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(54) Title: OXIDATIVE METHOD

(57) **Abrégé/Abstract:**

The present invention relates to a method of generating chlorine dioxide from chlorite salts in the presence of an iron ion-containing complex, a method of treating a substrate with a chlorine-containing oxidant in the presence of an iron ion-containing complex and related aqueous media, kits and compositions.

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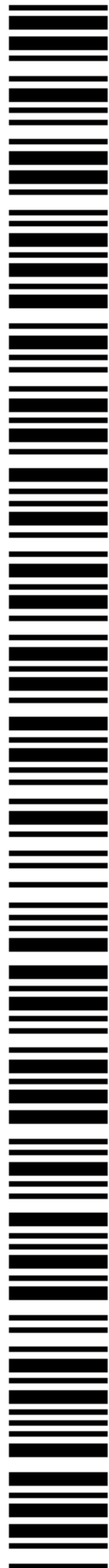
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OXIDATIVE METHOD

FIELD

5 The present invention relates to a method of generating chlorine dioxide from chlorite salts in the presence of an iron ion-containing complex, a method of treating a substrate with a chlorine-containing oxidant in the presence of an iron ion-containing complex and related aqueous media, kits and compositions.

BACKGROUND

10 The function of chlorine dioxide as an oxidant is useful for a variety of applications, such as for disinfection of, and removal of manganese and iron metals via formation of their oxides from, (surface) water, treatment of industrial water, such as in cooling towers, for taste and odour control, and for the bleaching of cellulosic substrates, particularly wood pulp. Besides significant usage in these applications,
15 chlorine dioxide is also used in food processing, such as in the washing of fruit and vegetables, cleaning of animal processing equipment and animal carcasses, and treatment of poultry and animal habitats.

Chlorine dioxide serves as a highly selective oxidant owing to a unique one-electron transfer mechanism in which it is reduced to chlorite (see Alternative
20 Disinfectants and Oxidants Guidance Manual,, United States Environmental Protection Agency, 1999 (www.epa.gov/ogwdw/mdbp/alternative_disinfectants_guidance.pdf) in particular Chapter 4 thereof ("Chlorine Dioxide")).

A wide variety of transition metal-based bleaching complexes have been studied to enhance the bleaching or delignification activity of hydrogen peroxide on
25 wood pulp. For example, dinuclear manganese complexes based on triazacyclononane ligands are known to be particularly active complexes. These complexes activate hydrogen peroxide towards the bleaching of cellulosic substrates, for example wood pulp or raw cotton (see for example EP 0 458 397 A2 (Unilever NV and Unilever plc), WO 2006/125517 A1 (Unilever plc *et al.*), US 2001/0025695 A1 (Patt
30 *et al.*), WO 2011/128649 (Unilever plc *et al.*), and WO 2011/141692 (Unilever plc *et al.*)). For a detailed review of the different classes of bleaching complexes active with hydrogen peroxide or dioxygen, reference is made to R Hage and A Lienke, *Angew. Chem., Int. Ed. Engl.*, **45**, 206-222 (2006).

Recently (see T P Umile & J T Groves (*Angew. Chem., Int. Ed. Engl.*, **50**, 695-
35 698 (2011)), T P Umile, D Wang & J T Groves (*Inorg. Chem.*, **50**, 10353-10362

(2011)), WO 2012/027216 (The Trustees of Princeton University) and S D Hicks *et al.* (*Angew. Chem., Int. Ed. Engl.*, **50**, 699-702 (2011))), it has been described that manganese complexes of porphyrins and porphyrazines can catalyse the formation of chlorine dioxide from sodium chlorite. In 2014, S D Hicks *et al.* (*J. Am. Chem. Soc.*, **136**, 3680-3686 (2014)) described the use of manganese complexes of the pentadentate N,N-bis(pyridin-2-ylmethyl)bis(pyridin-2-yl)methylamine (N4Py) and N-benzyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-diaminoethane (Bn-TPEN) in the catalytic formation of chlorine dioxide from chlorite.

Although the decomposition of chlorite catalysed by iron salts into chlorine dioxide, chlorate and various other species is known (see for example I Fábián in *Coord. Chem. Rev.*, **216-217**, 449-472 (2001)), porphyrin-based iron complexes, in contrast to manganese-ion -containing analogues, have been shown to dismutate chlorite into chlorate and chloride anions without forming chlorine dioxide (see M J Zdilla *et al.* (*Inorg. Chem.*, **48**, 2260-2268 (2009))).

In the publications concerning manganese complexes of porphyrins, porphyrazines, N4py and Bn-TPEN, it is suggested that the use of these may result in an alternative route for the production of chlorine dioxide from chlorite instead of using chlorate and a reducing agent. The latter process is the most common process to produce chlorine dioxide on large scale in, for example, pulp bleaching plants. For small-scale chlorine dioxide production, addition of a chemical oxidising agent (elemental chlorine, or hypochlorite + HCl) to chlorite solution, acidification of chlorite by HCl, or an electrochemical oxidation step is commonly employed. However, there is no teaching in these publications that related iron complexes could be of utility in the generation of chlorine dioxide from chlorite; or be of utility, *in situ*, in the bleaching and/or delignification of, for example, wood pulp or other cellulosic substrates by using chlorite salts or chlorine dioxide. Indeed, T P Umile *et al.* (*Inorg. Chem.*, 2011, *supra*) comment that the production of chlorine dioxide catalysed by the manganese porphyrins studied contrasts markedly from the oxygen-producing pathway catalysed by synthetic iron porphyrins.

Bleaching of raw cotton (cellulose) using chlorine dioxide is uncommon. This is because the optimal activity of chlorine dioxide is obtained at low pH whereas, for raw cotton, the most common method of removing fatty components from raw cotton, which is essential to obtain treated cotton suitable for subsequent dyeing processes, is conducted at high pH. Exposure of cotton to low pH only tends to take place when

cotton needs to be desized (which term refers to the removal of the protective layers put on the fibers to circumvent mechanical damage when weaving into garments).

Chlorine dioxide causes gross physical damage to bacterial cells and viral capsids. The efficacy of chlorine dioxide is at least as good as that of elemental chlorine, with 2-4 log inactivation when using a few mgs/L of chlorine dioxide.

It is undesirable, for reasons of safety, to produce chlorine dioxide in a chemical plant, and then store and ship it to where it is to be consumed, for example in a pulp mill or water treatment facility. Typically, therefore, chlorine dioxide is produced next to its place of use by allowing sodium chlorate to react with an acid such as sulfuric acid and a reducing agent (such as hydrogen peroxide, sulfur dioxide or methanol). In pulp treatment, for example, the resultant gaseous chlorine dioxide is then brought to another vessel, trapped in water and used as such to treat the pulp slurry.

Additional methods are known that produce chlorine dioxide from chlorite, either via acidification with hydrochloric acid or sulfuric acid, via oxidation of chlorite using chlorine, for example, or via electrochemical methods. Such processes are often used for small scale production of chlorine dioxide (for example in small units to deliver chlorine dioxide for hygiene/antimicrobial applications).

When chlorine dioxide acts as an oxidant, for example in its reaction with lignin moieties/residues during wood pulp and other bleaching processes, one-electron reactions occur, yielding the chlorite anion. Chlorite is not very reactive as an oxidant, in particular towards lignin or lignin residues, and may therefore be regarded as a waste product. Considering only the reduction of chlorine dioxide (oxidation state +4) to chlorite (oxidation state +3) means that only one electron per chlorine dioxide molecule is used (whilst in principle 5 electrons could be received by chlorine dioxide to yield chloride (oxidation state -1). Although other chlorine-containing oxidants may be generated (the chemistry is complicated), it is undeniable that the inherent oxidative efficiency of chlorine dioxide in existing processes is not being fully harnessed.

Although chlorine dioxide is of great benefit and is used in a variety of applications, it would be of benefit to the art to improve and/or develop alternative methods of using this chemical. This invention addresses that need.

SUMMARY

We have surprisingly found that iron complexes comprising a variety of polydentate nitrogen donor ligands are of utility in the preparation of chlorine dioxide from chlorite salts. Given that chlorite arises as a by-product upon the oxidation of

substrates with chlorine dioxide, this finding has utility not only in the preparation of chlorine dioxide but also in allowing provision of alternative methods of treatment of various substrates with chlorine dioxide. Accordingly, use of the iron ion-containing complexes and associated polydentate ligands described herein enhances the possibilities for using chlorite salts and chlorine dioxide.

Viewed from a first aspect, therefore, the invention provides a method of generating chlorine dioxide from a chlorine-containing chemical, which is a chlorite salt, comprising contacting, in an aqueous medium, a chlorite salt and a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

Viewed from a second aspect, the invention provides a method of treating a substrate comprising contacting, in an aqueous medium, (i) the substrate (ii) an amount of a chlorine-containing chemical, which is chlorine dioxide and/or a chlorite salt; and (iii) a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

Viewed from a third aspect, the invention provides an aqueous medium comprising a chlorine-containing chemical, which is chlorine dioxide and/or a chlorite salt, and a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

Viewed from a fourth aspect, the invention provides a kit comprising a chlorite salt and, separately, a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

Viewed from a fifth aspect, the invention provides a composition comprising a chlorite salt and a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

The use of chlorine dioxide or chlorite salts according to the present invention in the context of wood pulp bleaching and/or delignification, involving use of the iron ion-containing complexes described herein, allows better and/or more flexible use of these chemicals, and offers an alternative to existing methods, including those reliant on hydrogen peroxide. The invention is, however, not limited to the treatment of wood pulp. Other substrates, including cellulosic substrates such as raw cotton or stained cotton garments, may be treated in accordance with this invention, for example with detergent or other formulations comprising chlorine dioxide or solid chlorite salts and the complexes or polydentate ligands described herein. Such formulations may be used in cleaning and hygiene methods *in lieu* of formulations containing more traditional peroxy-based bleaches. As is discussed in more detail below, the invention is also of use in the treatment of water, for example to ameliorate microbial contamination, and other applications in which the antimicrobial effect of chlorine dioxide is of benefit.

Moreover, the invention permits alteration, e.g. improvement, of existing uses of the chlorine-based chemicals described herein (*viz* chlorine dioxide and chlorite salts), for example so as to allow a reduction in the temperature at which, or the duration for which, these chemicals are used. Furthermore, smaller dosages of chlorine dioxide or chlorite salts may be used than are used in the absence of the iron complexes described herein, for example so as to obtain antimicrobial activity. Another advantage of the invention is that, for example, solid chlorite salts in conjunction with an iron complex can be used for the antimicrobial applications, without needing to generate chlorine dioxide off line (*i.e. ex situ*).

Further aspects and embodiments of the invention will be evident from the discussion that follows below.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 depicts a UV-Vis spectrum of chlorine dioxide in water synthesised from chlorite as described in Experiment 1, at 20x dilution.

Fig.2 depicts a representative example of a UV-vis spectrum of chlorine dioxide measured after adding [Fe(N2py3o-C1)Cl]Cl (complex (1) to a buffered aqueous chlorite solution (N2py3o-C1 = Dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate). The peak at 261 nm is attributable to residual chlorite in the solution.

Fig. 3 depicts absorbance at 359 nm (indicative of the formation of chlorine dioxide) vs time upon mixing complex (1) (0.1 mM) with chlorite.

Fig. 4 depicts a plot of absorbance at 602 nm of Acid Blue 25 dye against time of 0.1 mM ClO_2 without complex (shown in middle of graph) and with 10 μM complex (1) (shown at bottom of graph), with absorbance decreasing over time. Shown at the top of the graph is a plot of absorbance against time in the presence of 10 μM complex 1 but in the absence of ClO_2 .

DETAILED DESCRIPTION

As summarised above, the present invention is based on the finding that complexes comprising iron ions and one or more polydentate ligands, which are either chelants capable of chelating at least one iron ion through at least three nitrogen atoms can convert chlorite to chlorine dioxide and thereby offer improvements or alternative to existing methods and compositions used for chlorine dioxide-based oxidations.

The methods of the first and second aspect of the invention involve use of, and the composition of the third aspect of the invention comprises, an aqueous medium, which will generally have at least 1 wt% water, by which is meant that the water-containing liquid constituting the liquid aqueous medium comprises at least 1% by weight water, more typically at least 10 wt%, even more typically 25 wt%, and most typically at least 50 wt% water. Typically the aqueous medium will be a solution (i.e. in which its various components, such as chlorine dioxide or chlorite salt(s) and the iron complex are dissolved). Although less typical, other aqueous (i.e. water-containing) media, including slurries and suspensions, may also be used as the aqueous medium. The aqueous medium comprises a liquid continuous phase, the liquid component of which is predominantly, i.e. between 50 and 100 wt% water, typically between 80 and 100 wt% water. Dependent on the use to which the aqueous medium referred to herein is being or is intended to be put, the liquid balance (if any) of the aqueous medium that is not water may be any convenient liquid, for example a liquid alcohol, e.g. a C_{1-4} alcohol such as methanol or ethanol. Where present, additional liquids will typically be water-miscible. Although the liquid continuous phase will often be entirely water, it will be understood that this does not exclude the presence of small amounts of other liquids (e.g. in a total amount of less than about 10 wt%, more typically less than about 5 wt%), e.g. as contaminants in the other materials with which the liquid continuous phases are brought into contact.

The pH of the liquid continuous phase of the aqueous media described herein need not be particularly limited. According to some embodiments, it may be between about 2 and about 11. In others, the pH may be between about 3 and about 7, for example a pH range of about 3.5 to about 7, often in the pH range of about 4 to about 6. Solutions or other systems having this pH may be readily prepared by the skilled person. For example, as the skilled person will recognise, appropriate buffers will allow control over pH to be achieved within the normal ability of those of normal skill. Suitable buffer systems include phosphate- or carboxylate-containing buffers, e.g. acetate-, benzoate- and citrate-based buffers. In some embodiments, the buffer system serves to achieve a pH between about 4.5 and about 5.5.

The chlorite salt used in accordance with the various aspects of the invention is typically an inorganic chlorite salt, the nature of which is not critical to the operation of the invention. One or more chlorite salts may be used in any given method although typically only one chlorite salt will be used. Non-limiting examples of chlorite salts that may be used include sodium chlorite (NaClO_2), potassium chlorite (KClO_2), lithium chlorite (LiClO_2), calcium chlorite ($\text{Ca}(\text{ClO}_2)_2$), barium chlorite ($\text{Ba}(\text{ClO}_2)_2$) and magnesium chlorite ($\text{Mg}(\text{ClO}_2)_2$). Typically sodium chlorite or potassium chlorite is used. More typically, the chlorite salt used is sodium chlorite.

As described above, the method according to the first aspect of the invention comprises contacting, in an aqueous medium, a chlorite salt and a complex comprising one or more iron ions (which complexes are interchangeably referred to herein as iron complexes) and one or more polydentate ligands (as defined herein). It will be understood that contacting may be achieved in a variety of ways. For example, an aqueous medium may be prepared, to which chlorite salt and metal complex are added, separately or in combination. The chlorite salt may be added as a solid, for example as a powder or granulate, or as an optionally buffered solution in water. Likewise, the iron complex may be added as a solid, for example as a powder, crystal granulate, either on its own or, for example diluted with a salt. Alternatively, it may be added as an optionally buffered solution in water, or as a solution in an alternative solvent such as an alcohol. Where added as a solution, the solution is typically formed by dissolving the iron complex in (optionally buffered) water. Alternatively, an aqueous medium (e.g. and typically a solution) containing a chlorite salt may be prepared to which may be added the iron complex, or *vice versa*.

Further permutations are also possible and may be easily envisaged by the skilled person. For example, the iron complex may not be added as such: iron ions

may be present in, or may be added to, an aqueous liquid and an iron complex formed *in situ* by addition of an appropriate ligand. For example, aqueous mixtures comprising wood pulp may comprise sufficient quantities of iron ions that useful quantities of the iron complexes described herein can be generated *in situ* by addition of an appropriate amount of the polydentate ligands described herein.

Alternatively, in accordance with the fourth and fifth aspects of the invention, a kit or composition comprising both a polydentate ligand as defined herein and a chlorite salt may be provided from which the aqueous medium in accordance with the third aspect of the invention may be prepared. Although the polydentate ligand in the kit or composition is part of an iron complex, it will be understood from the previous paragraph that it is not necessary that the aqueous medium is prepared by introduction of an iron complex as such, since the iron complex may be made *in situ* by provision of an appropriate source of iron ions.

Compositions in accordance with the fifth aspect of the invention may be added to a liquid medium to form an aqueous medium in accordance with the third aspect of the invention, which may be used in accordance with the first and second aspects of the invention, for example in those embodiments of the second aspect of the invention described herein relating to the treatment of water.

Analogously, it will be understood that kits in accordance with the fourth aspect of the invention may likewise be used to form an aqueous medium in accordance with the third aspect of the invention, which may be used in accordance with the first and second aspects of the invention, for example in those embodiments of the second aspect of the invention described herein relating to the treatment of water.

According to particular embodiments, the kit of the invention may take the form of a cartridge comprising separated compartments, for example of the type described in WO 2012/027216 A1 (*supra*), comprising the components of the kit, i.e. the chlorite salt and one or more iron complexes. For instance, in particular embodiments, the iron complex may be adsorbed (immobilised) on a solid support, permitting generation of chlorine dioxide by allowing water to flow through the cartridge. Advantageously, it will be understood that, where iron complexes are immobilised in such systems, these may be reused upon replacement of the chlorite salt.

The aqueous medium used in accordance with the second aspect of the invention, and of the third aspect of the invention, may be similarly prepared to that used in accordance with the first aspect of the invention except that the aqueous medium may alternatively or additionally comprise chlorine dioxide.

Irrespective of how the aqueous media of the various aspects of the invention are prepared, the one or more chlorite salts in it are typically present at a concentration of between about 0.01 and about 50 mM, for example between about 1 and about 30 mM. Where an aqueous medium (for example for use in the first or second aspect of the invention or of the third aspect) is for use in the treatment of a cellulosic substrate, the one or more chlorite salts in it are often present at a concentration of between about 0.1 and about 50 mM, for example between about 5 and about 30 mM. It will of course be recognised that the skilled person will be able to employ an appropriate concentration of chlorite salt, as with concentrations/amounts of other components described herein, without undue burden.

As well as the chlorite salt, the aqueous media used in or of the various aspects of the invention comprise an iron complex comprising one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

We use term porphyrin herein in accordance with its customary meaning in the art to mean a tetradentate tetracyclic macrocycle, comprising four pyrrole rings linked by four methine bridges, each of the pyrrole rings being connected at its 2- and 5-carbon atoms to an adjacent pyrrole moiety through a methine (=C(H)-) biradical. The parent compound is named porphyrine; when substituted, the resultant compounds are known as porphyrins.

According to particular embodiments of all aspects of the invention, the polydentate ligand is not a porphyrin or a porphyrazine ligand. Analogously to our use of the term porphyrin herein, we use term porphyrazine herein in accordance with its customary meaning in the art to refer to a class of macrocycle related to porphyrins, but in which the four pyrrole rings are linked linked by -N=, rather than methine, bridges, with the parent compound being known as porphyrazine and its derivatives as porphyrazines. For the avoidance of doubt, will be understood that porphyrazine derivatives comprising cyclic moieties fused to the 3- and 4-carbon atoms of the pyrrole moieties within porphyrazine are porphyrazines.

According to particular embodiments, the polydentate ligand is not a tetrapyrrole-containing compound. By "tetrapyrrole-containing compound" is meant herein a compound comprising four pyrrole rings or reduced forms thereof (such as the pyrroline ring found in the chlorin ring of chlorophylls; a chlorin ring being made up of three pyrrole and one pyrroline (3,4-dihydropyrrole) moieties linked by four methine (-

C(H)=) bridges, each of the pyrrole and pyrroline moieties being connected at its 2- and 5-carbon atoms to an adjacent pyrrole or pyrroline moiety through a methine biradical).

In addition to porphyrins, porphyrazines and chlorins, there are a variety of other macrocyclic compounds based either on four pyrrole or reduced pyrrole units linked either through methine or imine (-N=) bridges. For example, corrin rings comprise four pyrroline moieties linked by three methine bridges, all but one of the pyrroline moieties being connected at their 2- and 5-carbon atoms to an adjacent pyrroline moiety through a methine biradical; two of the pyrroline moieties, however, are directly connected, from the 2-carbon of one to the 5-carbon atom of the other. Phthalocyanines are macrocycles comprising four pyrrole-based five-membered rings linked by four imine bridges, each of the five-membered rings having a benzene ring fused to the 3- and 4-positions of the five-membered ring, and each of the five-membered rings being connected at its 2- and 5-carbon atoms to an adjacent five-membered ring through an imine biradical.

According to those embodiments of the invention in which the polydentate ligand is not a tetrapyrrole-containing compound, each of these immediately aforementioned classes of macrocycle is excluded, it being understood that use of the term tetrapyrrole-containing compounds to embrace compounds not necessarily comprising four pyrrole rings is consistent with the use prevalent in the art to describe, as tetrapyrrole-containing compounds, compounds such as phthalocyanines and chlorins, even although these compounds, strictly speaking structurally, do not comprise four pyrrole rings.

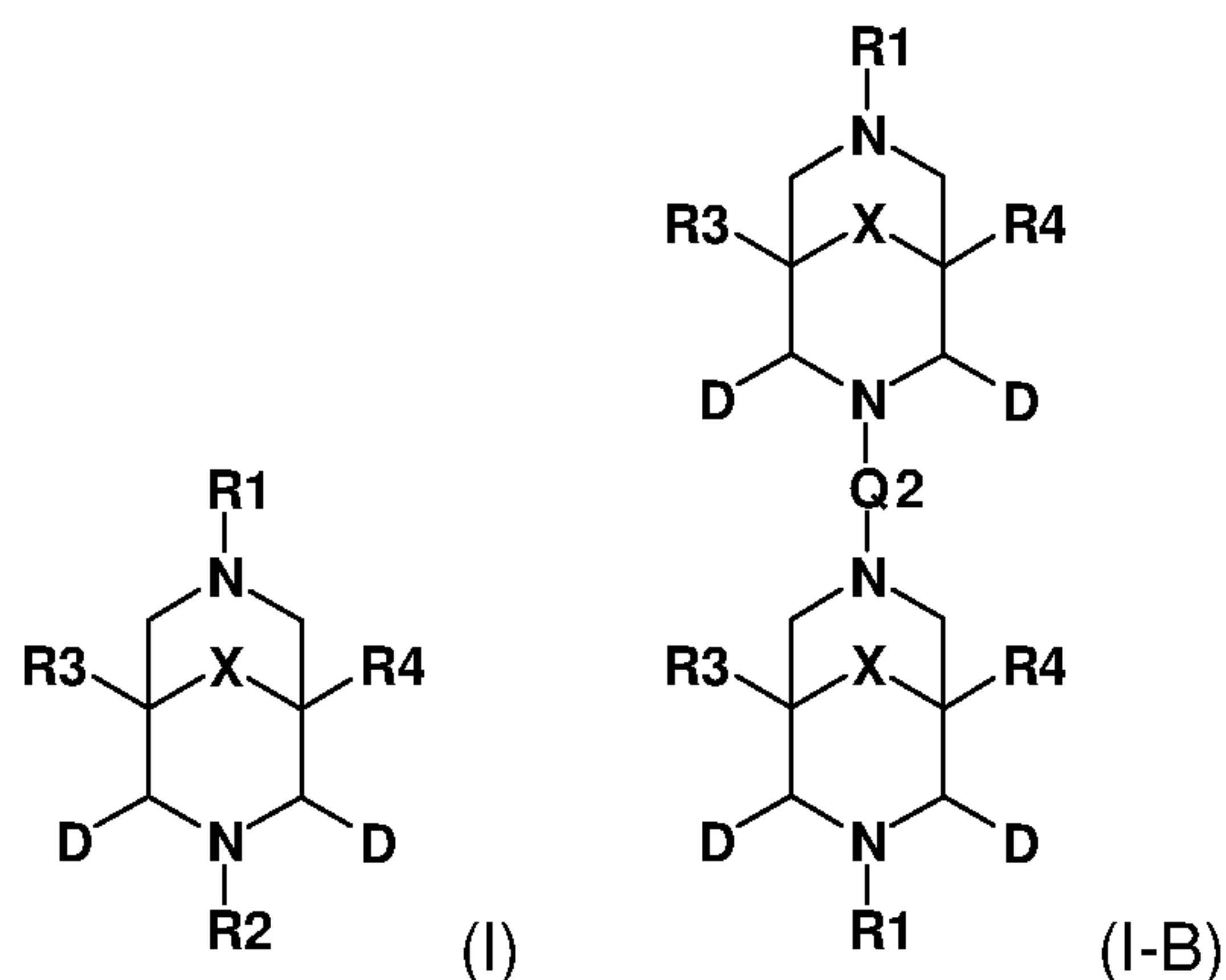
By a chelant capable of chelating at least one iron ion through at least three nitrogen atoms is meant a polydentate ligand capable of chelating one or more iron ions by the formation of coordinate bonds between three or more nitrogen atoms of the chelant and a common iron ion, chelation in this context and as the term is customarily used in the art requiring that the nitrogen atoms of the chelant coordinate to the same transition metal ion, in this case an iron ion. The chelants are thus at least tridentate. When bound to one iron ion, the chelant can be tridentate, tetradentate, pentadentate, hexadentate, heptadentate, or octadentate, with tridentate, tetradentate, pentadentate, hexadentate being most common. Further, some of the chelants described herein having a denticity of greater than six, for example eight, with octadentate ligands being capable of coordinating through eight nitrogen atoms. With these chelants, however, chelation is then often achieved by the formation of coordinate bonds between four nitrogen atoms and a common iron ion: for example four of the eight nitrogen atoms in

these octadentate chelants can chelate to a first iron ion and four of these nitrogen atoms can chelate to a second iron ion. This is generally achieved by such octadentate ligands having two portions of their structure giving rise to two separate regions of chelation, often separated by a bridge, as is explained and exemplified in greater detail below with reference to specific polydentate ligands useful in accordance with the present invention.

Often, the chelants of the invention capable of chelating at least one iron ion through at least three nitrogen atoms are chelants capable of chelating at least one iron ion through four, five or six nitrogen atoms. For the avoidance of doubt, whilst a chelant capable of chelating at least one iron ion through four nitrogen atoms may have a denticity of greater than four, such a chelant does not permit chelation through five (or more) or three (or fewer) nitrogen atoms. Similarly, for example, a chelant capable of chelating at least one iron ion through three nitrogen atoms may have a denticity of greater than three, such a chelant does not permit chelation through four (or more) or two (or fewer) nitrogen atoms and so on.

It will be understood that the denticity (and thus the terms tridentate, tetradentate, pentadentate or hexadentate, heptadentate, or octadentate) refers to the number of metal ion-binding donor atoms that can bind to a metal ion. A chelant which is, for example, a tetradentate nitrogen donor thus refers to an organic molecule comprising four nitrogen atoms with lone pairs, which can bind to a common transition metal ion, which according to the present invention is an iron ion. These nitrogen donor atoms may be either aliphatic, either tertiary, secondary or primary amines, or may belong to a heteroaromatic ring, for example pyridine.

According to particular embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formulae (I) or (I-B):



wherein:

each D is independently selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl and thiazol-2-yl, each of which may be optionally substituted by one or more groups independently selected from the group consisting of -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl, and -C₁-C₄alkyl;

the or each R1 and R2 are independently selected from the group consisting of C₁-C₂₄alkyl, C₆₋₁₀arylC₁-C₆alkyl, C₆₋₁₀aryl, C₅-C₁₀heteroarylC₁-C₆alkyl, each of which may be optionally substituted by one or more groups selected from -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl and -SC₁-C₄alkyl; and CH₂CH₂N(R10)(R11),

wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

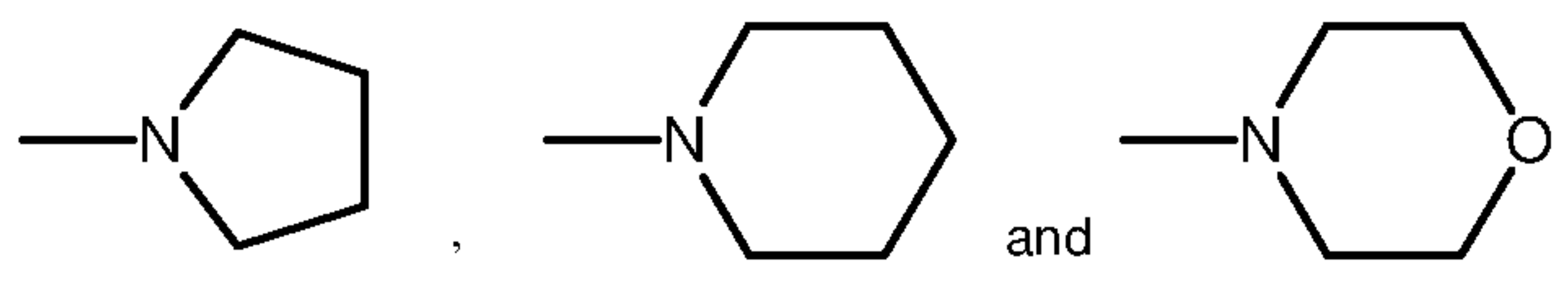
R3 and R4 are independently selected from hydrogen, C₁-C₈alkyl, C₁-C₈alkyl-O-C₁-C₈alkyl, C₆-C₁₀aryloxyC₁-C₈alkyl, C₆-C₁₀aryl, C₁-C₈hydroxyalkyl, C₆-C₁₀arylC₁-C₆alkyl and C₅-C₁₀heteroarylC₁-C₆alkyl, and -(CH₂)₀₋₄C(O)OR5 wherein R5 is independently selected from: hydrogen, C₁-C₈alkyl and C₆₋₁₀aryl;

Q2 represents a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge is optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

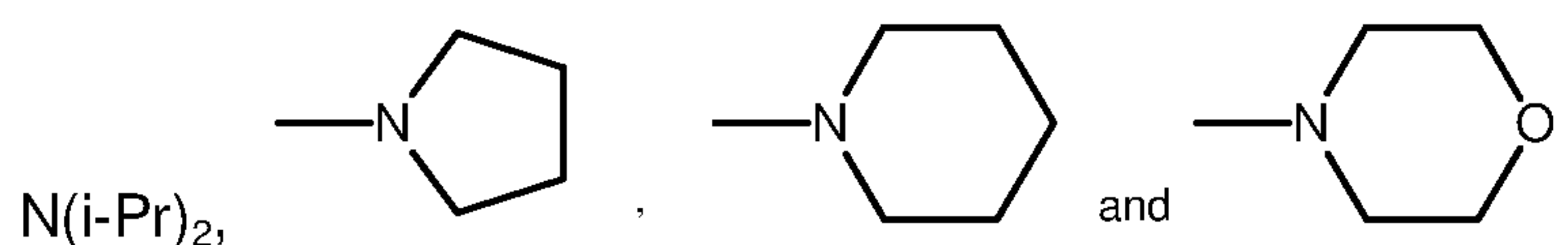
X is selected from C=O, -[C(R6)₂]₀₋₃- wherein each R6 is independently selected from hydrogen, hydroxyl, C₁-C₄alkoxy and C₁-C₄alkyl.

Such ligands (i.e. of formula (I) and (I-B)) are known in the art as bispidons. The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of bispidons:

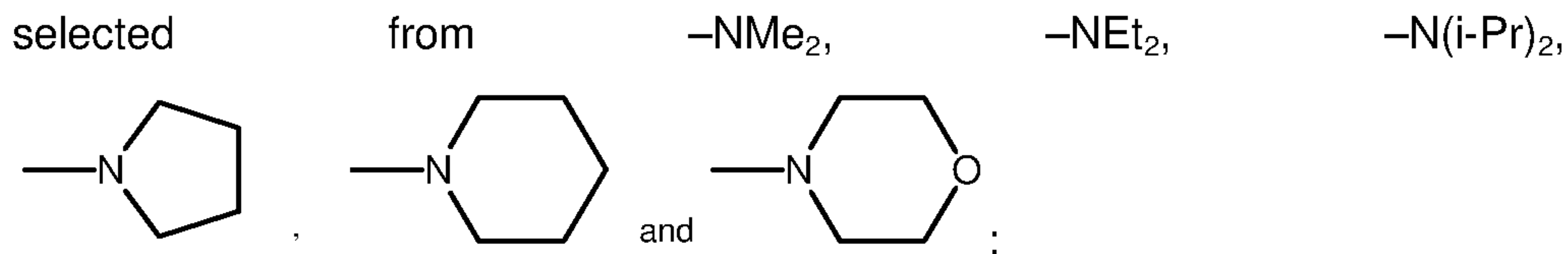
- each D group is either unsubstituted or substituted with one or more, often one, C₁-C₄alkyl groups;
- each D group is the same;
- each D group is an optionally substituted pyridin-2-yl;
- each D group is unsubstituted pyridin-2-yl group;
- Q2 is selected from -CH₂CH₂-, -CH₂CH₂CH₂- and -CH₂CHOHCH₂-, each of which is optionally C₁-C₆alkyl-substituted, with the bridge typically being unsubstituted;
- each R1 and R2 group is independently selected from C₁-C₂₄alkyl, C₆-C₁₀aryl, C₆₋₁₀arylC₁-C₆alkyl, C₅-C₁₀heteroarylCH₂ and CH₂CH₂N(R10)(R11), whereby -N(R10)(R11) is selected from -NMe₂, -NEt₂, -N(i-Pr)₂,



- in case any R1 or R2 group is independently a C₁-C₂₄alkyl, a C₆-C₁₀aryl, or a C₆₋₁₀arylC₁-C₆alkyl group, it is more typically independently selected from C₁-C₁₈alkyl and C₆-C₁₀arylC₁-C₆alkyl, and even more typically independently selected from: C₁-C₈alkyl and C₆-C₁₀arylCH₂;
- in case any R1 or R2 is independently a C₅-C₁₀heteroarylCH₂ group, it is preferably selected from pyridin-2-ylmethyl, pyrazin-2-ylmethyl, quinolin-2-ylmethyl, pyrazol-1-ylmethyl, pyrazol-3-ylmethyl, pyrrol-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, benzimidazol-2-ylmethyl, pyrimidin-2-ylmethyl, 1,2,3-triazol-1-ylmethyl, 1,2,3-triazol-2-ylmethyl, 1,2,3-triazol-4-ylmethyl, 1,2,4-triazol-3-ylmethyl, 1,2,4-triazol-1-ylmethyl and thiazol-2-ylmethyl, with pyridin-2-ylmethyl, quinolin-2-ylmethyl, imidazol-2-ylmethyl, and thiazol-2-ylmethyl being more typical;
- often one of the R1 and R2 groups is C₁-C₂₄alkyl or C₆₋₁₀arylC₁-C₆alkyl, whilst the other of the R1 and R2 groups is a C₅-C₁₀heteroarylCH₂ group or CH₂CH₂N(R10)(R11), whereby -N(R10)(R11) is selected from -NMe₂, -NEt₂, -



- one of the R1 and R2 groups is most typically C₁-C₁₈alkyl, with C₁-C₁₂alkyl more preferred, C₁-C₈alkyl even more preferred and with CH₃ being most preferred; and the other R1 or R2 group typically an optionally substituted pyridin-2-ylmethyl, with unsubstituted pyridin-2-ylmethyl being most typical, or is selected from



- R1 is the same as R2 (for formula (I)) or each R1 is the same (for formula (II)), often methyl or pyridin-2-ylmethyl; and
- groups R3 and R4 are the same.

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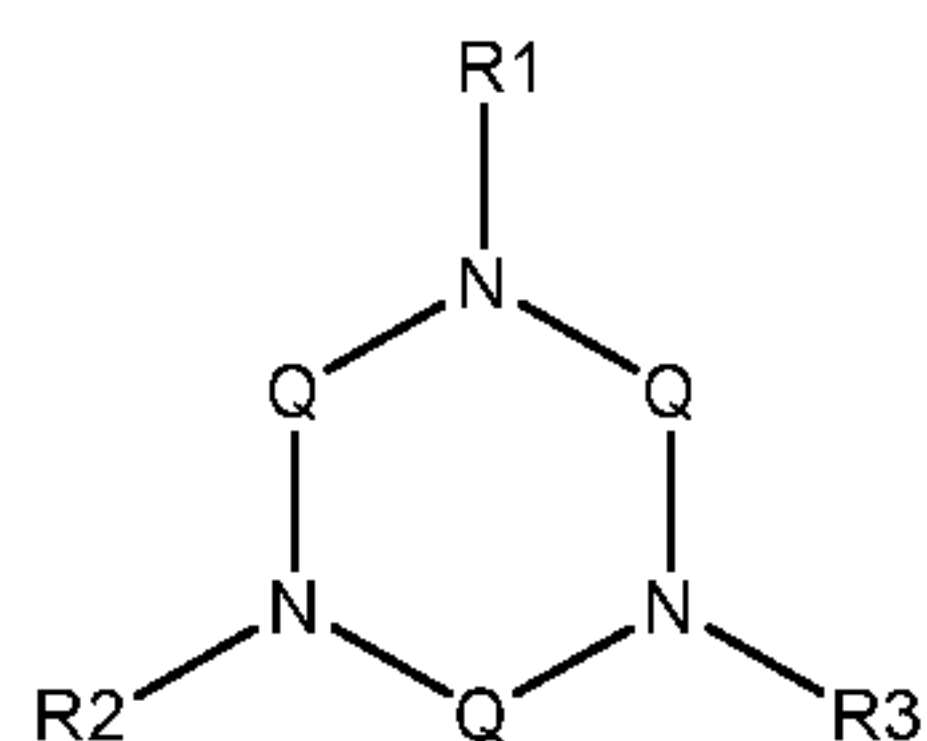
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According to specific embodiments, the bispidon is one of the following ligands:

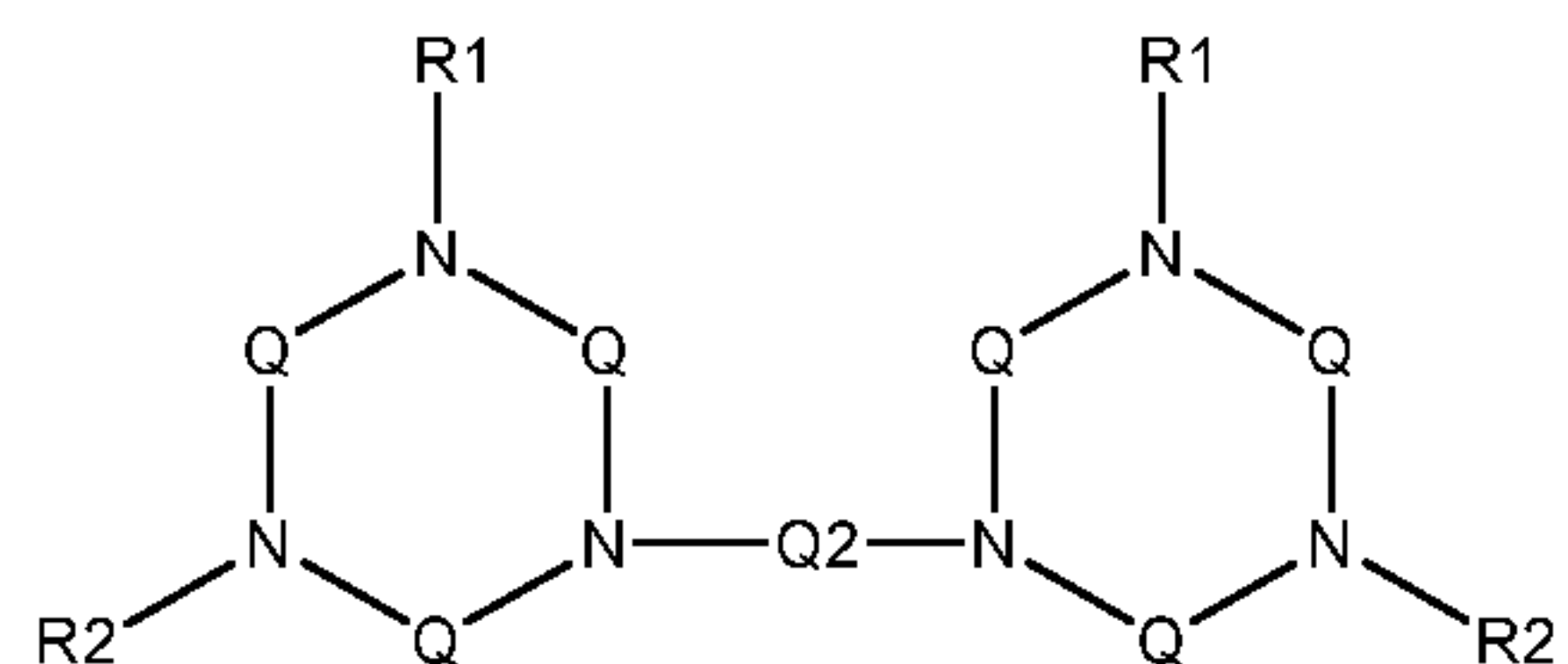
dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-C1), dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3u-C1), and the iron complexes thereof (FeN2py3o-C1, FeN2py3u-C1) which are described in WO 02/48301. Another particular preferred bispidon is dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate and the iron complex thereof as described in WO 03/104234. Other preferred bispidons are those that have instead of having R¹ = methyl, other N-alkyl groups are present, for example isobutyl, (n-hexyl) C6, (n-octyl) C8, (n-dodecyl) C12, (n-tetradecyl) C14, (n-octadecyl) C18. Similarly the analogous 3-pyridin-2ylmethyl)-7-alkyl isomeric ligands and their iron complexes thereof are preferred. Examples of such bispidons are described in WO 02/48301, WO 03/104379 and WO 2005/049778. Also preferred tetradentate bispidons, in particular, dimethyl 2,4-di-(2-pyridyl)-3,7-dimethyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py2), and the iron complexes thereof are mentioned. Various Fe(N2py2)X₂ complexes with X= e.g. thiocyanate and acetate are known to the skilled person (see for example P. Comba and co-workers, *Inorg. Chim. Acta*, **337**, 407-419 (2002)).

According to further embodiments, the chelant capable of chelating at least one iron ion through nitrogen atoms is of formulae (II) and (II-B):

15



(II)



(II-B)

wherein:

each Q is independently selected from -CR₄R₅CR₆R₇-
 5 and -CR₄R₅CR₆R₇CR₈R₉-;

R₄, R₅, R₆, R₇, R₈, and R₉ are independently selected from: H, C₁-C₄alkyl and hydroxyC₁-C₄alkyl;

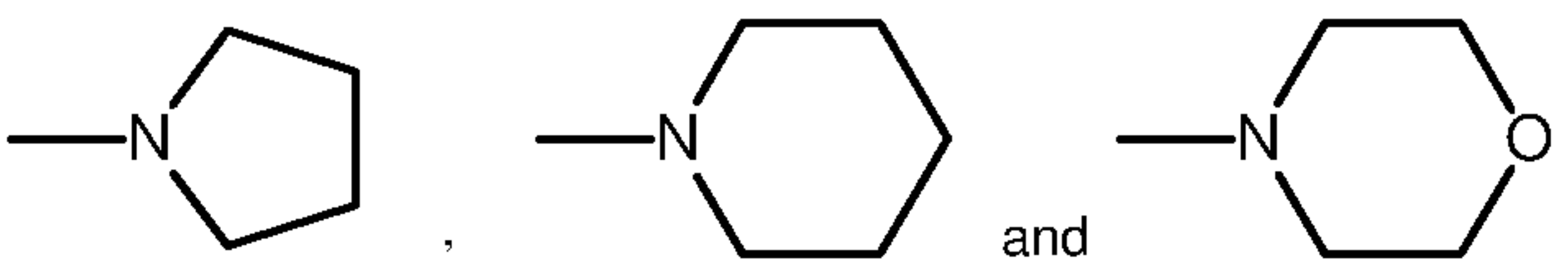
each R₁, R₂, and R₃ is independently selected from the group consisting of hydrogen, C₁-C₂₄alkyl, CH₂CH₂OH, CH₂COOH, CH₂PO₃H₂, C₅-C₁₀heteroarylC₁-C₆alkyl
 10 and CH₂CH₂N(R₁₀)(R₁₁),

wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁-
 44alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently
 optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in
 which each of the aryl groups is independently optionally substituted with one or more
 15 C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached
 represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl
 groups, which is connected to the remainder of R₁ through the nitrogen atom N;
 di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is
 independently optionally substituted with one or more C₁₋₂₀alkyl groups; and
 20 di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently
 optionally substituted with one or more C₁₋₂₀alkyl groups; and

Q₂ is a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆-
 10arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆-
 10arylene unit, which bridge may be optionally substituted one or more times with
 25 independently selected C₁₋₂₄alkyl groups and OH groups.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formulae (II) and (II-B):

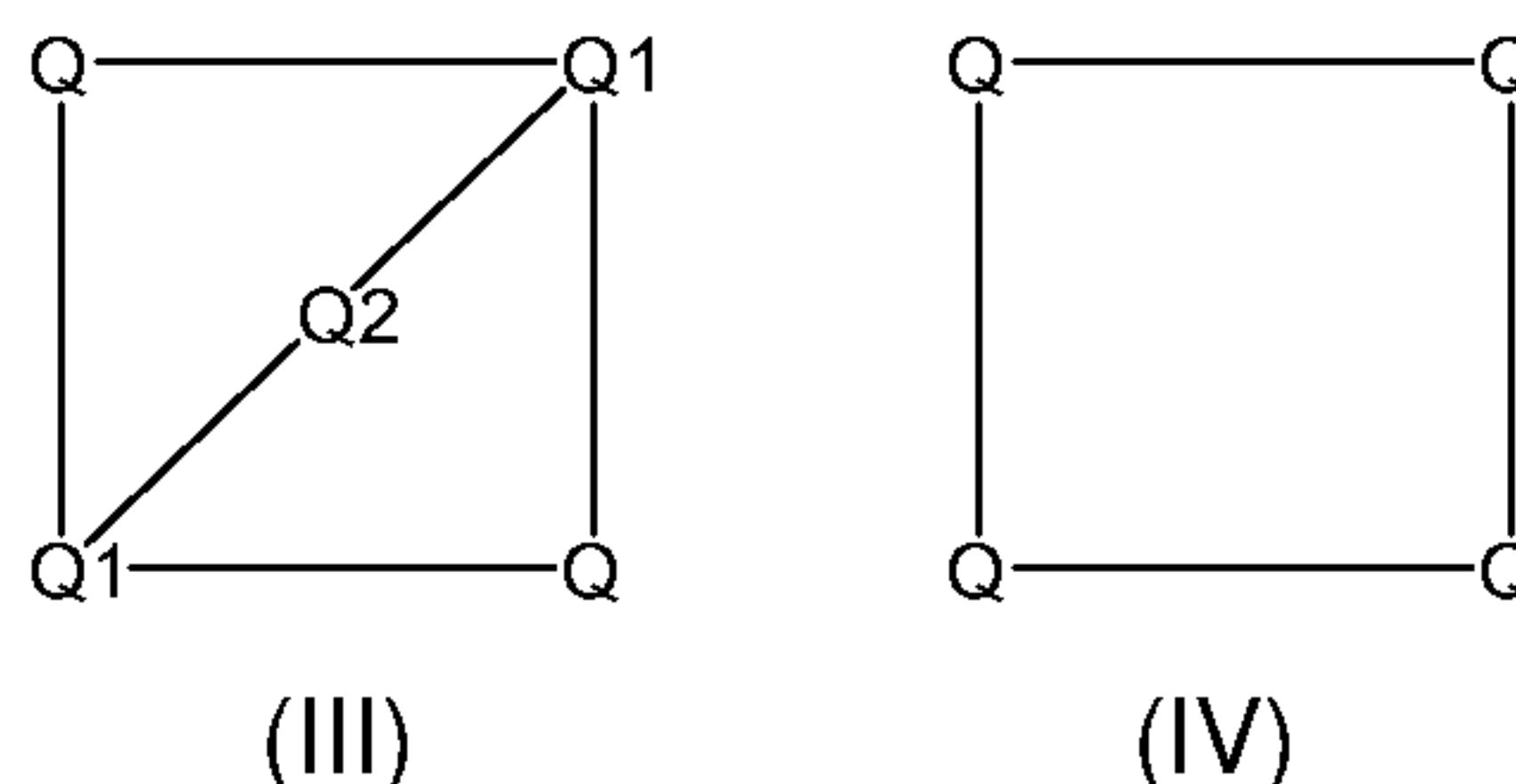
- where a ligand is of formula (II-B), the ligand is symmetrical, i.e. each R₁ is the
 30 same and each R₂ is the same; and each Q group at the same position (e.g. between the bridging moiety-bearing and R₂-substituted nitrogen atoms) in each ring is the same;

- each Q is the same, for example each Q is -CR₄R₅CR₆R₇-, in which R₄, R₅, R₆ and R₇ are often H, which limitation defines the class of ligands often known as 1,4,7-triazacyclononane ligands;
- if any of R₁, R₂, and/or R₃ is a C₅-C₁₀heteroarylC₁-C₆alkyl group, such groups are selected from pyridin-2-ylmethyl, quinolin-2-ylmethyl, imidazol-2-ylmethyl, benzimidazol-2-ylmethyl, pyrazin-2-ylmethyl, 1,2,4-triazol-3-ylmethyl, 1,2,4-triazol-1-ylmethyl, thiazol-2-ylmethyl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, pyrazol-3-ylmethyl and pyrazol-1-ylmethyl,;
- R₁, R₂, and/or R₃ are often independently C₁-C₂₄alkyl, pyridin-2-ylmethyl, or quinolin-2-ylmethyl.
- if R₁, R₂, and/or R₃ is a heteroarylmethyl group this will often be pyridin-2-ylmethyl;
- -R₁, -R₂, and/or -R₃ is -CH₂CH₂N(R₁₀)(R₁₁) in which any R₁₀ and/or R₁₁ moiety referred to as being optionally substituted with one or more C₁₋₂₀alkyl groups is typically either unsubstituted or only substituted with one C₁₋₂₀alkyl group;
- where R₁, R₂, and/or R₃ is CH₂CH₂N(R₁₀R₁₁), non-limiting examples of such groups include: di(*p*-methylbenzyl)amino, as an example of a di(C₆₋₁₀arylC₁₋₄alkyl)amino; pyrrolidinyl, piperidinyl or morpholinyl, as examples of NR₇; di(piperidineylethyl)amino, as an example of di(heterocycloalkylC₁₋₆alkyl)amino; and di(pyridin-2-ylethyl)amino, as an example of a di(heteroarylC₁₋₆alkyl)amino.
- if present, each -N(R₁₀)(R₁₁) is independently selected from the group consisting of -NMe₂, -NEt₂, -N(*i*-Pr)₂,

- if R₁, R₂ and/or R₃ is C₁-C₂₄alkyl, this is a C₁-C₆alkyl, and often methyl; and
- for ligands of formula (II-B), bridge Q₂ is typically C₁₋₆alkylene, often ethylene or n-propylene, and most often ethylene.

According to particular embodiments of the invention, ligands of formula (II) or (II-B) are selected from the group consisting of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃-TACN), 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me₄-DTNE), 1-(pyridin-2-ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, 1,4-bis(pyridin-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane, 1,4,7-tris(pyridin-2-ylmethyl)-1,4,7-triazacyclononane, 1,2-bis(4-methyl-7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-ethane and 1,3-bis(4-methyl-

7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-propane. According to particular embodiments, the ligand where of formula (II) is selected from 1-(pyridin-2-ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane and 1,4-bis(pyridin-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane.

- 5 According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formulae (III) or (IV):



wherein:

- 10 each -Q- is independently selected from -N(R)C(R₁)(R₂)C(R₃)(R₄)- and -N(R)C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

each -Q1- is independently selected from -N(R')C(R₁)(R₂)C(R₃)(R₄)- and -N(R')C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

- 15 each R is independently selected from: hydrogen; the group consisting of C₁-C₂₀alkyl, C₂-C₂₀alkenyl, C₂-C₂₀alkynyl, C₆-C₁₀aryl and C₇-C₂₀arylalkyl, each of which may be optionally substituted with C₁-C₆alkyl, C₅-C₁₀heteroarylC₁-C₆alkyl; and CH₂CH₂N(R₁₀)(R₁₁),

- 20 wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁-C₄alkyl)amino; di(C₆-C₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁-C₂₀alkyl groups; di(C₆-C₁₀arylC₁-C₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁-C₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁-C₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N;
- 25 di(heterocycloalkylC₁-C₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁-C₂₀alkyl groups; and di(heteroarylC₁-C₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁-C₂₀alkyl groups;

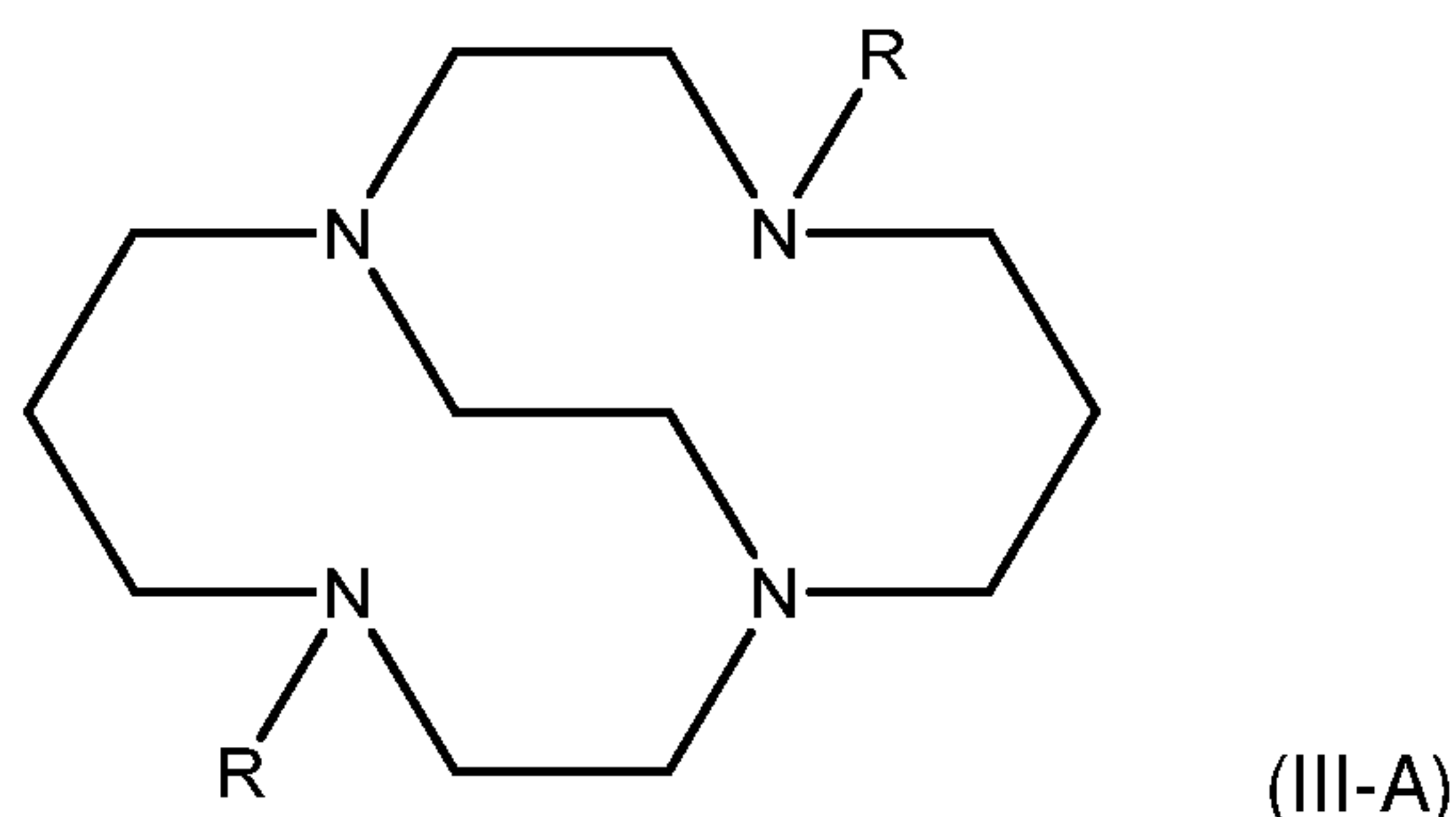
the two -R' groups of the two Q1 groups together form bridging moiety -Q2-;

- 30 Q2 is a bridge selected from the group consisting of a C₂-C₆alkylene moiety, a C₆-C₁₀arylene moiety, or a moiety comprising one or two C₁-C₃alkylene units and one C₆-C₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁-C₂₄alkyl groups; and

R_1 - R_6 are each independently selected from: H, C_{1-4} alkyl and hydroxy C_{1-4} alkyl.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formulae (III) and (IV):

- 5 • Q2, which may be present in chelants of formula (III), is an ethylene or n-propylene bridge;
- each -Q- is independently selected from -N(R)(CH₂)₂- and -N(R)(CH₂)₃-;
- each -Q1- is independently selected from -N(R')(CH₂)₂- and -N(R')(CH₂)₃-;
- 10 • each R is each selected from: hydrogen, C_1 - C_{20} alkyl, C_6 - C_{10} aryl, C_7 - C_{20} arylalkyl, pyridin-2-ylmethyl, quinolin-2-ylmethyl, imidazol-2-ylmethyl, benzimidazol-2-ylmethyl, more typically hydrogen, methyl, ethyl, benzyl, or pyridin-2-ylmethyl, yet more typically hydrogen, methyl, or benzyl;
- R_1 - R_6 are each typically hydrogen or C_{1-4} alkyl, more typically still hydrogen or methyl, for example hydrogen; and
- 15 • the ligand is of formula (III-A), i.e. a cross-bridged tetraaza-1,4,8,11-cyclotetradecane ligand:



20 wherein R is as defined for formulae (III) and (IV) above, including the particular embodiments immediately hereinbefore described.

Typically each R in formula (III-A) is independently selected from the group consisting of methyl, ethyl and benzyl. Typically, each R is the same, often methyl. Other suitable cross-bridged ligands (so-called because of the presence of a bridge linking two non-adjacent nitrogen atoms of the tetrazacycloalkane) are described in in
25 WO 98/39098 A1 (The University of Kansas).

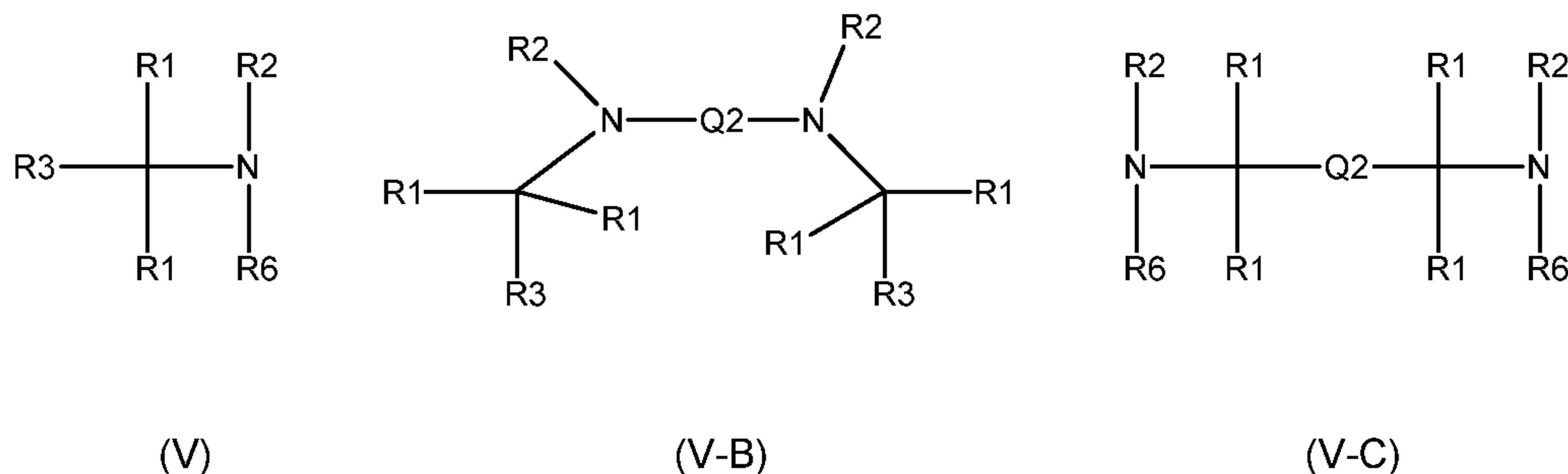
Typical ligands of formula (IV) are tetraaza-1,4,7,10-cyclododecane and tetraaza-1,4,8,11-cyclotetradecane, in either of which each of the hydrogen atoms attached to the four nitrogen atoms may be independently substituted for a C_1 - C_{20} alkyl, C_6 - C_{10} aryl or a C_7 - C_{20} arylalkyl group. According to particular embodiments, ligands of
30 formula (IV) may be tetraaza-1,4,7,10-cyclododecane-based and tetraaza-1,4,8,11-

cyclotetradecane-based ligands of formula (IV) wherein each R group is hydrogen, C₁₋₂₀alkyl, or heteroarylmethyl. Within these ligands, R is typically hydrogen, methyl, or pyridin-2ylmethyl. According to particular embodiments, ligands of formula (IV) include

1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane,

5 1,4,7,10-tetrakis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1-methyl-4,7,10-tris(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4-dimethyl-7,10-bis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4,7-trimethyl-11-(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4,8,11-tetraazacyclododecane, 1,4,8,11-tetrakis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1-methyl-4,8,11-tris(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1,4-dimethyl-8,11-bis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, and 1,4,8-trimethyl-11-(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclododecane.

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formulae (V), (V-B) or (V-C):



wherein:

each -R1 independently is selected from -CH₂N(C₁-C₂₄alkyl)₂, -CH₂NR₇ or an optionally C₁-C₆alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl;

each -R2 independently represents -R₄-R₅;

each -R3 and each -R6 each independently represents hydrogen, or a group selected from C₁-C₆alkyl, C₆-C₁₀aryl, C₅-C₁₀heteroaryl, C₆-C₁₀arylC₁-C₆alkyl and C₅-C₁₀heteroarylC₁-C₆alkyl, each of which groups may be optionally C₁-C₆alkyl-substituted;

each -R₄- independently represents optionally C₁-C₆alkyl-substituted C₁-C₆alkylene;

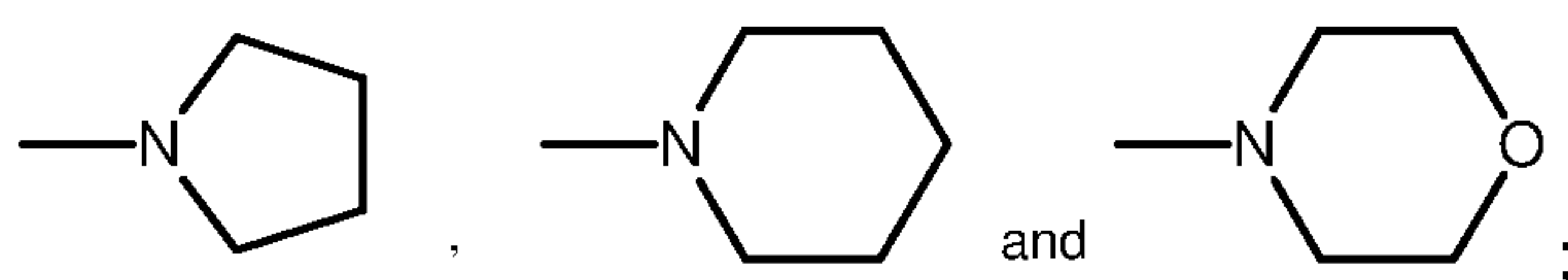
each -R5 independently represents an $-\text{CH}_2\text{N}(\text{C}_1\text{-C}_{24}\text{alkyl})_2$ group, $-\text{CH}_2\text{NR}_7$ or an optionally $\text{C}_1\text{-C}_6$ alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl;

each -NR7 independently represents a moiety in which R7 and the nitrogen atom N to which it is attached represents a heterocycloalkyl group optionally substituted with one or more C_{1-20} alkyl groups, which is connected to R4 through the nitrogen atom N; and

Q2 represents a bridge selected from the group consisting of a C_{1-6} alkylene moiety C_{6-10} arylene moiety or a moiety comprising one or two C_{1-3} alkylene units and one C_{6-10} arylene unit, which bridge is optionally substituted one or more times with independently selected C_{1-24} alkyl groups and OH groups.

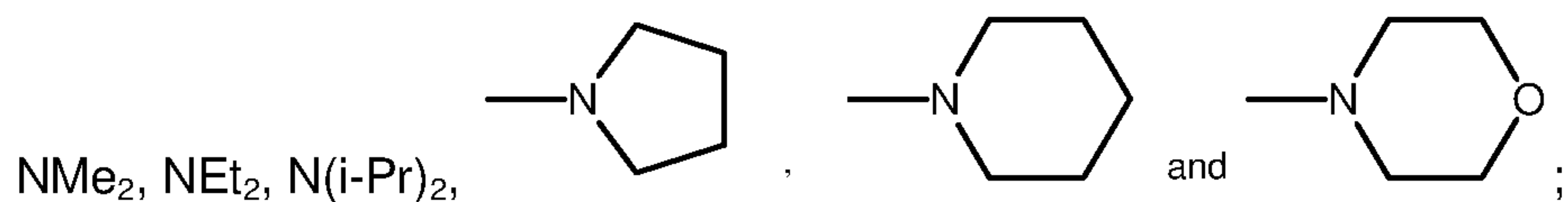
It will be understood that ligands of formulae (V-B) and (V-C) are effectively dimers of ligands of formula (V) in which bridge Q2 takes the place of the R6 groups, or the R3 groups respectively. Of the ligands of formulae (V), (V-B) and (V-C), ligands of formula (V) are most typical. Amongst the bridge-containing ligands, ligands of formula (V-B) more typical than ligands of formula (V-C). Additionally, the following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formulae (V), (V-B) and (V-C):

- groups having the same descriptor, e.g. R1, R2 (and, within the definition of R2, R4 and R5), R3, R6 and Q2 etc, are the same;
- R1 is optionally substituted pyridin-2-yl, in particular unsubstituted pyridin-2-yl;
- in embodiments in which -R1 is selected from $-\text{CH}_2\text{N}(\text{C}_{1-24}\text{alkyl})_2$ and $-\text{CH}_2\text{NR}_7$, the nitrogen-containing group attached to the methylene group recited for these possibilities is selected from the group consisting of $-\text{NMe}_2$, $-\text{NEt}_2$, $-\text{N}(\text{i-Pr})_2$,



- R4- is $-\text{CH}_2-$.
- where an alkyl-substituted heteroaryl group, R5 is optionally substituted pyridin-2-yl, with the unsubstituted pyridin-2-yl being most typical;
- according to other particular embodiments, R5 may be $-\text{CH}_2\text{N}(\text{C}_1\text{-C}_{24}\text{alkyl})_2$ group or $-\text{CH}_2\text{NR}_7$, the nitrogen-containing group attached to the methylene

group recited for these possibilities being selected from the group consisting of



- each R3 and each R6 each independently represents hydrogen, or a group selected from C₁-C₆alkyl, C₆-C₁₀aryl, C₆-C₁₀arylC₁-C₆alkyl C₅-C₁₀heteroaryl, C₆-C₁₀arylC₁-C₆alkyl and C₅-C₁₀heteroarylC₁-C₆alkyl, each of which groups may be optionally C₁-C₆alkyl-substituted;
- each R3 is selected from hydrogen, methyl and benzyl;
- Q2 is selected from -CH₂CH₂-, -CH₂CH₂CH₂- and -CH₂CHOHCH₂-, each of which is optionally C₁-C₆alkyl-substituted, with the bridge typically being unsubstituted; and
- each R6 is typically selected from hydrogen, methyl, benzyl, and pyridin-2ylmethyl, with R6 most typically being selected from methyl and pyridin-2ylmethyl.

According to particular embodiments, the ligand of formula (V) is N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (MeN3Py) or N-benzyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (BzN3Py), both which are disclosed by Klopstra *et al.* (*Eur. J. Inorg. Chem.*, **4**, 846-856 (2006)). Further selected preferred ligands of formula (V) are N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (N4Py), which is disclosed in WO 95/34628; N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane (MeN4py), as disclosed in EP 0 909 809, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane as disclosed in EP 0 909 809. Additional examples of ligands of formula (V) include: N-methyl-N-(pyridin-2-ylmethyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N-benzyl-N-(pyridin-2-ylmethyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N-methyl-N-(pyridin-2-ylmethyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane and N-benzyl-N-(pyridin-2-ylmethyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane.

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formula (VI):



wherein:

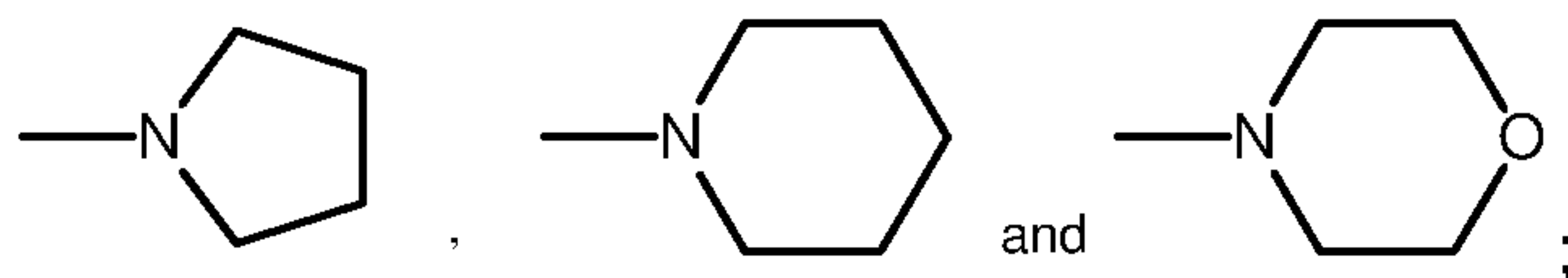
each -R1 is independently selected from -CY₂N(C₁-C₂₄alkyl)₂; -CY₂NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl

group optionally substituted with one or more C₁₋₆alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; or represents an optionally C₁₋₆alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-1-yl, pyrazol-3-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl; and

each Y is independently selected from H, CH₃, C₂H₅, C₃H₇.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formula (VI):

- each Y is H;
- -R1 is selected from -CH₂N(C₁-C₂₄alkyl)₂ and -CH₂NR7, with particular embodiments being those in which the nitrogen-containing group attached to the methylene group recited for these possibilities is selected from the group consisting of -NMe₂, -NEt₂, -N(i-Pr)₂,



- each R1 is often optionally substituted pyridin-2-yl and each R1 is more often unsubstituted pyridin-2-yl.

According to a specific embodiment, the ligand of formula (VI) is N,N,N-tris(pyridin-2-yl-methyl)amine (TPA), which has, for example, been described in US Patent Nos 5,850,086 (Que, Jr. *et al.*) and 6,153,576 (Blum *et al.*).

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formulae (VII) or (VII-B):

R1R2N-X-NR1R2 (VII); and R1R2N-X-NR2(-Q2-R2N)_n-X-NR1R2 (VII-B);

wherein:

-X- is selected from -CY₂CY₂-, cis- or trans-1,2-cyclohexylene, -CY₂CY₂CY₂-, -CY₂C(OH)YCY₂-, with each Y being independently selected from H, CH₃, C₂H₅ and C₃H₇;

n is an integer from 0 to 10;

each R1 group is independently an alkyl, heterocycloalkyl, heteroaryl, aryl, arylalkyl or heteroarylalkyl group, each of which may be optionally substituted with a substituent selected from the group consisting of hydroxy, alkoxy, phenoxy,

phosphonate, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, mono- or dialkylamine and $N^+(R3)_3$, wherein R3 is selected from hydrogen, alkyl, alkenyl, arylalkyl, arylalkenyl, hydroxyalkyl, aminoalkyl, and alkyl ether;

each R2 is $-CZ_2-R4$, with each Z being independently selected from H, CH_3 , C_2H_5 , C_3H_7 ; and each $-R4$ being independently selected from an optionally C_1-C_6 alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl; and $CH_2N(R10)(R11)$,

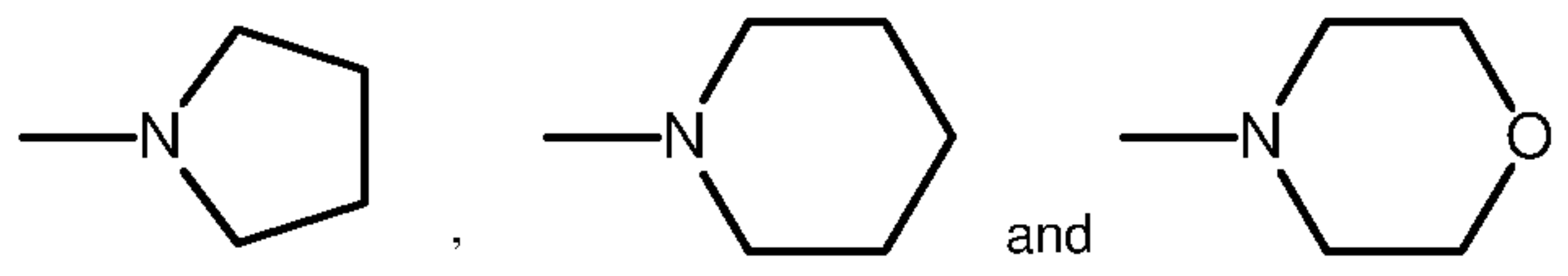
wherein $N(R10)(R11)$ is selected from the group consisting of $di(C_{1-44}alkyl)amino$; $di(C_{6-10}aryl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; $di(C_{6-10}arylC_{1-6}alkyl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; $NR7$, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more $C_{1-20}alkyl$ groups, which is connected to the remainder of R1 through the nitrogen atom N; $di(heterocycloalkylC_{1-6}alkyl)amino$, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; and $di(heteroarylC_{1-6}alkyl)amino$, wherein each of the heteroaryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; and

Q2 is a bridge selected from the group consisting of a $C_{1-6}alkylene$ bridge, a $C_{6-10}arylene$ bridge or a bridge comprising one or two $C_{1-3}alkylene$ units and one $C_{6-10}arylene$ unit, which bridge may be optionally substituted one or more times with independently selected $C_{1-24}alkyl$ groups and OH groups.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formulae (VII) and (VII-B):

- each Y is typically H;
- X is typically $-CH_2CH_2-$ or 1,2-cyclohexylene;
- n is typically an integer from 0 to 4, more typically from 0 to 3, even more typically 0 to 2, and most typically $n=0$ or 1.
- Q2 is typically an ethylene, n-propylene bridge, or cis- or trans-1,2-cyclohexylene;
- each Z is typically hydrogen;
- often $X=Q2$;

- R4 is selected from the group consisting of -NMe₂, -NEt₂, -N(i-Pr)₂,

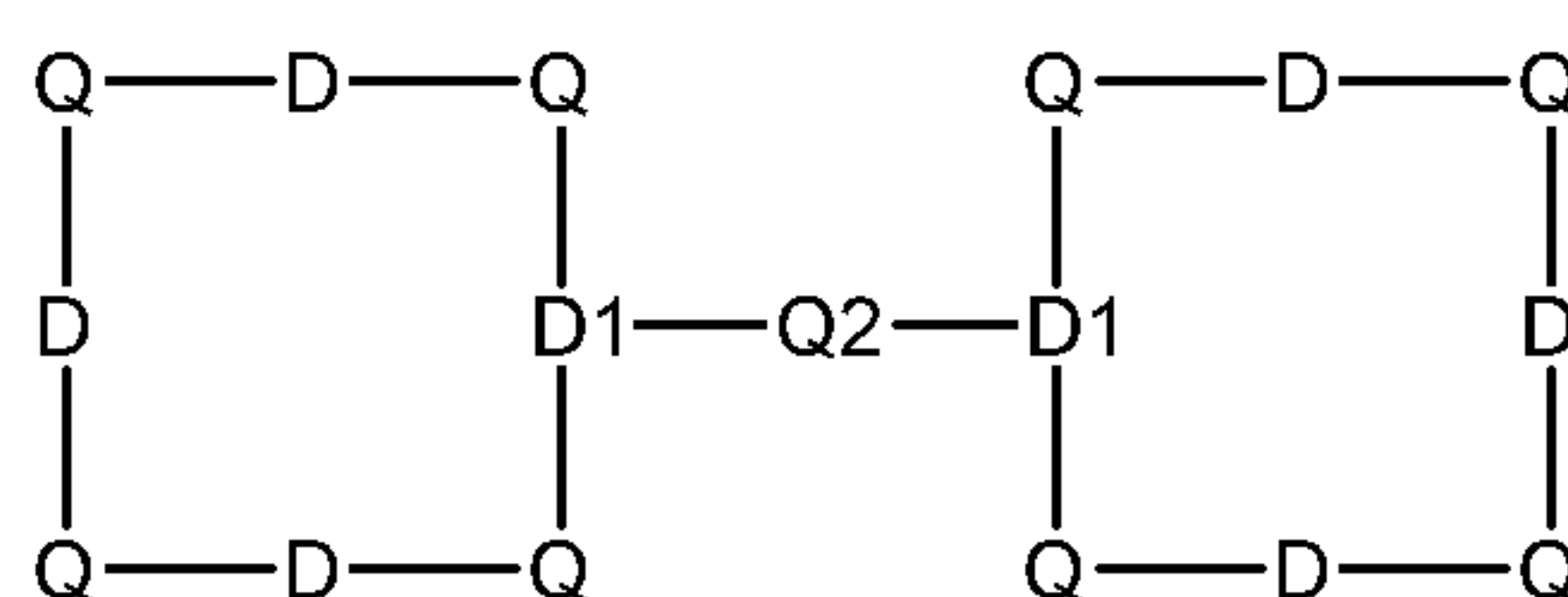
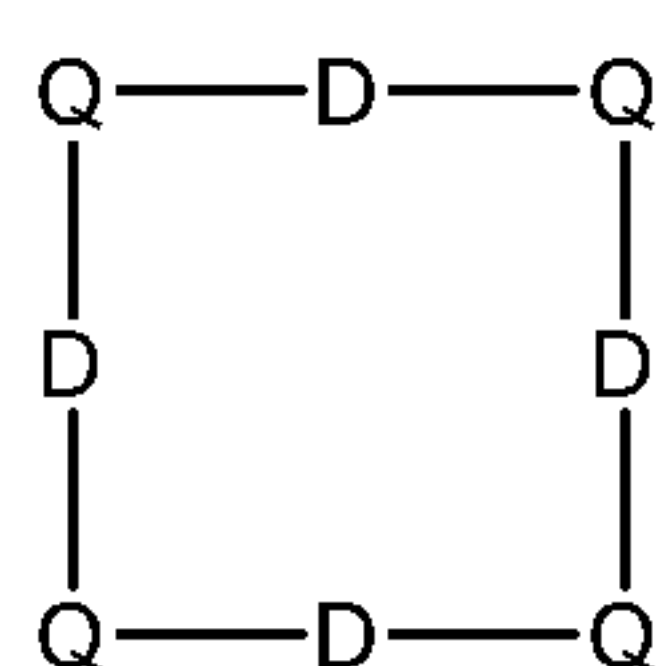


- where R4 is selected from the group consisting of optionally C₁-C₆alkyl-substituted pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl or thiazol-2-yl group, this will be typically be selected from optionally C₁-C₆alkyl-substituted pyridin-2-yl, imidazol-2-yl, imidazol-4-yl or benzimidazol-2-yl group, with unsubstituted pyridin-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl groups being more typical, and unsubstituted pyridin-2-yl most typical;
- either one or both R1 groups in Formulae (VII) or (VII-B) can be independently optionally substituted C₁-C₂₄ alkyl groups, more typically unsubstituted C₁-C₂₄ alkyl groups, for example C₁-C₁₈ alkyl groups, such as wherein one or both R1 groups are methyl;
- either one or both R1 groups in Formula (VII) or (VII-B) can be independently optionally substituted C₆-C₁₀arylC₁-C₂₄alkyl groups, more typically unsubstituted C₆-C₁₀arylC₁-C₂₄alkyl groups, for example C₆-C₁₀arylC₁-C₁₂alkyl groups, most typically benzyl;
- either one or both R1 groups in Formulae (VII) or (VII-B) can be independently CZ₂R4, whereby to define ligands of Formulae (VII') and (VII'-B) as referred to hereinafter, wherein Z is as defined for moiety R2 and typically hydrogen, R4 can be an optionally C₁-C₆alkyl-substituted pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl, this will be typically be selected from optionally C₁-C₆alkyl-substituted pyridin-2-yl, imidazol-2-yl, imidazol-4-yl, and benzimidazol-2-yl, more typically pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl;
- often all R1 groups in Formulae (VII) or (VII-B) are the same and typically selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl.

- more often, for formula (VII) one R1 group is the same as both R2 groups and typically all selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl. Equally often, both R1 groups are selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl;
- often all R1 groups in Formulae (VII') or (VII'-B) are the same and typically selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl.
- more often, for formula (VII') one R1 group is the same as both R2 groups and typically all selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl. Equally often, both R1 groups are selected from pyridin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, or benzimidazol-2-ylmethyl.

Specific embodiments of ligands of formula (VII) are N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)ethylene-1,2-diamine and N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine, as disclosed by J Glerup *et al.* (*Inorg. Chem.*, **33**, 4105-4111 (1994)). Specific embodiments of ligands of formula (VII) are those wherein one R1 and two R2 are -CH₂-R4 are described in WO 02/077145 and EP 1 001 009 A (trispicen ligands). Examples of most suitable trispicen ligands are N-C₁-C₂₀-alkyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, with N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, and N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine being most preferred. The ligand Tpen (N, N, N', N'-tetrakis(pyridin-2-ylmethyl)ethylene-1,2-diamine) is described in WO 97/48787. The synthesis of the ligand N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine has been described by S. Tong *et al.* (*Open Journal of Inorganic Chemistry*, **2**, 75-80 (2012)). Other suitable trispicens are described in WO 02/077145 and EP 1 001 009 A. Further examples of trispicens are described in WO 00/12667, WO2008/003652, WO 2005/049778, EP 2 228 429 and EP 1 008 645.

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formulae (VIII) or (VIII-B):



(VIII)

(VIII-B)

wherein:

each Q group independently represents $-CY_2-$ or $-CY_2CY_2-$, in which each Y is independently selected from hydrogen, C_{1-24} alkyl, or a C_{6-10} aryl;

5 each D group independently represents a heteroarylene group or a group of the formula $-NR-$, with the proviso that at least one D group represents a heteroarylene group;

each D1 group represents a group of the formula $-NR'-$;

the two $-R'$ groups of the two D1 groups together form bridging moiety $-Q2-$;

10 $Q2$ is a bridge selected from the group consisting of a C_{1-6} alkylene moiety, a C_{6-10} arylene moiety, or a moiety comprising one or two C_1-C_3 alkylene units and one C_6-C_{10} arylene unit, which bridge may be optionally substituted one or more times with independently selected C_{1-24} alkyl groups and OH groups; and

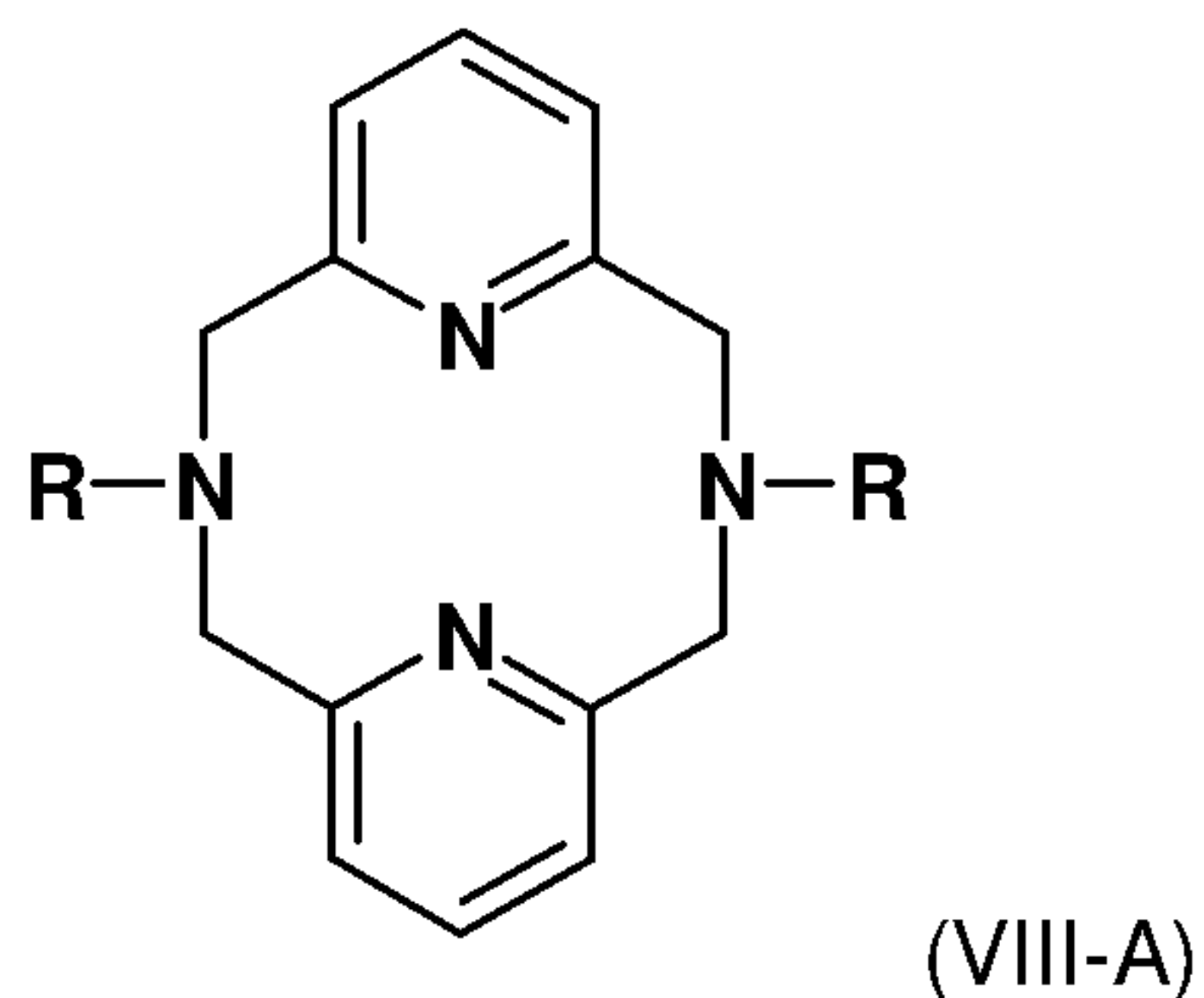
15 each R group independently represents H, C_{1-24} alkyl, C_{6-10} aryl or C_{5-10} heteroaryl.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formulae (VIII) and (VIII-B):

- each R is typically independently selected from hydrogen or methyl;
- 20 • where a bridge $Q2$ is present, this is typically an ethylene or *n*-propylene bridge;
- each R group is typically the same;
- each Q is typically $-CY_2-$;
- Y is typically hydrogen and thus each Q is typically $-CH_2-$; and
- 25 • where a group D is heteroarylene, this is typically pyridylene, in particular pyridin-2,6-diyl.

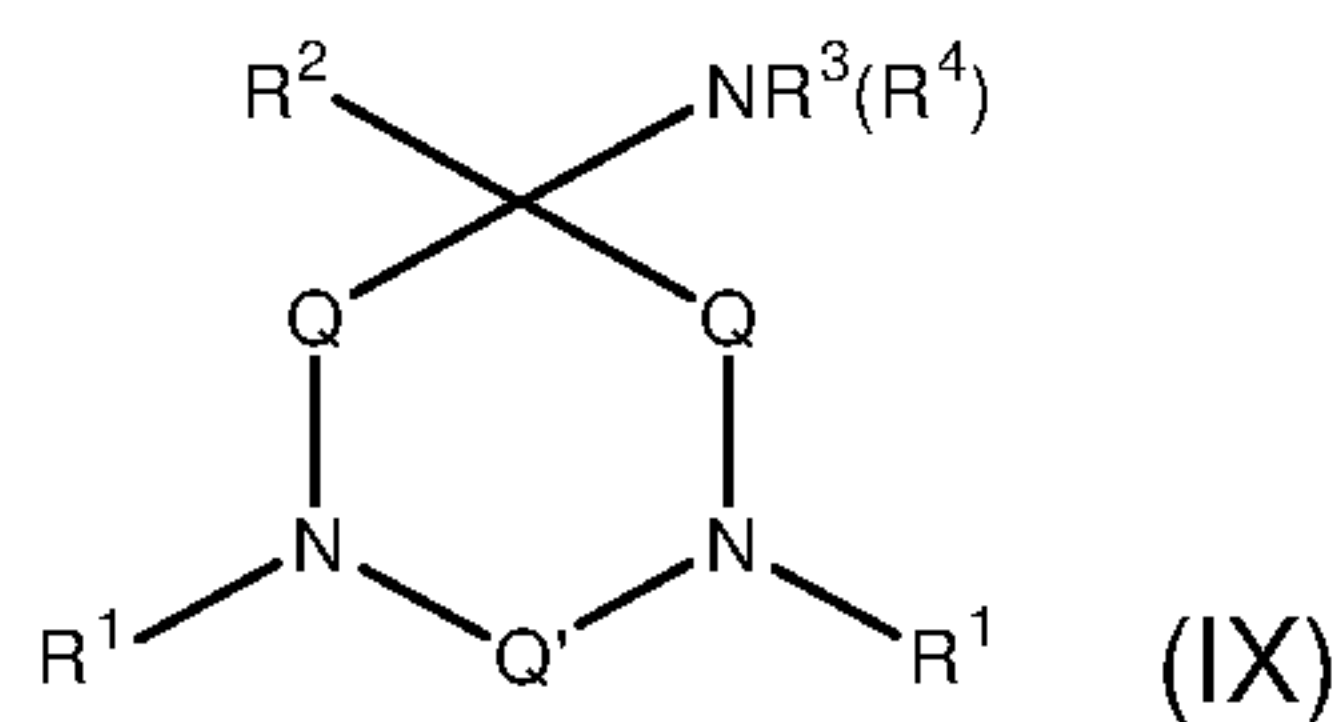
According to particular embodiments, ligands of formula (VIII) are of formula (VIII-A), in which wherein R is as defined for formulae (VIII) and (VIII-B), including the particular embodiments immediately hereinbefore described:

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According to specific embodiments, ligands of formula (VIII) (and formula (VIII-A)) are selected from 2,11-diaza[3.3](2,6-pyridinophane) (a compound of formula (VIII-A) in which each R is hydrogen) and N,N'-dimethyl-2,11-diaza[3.3](2,6-pyridinophane) (a compound of formula (VIII-A) in which each R is methyl), as described in WO 99/065905 A1 (Unilever plc *et al.*).

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formula (IX):



wherein:

each of -R¹, -R², -R³ and -R⁴ independently represents -H, -C₁₋₂₄alkyl, -C₆₋₁₀aryl or a group comprising a heteroatom capable of coordinating to a metal ion, which aryl and heteroatom-comprising groups may each be optionally substituted with one or more C₁₋₄alkyl groups;

Q represents methylene or ethylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group; and

Q' represents ethylene or n-propylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group.

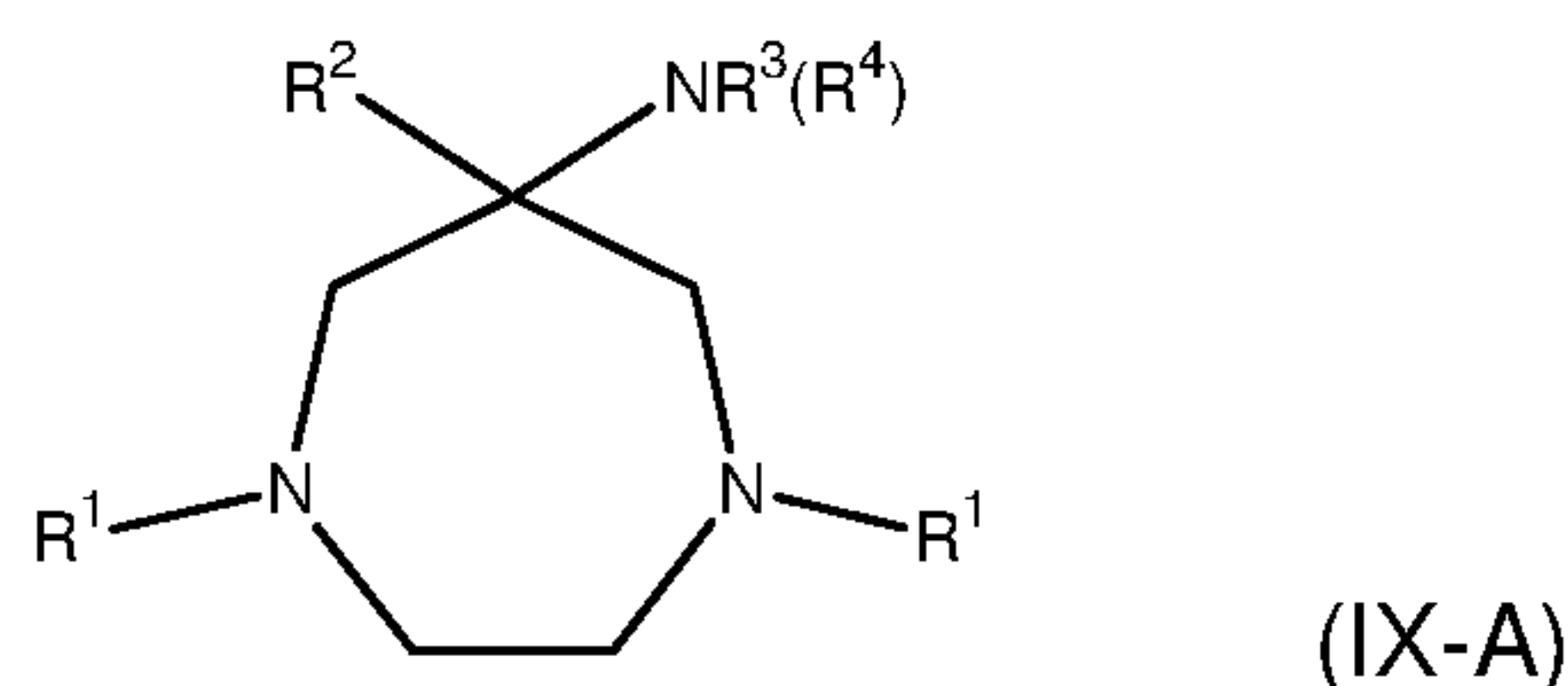
The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formula (IX):

- any of R¹, R², R³ or R⁴ is a C₁₋₂₄alkyl, which is often a C₁₋₁₀alkyl, and which is more often C₁₋₆alkyl, e.g. methyl.

- where any of R^1 , R^2 , R^3 or R^4 is a group comprising a heteroatom capable of coordinating to a metal ion, such groups may be the same or different. The heteroatom is typically present in a heteroaryl or non-aromatic heterocyclic ring, often a heteroaryl-containing group, which is optionally substituted with one or more (typically no or one) C_{1-4} alkyl groups. Often, groups containing a heteroatom comprise one or more nitrogen atoms, for example one or two nitrogen atoms, often one nitrogen atom; and/or the ring containing the heteroatom (e.g. the one or more nitrogen atoms, for example one or two nitrogen atoms, often one nitrogen atom) is connected to the remainder of formula (IX) through an alkylene linker, typically a straight-chain alkylene linker, comprising from 1 to 6 carbon atoms (i.e. typically methylene, ethylene, n-propylene, n-butylene, n-pentylene and n-hexylene), often methylene or ethylene and particularly often methylene.
- where one or more of R^1 , R^2 , R^3 and R^4 comprises a heteroaryl group as described herein, the heteroaryl group may be, for example, pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, 1,2,3- or 1,2,4-triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. According to particular embodiments, the heteroaryl group is pyridine. Where any of R^1 , R^2 , R^3 or R^4 comprises a heteroaryl group, the heteroaryl group may be optionally substituted one or more times with C_{1-4} alkyl groups. Typically, any heteroaryl groups in R^1 , R^2 , R^3 or R^4 are either unsubstituted or substituted once with a C_{1-4} alkyl group. In particular embodiments, such heteroaryl groups are unsubstituted.
- typically, although not necessarily, where one or more of R^1 , R^2 , R^3 and R^4 comprises a pyridine ring, this is connected to the remainder of formula (IX) through the 2-position (i.e. the heteroaryl group is an optionally C_{1-4} alkyl-substituted 2-pyridyl, e.g. 2-pyridyl). More typically still, although also not necessarily, pyridyl groups (in particular 2-pyridyl groups) are connected to the remainder of formula (IX) through alkylene linkers (as described herein), for example methylene. According to particular embodiments, one or more of R^1 , R^2 , R^3 and R^4 is 2-pyridylmethyl. According to other particular embodiments one or more of R^1 , R^2 , R^3 and R^4 is 2-pyridylmethyl and optionally R^2 is hydrogen or methyl.
- Q and Q' are optionally substituted alkylene groups as hereinbefore defined. The C_{1-24} alkyl groups with which these alkylene groups may be substituted are

typically C₁₋₁₈ alkyl groups. The C₆₋₁₀ aryl groups may be phenyl or naphthyl. According to other particular embodiments, Q is an optionally substituted methylene and Q' is an optionally substituted ethylene. According to still more particular embodiments, Q and Q' are unsubstituted, for example Q is an unsubstituted methylene and Q' is an unsubstituted ethylene.

Reflecting, in part, some of the particular embodiments of chelants of formula (IX) described above, particular embodiments of chelants of formula (IX) may be defined by chelants of formula (IX-A):



wherein:

each -R¹ is independently -H, -C₁₋₂₄alkyl, -C₆₋₁₀aryl or pyridin-2ylmethyl, which aryl or pyridine-2-yl is optionally substituted with C₁₋₄alkyl;

-R² represents -H or -CH₃; and

each -R³ and -R⁴ is independently -C₁₋₂₄alkyl, -C₆₋₁₀aryl or pyridin-2ylmethyl, which aryl or pyridine-2-yl is optionally substituted with C₁₋₄alkyl, for example wherein:

each -R¹ is independently -H, -C₁₋₂₄alkyl or pyridin-2ylmethyl, which pyridine-2-yl is optionally substituted with C₁₋₄alkyl;

-R² represents -H or -CH₃; and

each -R³ and -R⁴ is independently -C₁₋₂₄alkyl or pyridin-2ylmethyl, which pyridinyl is optionally substituted with C₁₋₄alkyl.

In many embodiments of the chelants of formula (IX) (and (IX-A)), the two R¹ groups are the same.

According to further particular embodiments of the chelants of formula (IX) (and (IX-A)), each R¹ independently represents methyl or pyridin-2ylmethyl, -R² represents methyl and -R³ and -R⁴ each independently represents a -C₁₋₂₄alkyl or -C₆₋₁₀aryl or pyridin-2ylmethyl.

Particular chelants of formulae (IX) and (IX-A) are:

6-dimethylamino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane;

6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane;

1,4,6-trimethyl-6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-diazacycloheptane;

- 6-amino-1,4,6-trimethyl-1,4-diazacycloheptane;
 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane;
 1,4,6-trimethyl-6-(pyridin-2-ylmethyl)amino)-1,4-diazacycloheptane;
 6-{N,N-bis(pyridin-2-ylmethyl)amino}-1,4,6-trimethyl-1,4-diazacycloheptane; and
 5 6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane.

According to further embodiments, the chelant capable of chelating at least one iron ion, particularly in its II, III, IV or V oxidation state, through at least three nitrogen atoms is a macrocyclic tetradentate ligand of formula (X):



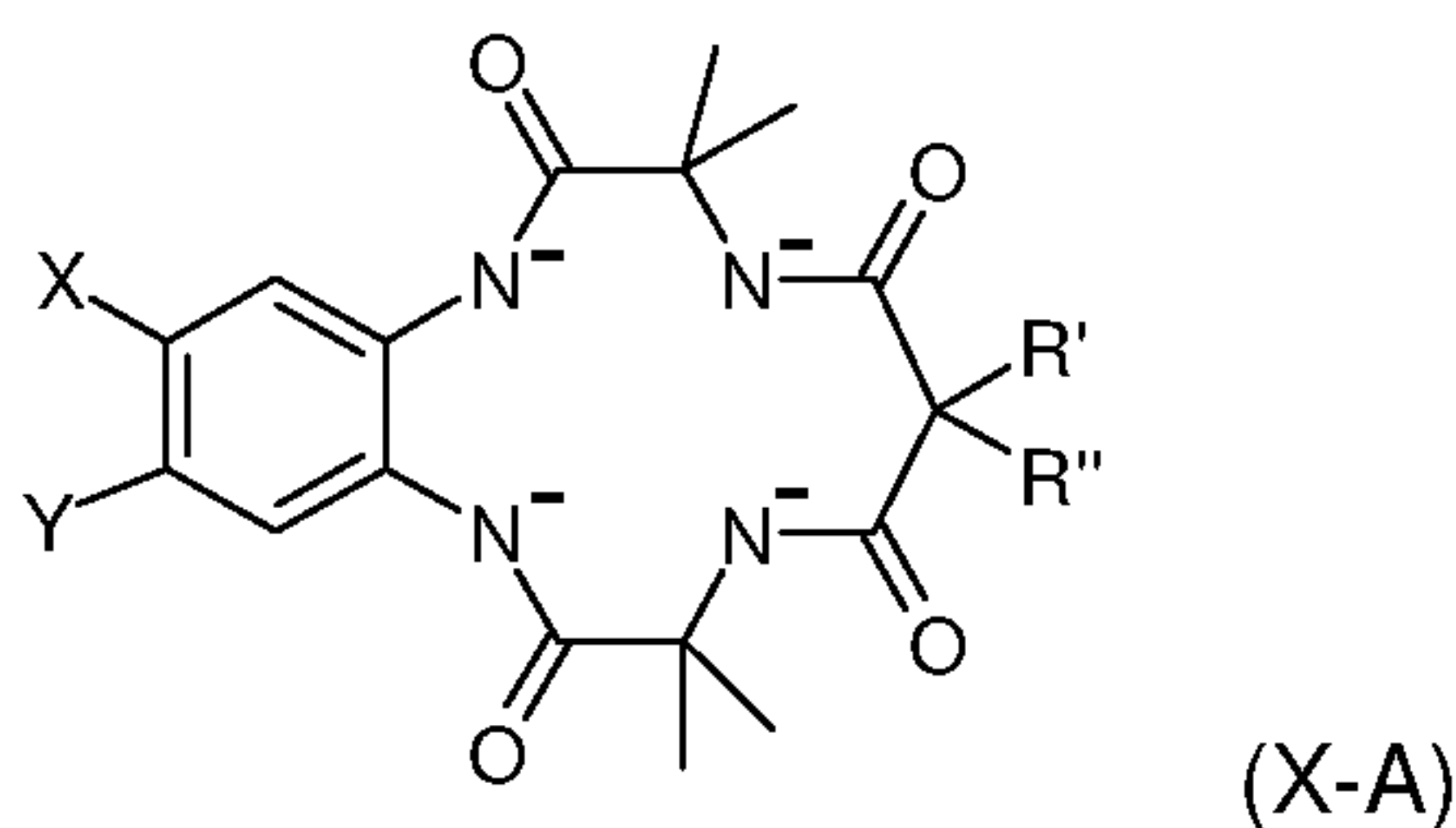
wherein:

- each X_2 and X_3 independently represents a bridging group $(CRR')_n$, wherein:
 n is an integer between 0 and 3; and
 15 each R and R' is independently selected from a group consisting of C_1 - C_{24} alkyl, cyclo- C_3 - C_8 alkyl, cyclo- C_4 - C_8 alkenyl, C_1 - C_{24} alkenyl, C_6 - C_{10} aryl, C_1 - C_{24} alkynyl and C_6 - C_{10} aryl- C_1 - C_{24} alkyl, C_1 - C_{24} alkoxy and phenoxy each of which may be optionally C_1 - C_6 alkyl-substituted, H, F, Cl, Br, I, CH_2CF_3 and CF_3 ; or one R and one R' attached to a common carbon atom may together with that carbon atom form a substituted or
 20 unsubstituted 1,2-phenylene moiety or a cycloalkylene, cycloalkenylene, heterocycloalkylene or heterocycloalkenylene moiety.

Examples of CRR' moieties where cycloalkylene are cyclopropylene, cyclobutylene, cyclopentylene and cyclohexylene.

- Particular preferred tetraamido macrocyclic ligands of formula (X) are those
 25 having a substituted aromatic substituent fused directly into the ligand's cyclic structure. For example, a useful subclass of these ligands has the structure (X-A):

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wherein:

X and Y may be independently selected from H; electron-donating groups
 5 selected from C₁-C₂₄alkyl, C₁-C₂₄alkoxy, C₆-C₁₀aryloxy and C₆-C₁₀arylC₁-C₂₄alkyloxy;
 and electron-withdrawing groups selected from F, Cl, Br, I, COOR (R is C₁-C₂₄alkyl),
 CONH(CH₂)₂N(R)₃⁺ (R is C₁-C₂₄alkyl), SO₃⁻, OSO₃⁻, OSO₃R (R is selected from H, C₁-
 C₂₄alkyl, C₆-C₁₀aryl, C₆-C₁₀arylC₁-C₂₄alkyl), CH₂CF₃, CF₃ and NO₂; and

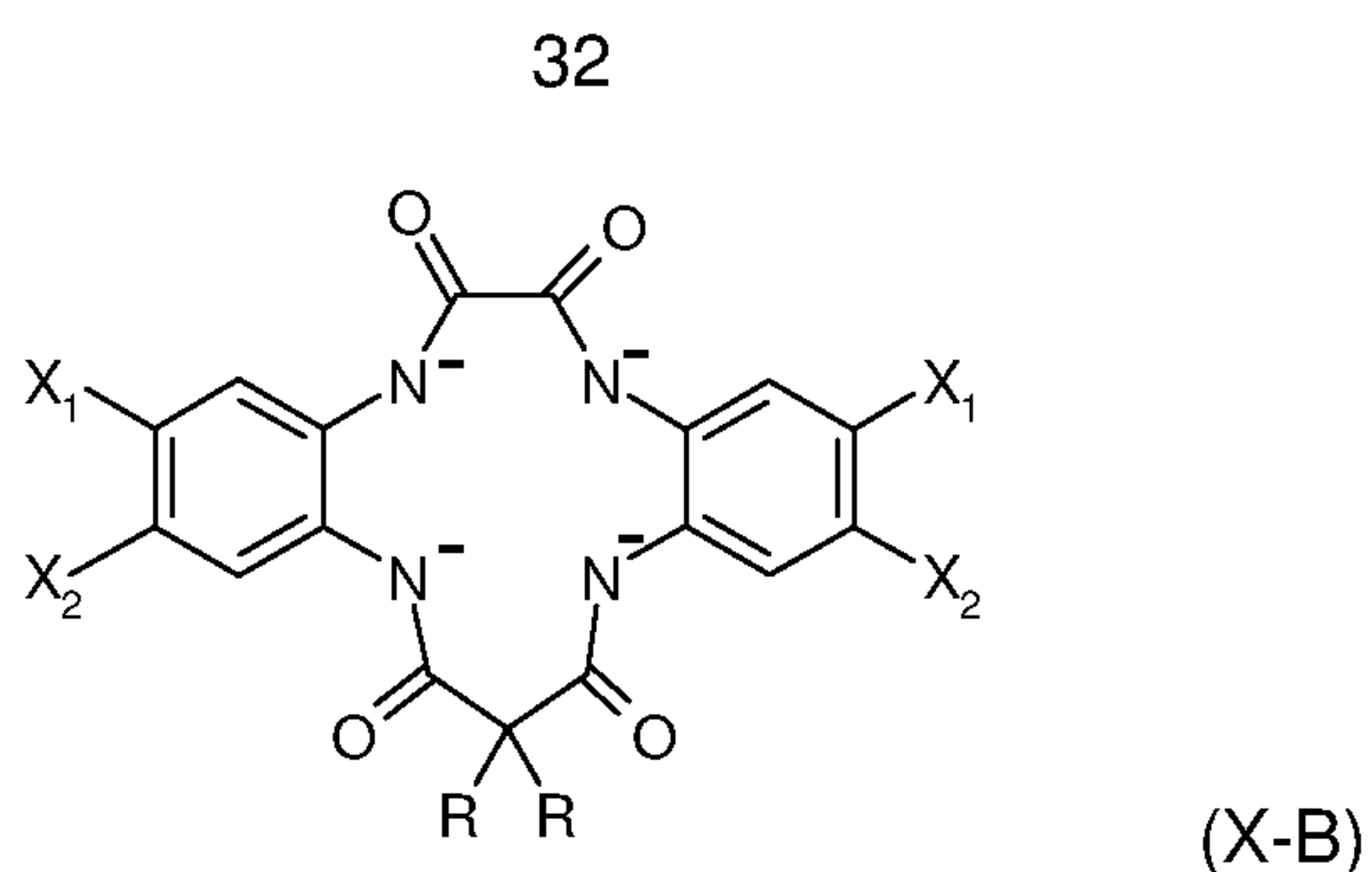
R' and R'' may each be independently selected from the group consisting of H,
 10 C₁-C₂₄alkyl, C₃-C₂₄cycloalkyl, C₃-C₂₄cycloalkenyl, C₂-C₂₄alkenyl, C₆-C₁₀aryl, C₂-
 C₂₄alkynyl, C₆-C₁₀arylC₁-C₂₄alkyl, halogen, C₁-C₂₄alkoxy and phenoxy substituents; or
 together with the carbon atom to which R and R'' are attached form a C₃-
 C₂₄cycloalkylene or C₃-C₂₄cycloalkenylene ring.

Examples of suitable X and Y groups, and as possibilities for the optionally
 15 substituted 1,2-phenylene moiety referred to in the definition for formula (X) are
 independently selected from hydrogen, C₁-C₆alkyl (e.g. methyl), methoxy, nitro, chloro,
 SO₃⁻, OSO₃⁻, COOR with R=H or CH₃, and CONH(CH₂)₂N(CH₃)₃⁺.

Often R' and R'' are identical, and selected from methyl, ethyl, fluoro; or
 together with the carbon atom to which they are attached form a three-membered
 20 carbon ring (cyclopropylene) or four-membered carbon ring (cyclobutylene).

Tetraamido macrocyclic iron complexes are usually penta-coordinate species,
 usually with an axial aqua ligand (X according to formula (A1) below) in the solid state,
 but may be hexa-coordinate with any combination of two suitable axial ligands (X) with
 the two being the same or different. The aqua complexes are synthesized as such or
 25 as the corresponding chloro species with Cl⁻ instead of H₂O as axial ligand in a five-
 coordinate species. Suitable cationic counterions are those outlined below in the
 discussion of generic formula (A1) below.

Other preferred tetradentate macrocyclic ligands according to formula (X) belong
 to generic formula (X-B):



wherein:

$X_1=X_2=H$, $X_1=X_2=Cl$, or $X_1=NO_2$ and $X_2 = H$, and $R=$ methyl.

5 The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of complexes comprising the ligands of formula (X) (including formulae (X-A) and (X-B)):

- the tetradentate macrocyclic ligands, will be typically bound to an iron ion, as defined in (A1) wherein $a=k=1$.
- 10 • when bound to the iron ion, the tetradentate macrocyclic ligands are quadrupally negatively charged, leading to anionic transition metal complexes if the oxidation state of the metal ion is II or III (the structures in formulae (X), (X-A) and (X-B) have been depicted in their deprotonated form, i.e. quadrupally negatively charged). When not bound to a metal, the ligands of formulae (X),
- 15 (X-A) and (X-B) will most often contain neutral amide groups, i.e. the amidate structures as depicted above will be protonated.
- suitable cationic counterions are those outlined below generic formula (A1). Non-coordinating cationic counterions that are particular suitable are Li^+ , K^+ and Na^+ .

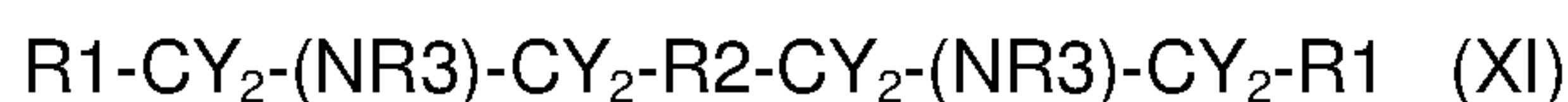
20 As outlined above, the iron complex contains optionally axial ligands such as chloride or water. The non-coordinating counterion is typically cationic and are listed below the generic formula (A1). Preferred ligands of formula (X) are 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H), 5,6(4,5-di-chlorobenzo)-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetracyclotridecane, 5,6(4,5-di-chlorobenzo)-3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 5,6-benzo-3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 3,4,8,9-tetrahydro-6,6-difluoro-3,3,9,9-tetramethyl-13-nitro-1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetraoxo, 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H), 3,4,8,9-tetrahydrospiro-3,3,9,9-tetramethyl-6,1'-cyclopropane-

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1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetraoxo, 15,15-dimethyl-5,8,13,17-tetrahydro-5,8,13,17-tetraazadibenzo[a,g]cyclotridecene-6,7,14,16-tetraoxo, and have been disclosed in for example US7060818, WO2011/137190 and in. *J. Am. Chem. Soc.*, **132**, 9774 (2010). A particular chelant is 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H). Various methods for making tetradentate macrocyclic ligands of formula (X), further details about and uses for these macrocyclic ligands are disclosed in the following U.S. patents: U.S. Patents Nos. 5, 847,120, 5,853,428, 5,876,625, 6,011,152, 6,051,704, 6,054,580, 6,099,586, 6,100,394, 6,136,223, 6,241,779, 6,992,184, and 7,060,818, the disclosures of each of which is hereby incorporated herein by reference.

According to further embodiments, the chelant capable of chelating at least one iron ion through at least three nitrogen atoms is of formula (XI):



15

wherein:

each Y is independently selected from H, CH₃, C₂H₅ and C₃H₇;

each R1 is independently selected from an optionally C₁-C₆alkyl-substituted C₅-C₁₀heteroaryl group, whereby the C₅-C₁₀heteroaryl group is selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl;

R2 is selected from an optionally C₁-C₆alkyl-substituted C₅-C₆heteroarylene group, whereby the C₅-C₆heteroarylene group is selected from pyridin-2,6-diyl, pyrazin-2,6-diyl, pyrazol-3,5-diyl, pyrazol-1,3-diyl, pyrrol-2,5-diyl, imidazol-2,5-diyl, imidazol-1,4-diyl, pyrimidin-2,6-diyl, 1,2,4-triazol-3,5-diyl, 1,2,4-triazol-1,3-diyl, 1,2,4-triazol-2,4-diyl, 1,2,3-triazol-1,4-diyl, 1,2,3-triazol-2,5-diyl, and thiazol-2,5-diyl;

each R3 is independently selected from optionally C₁-C₆-substituted C₁₋₂₄alkyl, C₆₋₁₀aryl, C₆₋₁₀arylC_{1-C24}alkyl, C₅₋₁₀heteroaryl, C₅₋₁₀heteroarylC_{1-C24}alkyl.

The following features, alone or in combination, as the context permits (i.e. where not conflicting) are typical (but not essential) features of the ligands of formula (XI):

- each Y is typically hydrogen;

- each R1 is independently selected from an unsubstituted C₅-C₁₀heteroaryl group, the C₅-C₁₀heteroaryl group being typically independently selected from pyridin-2-yl, quinolin-2-yl, imidazol-2-yl, and thiazol-2-yl;
- each R1 is the same;
- 5 • each R1 = pyridin-2-yl is most typical;
- R2 is typically unsubstituted pyridin-2,6-diyl;
- each R3 is independently selected from C₁-C₆ substituted C₁₋₁₈alkyl, C₆₋₁₀arylC₁₋₁₈alkyl, pyridin-2-ylmethyl, pyrazin-2-ylmethyl, quinolin-2-ylmethyl, pyrazol-1-ylmethyl, pyrazol-3-ylmethyl, pyrrol-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, benzimidazol-2-ylmethyl, pyrimidin-2-ylmethyl, 1,2,3-triazol-1-ylmethyl, 1,2,3-triazol-2-ylmethyl, 1,2,3-triazol-4-ylmethyl, 1,2,4-triazol-3-ylmethyl, 1,2,4-triazol-1-ylmethyl, and thiazol-2-ylmethyl;
- 10 • often, each R3 is independently selected from unsubstituted C₁₋₁₂alkyl, C₆arylC₁₋₁₂alkyl, pyridin-2-ylmethyl, quinolin-2-ylmethyl, pyrazol-1-ylmethyl, pyrazol-3-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, benzimidazol-2-ylmethyl, 1,2,3-triazol-1-ylmethyl, 1,2,3-triazol-2-ylmethyl, 1,2,3-triazol-4-ylmethyl, 1,2,4-triazol-3-ylmethyl, 1,2,4-triazol-1-ylmethyl, and thiazol-2-ylmethyl;
- 15 • more typically, each R3 is independently selected from unsubstituted C₁₋₈alkyl, C₆arylCH₂, pyridin-2-ylmethyl, quinolin-2-ylmethyl, imidazol-2-ylmethyl, imidazol-4-ylmethyl, benzimidazol-2-ylmethyl; and
- 20 • even more typically each R3 is independently selected from methyl, CH₂C₆H₅, and pyridin-2-ylmethyl;
- each R3 is the same.

25 In a specific embodiment of the ligands of formula (XI), Y=H, R1 = pyridin-2-yl, R2=pyridin-2,6-diyl, and R3 = methyl, i.e., is 2,6-bis[(*N*-methyl-{*N*-(2-pyridylmethyl)}amino)methyl]pyridine.

30 It will be understood that, in the polydentate ligands of formulae (I-B), (II-B), (V-B), (V-C), (VII-B) and (VIII-B), each of which comprises a bridge, the resultant polydentate ligands are capable of chelating two iron ions. Such polydentate ligands, as well as the other polydentate ligands described herein may be readily accessed by the skilled person.

35 For example, with regard to ligands of formulae (I-B), the skilled person will recognise, for example, if Q=1,3-propylene (-CH₂CH₂CH₂-), that by reacting the appropriate piperidone precursor, formaldehyde and 1,3-diamino-propane, the desired

bridged bispidon ligand can be obtained, as described by K. Born *et al.* (*J. Biol. Inorg. Chem.*, **12**, 36-48 (2007)).

With regard to ligands of formulae (II-B), reference is made to the procedure described by K-O Schaefer *et al.* (*J. Am. Chem. Soc.*, **120**, 131040-13120 (1998)),
5 describing the synthesis of bridged triazacyclononane (TACN) compounds.

With regard to ligands of formulae (V-B), the skilled person will recognise, for example, that N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (N3py) (the synthesis of which is described by G. Roelfes *et al.* (*J. Am. Chem. Soc.*, **122**, 11517-11518 (2000)), may be reacted with, 1,2-dibromoethane, for example to yield 1,2-bis(N-
10 (pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine)-ethane, analogously to the synthesis of the TACN-bridged ligands described by K-O Schaefer *et al.* (*supra*) or the procedure described by M Klopstra *et al.* (*Eur. J. Inorg. Chem.*, 846-856 (2000)) involving reaction N3py with benzylchloride to produce benzyl-N3py.

With regard to ligands of formulae (V-C), the skilled person will recognise, for example, that N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (MeN3py)
15 (the synthesis of which is described by M Klopstra *et al.* (*supra*)) may be reacted with BuLi at low temperature and then with, for example, dibromoethane to yield the bridged ligand, analogously to the synthesis of MeN4py and benzylN4py described elsewhere (see for example EP0909809B).

With regard to ligands of formula (VII-B), the skilled person will recognise, for example that N,N'-bis(2-pyridylmethyl)ethylene diamine (prepared as described by L Xu *et al.* (*Inorg. Chem.*, **39**, 5958-5963 (2000)) can be reacted with, for example, 1,3-dibromopropane (analogously to the synthesis of the TACN-bridged ligands described by K-O Schaefer *et al.* (*supra*)), to yield 1,3-bis(N,N'-bis(2-pyridylmethyl)ethylene
20 diamine)-propane. Subsequently, methylation can be effected to access the methylated ligand, 1,3-bis(N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethylenediamine)-propane, analogously to synthesis of MeN3py by M Klopstra *et al.* (*supra*).

In case a polyamine based ligand of formula (VII-B) is sought (i.e. wherein $n \geq 1$) with each R1 group = pyridin-2ylmethyl according to formula (VII-B), the skilled
30 person will understand that in such a case, the appropriate polyamine precursor, such as 1,4,7,10-tetraazadecane, can be allowed to react with picolylchloride, such as described in many articles (see e.g. L Xu *et al.* (*Inorg. Chem.*, **39**, 5958-5963 (2000)), to yield N,N,N',N'',N''',N''''-pentakis(pyridine-2-ylmethyl)-1,4,7,10-tetraazadecane. Numerous permutations with other R1 groups or number of aliphatic amine groups
35 according to formula (VII) can be invented by the skilled person.

With regard to ligands of formulae (VIII-B), the skilled person will recognise, for example that 2,11-diaza[3.3](2,6-pyridinophane (see WO 99/065905 A1) can be reacted with 1,2-dibromoethane (analogously to the synthesis of the TACN-bridged ligands described by K-O Schaefer *et al.* (*supra*)), to yield 1,2-bis(2,11-diaza[3.3](2,6-pyridinophane)ethane. Subsequently, methylation can be effected to access the methylated ligand, 1,2-bis(11-methyl-2,11-diaza[3.3](2,6-pyridinophane)ethane, analogously to synthesis of MeN3py by M Klopstra *et al.* (*supra*).

Ligands of formula (XI) can be either prepared by procedures as outlined above for different bridged ligands via a reaction of the appropriate amine-based precursor with e.g. dibromo-ethane, but they may also be prepared by reacting the appropriate free polyamine precursor with e.g. picolinic chloride, via the well-established procedures to couple picolinic chloride to free amines (see various references of the examples given in the patent application).

It will be understood that the procedures outlined above can be adapted to access other polydentate ligands of formulae (I-B), (II-B), (V-B), (V-C), (VI-B), (VII-B), (VIII-B) and (XI) within the normal ability of those of skill in the art and that alternative synthetic procedures will be readily evident to the skilled person.

Notwithstanding the discussion of polydentate ligands of formulae (I-B), (II-B), (V-B), (V-C), (VI-B), (VII-B), (VIII-B), and (XI) however, the polydentate ligands of the invention are often capable of chelating one iron ion and thus, of the chelants described above, chelants selected from the group consisting of ligands of formula (I), (II), (III), including (III-A), (IV), (V), (VI), (VII), (VIII), including (VIII-A), (IX), including (IX-A), (X), including (X-A) and (X-B), and (XI) are typical.

As described herein, the iron complexes referred to in connection with the various aspects of this invention are formed from a chelant capable of chelating at least one iron ion through at least three nitrogen atoms, including the specific examples of such ligands described in detail herein. These ligands comprise donor atoms, which coordinate to one or more iron ions of the iron complexes described herein.

The concentration of the iron complexes in the aqueous media described herein is typically between about 0.001 and about 50 μ M, often between about 0.01 and 20 μ M, and according to particular embodiments between about 0.1 and about 5 μ M.

It is to be understood that, whilst the complexes may be introduced into the methods of the first and second aspect of the invention, and the aqueous medium in accordance with the third aspect of the invention may be prepared from such

complexes, *per se*, which we refer to herein as well-defined complexes, well-defined complexes are not an essential feature of the invention.

By a well-defined complex is meant herein (as the term is used customarily in the art) a pre-formed complex (i.e. not one prepared *in situ*), which has been, or may be, isolated such that it is susceptible to characterisation (i.e. definition) and analysis (e.g. to determine its structure and degree of purity). In contrast, a complex that is not well-defined is one that is prepared *in situ* without isolation from the medium (e.g. reaction medium) in which it is prepared, and optionally used. Well-defined complexes are not a mandatory feature of the present invention, however: an appropriate iron complex may be prepared by mixing an appropriate amount of polydentate ligand with an appropriate amount and source of iron ions, in a desired stoichiometry.

It will be understood that there is no particular limitation as to the source of the iron ions from which the iron complexes described herein may be prepared. Typically, however, salts are selected from the group consisting of optionally hydrated FeCl_2 , FeBr_2 , $\text{Fe}(\text{NO}_3)_2$, FeSO_4 , $\text{Fe}(\text{CF}_3\text{SO}_3)_2$, $\text{Fe}(\text{acetylacetonate})_2$, $\text{Fe}(\text{acetylacetonate})_3$, $\text{Fe}(\text{R}_5\text{COO})_3$ (including $\text{Fe}(\text{acetate})_3$) and $\text{Fe}(\text{R}_5\text{COO})_2$, wherein R_5 is selected from a C_1 - C_{24} alkyl. Where the salt comprises two or more R_5 groups, these can be the same or different. The alkyl moieties, by which is meant saturated hydrocarbyl radicals, may be straight-chain or comprise branched and/or cyclic portions. Often the iron salt is selected from the group consisting of optionally hydrated FeCl_2 , FeBr_2 , $\text{Fe}(\text{NO}_3)_2$, FeSO_4 and $\text{Fe}(\text{OAc})_2$.

The term optionally hydrated is well known in the art. Metal salts often contain water molecules within a crystal lattice, which will remain present unless the hydrated metals salts are subjected to specific drying steps by heating or drying under reduced pressure. However, partially or fully dehydrated metal salts can also be used. For example, iron(II)chloride can be bought as a tetrahydrate salt or as a dehydrated (anhydrous) salt. Commercial iron sulfate is commercially available in dehydrated (anhydrous), monohydrate, and heptahydrate forms.

According to particular embodiments of the invention, the complex used in accordance with the first and second aspect of the invention, or present in the aqueous medium of the third aspect, kit of the fourth aspect, or composition of the fifth aspect, of the invention, is pre-formed (used interchangeably herein with the term “well-defined”). Often it is desirable to use preformed iron complexes.

The iron complexes of use according to the various aspects of the invention are typically of the general formula (A1):



in which:

Fe represents an iron ion selected from Fe(II), Fe(III), Fe(IV) and Fe(V);

5 L represents a polydentate ligand, which is a chelant capable of chelating at least one iron ion through at least three nitrogen atoms, as defined herein, or a protonated or deprotonated derivative thereof;

each X independently represents a coordinating species selected from any mono-, bi- or tri-charged anion or a neutral molecule able to coordinate an iron ion in a mono-, bi- or tridentate manner, preferably selected from O^{2-} , RBO_2^{2-} , RCOO^- , RCONR^- , OH^- , NO_3^- , NO , S^{2-} , RS^- , PO_4^{3-} , $\text{PO}_3\text{OR}^{3-}$, H_2O , CO_3^{2-} , HCO_3^- , ROH , N(R)_3 , ROO^- , O_2^{2-} , O_2^- , RCN , Cl^- , Br^- , OCN^- , SCN^- , CN^- , N_3^- , F^- , I^- , RO^- , ClO_4^- , and CF_3SO_3^- , and more preferably selected from O^{2-} , RBO_2^{2-} , RCOO^- , OH^- , NO_3^- , S^{2-} , RS^- , PO_3^{4-} , H_2O , CO_3^{2-} , HCO_3^- , ROH , N(R)_3 , Cl^- , Br^- , OCN^- , SCN^- , RCN , N_3^- , F^- , I^- , RO^- , ClO_4^- , and CF_3SO_3^- ;

15 each R independently represents a group selected from hydrogen, hydroxyl, $-\text{R}''$ and $-\text{OR}''$, wherein $\text{R}'' = \text{C}_1\text{-C}_{20}\text{alkyl}$, $\text{C}_2\text{-C}_{20}\text{alkenyl}$, $\text{C}_1\text{-C}_{20}\text{heterocycloalkyl}$, $\text{C}_6\text{-C}_{10}\text{aryl}$, $\text{C}_5\text{-C}_{10}\text{heteroaryl}$, $(\text{C}=\text{O})\text{H}$, $(\text{C}=\text{O})\text{-C}_1\text{-C}_{20}\text{alkyl}$, $(\text{C}=\text{O})\text{-C}_6\text{-C}_{10}\text{aryl}$, $(\text{C}=\text{O})\text{OH}$, $(\text{C}=\text{O})\text{O-C}_1\text{-C}_{20}\text{alkyl}$, $(\text{C}=\text{O})\text{O-C}_6\text{-C}_{10}\text{aryl}$, $(\text{C}=\text{O})\text{NH}_2$, $(\text{C}=\text{O})\text{NH}(\text{C}_1\text{-C}_{20}\text{alkyl})$, $(\text{C}=\text{O})\text{NH}(\text{C}_6\text{-C}_{10}\text{aryl})$, $(\text{C}=\text{O})\text{N}(\text{C}_1\text{-C}_{20}\text{alkyl})_2$, $(\text{C}=\text{O})\text{N}(\text{C}_6\text{-C}_{10}\text{aryl})_2$, R'' being optionally substituted by one or more functional groups E, wherein E independently represents a functional group selected from $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{OR}'$, $-\text{NH}_2$, $-\text{NHR}'$, $-\text{N(R}')_2$, $-\text{N(R}')_3^+$, $-\text{C(O)R}'$, $-\text{OC(O)R}'$, $-\text{COOH}$, $-\text{COO}^- (\text{Na}^+, \text{K}^+)$, $-\text{COOR}'$, $-\text{C(O)NH}_2$, $-\text{C(O)NHR}'$, $-\text{C(O)N(R')}_2$, heteroaryl, $-\text{R}'$, $-\text{SR}'$, $-\text{SH}$, $-\text{P(R')}_2$, $-\text{P(O)(R')}_2$, $-\text{P(O)(OH)}_2$, $-\text{P(O)(OR')}_2$, $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_3^-(\text{Na}^+, \text{K}^+)$, $-\text{S(O)}_2\text{R}'$, $-\text{NHC(O)R}'$, and $-\text{N(R')C(O)R}'$, wherein R' represents $\text{C}_6\text{-C}_{10}\text{aryl}$, $\text{C}_7\text{-C}_{20}\text{arylalkyl}$, or $\text{C}_1\text{-C}_{20}\text{alkyl}$ each of which may be optionally substituted by $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{NH}_3^+$, $-\text{SO}_3\text{H}$, $-\text{SO}_3^-(\text{Na}^+, \text{K}^+)$, $-\text{COOH}$, $-\text{COO}^-(\text{Na}^+, \text{K}^+)$, $-\text{P(O)(OH)}_2$, or $-\text{P(O)(O}^-(\text{Na}^+, \text{K}^+))_2$, and preferably each R independently represents hydrogen, $\text{C}_1\text{-C}_{40}\text{alkyl}$ or optionally $\text{C}_1\text{-C}_{20}\text{alkyl}$ -substituted $\text{C}_6\text{-C}_{10}\text{aryl}$, more preferably hydrogen or optionally substituted phenyl or naphthyl, or $\text{C}_{1-4}\text{alkyl}$;

30 Y is a non-coordinating counterion;

a is an integer from 1 to 10, typically from 1 to 4, more typically still 1 or 2;

k is an integer from 1 to 10 typically from 1 to 4, more typically still 1 or 2;

n is an integer from 1 to 10, typically from 1 to 4; and

m is zero or an integer from 1 to 20, and is typically an integer from 1 to 8.

Generally, the iron ion(s) of the complex are selected from the group consisting of Fe(II), Fe(III) and Fe(IV). Often, the complex comprises one or two such iron ions. Where the complex comprises two or more iron ions they may be of the same oxidation state or different oxidation states.

5 As used herein, within the definitions provided above for formula (A1) and elsewhere, unless a context expressly dictates to the contrary, the following definitions apply:

- 10 • By alkyl is meant herein a saturated hydrocarbyl radical, which may be straight-chain, cyclic or branched. By alkylene is meant an alkyl group from which a hydrogen atom has been formally abstracted. Typically alkyl and alkylene groups will comprise from 1 to 25 carbon atoms, more usually 1 to 10 carbon atoms, more usually still 1 to 6 carbon atoms. The simplest alkylene group is methylene (-CH₂-).
- 15 • By alkenyl is meant an unsaturated hydrocarbyl radical, which may be straight-chain, cyclic or branched, comprising one or more, typically one, non-aromatic carbon-carbon double bonds. By alkenylene is meant an alkenyl group from which a hydrogen atom has been formally abstracted. Typically alkenyl and alkenylene groups will comprise from 2 to 25 carbon atoms, more usually 2 to 10 carbon atoms, more usually still 2 to 6 carbon atoms. The simplest
20 alkenylene group is ethenylene (-CH=CH-).
- 25 • By alkynyl is meant an unsaturated hydrocarbyl radical, which may be straight-chain, cyclic or branched, comprising one or more, typically one, carbon-carbon triple bonds. By alkynylene is meant an alkynyl group from which a hydrogen atom has been formally abstracted. Typically alkynyl and alkynylene groups will
30 comprise from 2 to 25 carbon atoms, more usually 2 to 10 carbon atoms, more usually still 2 to 6 carbon atoms.
- The term aromatic used herein embraces within its scope heteroaromatic. As known to those skilled in the art, and used herein, heteroaromatic moieties may be regarded a subset of aromatic moieties that comprise one or more
35 heteroatoms, typically oxygen, nitrogen or sulfur, often nitrogen, in place of one or more ring carbon atoms and any hydrogen atoms attached thereto. Examples of heteroaromatic moieties, for example, include pyridine, furan, pyrrole and pyrimidine.
- Aromatic moieties may be polycyclic, i.e. comprising two or more fused aromatic (including heteroaromatic) rings. Naphthalene and anthracene are

examples of polycyclic aromatic moieties, and benzimidazole is an example of a polycyclic heteroaromatic moiety.

- 5 • Aryl radicals and arylene diradicals are formed formally by abstraction of one and two hydrogen atoms respectively from an aromatic moiety. Thus phenyl and phenylene are the aryl radical and arylene diradical corresponding to benzene. Similarly, pyridyl and pyridylene (synonymous with pyridindyl) are the heteroaryl radical and heteroarylene diradical corresponding to pyridine. Unless a context dictates to the contrary, pyridyl and pyridylene are typically 2-pyridyl and pyridine-2,6-diyl respectively.
- 10 • By heterocycloalkane is meant a cycloalkane, typically a C₅₋₆cycloalkane, in which one or more CH₂ moieties are replaced with heteroatoms, typically selected from the group consisting of nitrogen, oxygen and sulfur. Where the heteroatom is nitrogen, it will be understood that the CH₂ moiety is formally replaced with NH, not N. By heterocycloalkyl is meant herein a radical formed
15 formally by abstraction of a hydrogen atom from a heterocycloalkane. Typical examples of heterocycloalkyl groups are those in which the heterocycloalkyl is formed formally by abstraction of a hydrogen atom from the nitrogen atom. Typical heterocycloalkyl groups include pyrrolidin-1-yl, piperidin-1-yl and morpholin-4-yl, i.e. in which the heterocycloalkyl is formed formally by
20 abstraction of a hydrogen atom from the nitrogen atom of the parent heterocycloalkane.
- By arylalkyl is meant aryl-substituted alkyl. Analogously, by aminoalkyl is meant amino-substituted alkyl, by hydroxyalkyl is meant hydroxy-substituted alkyl and so on.
- 25 • Various alkylene bridges are described herein. Such alkylene bridges are typically although not necessarily straight chain alkylene bridges. They may, however, be cyclic alkylene groups (e.g. a C₆alkylene bridge may be cyclohexylene, and if so is typically cyclohexyl-1,4-ene). Where a bridge is, for example, a C₆-C₁₀arylene bridge, this may be, for example, phenylene or the
30 corresponding arylene formed by abstraction of two hydrogen atoms from naphthalene. Where a bridge comprises one or two C₁-C₃alkylene units and one C₆-C₁₀arylene unit, such bridges may be, for example, -CH₂C₆H₄CH₂- or -CH₂C₆H₄-. Where present, phenylene is typically phenyl-1,4-ene. It will be understood that each of these bridges may be optionally substituted one or

more times, for example once, with independently selected C₁-C₂₄ alkyl (e.g. C₁-C₁₈ alkyl) groups.

- By carboxamide is meant a compound or radical comprising the functional group -N(H)C(O)-.
- 5 • By carboxylic ester is meant a compound or radical comprising the functional group -OC(O)-.
- By alkyl ether is meant a radical of the formula -alkylene-O-alkyl, wherein alkylene and alkyl are as herein defined.

The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand(s) L, iron ion(s) and coordinating species X. If the charge z is positive, as it is in most cases, the iron complex comprises one or more iron ions and one or more non-coordinating counteranions Y. Examples of counteranions Y include RCOO⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻, S₂O₆²⁻, NO₃⁻, F⁻, Cl⁻, Br⁻, or I⁻, with R being hydrogen, C₁-C₄₀alkyl or optionally C₁-C₂₀alkyl-substituted C₆-C₁₀aryl.

15 Where z is positive, the identity of the counteranion(s) Y is, however, not an essential feature of the invention. Suitable counterions Y include those which give rise to the formation of storage-stable solids. Often counterions, including those for the preferred metal complexes, are selected from Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, PF₆⁻, RSO₃⁻, SO₄²⁻, RSO₄⁻, CF₃SO₃⁻, and RCOO⁻, with R in this context being selected from H, C₁₋₁₂ alkyl, and optionally C₁₋₆alkyl-substituted C₆H₅ (i.e. wherein C₆H₅ is substituted one or more times (e.g. once) with a C₁₋₆alkyl group; often C₆H₅ is unsubstituted). Often, these will be selected from Cl⁻, NO₃⁻, PF₆⁻, tosylate, SO₄²⁻, CF₃SO₃⁻, acetate, and benzoate. Particularly often, these will be selected from the group consisting of Cl⁻, NO₃⁻, SO₄²⁻ and acetate.

25 If the charge z is negative, then suitable counterions include alkali metal, alkaline earth metal or (alkyl)ammonium cation, tetraarylphosphonium cations, and bis(triphenylphosphoranylidene)-ammonium cations for balancing the charge of the compound on a stoichiometric basis. The tetraarylphosphonium ions include, for example, tetraphenylphosphonium ions, or a related ion with four aryl or four alkyl groups on phosphorus including any combination of mixed aryl or alkyl, or mixed aryl and alkyl groups on the phosphorus atom in the one ion. The tetraalkylammonium ions may include, for example, tetraethyl ammonium, tetrapropyl ammonium and tetrabutyl ammonium ions, and tetraalkyl ammonium ions with longer (e.g. C₅-C₂₄) straight chain groups including ammonium ions with mixed straight chain alkyl groups, or with four branched alkyl groups or with mixtures of branched and straight chain alkyl. If the

charge z is negative, preferred counterions are those of alkali metal or alkaline earth metals, with Na^+ , K^+ , and Li^+ being particularly preferred.

Those complexes that comprise chelants capable of chelating at least one iron ion through at least three nitrogen atoms are typically mononuclear iron complexes comprising other monodentate ligands (X according to formula (A1)). Examples of suitable monodentate ligands include chloride, bromide or triflate (CF_3SO_3^-) anions. If for example iron (II) species are used with chelants capable of chelating at least one iron ion through four neutral nitrogen atoms, two monanionic, monodentate ligands will neutralise the charge of the iron ion and no additional non-coordinating counterions will be present. However, if iron(III) or iron(IV) species are formed, then additional counterions X will be present, such as those defined in formula (A1), chloride, triflate or hexafluorophosphate being most preferred. Other possibilities may be envisaged, such as a neutral tridentate nitrogen donor bound to an iron(III) species, with three anionic monodentate ligands, such as chloride, bromide or triflate, rendering the charge of the complex zero.

In addition to anionic counterions, neutral monodentate ligands, such as acetonitrile or water, may be bound to the iron ion(s). It will be understood that this possibility may also give rise to a charged iron complex (i.e. with a bound Fe(II) ion, and thus occasions the presence of non-coordinating counterions. This discussion is premised on an iron ion binding to 6 donor atoms. Although this is generally the case, it is not always so: Fe(II) or Fe(III) ions are, for example, known to give rise to 4, 5 or 7-coordinate complexes.

Complexes of formula (A1) typically comprise one or two iron ions.

For dinuclear iron complexes (i.e. iron complexes comprising two iron ions), there are often bridging ionic ligands presents, i.e. in addition to the bichelating polydentate ligands described herein. Examples of such additional bridging ligands include oxide (O^{2-}), hydroxide (OH^-) or C_{1-6} carboxylate (i.e. RCO_2^- wherein R is a C_{1-5} alkyl group) ions, which bridge the two iron ions. Where present, an alkylcarboxylate ion is typically acetate. Typically, dinuclear complexes comprise two bridging ions, for example, two acetate ions.

The substrate according to the second aspect of the invention need not be particularly limited and may be any substrate of which treatment with chlorine dioxide is desirable. According to some embodiments, the substrate is, or comprises, a polysaccharide, for example cellulose or starch, often cellulose. An example of a particularly important embodiment in this respect is the treatment of wood pulp.

However, a wide variety of other substrates may be treated in accordance with the present invention. For example, the present invention is of broad utility in the treatment of food products, including but not limited to fruit & vegetables, meat and fish; in the treatment of hard surfaces, including but not limited to the sanitation of poultry & animal processing equipment and poultry and animal habitats; and in the treatment of biofilms.

In many of these applications, the aim is sterilisation: by treatment of a food product, for example, including but not limited to fruit, vegetables, meat and fish; a hard surface, such as those of equipment used in food processing (including poultry & animal processing), medical or laboratory equipment and equipment used in poultry and animal husbandry; and biofilms, for example on membranes, the aim is generally to effect sterilisation so as to eradicate or treat microorganisms, such as viruses, bacteria, and protozoa.

The IUPAC definition for biofilms (*Pure Appl. Chem.*, **84**(2), 377-410 (2012)) is adopted herein, that is an aggregate of microorganisms in which cells that are frequently embedded within a self-produced matrix of extracellular polymeric substance adhere to each other and/or to a surface. Biofilms are frequently found on membranes present in all types of filtration apparatus. All such membranes are susceptible to fouling with biofilms, particularly those found in reverse osmosis systems. Accordingly, treatment of substrates susceptible to the formation of biofilm is a particularly useful embodiment of the present invention: prevention and/or treatment of biofilms reduces the need for servicing and cleaning, and thus can lead to lower maintenance and system operating costs. As well as equipment such as membranes, equipment susceptible to biofilm formation include, but are not limited to, pipes; cleaning (including laundry, dishwashing and bathing) equipment, such as sinks, baths, showers, dishwashers and washing machines, including the surfaces thereof (e.g. shower room walls and floors); cooling and heating systems; and marine apparatus (including hulls of ships and boats). Often biofilms form in environments frequently or permanently in contact with water. However, it will be understood that this is not necessarily the case, biofilm formation being a significant problem in the oil and gas industry, for example in pipelines and other production equipment.

It is therefore to be understood that the second aspect of the invention is of particular commercial utility in the treatment or prevention of biofilms, the method comprising treating any substrate on which a biofilm may be found, such as the equipment referred to in the previous paragraph.

In addition to the treatment or prevention of biofilms, microbiological control in water can also be achieved by employing present invention. It is therefore to be understood that the second aspect of the invention is also of particular commercial utility in the treatment of water. In this context, it will be understood that the method according to the second aspect of the invention provides a method of treating water, comprising contacting the water with an amount of a chlorine-containing chemical, which is chlorine dioxide and/or a chlorite salt; and a complex comprising one or more iron ions and one or more polydentate ligands, which are either chelants capable of chelating at least one iron ion through three, four, five, or six nitrogen atoms.

The water that may be treated in accordance with the present invention is not limited. It may be, for example, water in municipal, commercial, industrial and domestic water systems, including drinking water, plant process water, cooling water or water found in swimming pools, boilers, conditioning equipment, or other industrial plant process water.

Although the subsequent discussion focuses on the treatment of cellulosic substrates, and in particular wood pulp (reflecting the commercial reality of the majority of chlorine dioxide usage), it is to be understood that the discussion in this respect is not limiting with the present invention being applicable *mutatis mutandis* to the treatment of other polysaccharide-containing substrates and indeed other classes substrates, including the treatment of water as described herein.

According to many embodiments of the invention, the substrate that is treated in accordance with the second aspect of the invention is or comprises a polysaccharide. Within the ambit of polysaccharide-containing substrates, cellulosic (i.e. cellulose-containing) substrates are particularly important commercially. Cellulosic substrates include primarily wood pulp and cotton (and thus cotton -containing material), as well as other plant-derived materials such as bagasse and jute. Treatment of cellulosic substrates is thus widespread, with the bleaching of both wood pulp and cotton being massive industries, cotton being subject to bleaching both in the treatment of raw cotton in the cotton-processing industry and also in laundry (domestic, industrial and institutional). In each case, the objective of the treatment is to bleach these substrates, by which is meant the oxidative removal of undesirable contaminants. In the treatment of raw cotton and wood pulp (and other plant-derived materials), these contaminants are generally polyphenolic materials, with lignin, which is responsible for the dark colour of unbleached wood pulp, comprising a significant proportion of wood. In

laundry applications, the undesirable contaminants particularly targeted by bleaching include those responsible for stains.

In order to produce high quality paper grades, wood pulp needs to be delignified and bleached to a sufficient extent to produce white pulp which is also stable towards light- and time-induced yellowing/ageing. Typically, wood is ground, pulped and then
5 treated at high temperatures with alkaline sulfide or sulfite to remove the majority of the lignin. The thus-treated pulp is generally referred to as chemical pulp.

An overview of the use of chlorine dioxide (and other bleaching agents) for wood pulp treatment can be found in Pulp Bleaching, Principles and Practice, C.W.
10 Dence and D.W. Reeve, ed., Tappi, 1996.

Often in a first step, an oxygen delignification process is carried out, to remove about half of the lignin remaining in the chemical pulp. Then, this partly delignified pulp is often treated separately with chlorine dioxide and hydrogen peroxide. Dependent on the type of wood and the paper quality (brightness) desired, up to 2 to 3 separate steps
15 employing chlorine dioxide and 1 to 2 stages with hydrogen peroxide are carried out. Alternatively, delignified and bleached pulp is frequently produced without the use of any chlorine-based bleaching chemicals, resulting in so-called total chlorine free (TCF) pulp.

In the first step after the oxygen delignification step, chlorine dioxide is used
20 mainly as a delignification agent (D0-stage). In some cases, elemental chlorine is also used as a bleaching chemical, which can give good activity in conjunction with chlorine dioxide. Application of chlorine alone (i.e. without chlorine dioxide) is no longer practised, since this can result in the formation of undesirably large amounts of chlorinated waste products. In later stages of the pulp bleaching process (D1 or D2
25 stages), chlorine dioxide is mainly used to further bleach the pulp, which contains small residues of lignin.

Loadings of chlorine dioxide in pulp mills are typically between about 2 and about 10 wt% (with respect to oven-dry pulp), with processing carried out at about 40-100 °C. The duration of the delignification varies but this typically from less than 1 h to
30 4 h.

It will be understood that the various aspects of the present invention are of utility in each step in wood pulp processing, for example those described above, in which chlorine dioxide may be used.

As noted above, the concentration of the chlorine-based bleaching chemical
35 (chlorine dioxide or chlorite salt) in the aqueous media described herein is between

about 0.1 and about 50 mM for example between about 5 and about 30 mM. The skilled person in the art will be able to optimise the amount required to attain the right level of bleaching or delignification of the wood pulp. The concentration of bleaching chemical, such as chlorine dioxide, is most often expressed in the context of pulp bleaching as kg/ton oven dry pulp (odp). Typical concentrations of chlorine dioxide currently used vary between about 5 and about 20 kg/ton odp. If the pulp is bleached at 10 % consistency level, which means 100 g per kg odp in the bleaching liquor, the concentration of ClO_2 will be between 0.5 and 2 g/L (which on a molar basis equates to between 7.4 and 29.4 mM. However, it will be understood that the amount of chlorine dioxide or chlorite salt used in accordance with the present invention may be less than these whilst still retaining the desired extent of bleaching. Of course, the skilled person will be able to determine the appropriate quantity of chlorine dioxide or chlorite salt to use for any given method.

A further advantage of the present invention, particularly but not necessarily in the context of wood pulp processing arises from the reaction between hypochlorite and chlorite to form chloride and chlorine dioxide. Where aqueous media (e.g. solutions) contain chlorite, this will react with any hypochlorite, which may be formed after reaction of chlorine dioxide with partially oxidised lignin residues (cf *Pulp Bleaching, Principles and Practice*, C.W. Dence and D.W. Reeve, ed., Tappi, 1996). Hypochlorite as a side product is less desirable as it may react with lignin residues to form chlorinated phenols. However, being a strong oxidant, hypochlorite reacts very efficiently with chlorite to form chloride and chlorine dioxide (cf Z Jia *et al.*, *Inorg. Chem.*, **39**(12), 2614–2620 (2000)), and so will react chlorite salt present, preventing hypochlorite reacting further to yield chlorinated side products.

Where used to obtain antimicrobial effect the amount of chlorine dioxide or is generally much lower than that used in the context of pulp bleaching, typically between 1 and 30 mg/l. It will be understood that the amount of chlorine dioxide (or chlorite salt) used in accordance with the present invention may be less than these whilst still retaining the desired extent of activity. Again, the skilled person will be able to determine the appropriate quantity of chlorine dioxide or chlorite salt to use for any given method.

In all methods according to the present invention, it will be appreciated that a particular benefit, where chlorite salts are used, is that chlorine dioxide does not need to be generated *ex situ*, as is the case presently.

Where the substrate treated in accordance with the methods of the first and second aspect of the invention is a polysaccharide substrate, and in particular a cellulosic substrate, the pH of the aqueous medium is generally between about 2 and about 11, more typically between about pH 3 and about pH 7. The pH of the aqueous medium can be easily set using the right level of alkali or acid (for example NaOH or HCl) or by using a buffered solution (as described elsewhere herein).

A much wider pH range may be used to obtain antimicrobial activities of chlorite or chlorine dioxide than for cellulosic treatment. In general a pH range between 3 and 11 can be employed for this application.

The temperature for practice of the methods of the invention may be determined by the skilled person. For example, cellulose treatment processes can be carried out at similar temperatures to those currently practised. Clearly, the optimum temperature will be substrate-dependent, and will often be between about 50 and about 70 °C for wood pulp bleaching, although improved bleaching processes have been achieved by increasing the temperature, known in the art as the D_{HOT} process, for example to treat eucalyptus wood pulp. However, it should be noted that the methods described herein may achieve the same bleaching activity at lower temperatures than those achievable absent the iron complexes described herein. Therefore, whilst the currently used temperature ranges for wood-pulp bleaching are typically between 50 and 100 °C, use of the iron complexes described herein may allow these temperatures to be lowered. For the treatment of polysaccharide-based substrates, temperatures of between about 30 and 100 °C are typical, for example between 40 and 95 °C. For treatment of water or other substrates to attain antimicrobial effect, ambient temperatures (e.g. 15 to 30 °C) are generally appropriate. Nevertheless, it will be appreciated that the exact temperature can be determined without undue burden by those conducting any given method.

Each and every patent and non-patent reference referred to herein is hereby incorporated by reference in its entirety, as if the entire contents of each reference were set forth herein in their entirety.

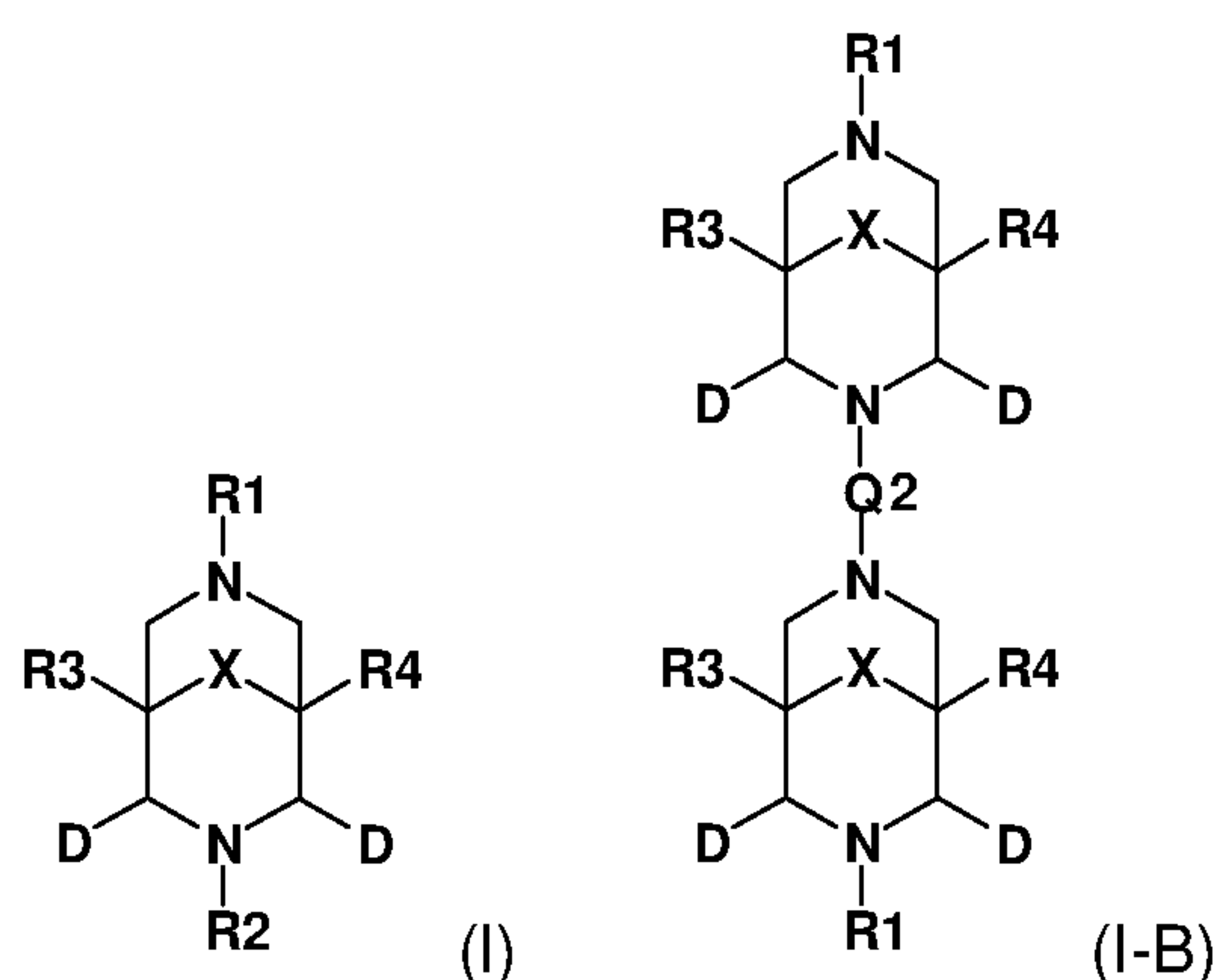
The invention may be further understood with reference to the following non-limiting clauses:

1. A method of generating chlorine dioxide from a chlorine-containing chemical, which is a chlorite salt, comprising contacting, in an aqueous medium, a chlorite salt and a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.
2. A method of treating a substrate comprising contacting, in an aqueous medium, (i) the substrate (ii) an amount of a chlorine-containing chemical, which is chlorine dioxide and/or a chlorite salt; and (iii) a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.
3. The method of clause 2, wherein the substrate is a cellulosic substrate.
4. The method of clause 2, wherein the substrate is wood pulp.
5. The method of clause 2, wherein the substrate is a food product or equipment used in food processing, medicine, laboratories or poultry or animal husbandry.
6. The method of clause 2, which is for use in the treatment or prevention of a biofilm.
7. The method of clause 2, which is a method of treating water, comprising contacting the water with an amount of the chlorine-containing chemical and the complex.
8. The method of any one of clauses 2 to 7, wherein the chlorine-containing chemical is a chlorite salt.

9. The method of any one preceding clause, wherein the chelant is capable of chelating at least one iron ion through three, four, five or six nitrogen atoms.

10. The method of any one preceding clause, wherein the chelant is capable of chelating at least one iron ion through three, four or five nitrogen atoms.

11. The method of any one preceding clause, wherein the complex comprises a chelant capable of chelating at least one iron ion through at least three nitrogen atoms, which is of formulae (I), (I-B), (II), (II-B), (III), (IV), (V), (V-B), (V-C), (VI), (VII), (VII-B), (VIII), (VIII-B), (IX), (X) or (XI):



wherein:

each D is independently selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl and thiazol-2-yl, each of which may be optionally substituted by one or more groups independently selected from the group consisting of -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl, and -C₁-C₄alkyl;

the or each R1 and R2 are independently selected from the group consisting of C₁-C₂₄alkyl, C₆₋₁₀arylC₁-C₆alkyl, C₆₋₁₀aryl, C₅-C₁₀heteroarylC₁-C₆alkyl, each of which may be optionally substituted by one or more groups selected from -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl and -SC₁-C₄alkyl; and CH₂CH₂N(R10)(R11),

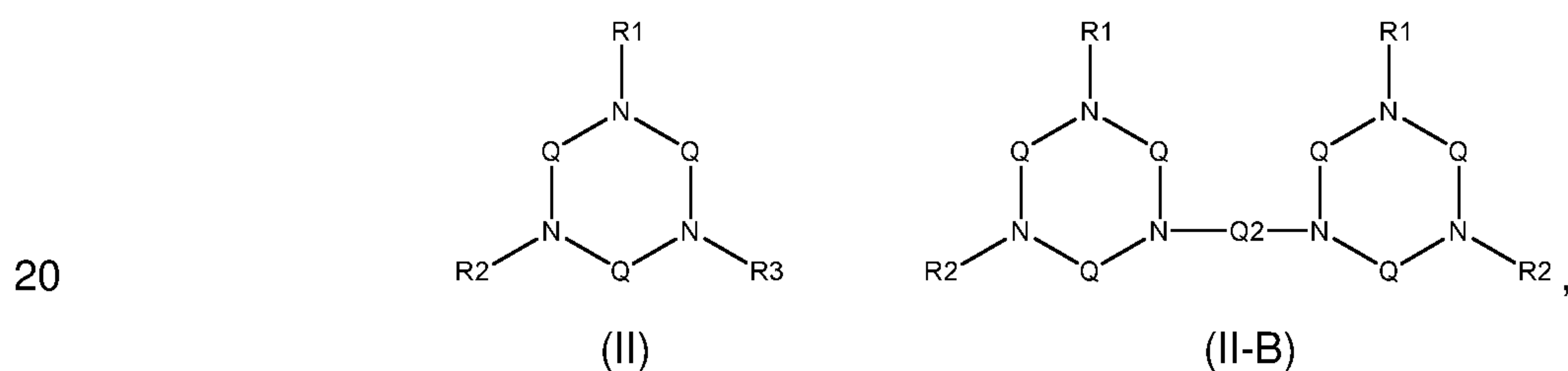
wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in

which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N;
 5 di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and
 di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

R₃ and R₄ are independently selected from hydrogen, C₁-C₈alkyl, C₁-C₈alkyl-O-C₁-C₈alkyl, C₆-C₁₀aryloxyC₁-C₈alkyl, C₆-C₁₀aryl, C₁-C₈hydroxyalkyl, C₆-C₁₀arylC₁-C₆alkyl
 10 and C₅-C₁₀heteroarylC₁-C₆alkyl, and -(CH₂)₀₋₄C(O)OR₅ wherein R₅ is independently selected from: hydrogen, C₁-C₈alkyl and C₆₋₁₀aryl;

Q₂ represents a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and
 15 one C₆₋₁₀arylene unit, which bridge is optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

X is selected from C=O, -[C(R₆)₂]₀₋₃- wherein each R₆ is independently selected from hydrogen, hydroxyl, C₁-C₄alkoxy and C₁-C₄alkyl;



wherein:

each Q is independently selected from -CR₄R₅CR₆R₇- and -CR₄R₅CR₆R₇CR₈R₉-;

25 R₄, R₅, R₆, R₇, R₈, and R₉ are independently selected from: H, C₁-C₄alkyl and hydroxyC₁-C₄alkyl;

each R₁, R₂, and R₃ is independently selected from the group consisting of hydrogen, C₁-C₂₄alkyl, CH₂CH₂OH, CH₂COOH, CH₂PO₃H₂, C₅-C₁₀heteroarylC₁-C₆alkyl and CH₂CH₂N(R₁₀)(R₁₁),

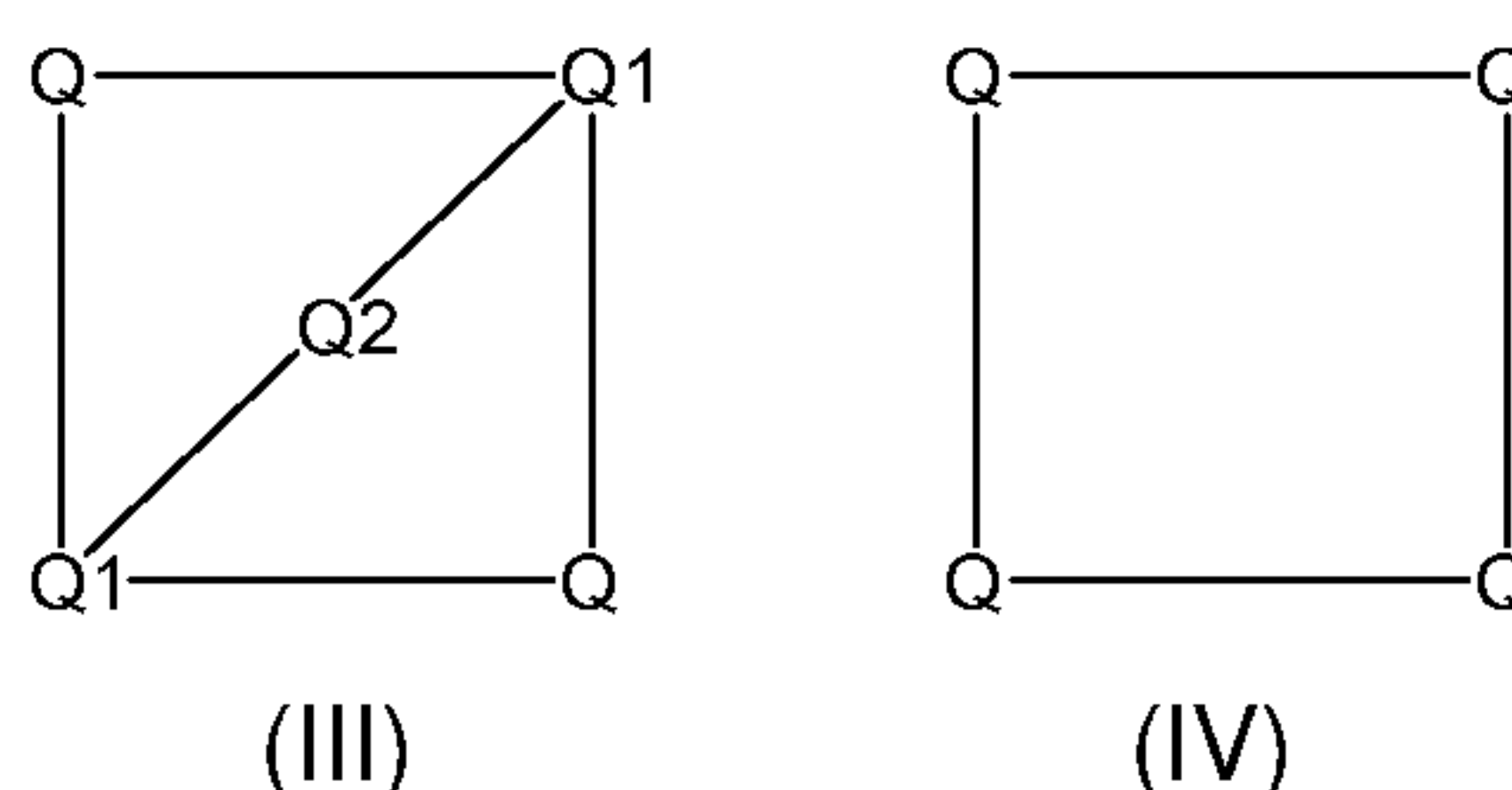
30 wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in

which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N;

5 di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and

di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and

10 Q₂ is a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups;



15 wherein:

each -Q- is independently selected from -N(R)C(R₁)(R₂)C(R₃)(R₄)- and -N(R)C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

each -Q₁- is independently selected from -N(R')C(R₁)(R₂)C(R₃)(R₄)- and -N(R')C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

20 each R is independently selected from: hydrogen; the group consisting of C₁₋₂₀alkyl, C₂₋₂₀alkenyl, C₂₋₂₀alkynyl, C₆₋₁₀aryl and C₇₋₂₀arylalkyl, each of which may be optionally substituted with C₁₋₆alkyl, C₅₋₁₀heteroarylC₁₋₆alkyl; and CH₂CH₂N(R₁₀)(R₁₁),

25 wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached

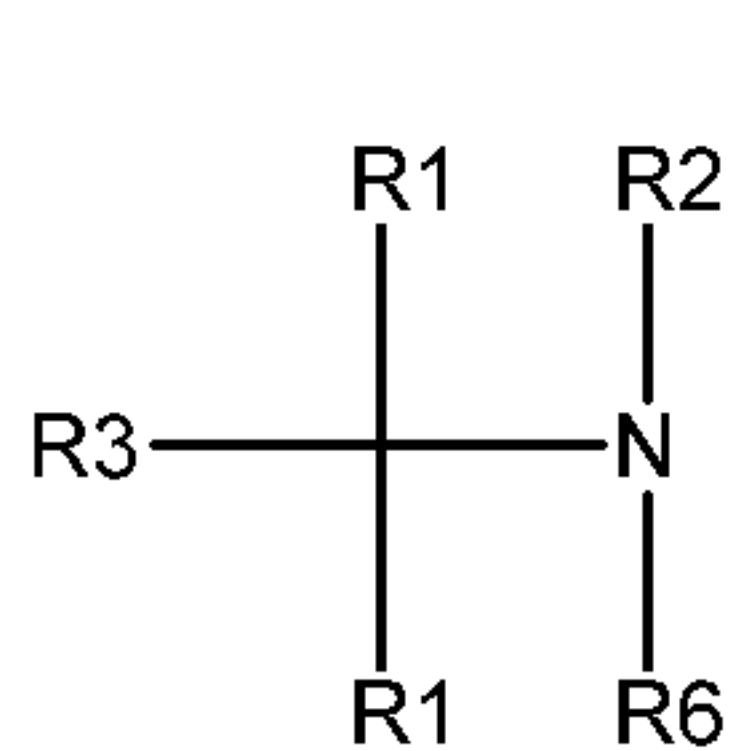
30 represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and

di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

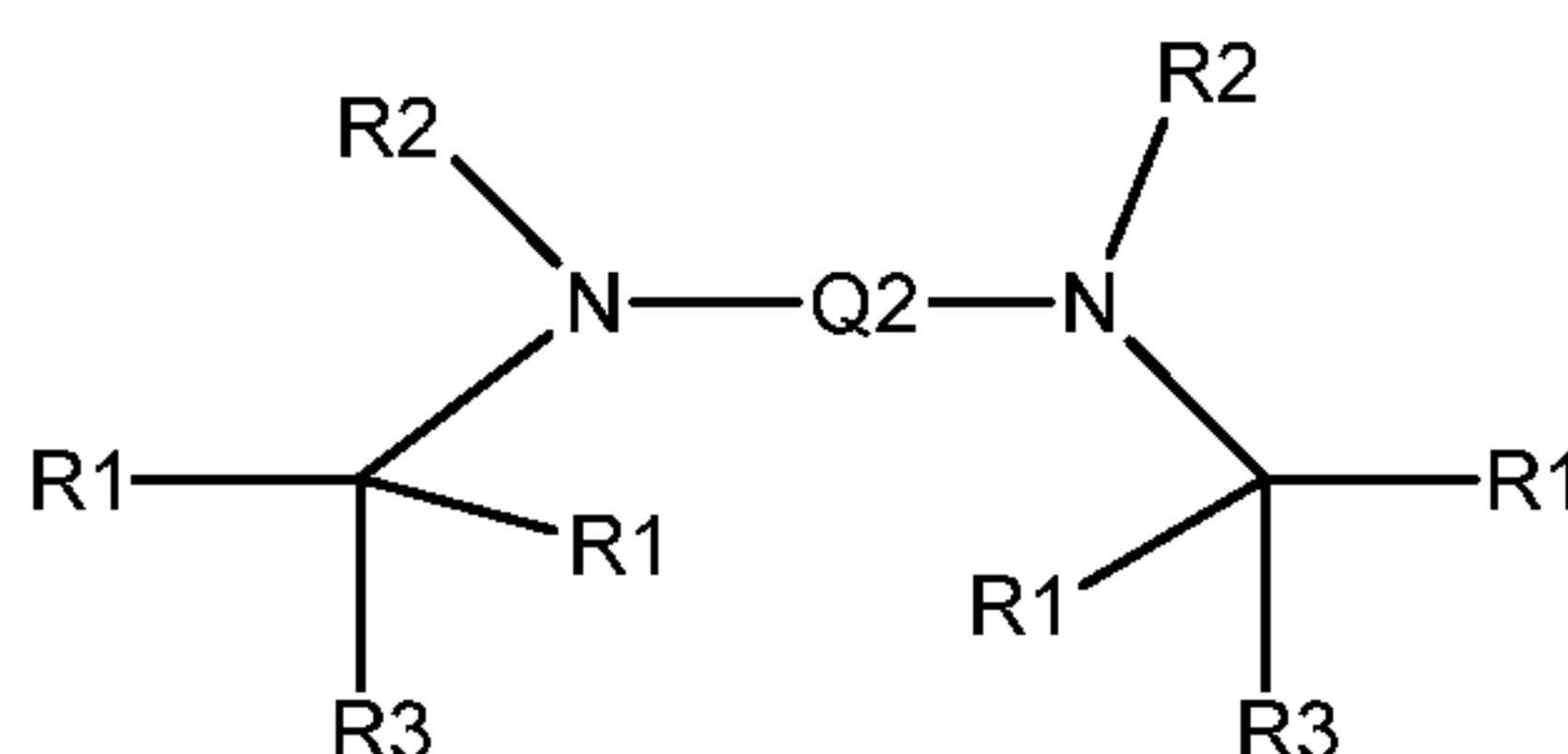
the two -R' groups of the two Q1 groups together form bridging moiety -Q2-;

Q2 is a bridge selected from the group consisting of a C₂₋₆alkylene moiety, a C₆₋₁₀arylene moiety, or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups; and

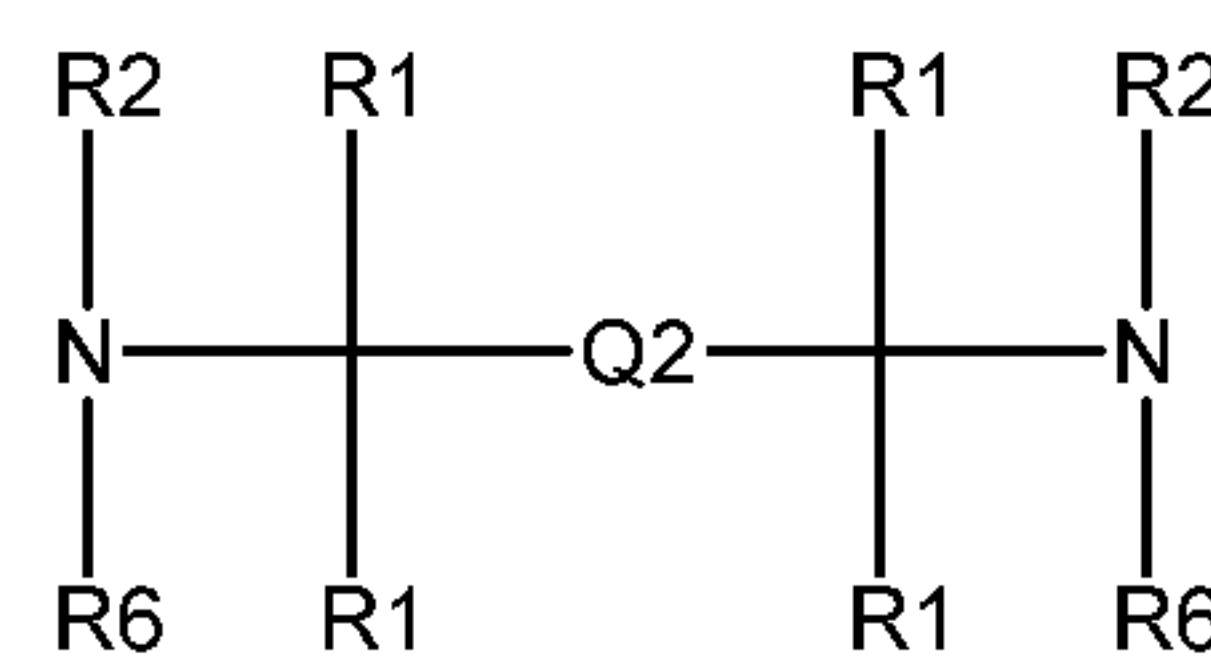
R₁-R₆ are each independently selected from: H, C₁₋₄alkyl and hydroxyC₁₋₄alkyl;



(V)



(V-B)



(V-C)

wherein:

each -R1 independently is selected from -CH₂N(C₁-C₂₄alkyl)₂, -CH₂NR7 or an optionally C₁-C₆alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl;

each -R2 independently represents -R4-R5;

each -R3 and each -R6 each independently represents hydrogen, or a group selected from C₁-C₆alkyl, C₆-C₁₀aryl, C₅-C₁₀heteroaryl, C₆-C₁₀arylC₁-C₆alkyl and C₅-C₁₀heteroarylC₁-C₆alkyl, each of which groups may be optionally C₁-C₆alkyl-substituted;

each -R4- independently represents optionally C₁-C₆alkyl-substituted C₁-C₆alkylene;

each -R5 independently represents an -CH₂N(C₁-C₂₄alkyl)₂ group, -CH₂NR7 or an optionally C₁-C₆alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl;

each -NR7 independently represents a moiety in which R7 and the nitrogen atom N to which it is attached represents a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to R4 through the nitrogen atom N; and

5 Q2 represents a bridge selected from the group consisting of a C₁₋₆alkylene moiety C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge is optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups;



10

wherein:

each -R1 is independently selected from -CY₂N(C₁-C₂₄alkyl)₂; -CY₂NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₆alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; or represents an optionally C₁-C₆alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-1-yl, pyrazol-3-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl; and

20 each Y is independently selected from H, CH₃, C₂H₅, C₃H₇;



wherein:

25 -X- is selected from -CY₂CY₂-, cis- or trans-1,2-cyclohexylene, -CY₂CY₂CY₂-, -CY₂C(OH)YCY₂-, with each Y being independently selected from H, CH₃, C₂H₅ and C₃H₇;

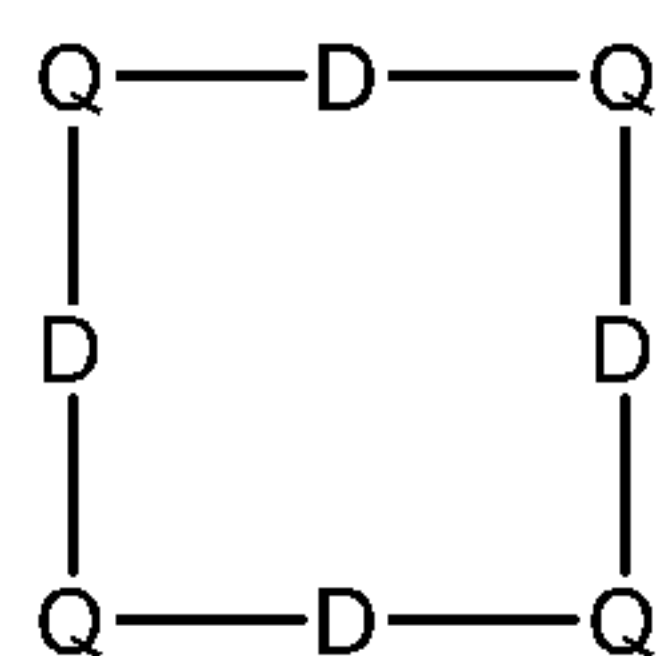
n is an integer from 0 to 10;

30 each R1 group is independently an alkyl, heterocycloalkyl, heteroaryl, aryl, arylalkyl or heteroarylalkyl group, each of which may be optionally substituted with a substituent selected from the group consisting of hydroxy, alkoxy, phenoxy, phosphonate, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, mono- or dialkylamine and N⁺(R3)₃, wherein R3 is selected from hydrogen, alkyl, alkenyl, arylalkyl, arylalkenyl, hydroxyalkyl, aminoalkyl, and alkyl ether;

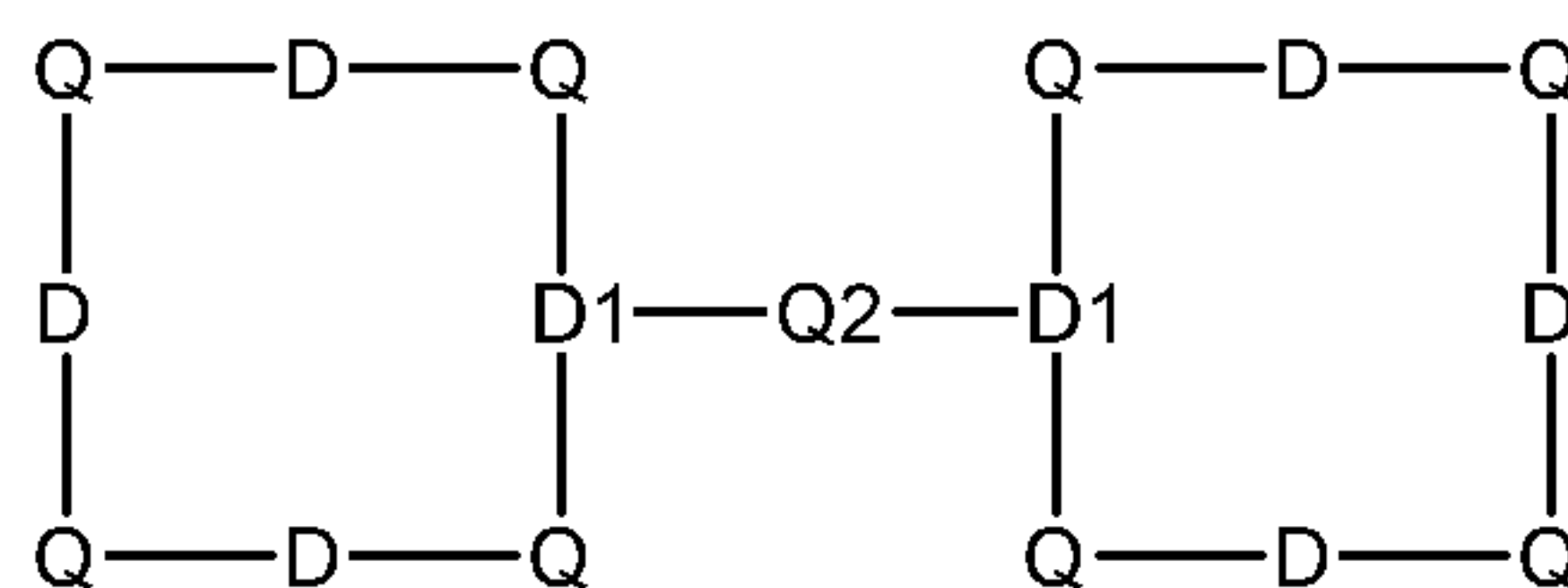
each R2 is $-CZ_2-R4$, with each Z being independently selected from H, CH_3 , C_2H_5 , C_3H_7 ; and each $-R4$ being independently selected from an optionally C_1-C_6 alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl; and $CH_2N(R10)(R11)$,

wherein $N(R10)(R11)$ is selected from the group consisting of $di(C_{1-44}alkyl)amino$; $di(C_{6-10}aryl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; $di(C_{6-10}arylC_{1-6}alkyl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more $C_{1-20}alkyl$ groups, which is connected to the remainder of R1 through the nitrogen atom N; $di(heterocycloalkylC_{1-6}alkyl)amino$, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; and $di(heteroarylC_{1-6}alkyl)amino$, wherein each of the heteroaryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; and

Q2 is a bridge selected from the group consisting of a $C_{1-6}alkylene$ bridge, a $C_{6-10}arylene$ bridge or a bridge comprising one or two $C_{1-3}alkylene$ units and one $C_{6-10}arylene$ unit, which bridge may be optionally substituted one or more times with independently selected $C_{1-24}alkyl$ groups and OH groups;



(VIII)



(VIII-B)

wherein:

each Q group independently represents $-CY_2-$ or $-CY_2CY_2-$, in which each Y is independently selected from hydrogen, $C_{1-24}alkyl$, or a $C_{6-10}aryl$;

each D group independently represents a heteroarylene group or a group of the formula $-NR-$, with the proviso that at least one D group represents a heteroarylene group;

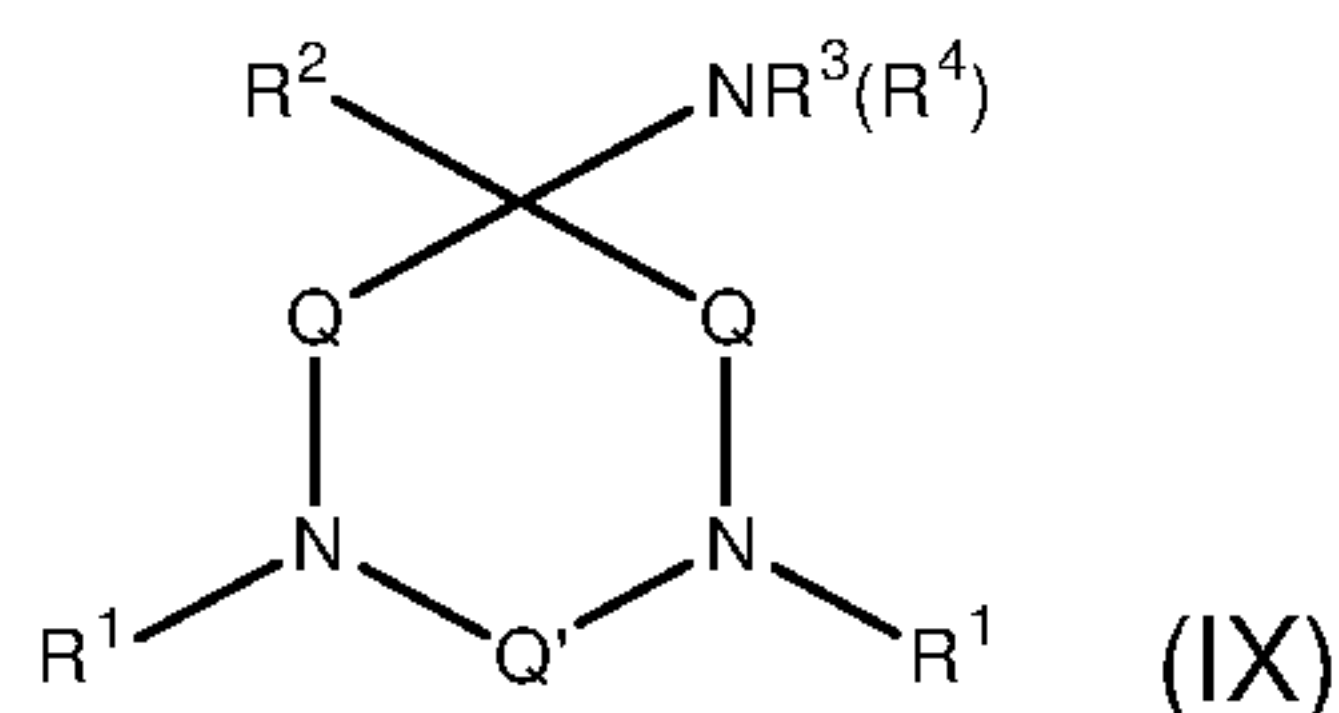
each D1 group represents a group of the formula $-NR'-$;

the two $-R'$ groups of the two D1 groups together form bridging moiety $-Q2-$;

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Q2 is a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety, or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

5 each R group independently represents H, C₁₋₂₄alkyl, C₆₋₁₀aryl or C₅₋₁₀heteroaryl;

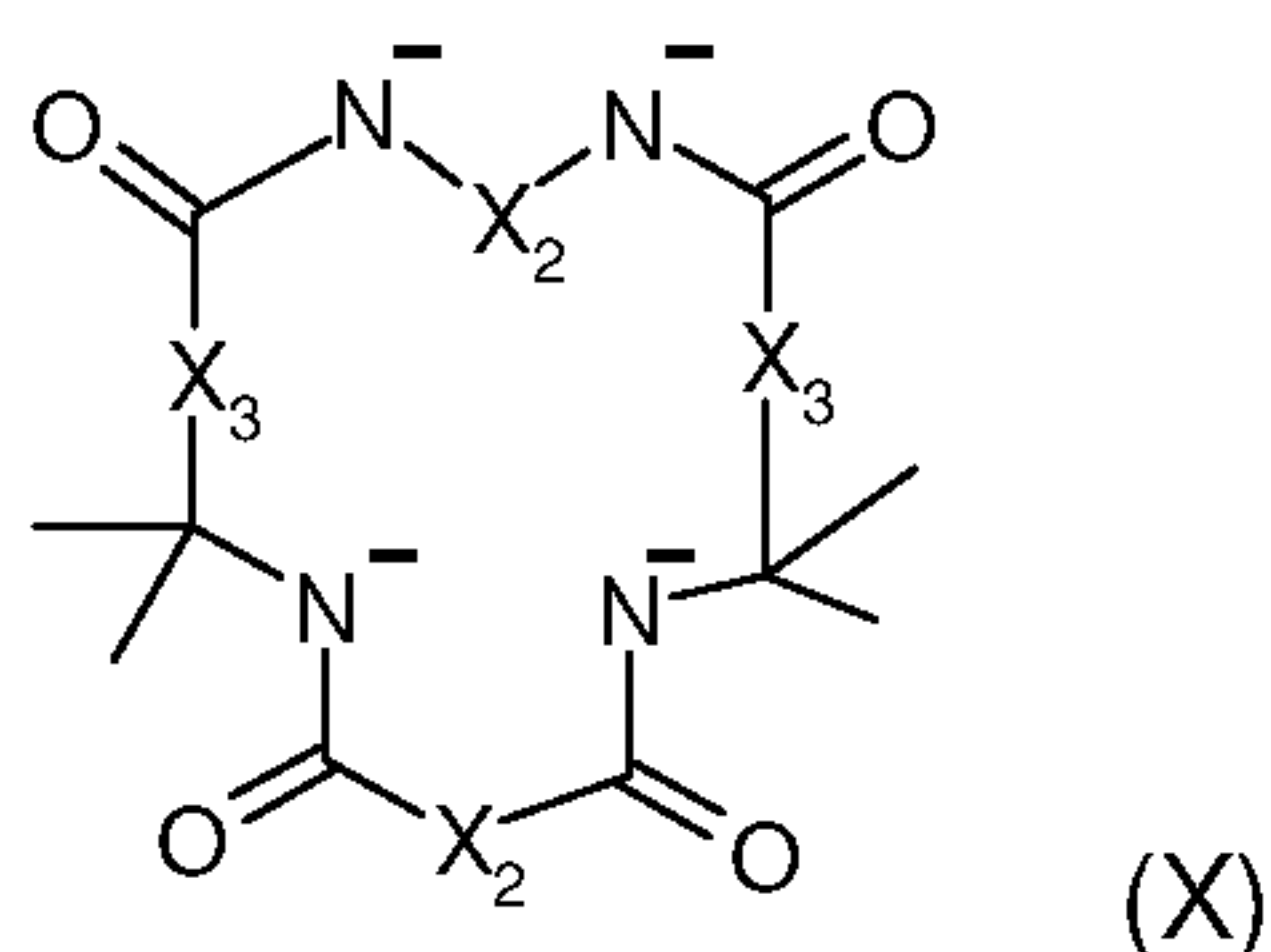


wherein:

10 each of -R¹, -R², -R³ and -R⁴ independently represents -H, -C₁₋₂₄alkyl, -C₆₋₁₀aryl or a group comprising a heteroatom capable of coordinating to a metal ion, which aryl and heteroatom-comprising groups may each be optionally substituted with one or more C₁₋₄alkyl groups;

15 Q represents methylene or ethylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group; and

Q' represents ethylene or n-propylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group;



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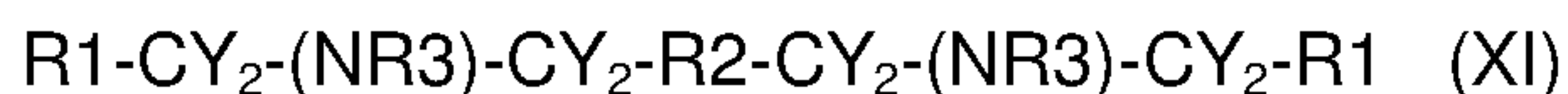
wherein:

each X₂ and X₃ independently represents a bridging group (CRR')_n, wherein:

n is an integer between 0 and 3; and

25 each R and R' is independently selected from a group consisting of C₁₋₂₄alkyl, cyclo-C₃₋₈alkyl, cyclo-C₄₋₈alkenyl, C₁₋₂₄alkenyl, C₆₋₁₀aryl, C₁₋₂₄alkynyl and C₆₋₁₀arylC₁₋₂₄alkyl, C₁₋₂₄alkoxy and phenoxy each of which may be optionally C₁₋₆alkyl-substituted, H, F, Cl, Br, I, CH₂CF₃ and CF₃; or one R and one R' attached to a common carbon atom may together with that carbon atom form a substituted or

unsubstituted 1,2-phenylene moiety or a cycloalkylene, cycloalkenylene, heterocycloalkylene or heterocycloalkenylene moiety;



5 wherein:

each Y is independently selected from H, CH₃, C₂H₅ and C₃H₇;

each R1 is independently selected from an optionally C₁-C₆alkyl-substituted C₅-C₁₀heteroaryl group, whereby the C₅-C₁₀heteroaryl group is selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl;

R2 is selected from an optionally C₁-C₆alkyl-substituted C₅-C₆heteroarylene group, whereby the C₅-C₆heteroarylene group is selected from pyridin-2,6-diyl, pyrazin-2,6-diyl, pyrazol-3,5-diyl, pyrazol-1,3-diyl, pyrrol-2,5-diyl, imidazol-2,5-diyl, imidazol-1,4-diyl, pyrimidin-2,6-diyl, 1,2,4-triazol-3,5-diyl, 1,2,4-triazol-1,3-diyl, 1,2,4-triazol-2,4-diyl, 1,2,3-triazol-1,4-diyl, 1,2,3-triazol-2,5-diyl, and thiazol-2,5-diyl;

each R3 is independently selected from optionally C₁-C₆-substituted C₁₋₂₄alkyl, C₆₋₁₀aryl, C₆₋₁₀arylC₁-C₂₄alkyl, C₅₋₁₀heteroaryl, C₅₋₁₀heteroarylC₁-C₂₄alkyl.

12. The method of clause 11, wherein the complex comprises a polydentate ligand selected from the group consisting of those of formulae (I), (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), (X) and (XI).

13. The method of any one of clauses 1 to 10, wherein the complex comprises a chelant capable of chelating at least one iron ion through at least three nitrogen atoms, which is of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (VII'), (VII'-B), (IX) or (XI), wherein the ligands of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (IX) or (XI) are as defined in clause 11 and the ligands of formulae (VII') and (VII'-B) are of the formulae:



wherein:

-X- is selected from -CY₂CY₂-, cis- or trans-1,2-cyclohexylene, -CY₂CY₂CY₂-, -CY₂C(OH)YCY₂-, with each Y being independently selected from H, CH₃, C₂H₅ and C₃H₇;

n is an integer from 0 to 10;

at most one R1 group is independently an alkyl, heterocycloalkyl, heteroaryl, aryl, arylalkyl or heteroarylalkyl group, each of which may be optionally substituted with a substituent selected from the group consisting of hydroxy, alkoxy, phenoxy, phosphonate, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, mono- or dialkylamine and $N^+(R3)_3$, wherein R3 is selected from hydrogen, alkyl, alkenyl, arylalkyl, arylalkenyl, hydroxyalkyl, aminoalkyl, and alkyl ether;

each R2 is $-CZ_2-R4$, with each Z being independently selected from H, CH_3 , C_2H_5 , C_3H_7 ; and each $-R4$ being independently selected from an optionally C_1 - C_6 alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl; and $CH_2N(R10)(R11)$,

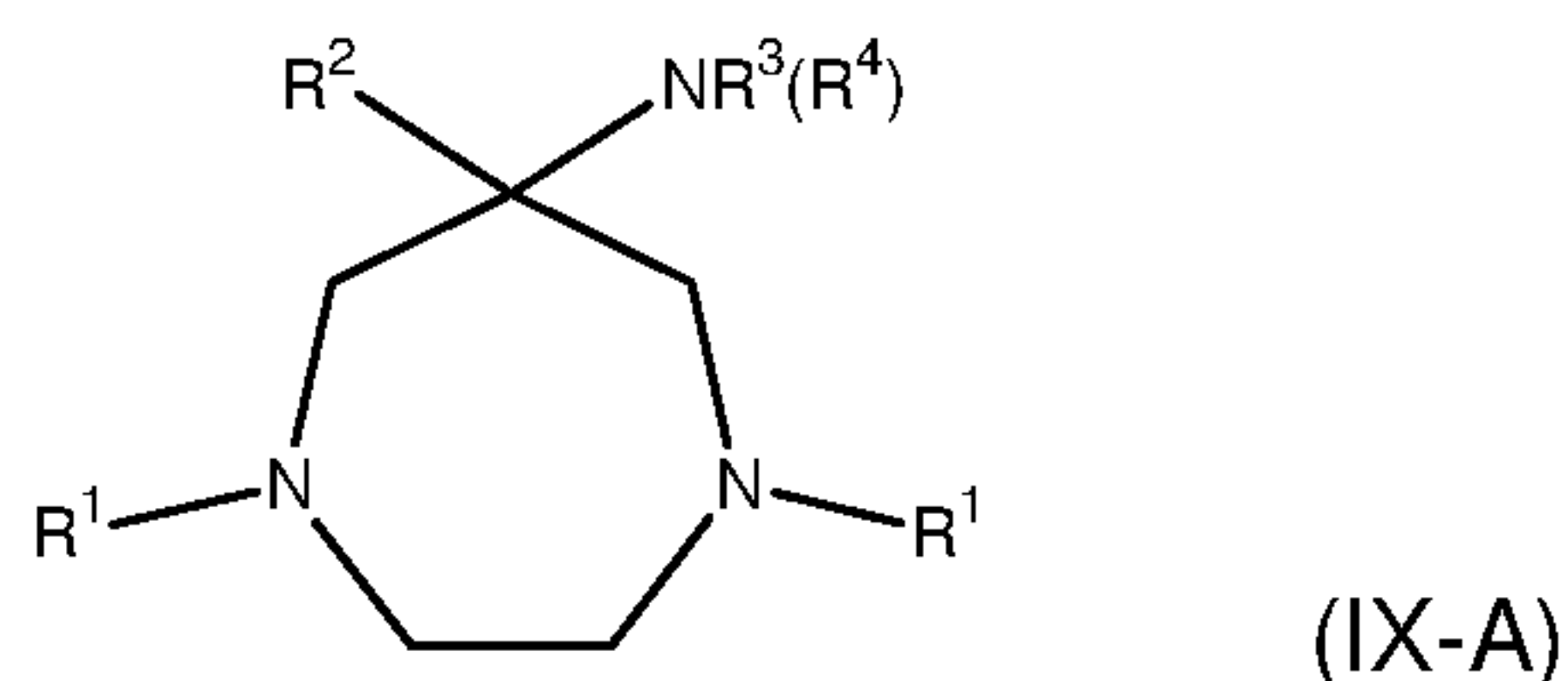
wherein $N(R10)(R11)$ is selected from the group consisting of $di(C_{1-44}alkyl)amino$; $di(C_{6-10}aryl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; $di(C_{6-10}arylC_{1-6}alkyl)amino$ in which each of the aryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more $C_{1-20}alkyl$ groups, which is connected to the remainder of R1 through the nitrogen atom N; $di(heterocycloalkylC_{1-6}alkyl)amino$, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups; and $di(heteroarylC_{1-6}alkyl)amino$, wherein each of the heteroaryl groups is independently optionally substituted with one or more $C_{1-20}alkyl$ groups;

Q2 is a bridge selected from the group consisting of a $C_{1-6}alkylene$ bridge, a $C_{6-10}arylene$ bridge or a bridge comprising one or two $C_{1-3}alkylene$ units and one $C_{6-10}arylene$ unit, which bridge may be optionally substituted one or more times with independently selected $C_{1-24}alkyl$ groups and OH groups; and

either one or both R1 groups are independently CZ_2R4 , wherein Z is as defined for moiety R2 and R4 is an optionally C_1 - C_6 alkyl-substituted pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl.

14. The method of clause 13, wherein the complex comprises a polydentate ligand selected from the group consisting of those of formulae (I), (V), (VI), (VII'), (IX) and (XI).

15. The method of any one of clauses 11 to 14, wherein the complex comprises a polydentate ligand of formula (IX), which is of formula (IX-A):



wherein:

each -R¹ is independently -H, -C₁₋₂₄alkyl, -C₆₋₁₀aryl or pyridin-2-ylmethyl, which aryl or pyridine-2-yl is optionally substituted with C₁₋₄alkyl;

-R² represents -H or -CH₃; and

each -R³ and -R⁴ is independently -C₁₋₂₄alkyl, -C₆₋₁₀aryl or pyridin-2-ylmethyl, which aryl or pyridine-2-yl is optionally substituted with C₁₋₄alkyl, for example wherein:

each -R¹ is independently -H, -C₁₋₂₄alkyl or pyridin-2-ylmethyl, which pyridine-2-yl is optionally substituted with C₁₋₄alkyl;

-R² represents -H or -CH₃; and

each -R³ and -R⁴ is independently -C₁₋₂₄alkyl or pyridin-2-ylmethyl, which pyridinyl is optionally substituted with C₁₋₄alkyl.

16. The method of clause 13, wherein the complex comprises a polydentate ligand selected from the group consisting of 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, 2,4-di-(2-pyridyl)-3,7-dimethyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N-benzyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, N,N,N-tris(pyridin-2-yl-methyl)amine, N-methyl-alkyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-octyl-N,N',N'-tris(pyridin-

2-ylmethyl)-1,2-ethylene-diamine, N, N, N', N'-tetrakis(pyridin-2-yl-methyl)ethylene-1,2-diamine, N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, N,N'-dimethyl-2,11-diaza[3.3](2,6-pyridinophane), 6-dimethylamino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-diazacycloheptane, 6-amino-1,4,6-trimethyl-1,4-diazacycloheptane, 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-(pyridin-2-ylmethyl)amino)-1,4-diazacycloheptane, 6-{N,N-bis(pyridin-2-ylmethyl)amino}-1,4,6-trimethyl-1,4-diazacycloheptane and 6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane.

17. The method of clause 13, wherein the complex comprises a polydentate ligand selected from the group consisting of dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine, N-methyl-N,N,N'-tris(imidazol-2-ylmethyl)ethylene diamine, N-ethyl-N,N,N'-tris(imidazol-2-ylmethyl)ethylene diamine, tris(pyridin-2-ylmethyl)amine and 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane.

18. The method of clause 11 or clause 13, wherein the complex comprises a chelant of formulae (I) or (I-B), wherein:

each D=pyridin-2-yl;

each R1 and R2 group is independently selected from C₁-C₂₄alkyl, C₆-C₁₀aryl, C₆₋₁₀arylC₁-C₆alkyl, with the proviso that either -R1 or -R2 or both -R1 and -R2 (for formula (I), or one or both -R1 groups (for formula (I-B) are -CH₂CH₂N(R10)(R11), wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a

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heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

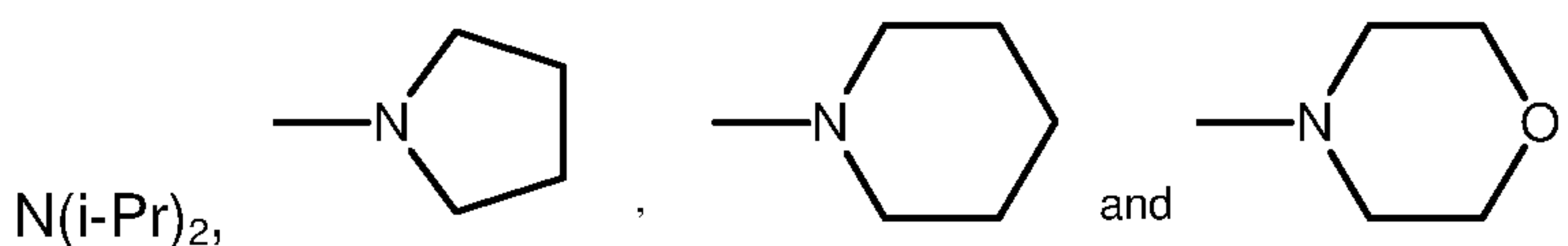
-Q2- if present is selected from -CH₂CH₂-, -CH₂CH₂CH₂- and -CH₂CHOHCH₂-;

X is either C=O or C(OH)₂; and

R3 and R4 are selected from -C(=O)OR5 wherein R5 is selected from C1-C8alkyl; and

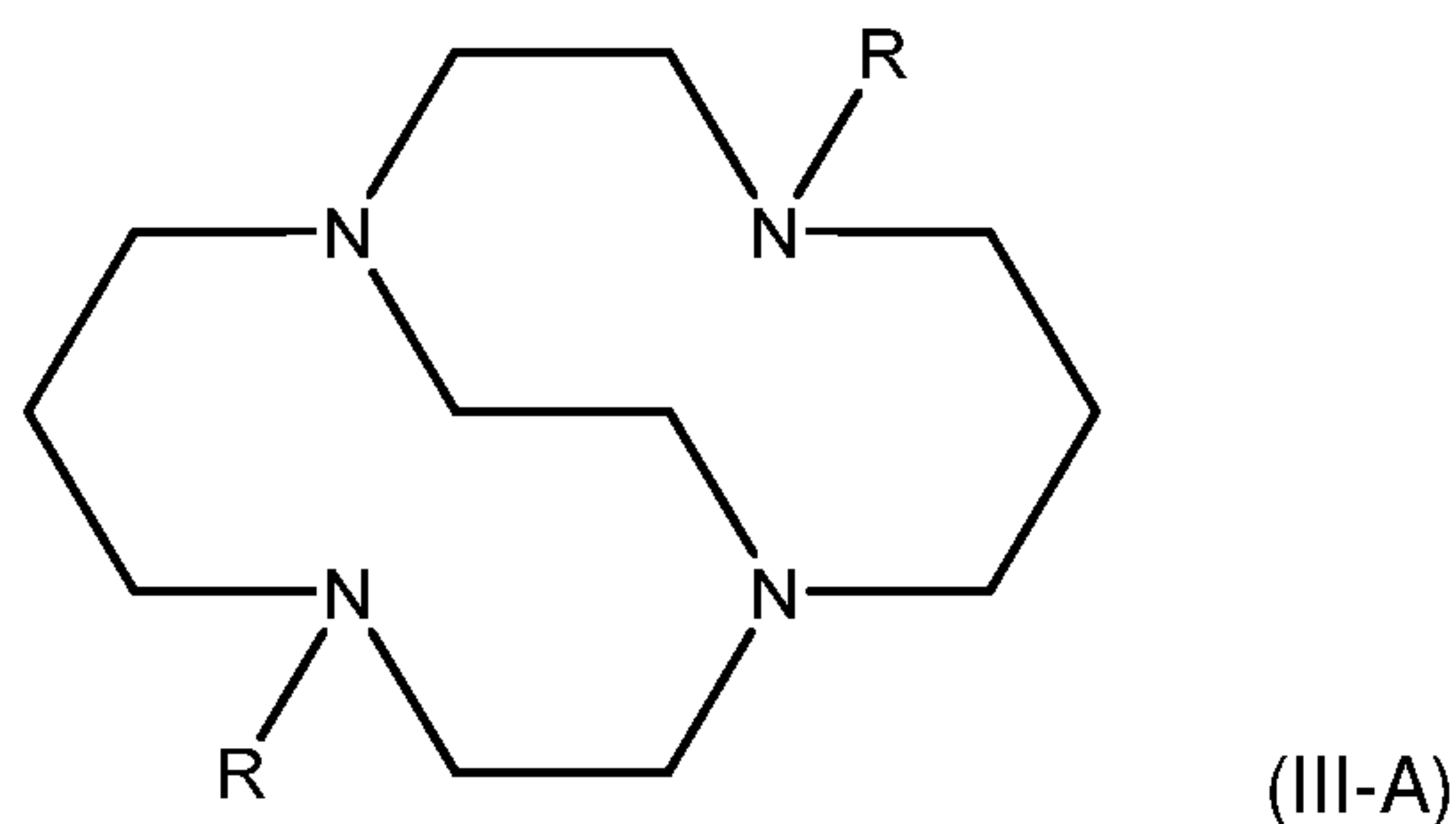
the pH of the aqueous medium is between about 7 and about 11.

19. The method of clause 18, wherein -N(R10)(R11) is selected from -NMe₂, -NEt₂, -



20. The method of clause 18 or clause 19, wherein the complex comprises dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(N,N-dimethyl-amine-ethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate.

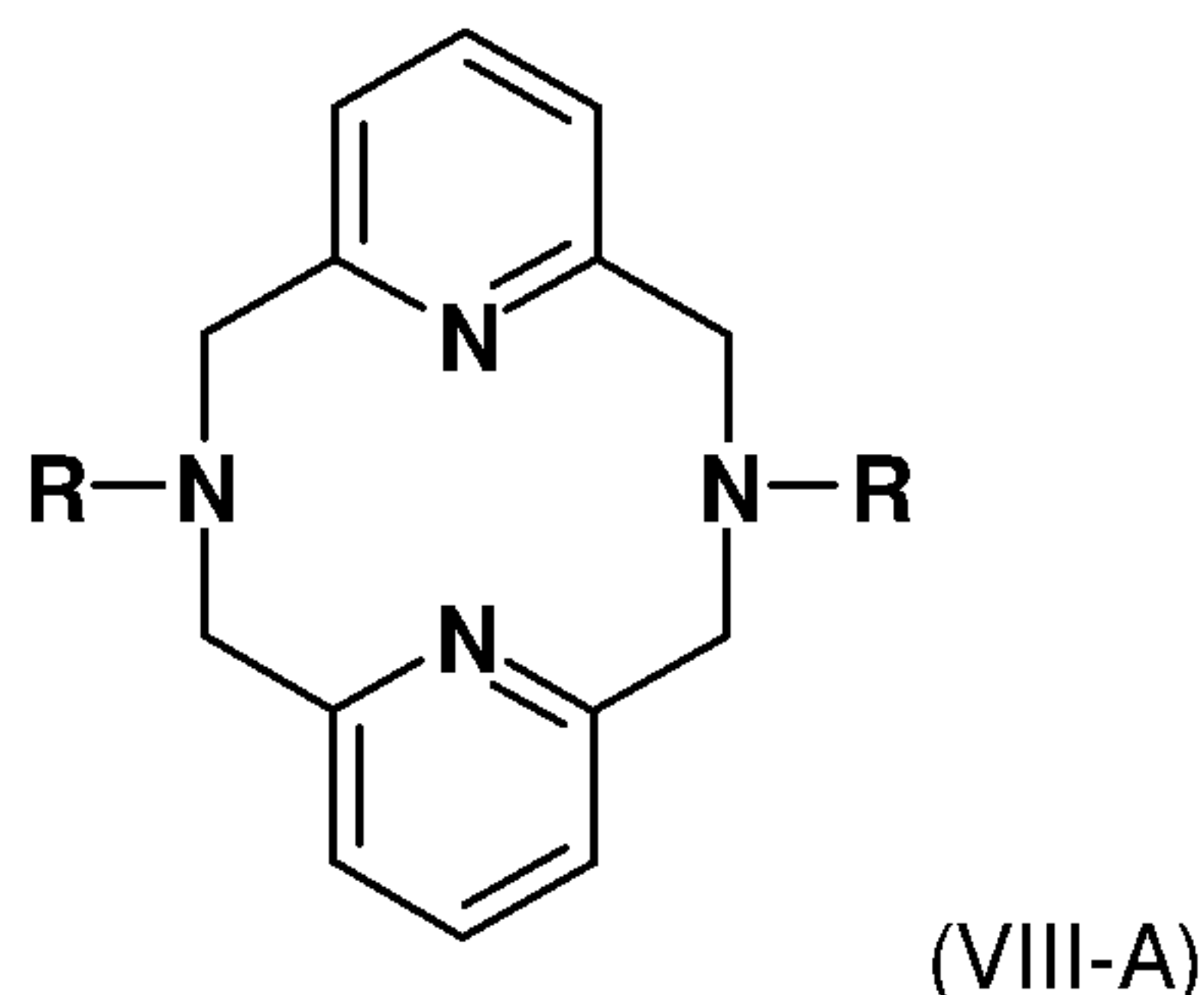
21. The method of clause 11 or clause 12, wherein the complex comprises a polydentate ligand of formula (III), which is of formula (III-A):



wherein R is as defined in clause 11 for formulae (III) and (IV).

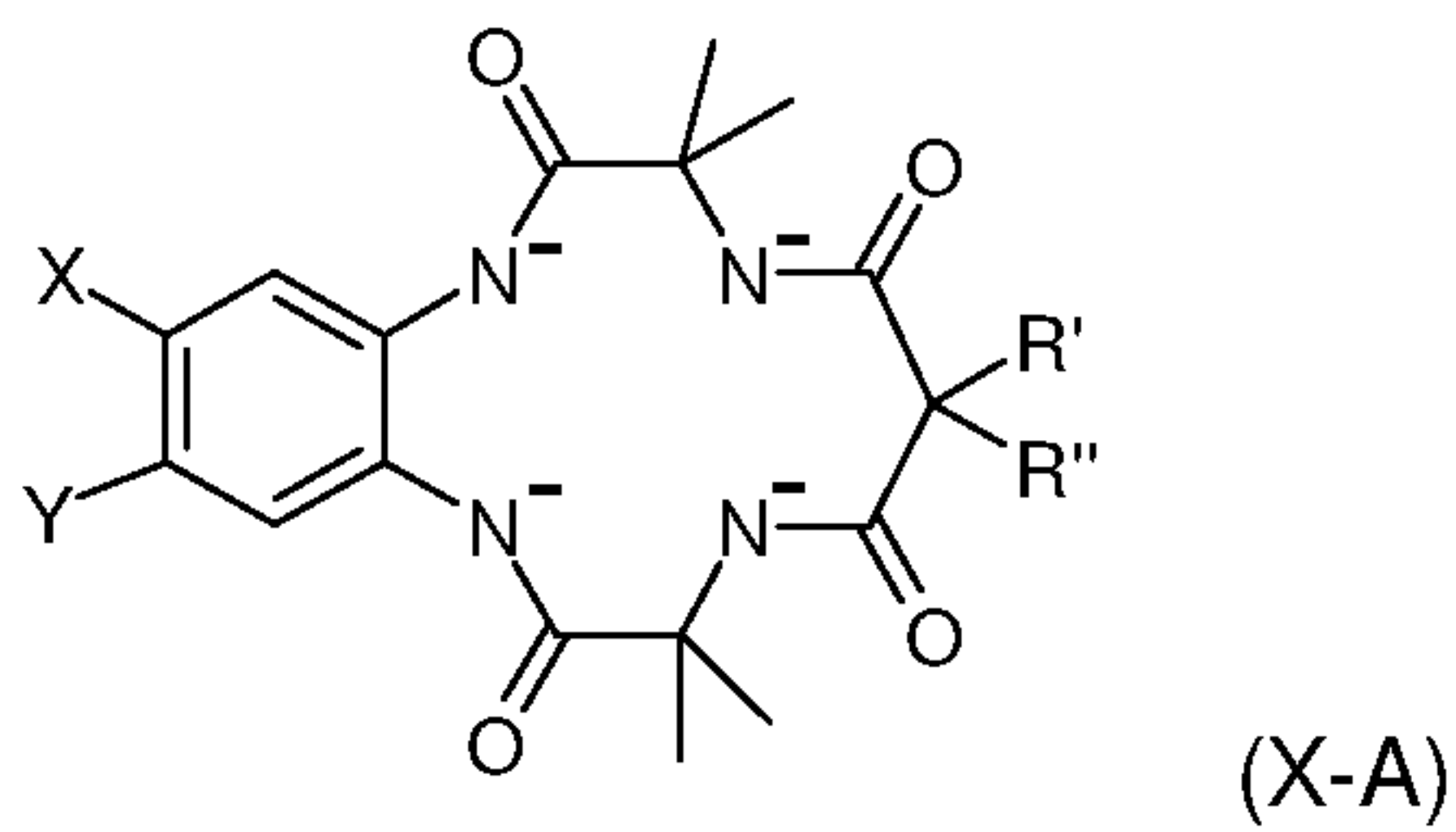
22. The method of clause 11 or clause 12, wherein the complex comprises a polydentate ligand of formula (VIII), which is of formula (VIII-A):

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wherein R is as defined in clause 11 for formulae (VIII) and (VIII-B).

23. The method of clause 11 or clause 12, wherein the complex comprises a polydentate ligand of formula (X), which is of formula (X-A):



wherein:

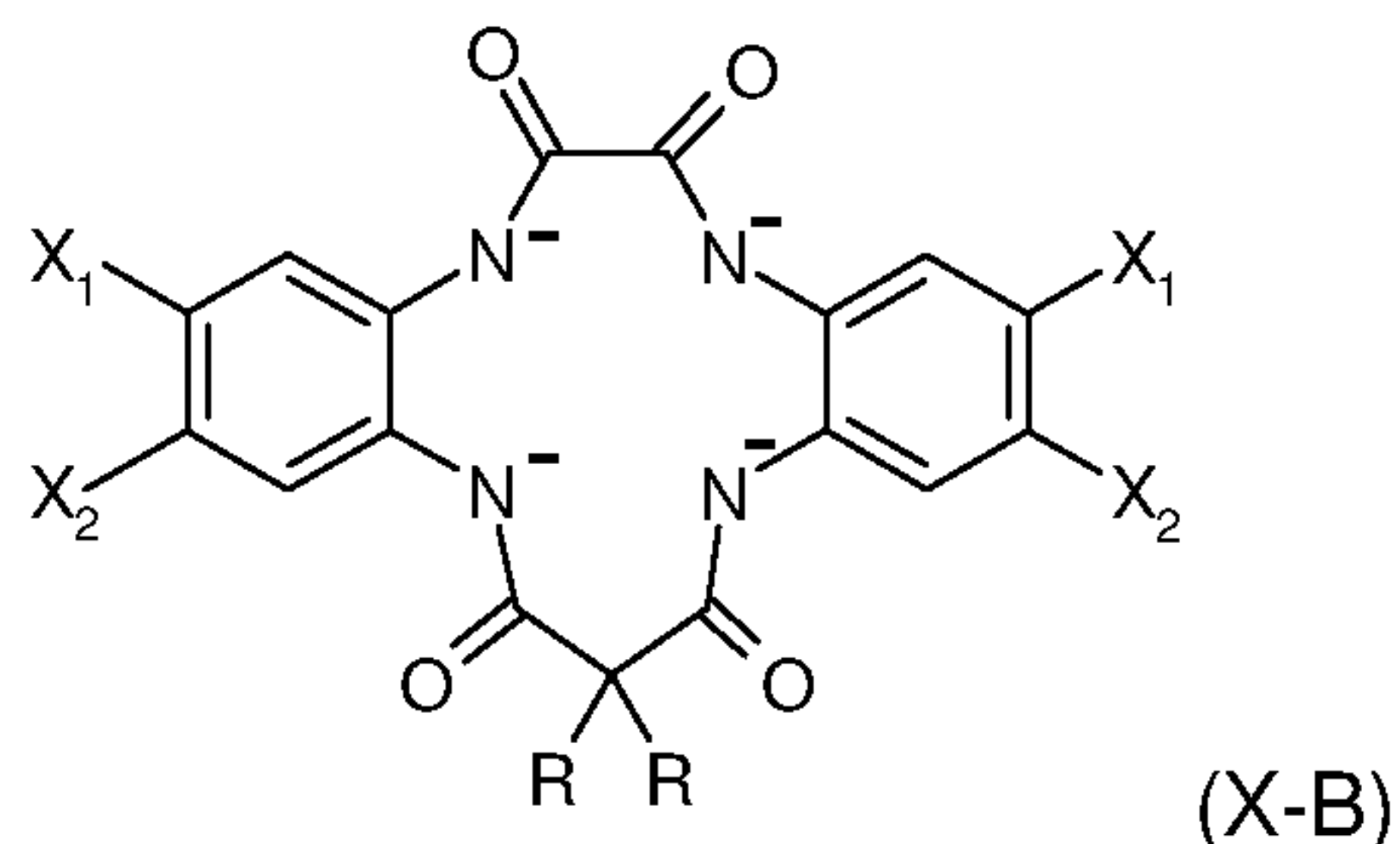
- X and Y may be independently selected from H; electron-donating groups selected from C₁-C₂₄alkyl, C₁-C₂₄alkoxy, C₆-C₁₀aryloxy and C₆-C₁₀arylC₁-C₂₄alkyloxy; and electron-withdrawing groups selected from F, Cl, Br, I, COOR (R is C₁-C₂₄alkyl), CONH(CH₂)₂N(R)₃⁺ (R is C₁-C₂₄alkyl), SO₃⁻, OSO₃⁻, OSO₃R (R is selected from H, C₁-C₂₄alkyl, C₆-C₁₀aryl, C₆-C₁₀arylC₁-C₂₄alkyl), CH₂CF₃, CF₃ and NO₂⁻, and

- R' and R'' may each be independently selected from the group consisting of H, C₁-C₂₄alkyl, C₃-C₂₄cycloalkyl, C₃-C₂₄cycloalkenyl, C₂-C₂₄alkenyl, C₆-C₁₀aryl, C₂-C₂₄alkynyl, C₆-C₁₀arylC₁-C₂₄alkyl, halogen, C₁-C₂₄alkoxy and phenoxy substituents; or together with the carbon atom to which R and R'' are attached form a C₃-C₂₄cycloalkylene or C₃-C₂₄cycloalkenylene ring.

24. The method of clause 23, wherein X and Y groups are independently selected from hydrogen, C₁-C₆alkyl (e.g. methyl), methoxy, nitro, chloro, SO₃⁻, OSO₃⁻, COOR with R=H or CH₃, and CONH(CH₂)₂N(CH₃)₃⁺; and/or wherein the R' and R'' are identical, and selected from methyl, ethyl, fluoro; or together with the carbon atom to which they are attached form a three-membered carbon ring (cyclopropylene) or four-membered carbon ring (cyclobutylene).

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25. The method of clause 11 or clause 12, wherein the complex comprises a polydentate ligand of formula (X), which is of formula (X-B):



wherein:

5 $X_1=X_2=H$, $X_1=X_2=Cl$, or $X_1=NO_2$ and $X_2=H$, and $R=$ methyl.

26. The method of clause 11, wherein the complex comprises a polydentate ligand selected from the group consisting of 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, 2,4-di-(2-pyridyl)-3,7-dimethyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane, 1-(pyridin-2-ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, 1,4-bis(pyridin-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane, 1,4,7-tris(pyridin-2-ylmethyl)-1,4,7-triazacyclononane, 1,2-bis(4-methyl-7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-ethane and 1,3-bis(4-methyl-7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-propane, 1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetrakis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1-methyl-4,7,10-tris(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4-dimethyl-7,10-bis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4,7-trimethyl-11-(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4,8,11-tetraazacyclododecane, 1,4,8,11-tetrakis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1-methyl-4,8,11-tris(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1,4-dimethyl-8,11-bis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, and 1,4,8-trimethyl-11-(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclododecane, 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N-benzyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N,N-bis(pyridin-2-yl-

methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, N,N,N-*tris*(pyridin-2-yl-
 methyl)amine, N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)ethylene-1,2-diamine, N,N'-
 dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine, N-methyl-alkyl-N,N',N'-
 tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)-
 5 1,2-ethylene-diamine, N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N,
 N, N', N'-tetrakis(pyridin-2-yl-methyl)ethylene-1,2-diamine, N, N, N', N'-
 tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, 2,11-diaza[3.3](2,6-
 pyridinophane), N,N'-dimethyl-2,11-diaza[3.3](2,6-pyridinophane), 6-dimethylamino-
 1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 6-amino-1,4-bis(pyridin-2-
 10 ylmethyl)-6-methyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-{N-(pyridin-2-ylmethyl)-N-
 methylamino}-1,4-diazacycloheptane, 6-amino-1,4,6-trimethyl-1,4-diazacycloheptane,
 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane,
 1,4,6-trimethyl-6-(pyridin-2-ylmethyl)amino)-1,4-diazacycloheptane, 6-{N,N-
 bis(pyridin-2-ylmethyl)amino}-1,4,6-trimethyl-1,4-diazacycloheptane, 6-{N-(pyridin-2-
 15 ylmethyl)-N-methylamino}-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane,
 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-
 2,5,7,10-tetrone (6H, 11H), 5,6(4,5-di-chlorobenzo)-3,8,11,13-tetraoxo-2,2,9,9-
 tetramethyl-12,12-diethyl-1,4,7,10-tetracyclotridecane, 5,6(4,5-di-chlorobenzo)-
 3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 5,6-benzo-
 20 3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 3,4,8,9-
 tetrahydro-6,6-difluoro-3,3,9,9-tetramethyl-13-nitro-1-H-1,4,8,11-
 benzotetracyclotridecine-2,5,7,10-tetraoxo, 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-
 1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H), 3,4,8,9-
 tetrahydrospiro-3,3,9,9-tetramethyl-6,1'-cyclopropane-1,4,8,11-
 25 benzotetracyclotridecine-2,5,7,10-tetraoxo, 15,15-dimethyl-5,8,13,17-tetrahydro-
 5,8,13,17-tetraazadibenzo[a,g]cyclotridecene-6,7,14,16-tetraoxo and 2,6-bis[{N-methyl-
 {N-(2-pyridylmethyl)}amino)methyl]pyridine.

27. The method of clause 11, wherein the complex comprises a polydentate ligand
 30 selected from the group consisting of dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-
 ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-
 pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-
 dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-
 dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, 1-(pyridin-2-
 35 ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, 1,4-bis(pyridin-2-ylmethyl)-7-methyl-

- 1,4,7-triazacyclononane, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine, N-methyl-N,N',N'-tris(imidazol-2-ylmethyl)ethylene diamine, N-ethyl-N,N',N'-tris(imidazol-2-ylmethyl)ethylene diamine, tris(pyridin-2-ylmethyl)amine, 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane and 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H).
- 10 28. The method of clause 11, wherein the complex comprises 1,4,7-trimethyl-1,4,7-triazacyclononane.
- 15 29. The method of any one of clauses 2 to 7, wherein the chlorine-containing chemical is chlorine dioxide and the complex comprises a chelant of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (VII'), (VII'-B), (IX) or (XI) as defined in clause 13.
30. The method of any one of clause 29, wherein the chelant is as defined in any one of clauses 13 to 20.
- 20 31. The method of any one preceding clause, wherein the complex is pre-formed.
32. The method of any one preceding clause, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III), Fe(IV) and Fe(V).
- 25 33. The method of clause 32, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III) and Fe(IV).
34. The method of any one preceding clause, wherein the complex comprises one or two iron ions.
- 30 35. The method of any one preceding clause, wherein the method comprises heating the aqueous medium to a temperature of between about 30 and about 100 °C.
- 35 36. The method of clause 35, wherein the temperature is between about 40 and about 95 °C.

37. The method of any one preceding clause, wherein the aqueous medium comprises at least 1 wt% of water.

5 38. The method of any one preceding clause, wherein the aqueous medium is a solution.

39. The method of any one preceding clause, wherein the aqueous medium comprises between about 0.001 and about 50 μM of the complex.

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40. The method of clause 39, wherein the aqueous medium comprises between about 0.01 and about 20 μM of the complex.

15 41. The method of clause 39, wherein the aqueous medium comprises between about 0.1 and about 5 μM of the complex.

42. The method of any one preceding clause, wherein the chlorine-containing chemical is present in the aqueous medium in a concentration of between about 0.01 and about 50 mM.

20

43. The method of clause 42, wherein the chlorine-containing chemical is present in the aqueous medium in a concentration of between about 1 and about 30 mM.

25 44. The method of any preceding clause, wherein the pH of the aqueous medium is between about 2 and about 11, for example wherein the pH of the aqueous medium is between about 3 and about 7.

45. The method of any one preceding clause, wherein the aqueous medium is buffered.

30

46. The method of any one preceding clause, wherein the method involves use of a chlorite salt selected from the group consisting of sodium chlorite, potassium chlorite, lithium chlorite, calcium chlorite, barium chlorite and magnesium chlorite.

47. The method of clause 46, wherein the chlorite salt is sodium chlorite or potassium chlorite.

48. The method of clause 46, wherein the chlorite salt is sodium chlorite.

5

49. An aqueous medium comprising a chlorine-containing chemical, which is chlorine dioxide and/or a chlorite salt, and a complex of one or more iron ions and one or more polydentate ligands, which are chelants that contain at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

10

50. The aqueous medium of clause 49, which comprises at least 1 wt% of water.

51. The aqueous medium of clause 49, which comprises between 50 and 100 wt% water, typically between 80 and 100 wt% water.

15

52. The aqueous medium of any one of clauses 49 to 51, which is as defined in any one of clauses 38 to 48.

53. The aqueous medium of any one of clauses 49 to 52, wherein the complex is as defined in any one of clauses 9 to 34.

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54. The aqueous medium of any one of clauses 49 to 52, wherein the complex is as defined in any one of clauses 9-12, 15 and 18-27.

25

55. The aqueous medium of clause 54, wherein the complex is pre-formed.

56. The aqueous medium of clause 54 or clause 55, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III), Fe(IV) and Fe(V).

30

57. The aqueous medium of clause 56, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III) and Fe(IV).

58. The aqueous medium of any one of clauses 54 to 57, wherein the complex comprises one or two iron ions.

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67

59. The aqueous medium of any one of clauses 49 to 58, wherein the chlorine-containing chemical is a chlorite salt.
- 5 60. The aqueous medium of any one of clauses 49 to 52, wherein the chlorine-containing chemical is chlorine dioxide and the complex is as defined in clause 13.
61. The aqueous medium of clause 60, wherein the chelant is as defined in any one of clauses 13 to 20.
- 10 62. The aqueous medium of clause 60 or clause 61, wherein the complex is pre-formed.
63. The aqueous medium of any one of clauses 60 to 62, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III),
15 Fe(IV) and Fe(V).
64. The aqueous medium of clause 63, wherein the complex comprises one or more iron ions selected from the group consisting of Fe(II), Fe(III) and Fe(IV).
- 20 65. The aqueous medium of any one of clauses 60 to 64, wherein the complex comprises one or two iron ions.
66. A kit comprising a chlorite salt and, separately, a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at
25 least one iron ion through at least three nitrogen atoms, with the proviso that the one or more polydentate ligands are not porphyrin ligands.
67. The kit of clause 66, wherein the chlorite salt is as defined in any one of clauses 46 to 48.
30
68. The kit of clause 66 or clause 67, wherein the complex is as defined in any one of clauses 9 to 34.
69. The kit of any one of 66 to 68, wherein the complex is as defined in any one of
35 clauses 54 to 58.

70. A composition comprising a chlorite salt and a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the one or more polydentate ligands are not porphyrin ligands.

5

71. The composition of clause 70, wherein the complex is as defined in any one of clauses 9 to 34.

10

72. The composition of clause 70 or clause 71, wherein the complex is as defined in any one of clauses 54 to 58.

73. The composition of any one of clauses 70 to 72, wherein the chlorite salt is as defined in any one of clauses 46 to 48.

15

The following non-limiting examples below serve to illustrate the invention further.

EXPERIMENTAL

20

Compound (1): $[\text{Fe}(\text{N}2\text{py}3\text{o}-\text{C}1)\text{Cl}]\text{Cl}$ ($\text{N}2\text{py}3\text{o}-\text{C}1$ = Dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate) was obtained as described in WO 02/48301 (Unilever).

25

Compound (2): $[\text{Fe}(\text{N}2\text{py}2\text{o}-\text{EtNMe}_2)\text{Cl}]\text{Cl}$ ($\text{N}2\text{py}2\text{o}-\text{EtNMe}_2$ = Dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(N,N-dimethyl-amine-ethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate) was obtained as described in WO 03/104379 (Unilever).

30

Compound (3): $[\text{Fe}(\text{III})_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{TACN})_2](\text{PF}_6)_2$ (Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) was prepared as disclosed by Wieghardt and co-workers, *J. Am. Chem. Soc.*, **109**, 7387-7396 (1987).

Compound (4): $[\text{Fe}(\text{II})(\text{Me}_2\text{PyTACN})(\text{CF}_3\text{SO}_3)_2]$ (Me_2PyTACN = 1,4-dimethyl-7-(pyridin-2-ylmethyl)-1,4,7-triazacyclononane) was prepared as described by M. Costas, et al., *Chem. Eur. J.*, **15**, 3359-3362 (2009).

35

Compound (5): $[\text{Fe}(\text{II})(\text{EtPy}2\text{TACN})\text{Cl}]\text{ClO}_4$ ($\text{EtPy}2\text{TACN}$ = 1-ethyl-4,7-bis(pyridin-2-ylmethyl)-1,4,7-triazacyclononane) was prepared as described elsewhere (WO2001/064826).

Compound **(6)**: $[\text{Fe}(\text{CyclenPy}_4)](\text{ClO}_4)_2$ (CyclenPy_4 = 1,4,7,10-tetrakis(2-pyridin-2-ylmethyl)-1,4,7,10-tetraazacyclododecane) was prepared as described by X-H Bu and co-workers, *Polyhedron*, **19**, 431-435 (2000) and **17**, 289-293 (1998).

- 5 Compound **(7)**: $[\text{Fe}(\text{Bcyclam})\text{Cl}_2]$, (Bcyclam = 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) was prepared as described by Busch and co-workers in WO 98/39098 and *J. Am. Chem. Soc.*, **122**, 2512-2522 (2000).

10 Compound **(8)**. 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane was prepared as disclosed elsewhere (EP1280794B). The iron complex was prepared *in situ* by mixing 0.2 mmol/l of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in water and 0.2 mmol/l of the ligand in water (for the ClO_2 formation and dye bleaching experiments). For the BC-1 experiments 2 mmol/l of iron chloride in water and 2 mmol/l of the ligand in water was mixed. All samples were left for at least 15 minutes before the subsequent bleaching or
15 ClO_2 formation experiments were done.

Compound **(9)**: 6-dimethylamino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane was prepared as disclosed elsewhere (EP1280794B). The iron complex was prepared as described for compound **(8)**.

20 Compound **(10)**: $[\text{Fe}(\text{MeN4py})\text{Cl}]\text{Cl}$ (MeN4py = N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane) and the corresponding iron(II) complex, $[\text{Fe}(\text{MeN4py})\text{Cl}]\text{Cl}$, were prepared as described in EP0909809 (Unilever).

25 Compound **(11)**: N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine (MeN3Py) was prepared as disclosed elsewhere (EP11657381B). The iron complex was prepared as described for compound **(8)**

30 Compound **(12)**: $[\text{Fe}(\text{bispicen})(\text{CF}_3\text{SO}_3)_2]$ (bispicen = N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)ethylenediamine) was prepared as published by Que et al (*J. Am. Chem. Soc.*, **123**, 12931-12932 (2001)).

Compound **(13)**: $[\text{Fe}(\text{trispicen})\text{Cl}]\text{Cl}$ (trispicen = N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)ethylenediamine) was prepared as published by I Bernal et al (*J. Chem. Soc., Dalton Trans*, **22**, 3667-3675 (1995)).
35

Compound **(14)**: $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2$ (tpen = N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine) was prepared as published by H Toftlund et al (*Acta*.

Chemica Scandinavica A, **35**, 575-585 (1981)). Tpen ligand (tpen=N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine) was prepared as published by H Toftlund et al (*Acta. Chemica Scandinavica A*, **35**, 575-585 (1981)).

- 5 Compound (15): $[\text{Fe}(\text{II})(\text{TPAA})](\text{ClO}_4)_2$ (TPPA = tris(N-pyridin-2-ylmethyl)-2-aminoethylamine) was prepared as described by I. Morgenstern *et al.*, *J. Am. Chem. Soc.*, **118**, 4567-4573 (1996) and *Inorg. Chim. Acta*, **297**, 338-350 (2000).

10 Compounds (16): N-ethyl-N,N',N'-tris(imidazol-2-ylmethyl)ethylene diamine) was prepared as disclosed elsewhere (EP1358309B). The iron complex with this ligand was prepared in-situ as described for compound (8).

15 Compound (17): $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)(\text{TPA})_2](\text{ClO}_4)_3$ (TPA = tris(pyridin-2-ylmethyl)amine) was prepared as described by L. Que *et al.*, *J. Am. Chem. Soc.*, **112**, 1554-1562 (1990).

20 Compound (18): $[\text{LFe}(\text{H}_2\text{O})]\text{Li} \cdot \text{H}_2\text{O}$: (H_4L =5,6-Benzo-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetraazacyclotridecane) was prepared as described in patent WO2004/076425 (Carnegie Mellon University).

Compound (19): $[\text{Fe}(\text{py}_2\text{N}_2)\text{Cl}_2]\text{Cl}$ (py_2N_2 = 2,11-diaza[3.3](2,6)pyridinophane) was made according to a procedure disclosed for a similar methoxy derivative as described in EP1087969B (Unilever).

25 Compound (20): The ligand, 2,6-bis[(N-methyl-{N-(2-pyridylmethyl)}amino)methyl]pyridine was prepared as described by G. Britovsek and co-workers in *Inorg. Chem.*, **52**, 11867-11874 (2013). The iron complex was prepared *in situ* as described above for the preparation of compound (8).

30 Experiment 1: Formation of chlorine dioxide from sodium chlorite

Experimental

35 As a reference, ClO_2 dissolved in water was prepared as follows: sodium chlorite (5 g, 80% purity, dissolved in 15 ml water) was mixed with an HCl solution (37 wt-%, 3 mL) in a flask with an nitrogen gas inlet and an outlet to a another flask containing water that was put in an ice-bath. A yellow solution slowly formed, which was then purged with nitrogen gas. The ClO_2 gas was then bubbled into the cold water from the other vessel, which led then to dissolution of ClO_2 in water. It should be noted

that chlorine dioxide dissolves well in cold water and also shows a fairly good stability. The amount of chlorine dioxide has been determined by UV-vis (359 nm, extinction coefficient of $1250 \text{ M}^{-1}\text{cm}^{-1}$). (*J. Am. Chem. Soc.*, **136**, 3680-3686 (2014)).

5 The UV-vis spectrum of ClO_2 is shown in Fig. 1, which shows ClO_2 in water synthesized from chlorite. Sample diluted 20x.

The formation of ClO_2 from sodium chlorite was tested as follows. In an aqueous solution of pH 5 using acetic acid buffer (50 mM) and sodium chlorite (10 mM) and 10 and 1 μM of each complex was heated at 60 °C for 15 min (results listed in Table 1 below). The formation of chlorine dioxide could be followed by monitoring the
10 UV-vis spectrum (increase in absorbance at 359 nm), as also disclosed in literature (see for example Figure 1 in *Angew. Chem., Int. Ed. Engl.*, **50**, 695-698 (2011)). Additionally, some of the complexes (**1**, **14** and **17**) were also tested for their activity to form ClO_2 at 40 and 25 °C.

15 *Results and Discussion*

In all cases, formation of chlorine dioxide has been observed under the conditions outlined above (whilst the blank did not furnish any significant amount of chlorine dioxide). Table 1 shows the data. A representative example of a UV-vis spectrum of chlorine dioxide measured after adding compound **1** to a buffered aqueous
20 chlorite solution is shown in Fig. 2 below, which shows the maximum concentration ClO_2 obtained by mixing 0.1 mM compound **1** with chlorite. The peak at 261 nm is due to residual chlorite in the solution.

The results in Table 1 show that some compounds furnish quicker ClO_2 than some others (e.g. **14** and **17** are quite rapid in maximum formation of ClO_2). In many
25 cases, a decrease in the absorbance at 359 nm could be observed, after having reached the maximum absorbance (see Fig. 3 as a representative example obtained by monitoring the absorbance at 359 nm after mixing compound **1** with chlorite, which shows absorbance at 359 nm (formation of ClO_2) vs time upon mixing 0.1 mM compound **1** with chlorite). The decrease in absorbance suggests that the ClO_2 formed
30 may be decomposed as well. Furthermore, the amount of ClO_2 formed in some cases was higher than what could have been analysed for by UV-vis at this concentration. For this reason, as well as for comparison with dye bleaching result (*vide infra*), various complexes were also tested at lower concentrations, with in many cases good results (see Table 1). Especially compounds **14** and **17** show even at 1 μM level very rapid
35 ClO_2 formation, and therefore these were also tested at 0.1 μM . Complex **14** shows

then still 0.7 a.u. at 359 nm due to ClO_2 formation after 900 seconds and complex **17** even a more intense band due to ClO_2 (2.5 a.u. at 359 nm after 900s).

The results of the complexes that were also tested at 40 °C and 25 °C for their activity on conversion of chlorite to ClO_2 and their dye bleaching activity are given in Table 2 below. Also at these lower temperatures the three complexes tested showed clear activity.

These results on ClO_2 formation show that the iron complexes tested, which comprise chelants capable of chelating at least one iron ion through at least three nitrogen atoms, are active and therefore could be used for different applications, such as cellulosic bleaching or antimicrobial treatment for example.

Table 1. Formation of chlorine dioxide (column 2 & 3) and Acid Blue 25 dye bleaching (column 4) by different complexes (10 and/or 1 μM) and sodium chlorite. 1 μM of each complex was used for the Acid Blue dye bleaching. In some cases also 10 μM of the complex was tested towards dye bleaching, denoted in parentheses in column 4).

Compound	ClO_2 formation		Acid Blue bleaching
	Max. abs. in A.u.(time to reach max abs) ^{1,2,3,4}		Δ Abs 602nm (15') ⁵
	10 μM	1 μM	1 μM (10 μM)
1	2.9 (900s)	0.7 (900s)	0.95
2	2.1 (900s)	0.2 (900s)	0.84
3		1.4 (900s)	1.04 (0.53)
4	1.7 (900s)	1.34 (900s)	0.92
5	2.9 (900s)	0.9 (900s)	0.68
6	2.7 (250s)	1.7 (900s)	1.04 (1.1)
7	0.4 (900s) ³		0.16
8	2.7 (40 s)	2.1 (300 s)	0.8
9	2.6 (160 s)	1.1 (300 s)	0.2 (0.9)
10	2.9 (700s)	1.1 (900s)	0.62
11	2.2 (900 s)	0.7 (900 s)	1.0 (1.0) ⁶
12	2.4 (900s)	0.3 (900s)	0.43
13	2.9 (450s)	0.2 (900s)	0.06 (1.2)
14	2.9 (150s)	2.9 (550s)	0.99
15	2.8 (900s)	0.9 (900s)	0.94
16	2.3 (430 s)	0.9 (900 s)	0.92
17	2.9 (130s)	2.8 (340s)	0.74

18	2.0 (900s)	1.2 (900s)	0.87
19	2.9 (700s)		0.1 (1.1)
20	1.8 (820 s)		0.9
No cat	<0.1 (900s)		No reaction

¹Maximum absorbance at 359 nm measured as measure of chlorine dioxide formed at 60 °C (see experimental section above for details).

²Time to reach highest absorbance of ClO₂ in seconds. A smaller value indicates that the complexes induces a faster formation of chlorine dioxide.

5 ³The reference sample iron chloride (at 100 μM) yielded 0.3 A.u. of chlorine dioxide within 900 sec, which is much less than any of the iron compounds tested. Compound 7 generated chlorine dioxide at 100 μM to yield an absorbance of 2.2 after 900 seconds.

⁴The absorbance that can be measured accurately is less than 2.5 A.u. Therefore, no conclusions regarding the exact amounts of ClO₂ can be made from these data if the absorbance is > 2.5 A.u.

10 ⁵Difference in absorbance at 602 nm between a solution with a complex (concentration given in the table) and a solution without an iron complex (blank) indicating Acid Blue 25 dye bleaching activity. The blank gives a decrease in absorbance at 602 nm of about 0.02 A.U. A higher value of the bleaching observed with respect to the blank (combined with lower level of complex) indicates a better bleaching activity. Values in parentheses denote the dye bleaching activity of 10 μM of the complex.

15 ⁶Full bleaching reached within 100 seconds.

Table 2. Formation of chlorine dioxide (columns 2, 3, 5, 6) and Acid Blue 25 dye bleaching (columns 4 and 7) by different complexes and sodium chlorite. The amount of complex used for the chlorine dioxide formation was 10 and 1 μM. 10 μM of each complex was used for the Acid Blue dye bleaching.

Compound	Max. abs. in A.u. (time to reach max abs) ^{1,2,3}		Δ Abs AB 602nm (15') ^{4,5}	Max. abs. in A.u. (time to reach max abs) ^{1,2,3}		Δ Abs AB 602nm (15') ^{4,5}
	10 μM 40 °C	1 μM 40 °C		10 μM 25 °C	1 μM 25 °C	
1	1.3 (900s)	1.4 (900s)	1.22	0.8 (900s)	0.4 (900s)	1.21
14	2.5 (160s)	0.5 (900s)	1.26	2.5 (200s)	0.9 (900s)	1.21
17	2.4 (280s)	2.3 (900s)	1.25	2.4 (400s)	2.9 (900s)	1.25
No Fe complex	<0.1		<0.1	<0.1		<0.1

¹Maximum absorbance at 359 nm measured as measure of chlorine dioxide formed at 40 or 25 °C (see experimental section above for details).

²See footnote 2 table 1.

³See footnote 4 table 1.

25 ⁴See footnote 5 table 1, except that only 10 μM of each complex has been used.

⁵Complete dye bleaching has been observed; the variation in the value of ΔAbs is due to differences in starting dye concentrations.

Experiment 2. Acid Blue 25 dye bleaching with chlorite.*Experimental*

In a buffered aqueous solution (50 mM acetic acid buffer pH 5), Acid Blue 25 dye was added to reach an absorbance of approximately 1 at 602 nm. Sodium chlorite was added to yield 10 mM in the solution. Then various amounts of complex were added to test their activity towards dye bleaching (in most cases 1 μ M, whilst some complexes were tested at 10 μ M concentration). All experiments were done at 60 °C (Table 1), whilst some of the more active complexes were also tested at 40 °C and 25 °C for their activity on their dye bleaching activity (Table 2). The decay of the absorbance at 602 nm was monitored (=bleaching of the dye) and the difference between starting absorbance and the absorbance measured at 15 minutes was noted (see Table 1).

Results and Discussion

As shown in Table 1, the complexes tested yielded improved dye bleaching activity as compared to the reference (without complex). A reference experiment using independently prepared ClO_2 (*vide supra*) yielded an immediate bleaching of the blue dye, suggested that the extent of dye bleaching is correlated to the ClO_2 formation measured as discussed above.

The complexes when tested also showed good dye bleaching activity at 40 °C and 25 °C as shown in Table 2.

The results on ClO_2 formation and dye bleaching presented in Tables 1 and 2, indicate that the complexes of the different classes of ligands as specified herein are active and therefore could be used for different applications, such as cellulosic bleaching, dye bleaching or antimicrobial treatment for example. Although not all complexes have been tested at lower temperatures, the ones that were tested show also clear activity towards ClO_2 formation at 40 and 25 °C, suggesting that these complexes may be employed at different temperatures ranging from ambient to at least 60 °C.

Experiment 3. Bleaching experiments of hardwood pulp with chlorite*Experimental*

Hardwood chemical pulp that has been delignified in an O_2 delignification step, with a starting ISO-brightness of 50.6 was treated as follows: 1 g of oven-dry pulp was added to a series of small beaker-glasses containing 19 mL of water with 50 mM

acetate buffer at pH 5 and 20 mg of NaClO₂. When appropriate, an aqueous solution of the iron complex was added to yield the desired level of complex (see Table 2 for concentration of each complex used). All experiments were carried out at 5% consistency (the exact amounts of pulp added therefore depended on the consistency of the starting pulp). The temperature was set at 60 °C and the reaction mixture was kept at this temperature for 1 h. Manual stirring was done twice or three times during the bleaching experiments. Subsequently the pulp mixture is filtrated through a Buchner funnel, washed with copious amounts of demineralised water and dried overnight at ambient conditions. The optical properties of the pulp heaps were then measured using a Minolta spectrophotometer CM-3700d, using L, a, b values which are converted to whiteness values through the following formula:

$$100 - \sqrt{(100 - L)^2 + a^2 + b^2}$$

The ISO-Brightness values are calculated through the following formula:

$$\text{ISO-Brightness} = (1.98 * \text{whiteness}) - 100.3.$$

Results and Discussion

The results of the experiment are given in Table 3.

Table 3. ISO-Brightness results of bleaching hardwood pulp using NaClO₂ and the transition-metal complexes at pH 5 at 60°C for 60 minutes. The numbers in parentheses indicate the amount of complex added in ppm (or mg per kg of oven dry pulp).

Compound	Δ Brightness pulp (wrt blank – no cat)
1	8(10 ppm)
2	10(10 ppm)
6	7(30 ppm)
10	9(10 ppm) 12(30 ppm)
14	7(10 ppm)
Tpen ligand	5(300 ppm)
FeCl ₂	2(100 ppm)

As shown in Table 3, a number of the complexes tested give good bleaching effects with sodium chlorite at low levels (10-30 ppm). The iron complexes **1**, **2**, **10**, and **14** show a good bleaching with chlorite at relatively low levels. The ligand of complex **14**, TPEN, gives also enhanced bleaching. Although the bleaching results with TPEN ligand were not further optimised (with respect to levels), it is assumed that transition-metal ions present in the wood pulp, like Fe, may bind to the ligand and then become active to activate chlorite for bleaching and/or chlorine dioxide formation.

Iron chloride gave a very low bleaching effect at 100 ppm did not show any significant bleaching with chlorite (as compared to chlorite alone). This also shows that the Fe complexes listed in the table above all yield significant bleaching effects on wood pulp and that these complexes have not been decomposed into the free iron species to a large extent.

Experiment 4. Acid Blue 25 and Acid Red 88 dye bleaching with chlorine dioxide.

Experimental

In a buffered aqueous solution (50 mM acetic acid buffer pH 5), Acid Blue 25 dye was added to reach an absorbance of approximately 1 at 602 nm. Chlorine dioxide was prepared from sodium chlorite and HCl as shown in experiment 1. Then chlorine dioxide was added to yield 0.1 and 0.15 mM of chlorine dioxide and various amounts of the Fe complex (compound **1**) were added to test the catalysed dye bleaching activity.

All experiments were done at 30 °C. The decay of the absorbance at 602 nm was monitored (=bleaching of the dye) and the difference between starting absorbance and the absorbance measured at 15 minutes was noted (see Table 4). A higher value indicates a better bleaching activity. A similar set of experiments was done using Acid Red 88 as dye (following the changes in absorbance at 502 nm, starting at an absorbance of 1.9).

Similarly, a wider screening of various catalysts at a concentration of 10 µM was done using Acid Blue 25 and 0.1 mM chlorine dioxide under the same conditions (see Table 4a).

Results and Discussion

As shown in Table 4, the addition of compound **1** to 0.1 and 0.15 mM ClO₂ resulted in much lower absorbances of Acid Blue 25 and Acid Red 88 after 15 minutes reaction time. There is therefore an improved dye bleaching activity as compared to the

reference (without compound **1**). As these absorbances were monitored after 15 minutes, they do not reflect the time dependencies of the bleaching. Therefore, Fig. 4 has been included to show a typical time-dependent bleaching by ClO₂ without and with the complex **1**. It shows absorbance at 602 nm of Acid Blue 25 dye vs time, of 0.1 mM ClO₂ without complex and with 10 μM complex **1**.

Addition of ClO₂ to the solution with the dye, led to a very rapid decrease of the dye intensity. This is shown in Fig. 4, where the addition of 0.1 mM ClO₂ led to a decrease in absorbance of approximately 1 to about 0.7. Addition of the complex to the dye and chlorine dioxide mixture leads to a slower continuation of the bleaching of the dye (see Fig. 4 – lowest line).

These observations are in agreement with the suggestion that, after bleaching of the dye by ClO₂, the chlorite presumably formed can be regenerated by the complex (as noted from the formation of ClO₂ out of chlorite when using complex **1**, see Experiment 1).

Table 4. Acid Blue 25 (AB25) and Acid Red 88 (AR88) dye bleaching by compound **1** and chlorine dioxide.

	0.1 mM ClO ₂ Δ Abs AB25 602nm (15 ') ¹	0.15 mM ClO ₂ Δ Abs AB25 602nm (15 ') ¹	0.1 mM ClO ₂ Δ Abs AR88 503nm (15 ') ²	0.15 mM ClO ₂ Δ Abs AR88 503nm (15 ') ²
Blank	0.3	0.5	0.65	0.95
3.5 μM 1	0.6	0.75	0.7	1.0
10 μM 1	0.75	0.8	0.9	1.2
30 μM 1	0.8	0.8	1.1	1.5

¹Change in absorbance at 602 nm of Acid Blue 25 dye between the initial value and the solution after 15 minutes reaction time. Comparisons are made between the differences in absorbance with the Fe complex (compound **1** in different concentrations) and those without. A larger difference suggests that the effect of the Fe complex increases the bleaching effect by ClO₂.

²Difference in absorbance at 503 nm using Acid Red 88 after 15 min reaction time.

The results of similar experiments conducted using a wider set of catalysts on Acid Blue 25 bleaching are shown in Table 4a. Addition of ClO₂ only (without catalyst) led to a decrease of the concentration of dye by 0.39 A.U. (at 602 nm).

Table 4a. Acid Blue 25 (AB25) dye bleaching by various compounds (10 μM) and chlorine dioxide (0.1 mM). Conditions are the same as shown in Table 4.

	0.1 mM ClO ₂ Δ Abs AB25 602nm (15 ‘) ¹
Blank	0.39
1	0.84
2	0.87
3	0.47
4	0.35
5	0.41
6	0.40
8	0.77
10	0.67
11	0.81
12	0.44
13	0.83
14	0.82
15	0.62
16	0.71
17	0.78
18	0.39

¹Change in absorbance at 602 nm of Acid Blue 25 dye between the initial value and the solution after 15 minutes reaction time. Comparisons are made between the differences in absorbance with the Fe complexes and those without. A larger difference suggests that the effect of the Fe complex increases the bleaching effect by ClO₂.

The results in Table 4a show that a wide variety of iron catalysts is active in the presence of ClO₂ towards dye bleaching. These observations are in agreement with the suggestion that, after bleaching of the dye by ClO₂, the chlorite presumably formed can be regenerated by a variety of iron catalysts (compounds **1**, **2**, **8**, **10**, **11**, **13**, **14**, **15**, **16**, and **17**). Compounds **3**, **4**, **5**, **6**, **12**, and **18** show a minor or no activity towards increased dye bleaching vs ClO₂ only. The inactive or less active compounds in this experiments showed clear ClO₂ formation activity when mixed with chlorite (Table 1) and were also capable in bleaching the same dye in the presence of chlorite.

Experiment 5: stain bleaching on cotton*Experimental*

In an aqueous solution of pH 5 using acetic acid buffer (50 mM), sodium chlorite (0.1 g/L), 10, 3 or 1 μ M of each complex, and 1 g of BC-1 tea stains (a well-known model for tea stains) was added and heated to 60 °C for 30 min while stirring continuously (Table 6). The total volume was 100 mL. After this, the BC-1 was washed two times in demineralized water and dried before measuring the reflectance at 460 nm using a Minolta spectrophotometer CM-3700d. Details of the procedures to measure the reflectance at 460 nm of BC1 stains can be found elsewhere (EP 0 909 809 B (Unilever plc and Unilever N.V.)).

Also one of the complexes, **1**, was tested with different levels of sodium chlorite at pH 5 (Table 5).

Four of the complexes, **1**, **2**, **14**, and **17** were also tested on their performance at 40 °C and 25 °C following the same procedure as shown above (Table 7).

Similar experiments were performed using 10 μ M of compound **2** between pH 7 and 11 without buffer. The results of these experiments are shown in Table 8 below.

Results and Discussion

The results of the BC-1 bleaching experiments of sodium chlorite without and with compound **1** are presented in Table 5 below. Whilst the bleaching activity of sodium chlorite in the absence of the complex is very low, addition of the complex leads to a large increase in reflectance at 460 nm (ΔR value), even when using very low levels of chlorite. For example, 10 mg/l of sodium chlorite shows an increase of around 10 ΔR points using 10 μ M of the complex.

Table 5. BC-1 bleaching (in ΔR) of sodium chlorite in the absence and presence of complex **1** at 60 °C for 30 min (pH 5).

NaClO ₂ (g/l)	No Fe complex	2 μ M 1	10 μ M 1
0.1	6.0		38.3
0.05	6.0	27.3	33.2
0.01			6.0
0.002	5.4		7.4

The results of the BC-1 bleaching experiments of sodium chlorite with different complexes are presented in Table 6 below. In all cases a clear enhancement in the bleaching activity was observed, even with lower levels of complexes. It should be noted that compound **17** shows an unusual behaviour, i.e. a higher activity was measured when lower levels of this complex were employed. This is likely related to the very high activity of this complex towards chlorine dioxide formation and decomposition found for this complex at 10 μM (table 1), so during most of the period during which the BC-1 stain was bleached, there will be little or no chlorine dioxide left to bleach the stain. Therefore, at lower levels of complex **17** the activity of ClO_2 decomposition decreases and the overall bleaching effect becomes larger. It was observed that this compound shows even at 0.1 μM level a significant bleaching effect.

Four of the identified active complexes above were also tested at lower temperatures (40 and 25 $^{\circ}\text{C}$); see Table 7 below for the bleaching results. From the results it is clear that also at lower temperatures, and even room temperature, the bleaching performance of these complexes are significantly higher than those of the blanks, in agreement with the results presented in Table 2 and discussed above on ClO_2 formation and dye bleaching.

Further it was observed that using the TPEN ligand of compound **14** (without iron) furnishes bleaching as well. Without being bound to theory, it is assumed that the BC-1 stain, derived from tea, which contains metal ions, binds to the TPEN ligand and then forms active catalytic species *in situ*.

Table 6. BC-1 bleaching (in ΔR) of sodium chlorite (100 mg/l) in the absence and presence of different compounds at 60 $^{\circ}\text{C}$ for 30 min.

Compound	10 μM	3 μM	1 μM	0.3 μM	0.1 μM
1	36.0	33.3	28.2		
2	34.8	31.7	23.2		
5	21.3	12.6			
6	23.5	28.8	7.3		
8	37.1	30.0	8.0		
10	29.7	32.2	24.6		
11	30.7	31.7	16.8		
12	13.5	9.2			

13	30.7	33.3	14.1		
14	27.7	26.3			
TPEN ligand (no Fe)		25.5			
14	26.4	18.8			
16	32.3	34.5	26.3		
17	11.4	15.3	27.5	29.5	15.5
18	34.3	21.3			
20	30.1	7.3			
No Fe complex	7.1				

Table 7. BC-1 bleaching (in ΔR) of sodium chlorite (100 mg/l) in the absence and presence of different compounds at 40 and 25 °C for 30 min.

Compound	10 μM 40 °C	3 μM 40 °C	1 μM 40 °C	0.3 μM 40 °C	10 μM 25 °C	3 μM 25 °C	1 μM 25 °C
1	27.4	-	-	-	16.9	-	-
2	22.1	-	-	-	13.4	-	-
14	26.8	31.5	30.2	-	24.6	19.6	-
17	14.2	22.8	29.0	24.8	13.1	18.8	17.0
No Fe complex	5.7				4.6		

5 The results of the BC-1 bleaching experiments of sodium chlorite with and with 10 μM of compound 2 at different pHs are presented in table 8 below. The results show that also at higher pHs the performance of one of the iron complexes, 2, is remarkably high (the blanks were not measured at all pHs, but in general will be expected to be lower than the blank at pH 5 (which is the expected optimum for chlorite only).

10

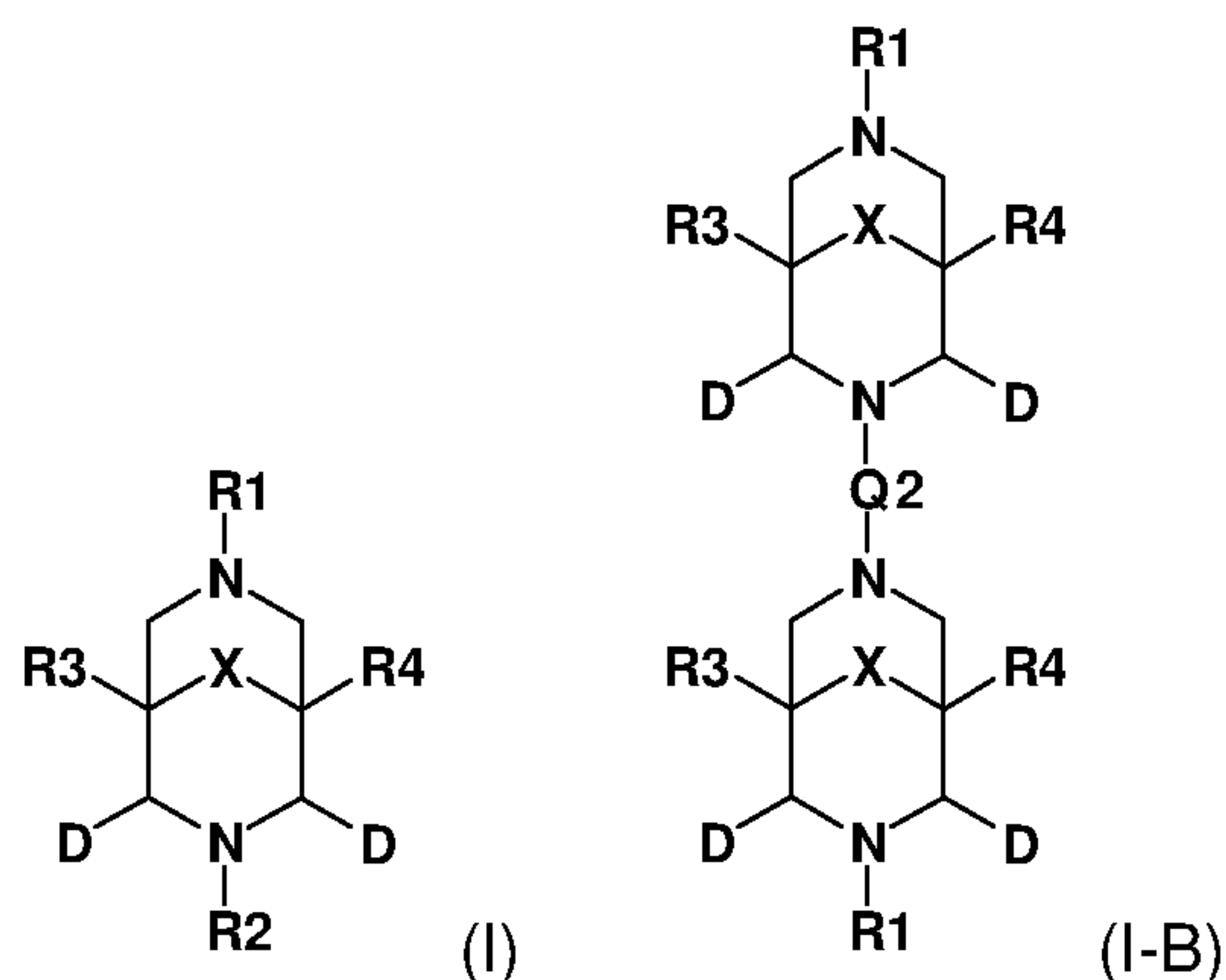
Table 8. BC-1 bleaching (in ΔR) of sodium chlorite with compound 2 at 60 °C for 30 min at different pH's in either 50 mM carbonate buffer or without buffer.

pH	10 μM 2	
	No buffer ΔR	carbonate buffer ΔR
7.0	24.8	
9.0	23.5	21.1
10.0	21.9	19.0
11.0	18.0	

CLAIMS:

1. A method of generating chlorine dioxide from a chlorine-containing chemical, which is a chlorite salt, comprising contacting, in an aqueous medium, a chlorite salt
5 and a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.
- 10 2. A method of treating a substrate comprising contacting, in an aqueous medium, (i) the substrate (ii) an amount of a chlorine-containing chemical, which is a chlorite salt; and (iii) a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least
15 three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.
3. The method of claim 2, wherein the substrate is a cellulosic substrate, for example wood pulp.
- 20 4. The method of claim 2, which is a method of treating water, comprising contacting the water with an amount of the chlorine-containing chemical and the complex.
- 25 5. The method of any one preceding claim, wherein the aqueous medium comprises between about 0.1 and about 5 μ M of the complex.
6. The method of any one preceding claim, wherein the method involves use of a chlorite salt selected from the group consisting of sodium chlorite, potassium chlorite, lithium chlorite, calcium chlorite, barium chlorite and magnesium chlorite.
30
7. The method of any one preceding claim, wherein the complex is pre-formed.
8. The method of any one preceding claim, wherein the complex comprises a chelant capable of chelating at least one iron ion through at least three nitrogen atoms,
35 which is of formulae (I), (I-B), (II), (II-B), (III), (IV), (V), (V-B), (V-C), (VI), (VII), (VII-B), (VIII), (VIII-B), (IX), (X) or (XI):

83



wherein:

each D is independently selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl and thiazol-2-yl, each of which may be optionally substituted by one or more groups independently selected from the group consisting of -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl, and -C₁-C₄alkyl;

the or each R1 and R2 are independently selected from the group consisting of C₁-C₂₄alkyl, C₆₋₁₀arylC₁-C₆alkyl, C₆₋₁₀aryl, C₅-C₁₀heteroarylC₁-C₆alkyl, each of which may be optionally substituted by one or more groups selected from -F, -Cl, -Br, -OH, -OC₁-C₄alkyl, -NH-CO-H, -NH-CO-C₁-C₄alkyl, -NH₂, -NH-C₁-C₄alkyl and -SC₁-C₄alkyl; and CH₂CH₂N(R10)(R11),

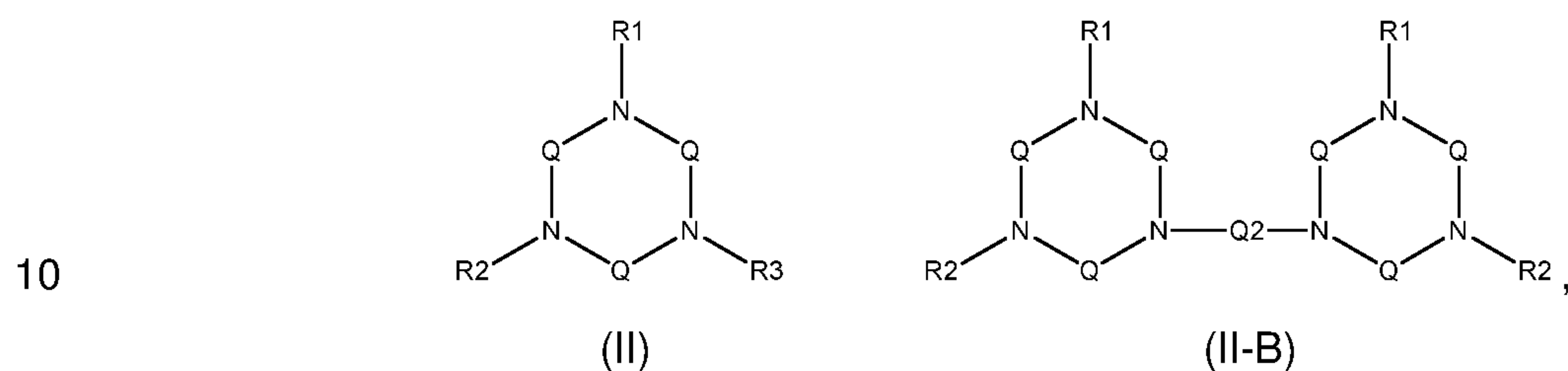
wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

R3 and R4 are independently selected from hydrogen, C₁-C₈alkyl, C₁-C₈alkyl-O-C₁-C₈alkyl, C₆-C₁₀aryloxyC₁-C₈alkyl, C₆-C₁₀aryl, C₁-C₈hydroxyalkyl, C₆-C₁₀arylC₁-C₆alkyl

and C₅-C₁₀heteroarylC₁-C₆alkyl, and -(CH₂)₀₋₄C(O)OR₅ wherein R₅ is independently selected from: hydrogen, C₁-C₈alkyl and C₆₋₁₀aryl;

Q₂ represents a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge is optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

X is selected from C=O, -[C(R₆)₂]₀₋₃- wherein each R₆ is independently selected from hydrogen, hydroxyl, C₁-C₄alkoxy and C₁-C₄alkyl;



wherein:

each Q is independently selected from -CR₄R₅CR₆R₇- and -CR₄R₅CR₆R₇CR₈R₉-;

15 R₄, R₅, R₆, R₇, R₈, and R₉ are independently selected from: H, C₁-C₄alkyl and hydroxyC₁-C₄alkyl;

each R₁, R₂, and R₃ is independently selected from the group consisting of hydrogen, C₁-C₂₄alkyl, CH₂CH₂OH, CH₂COOH, CH₂PO₃H₂, C₅-C₁₀heteroarylC₁-C₆alkyl and CH₂CH₂N(R₁₀)(R₁₁),

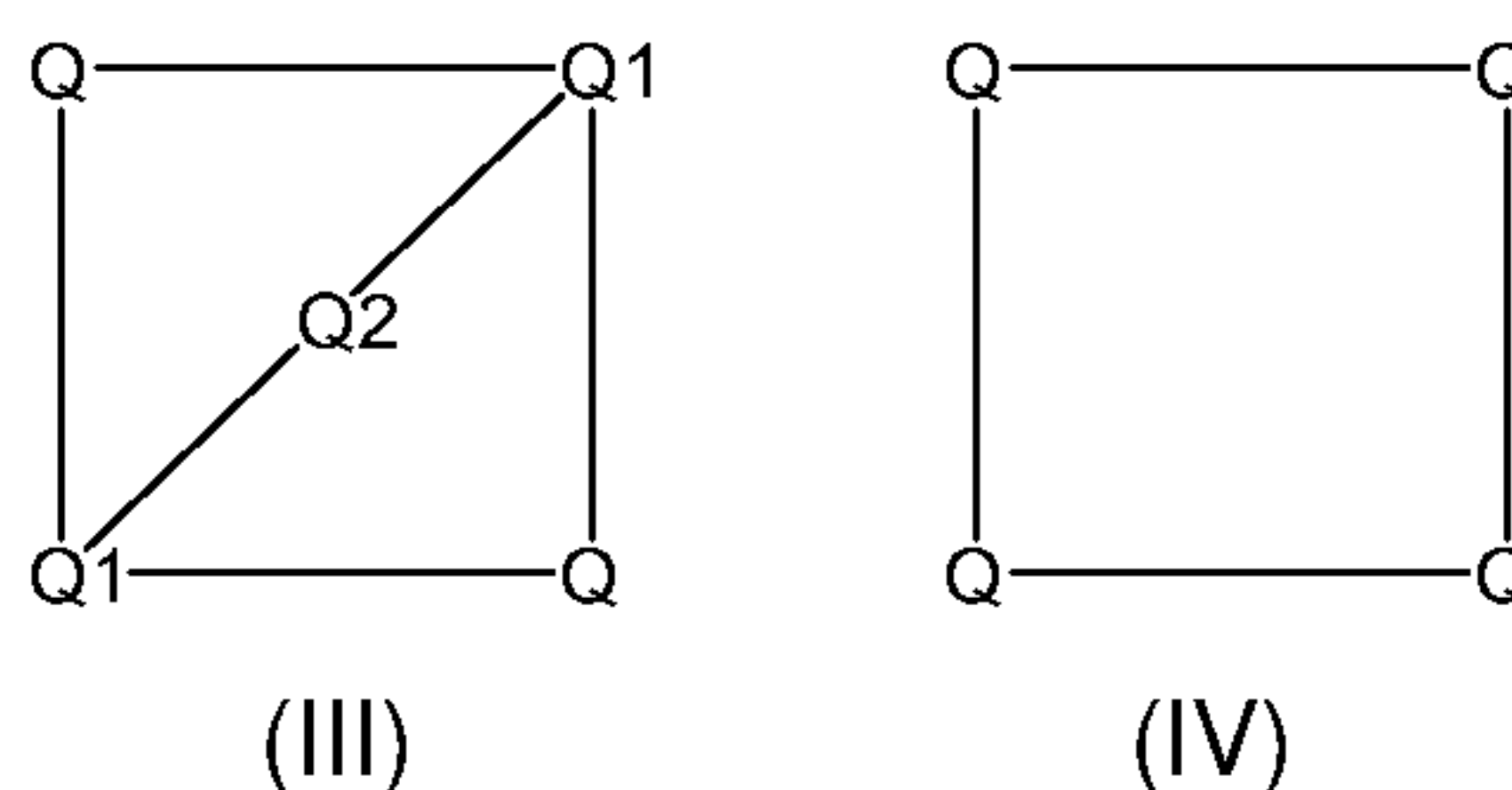
20 wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and

25

30

Q₂ is a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋

arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups;



5

wherein:

each -Q- is independently selected from -N(R)C(R₁)(R₂)C(R₃)(R₄)- and -N(R)C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

10 each -Q1- is independently selected from -N(R')C(R₁)(R₂)C(R₃)(R₄)- and -N(R')C(R₁)(R₂)C(R₃)(R₄)C(R₅)(R₆)-;

each R is independently selected from: hydrogen; the group consisting of C₁-C₂₀alkyl, C₂-C₂₀alkenyl, C₂-C₂₀alkynyl, C₆-C₁₀aryl and C₇-C₂₀arylalkyl, each of which may be optionally substituted with C₁-C₆alkyl, C₅-C₁₀heteroarylC₁-C₆alkyl; and CH₂CH₂N(R₁₀)(R₁₁),

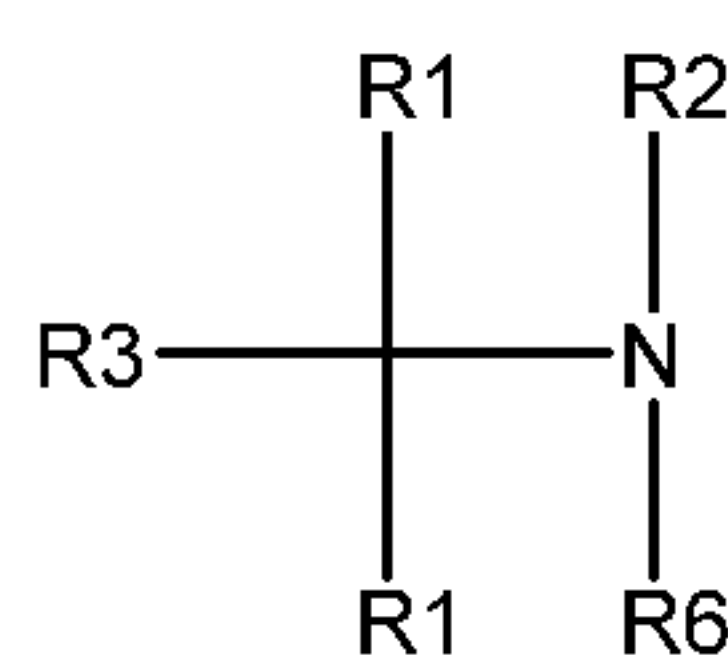
15 wherein N(R₁₀)(R₁₁) is selected from the group consisting of di(C₁-C₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR₇, in which R₇ and the nitrogen atom N to which it is attached
20 represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R₁ through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently
25 optionally substituted with one or more C₁₋₂₀alkyl groups;

the two -R' groups of the two Q1 groups together form bridging moiety -Q2-;

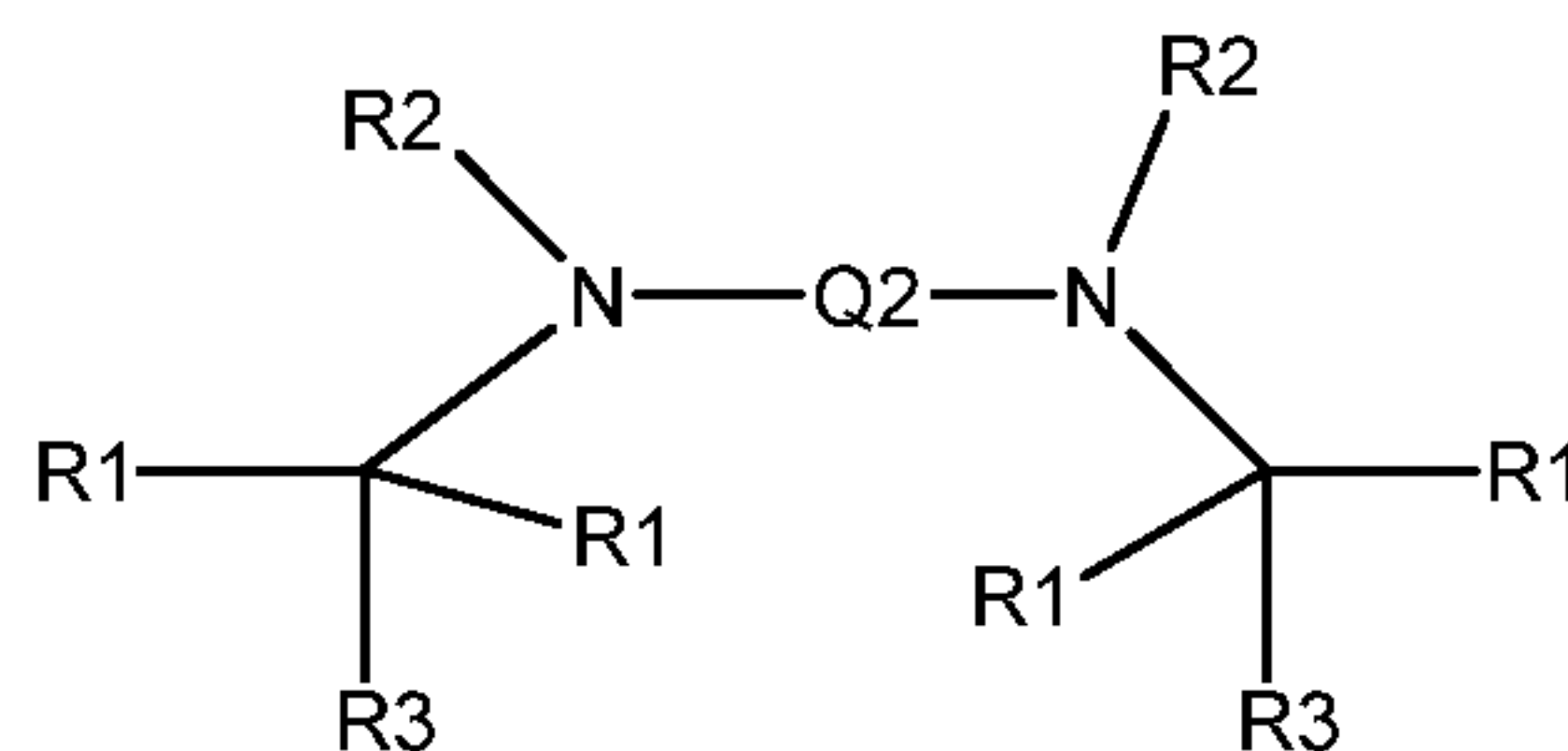
30 Q2 is a bridge selected from the group consisting of a C₂₋₆alkylene moiety, a C₆₋₁₀arylene moiety, or a moiety comprising one or two C₁-C₃alkylene units and one C₆-C₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups; and

R₁-R₆ are each independently selected from: H, C₁₋₄alkyl and hydroxyC₁₋₄alkyl;

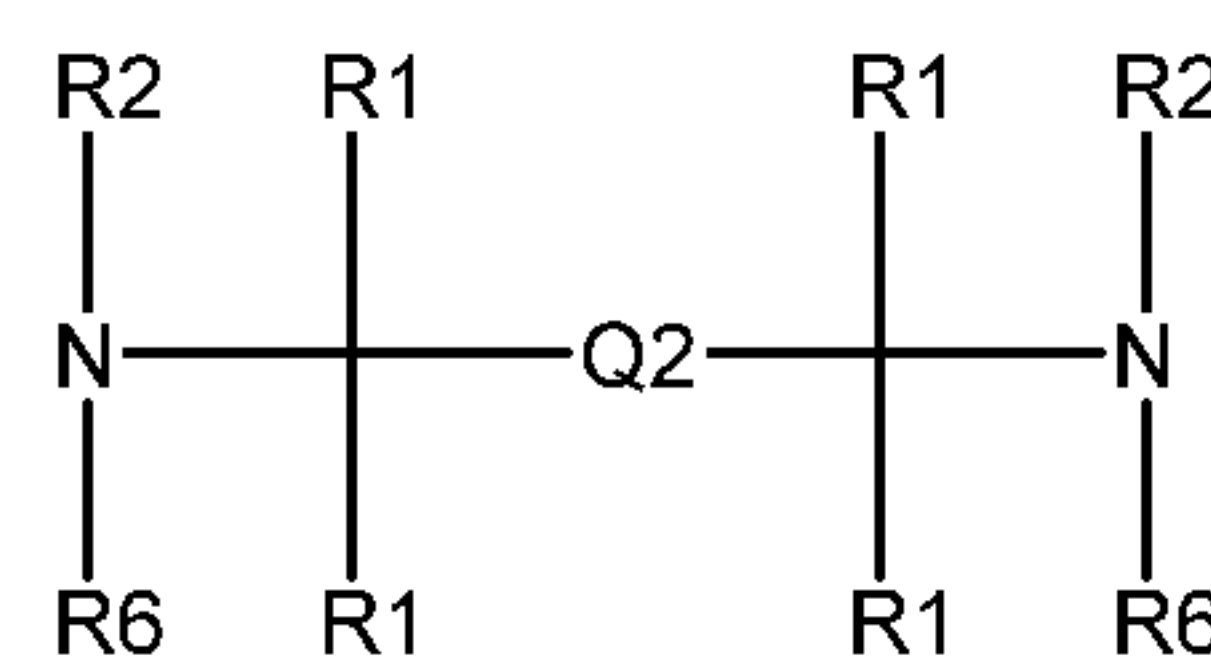
86



(V)



(V-B)



(V-C)

wherein:

each -R1 independently is selected from $-\text{CH}_2\text{N}(\text{C}_1\text{-C}_{24}\text{alkyl})_2$, $-\text{CH}_2\text{NR7}$ or an optionally $\text{C}_1\text{-C}_6$ alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl;

each -R2 independently represents -R4-R5;

each -R3 and each -R6 each independently represents hydrogen, or a group selected from $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_6\text{-C}_{10}$ aryl, $\text{C}_5\text{-C}_{10}$ heteroaryl, $\text{C}_6\text{-C}_{10}\text{arylC}_1\text{-C}_6$ alkyl and $\text{C}_5\text{-C}_{10}\text{heteroarylC}_1\text{-C}_6$ alkyl, each of which groups may be optionally $\text{C}_1\text{-C}_6$ alkyl-substituted;

each -R4- independently represents optionally $\text{C}_1\text{-C}_6$ alkyl-substituted $\text{C}_1\text{-C}_6$ alkylene;

each -R5 independently represents an $-\text{CH}_2\text{N}(\text{C}_1\text{-C}_{24}\text{alkyl})_2$ group, $-\text{CH}_2\text{NR7}$ or an optionally $\text{C}_1\text{-C}_6$ alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl;

each -NR7 independently represents a moiety in which R7 and the nitrogen atom N to which it is attached represents a heterocycloalkyl group optionally substituted with one or more C_{1-20} alkyl groups, which is connected to R4 through the nitrogen atom N; and

Q2 represents a bridge selected from the group consisting of a C_{1-6} alkylene moiety C_{6-10} arylene moiety or a moiety comprising one or two C_{1-3} alkylene units and one C_{6-10} arylene unit, which bridge is optionally substituted one or more times with independently selected C_{1-24} alkyl groups and OH groups;



wherein:

each -R1 is independently selected from -CY₂N(C₁-C₂₄alkyl)₂; -CY₂NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₆alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; or represents an optionally C₁-C₆alkyl-substituted heteroaryl group selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-1-yl, pyrazol-3-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-1-yl, 1,2,4-triazol-3-yl and thiazol-2-yl; and

each Y is independently selected from H, CH₃, C₂H₅, C₃H₇;

R1R2N-X-NR1R2 (VII); and R1R2N-X-NR2(-Q2-R2N)_n-X-NR1R2 (VII-B);

wherein:

-X- is selected from -CY₂CY₂-, cis- or trans-1,2-cyclohexylene, -CY₂CY₂CY₂-, -CY₂C(OH)YCY₂-, with each Y being independently selected from H, CH₃, C₂H₅ and C₃H₇;

n is an integer from 0 to 10;

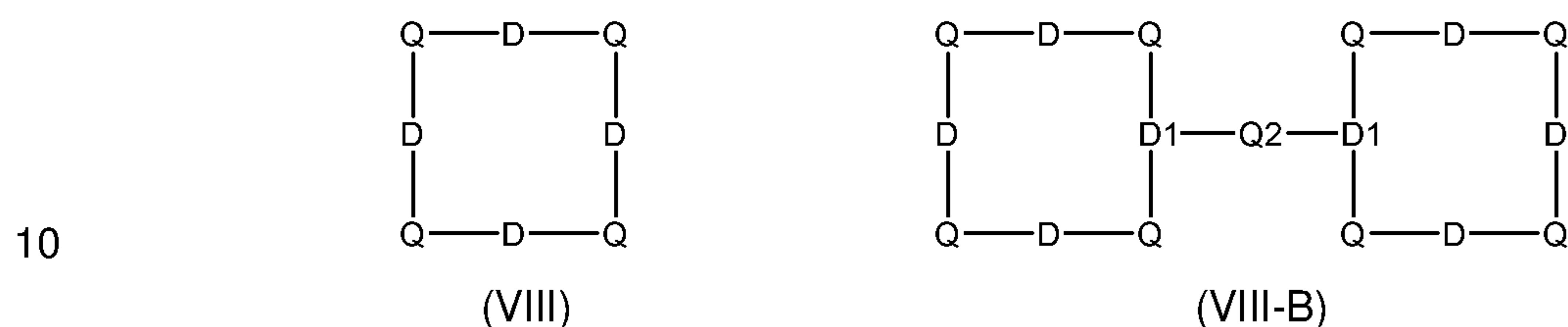
each R1 group is independently an alkyl, heterocycloalkyl, heteroaryl, aryl, arylalkyl or heteroarylalkyl group, each of which may be optionally substituted with a substituent selected from the group consisting of hydroxy, alkoxy, phenoxy, phosphonate, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, mono- or dialkylamine and N⁺(R3)₃, wherein R3 is selected from hydrogen, alkyl, alkenyl, arylalkyl, arylalkenyl, hydroxyalkyl, aminoalkyl, and alkyl ether;

each R2 is -CZ₂-R4, with each Z being independently selected from H, CH₃, C₂H₅, C₃H₇; and each -R4 being independently selected from an optionally C₁-C₆alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl; and CH₂N(R10)(R11),

wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N;

di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and

- 5 Q2 is a bridge selected from the group consisting of a C₁₋₆alkylene bridge, a C₆₋₁₀arylene bridge or a bridge comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups;



wherein:

each Q group independently represents -CY₂- or -CY₂CY₂-, in which each Y is independently selected from hydrogen, C₁₋₂₄alkyl, or a C₆₋₁₀aryl;

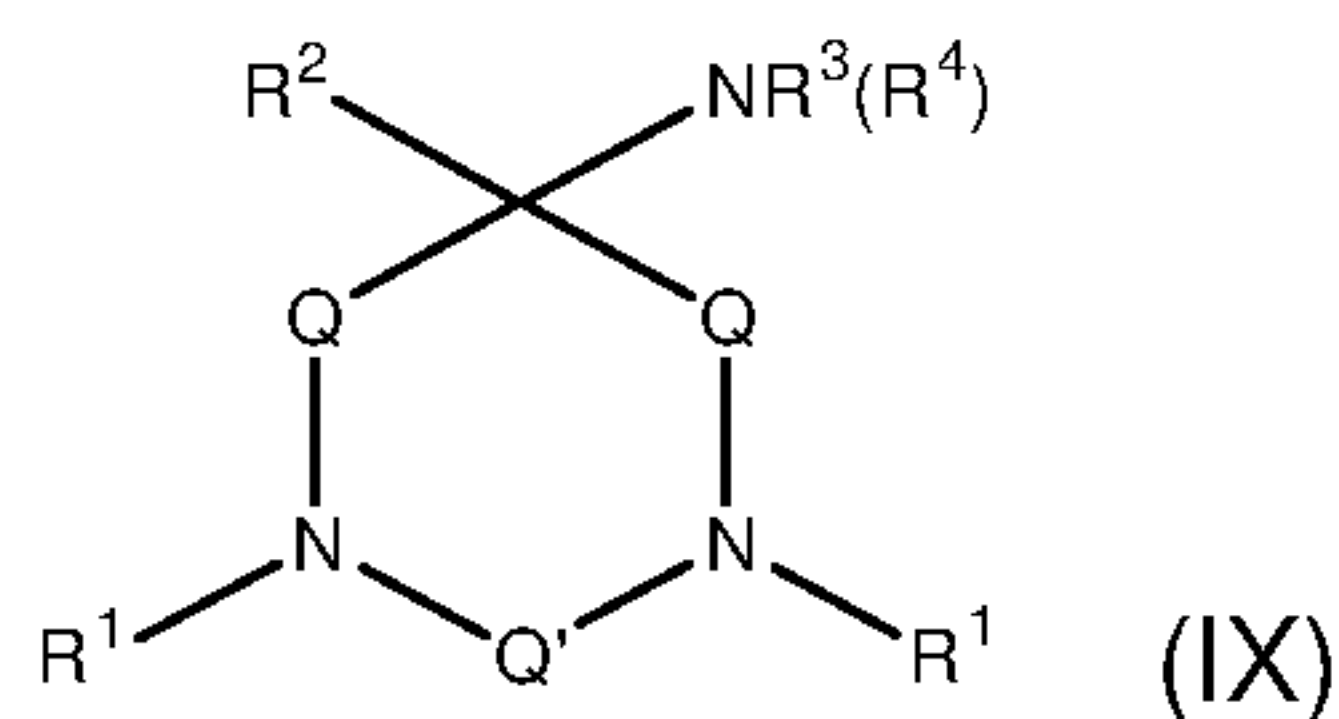
- 15 each D group independently represents a heteroarylene group or a group of the formula -NR-, with the proviso that at least one D group represents a heteroarylene group;

each D1 group represents a group of the formula -NR'-;

the two -R' groups of the two D1 groups together form bridging moiety -Q2-;

- 20 Q2 is a bridge selected from the group consisting of a C₁₋₆alkylene moiety, a C₆₋₁₀arylene moiety, or a moiety comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

- 25 each R group independently represents H, C₁₋₂₄alkyl, C₆₋₁₀aryl or C₅₋₁₀heteroaryl;



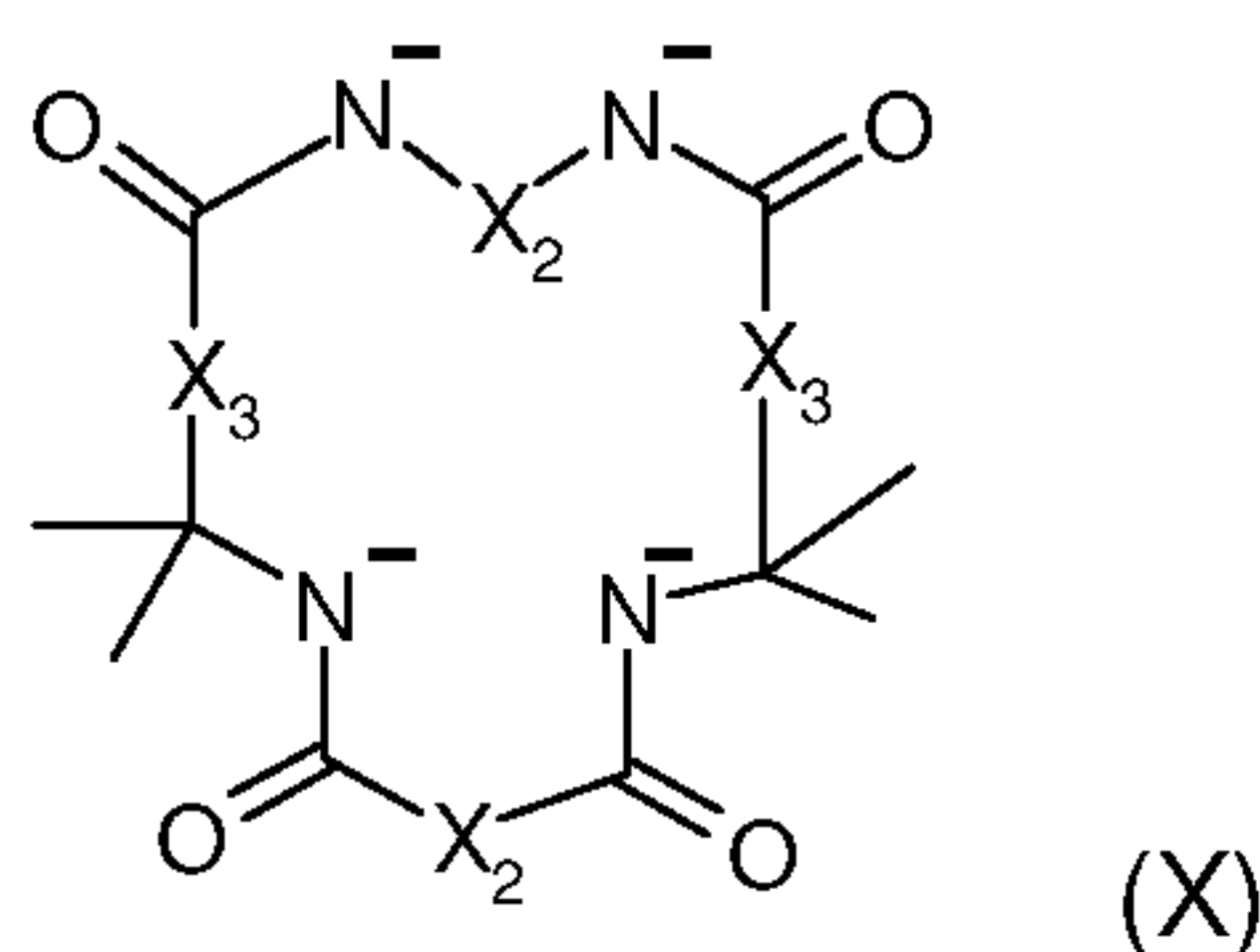
wherein:

each of -R¹, -R², -R³ and -R⁴ independently represents -H, -C₁₋₂₄alkyl, -C₆₋₁₀aryl or a group comprising a heteroatom capable of coordinating to a metal ion, which aryl

and heteroatom-comprising groups may each be optionally substituted with one or more C₁₋₄alkyl groups;

Q represents methylene or ethylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group; and

5 Q' represents ethylene or n-propylene, in which one or more hydrogen atoms may be optionally independently replaced with a C₁₋₂₄ alkyl or a C₆₋₁₀ aryl group;



10 wherein:

each X₂ and X₃ independently represents a bridging group (CRR')_n, wherein:

n is an integer between 0 and 3; and

15 each R and R' is independently selected from a group consisting of C₁-C₂₄alkyl, cyclo-C₃-C₈alkyl, cyclo-C₄-C₈alkenyl, C₁-C₂₄alkenyl, C₆-C₁₀aryl, C₁-C₂₄alkynyl and C₆-C₁₀arylC₁-C₂₄alkyl, C₁-C₂₄alkoxy and phenoxy each of which may be optionally C₁-C₆alkyl-substituted, H, F, Cl, Br, I, CH₂CF₃ and CF₃; or one R and one R' attached to a common carbon atom may together with that carbon atom form a substituted or unsubstituted 1,2-phenylene moiety or a cycloalkylene, cycloalkenylene, heterocycloalkylene or heterocycloalkenylene moiety; and

20



wherein:

each Y is independently selected from H, CH₃, C₂H₅ and C₃H₇;

25 each R1 is independently selected from an optionally C₁-C₆alkyl-substituted C₅-C₁₀heteroaryl group, whereby the C₅-C₁₀heteroaryl group is selected from pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl;

30 R2 is selected from an optionally C₁-C₆alkyl-substituted C₅-C₆heteroarylene group, whereby the C₅-C₆heteroarylene group is selected from pyridin-2,6-diyl, pyrazin-

2,6-diyl, pyrazol-3,5-diyl, pyrazol-1,3-diyl, pyrrol-2,5-diyl, imidazol-2,5-diyl, imidazol-1,4-diyl, pyrimidin-2,6-diyl, 1,2,4-triazol-3,5-diyl, 1,2,4-triazol-1,3-diyl, 1,2,4-triazol-2,4-diyl, 1,2,3-triazol-1,4-diyl, 1,2,3-triazol-2,5-diyl, and thiazol-2,5-diyl;

each R3 is independently selected from optionally C₁-C₆-substituted C₁₋₂₄alkyl,
 5 C₆₋₁₀aryl, C₆₋₁₀arylC₁-C₂₄alkyl, C₅₋₁₀heteroaryl, C₅₋₁₀heteroarylC₁-C₂₄alkyl.

9. The method of claim 8, wherein the complex comprises a polydentate ligand selected from the group consisting of those of formulae (I), (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), (X) and (XI).

10

10. The method of any one of claims 1 to 7, wherein the complex comprises a chelant capable of chelating at least one iron ion through at least three nitrogen atoms, which is of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (VII'), (VII'-B), (IX) or (XI), wherein the ligands of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (IX) or (XI) are as defined in
 15 claim 8 and the ligands of formulae (VII') and (VII'-B) are of the formulae:



wherein:

20

-X- is selected from -CY₂CY₂-, cis- or trans-1,2-cyclohexylene, -CY₂CY₂CY₂-, -CY₂C(OH)YCY₂-, with each Y being independently selected from H, CH₃, C₂H₅ and C₃H₇;

n is an integer from 0 to 10;

25

at most one R₁ group is independently an alkyl, heterocycloalkyl, heteroaryl, aryl, arylalkyl or heteroarylalkyl group, each of which may be optionally substituted with a substituent selected from the group consisting of hydroxy, alkoxy, phenoxy, phosphonate, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, mono- or dialkylamine and N⁺(R₃)₃, wherein R₃ is selected from hydrogen, alkyl, alkenyl, arylalkyl, arylalkenyl, hydroxyalkyl, aminoalkyl, and alkyl ether;

30

each R₂ is -CZ₂-R₄, with each Z being independently selected from H, CH₃, C₂H₅, C₃H₇; and each -R₄ being independently selected from an optionally C₁-C₆alkyl-substituted heteroaryl group selected from the group consisting of pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, and thiazol-2-yl; and CH₂N(R₁₀)(R₁₁),
 35

wherein N(R10)(R11) is selected from the group consisting of di(C₁₋₄₄alkyl)amino; di(C₆₋₁₀aryl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; di(C₆₋₁₀arylC₁₋₆alkyl)amino in which each of the aryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; NR7, in which R7 and the nitrogen atom N to which it is attached represent a heterocycloalkyl group optionally substituted with one or more C₁₋₂₀alkyl groups, which is connected to the remainder of R1 through the nitrogen atom N; di(heterocycloalkylC₁₋₆alkyl)amino, in which each of the heterocycloalkyl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups; and di(heteroarylC₁₋₆alkyl)amino, wherein each of the heteroaryl groups is independently optionally substituted with one or more C₁₋₂₀alkyl groups;

Q2 is a bridge selected from the group consisting of a C₁₋₆alkylene bridge, a C₆₋₁₀arylene bridge or a bridge comprising one or two C₁₋₃alkylene units and one C₆₋₁₀arylene unit, which bridge may be optionally substituted one or more times with independently selected C₁₋₂₄alkyl groups and OH groups; and

either one or both R1 groups are independently CZ₂R4, wherein Z is as defined for moiety R2 and R4 is an optionally C₁-C₆alkyl-substituted pyridin-2-yl, pyrazin-2-yl, quinolin-2-yl, pyrazol-3-yl, pyrazol-1-yl, pyrrol-2-yl, imidazol-2-yl, imidazol-4-yl, benzimidazol-2-yl, pyrimidin-2-yl, 1,2,3-triazol-1-yl, 1,2,3-triazol-2-yl, 1,2,3-triazol-4-yl, 1,2,4-triazol-3-yl, 1,2,4-triazol-1-yl, and thiazol-2-yl.

11. The method of claim 10, wherein the complex comprises a polydentate ligand selected from the group consisting of those of formulae (I), (V), (VI), (VII'), (IX) and (XI).

12. The method of claim 10, wherein the complex comprises a polydentate ligand selected from the group consisting of 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, 2,4-di-(2-pyridyl)-3,7-dimethyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N-benzyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, N,N,N-tris(pyridin-2-yl-methyl)amine, N-methyl-alkyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-

butyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N, N, N', N'-tetrakis(pyridin-2-yl-methyl)ethylene-1,2-diamine, N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, N,N'-dimethyl-2,11-diaza[3.3](2,6-pyridinophane), 6-dimethylamino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-diazacycloheptane, 6-amino-1,4,6-trimethyl-1,4-diazacycloheptane, 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-(pyridin-2-ylmethyl)amino-1,4-diazacycloheptane, 6-{N,N-bis(pyridin-2-ylmethyl)amino}-1,4,6-trimethyl-1,4-diazacycloheptane and 6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane.

13. The method of claim 10, wherein the complex comprises a polydentate ligand selected from the group consisting of dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, N-methyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N, N, N', N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine, N-methyl-N,N,N'-tris(imidazol-2-ylmethyl)ethylene diamine, N-ethyl-N,N,N'-tris(imidazol-2-ylmethyl)ethylene diamine, tris(pyridin-2-ylmethyl)amine and 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane.

14. The method of claim 8, wherein the complex comprises dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(N,N-dimethyl-amine-ethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate and the pH of the aqueous medium is between about 7 and about 11.

15. The method of any one of claims 1 to 7, wherein the complex comprises a polydentate ligand selected from the group consisting of 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-(2-pyridyl)-7-(1-(N,N-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-dicarboxylate, 2,4-di-(2-pyridyl)-3,7-dimethyl-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, 1,4,7-

trimethyl-1,4,7-triazacyclononane, 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane, 1-(pyridin-2-ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, 1,4-bis(pyridin-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane, 1,4,7-tris(pyridin-2-ylmethyl)-1,4,7-triazacyclononane, 1,2-bis(4-methyl-7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-ethane
 5 and 1,3-bis(4-methyl-7-pyridin-2-yl-1,4,7-triazacyclonon-1-yl)-propane, 1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane, 1,4,7,10-tetrakis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1-methyl-4,7,10-tris(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4-dimethyl-7,10-bis(pyridin-2ylmethyl)-1,4,7,10-tetraazacyclododecane, 1,4,7-trimethyl-11-(pyridin-2ylmethyl)-
 10 1,4,7,10-tetraazacyclododecane, 1,4,8,11-tetraazacyclododecane, 1,4,8,11-tetrakis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1-methyl-4,8,11-tris(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1,4-dimethyl-8,11-bis(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, and 1,4,8-trimethyl-11-(pyridin-2ylmethyl)-1,4,8,11-tetraazacyclododecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclododecane,
 15 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane, N-methyl-N-(pyridin-2-ylmethyl)-bis(pyridin-2-yl)methylamine, N-benzyl-N-(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, N,N,N-tris(pyridin-2-yl-
 20 methyl)amine, N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)ethylene-1-2-diamine, N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1-2-diamine, N-methyl-alkyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-butyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N-octyl-N,N',N'-tris(pyridin-2-ylmethyl)-1,2-ethylene-diamine, N,N,N',N'-tetrakis(pyridin-2-yl-methyl)ethylene-1,2-diamine, N,N,N',N'-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine, 2,11-diaza[3.3](2,6-pyridinophane), N,N'-dimethyl-2,11-diaza[3.3](2,6-pyridinophane), 6-dimethylamino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-diazacycloheptane, 6-amino-1,4,6-trimethyl-1,4-diazacycloheptane,
 30 6-dimethylamino-1,4,6-trimethyl-1,4-diazacycloheptane, 1,4,6-trimethyl-6-(pyridin-2-ylmethyl)amino-1,4-diazacycloheptane, 6-{N,N-bis(pyridin-2-ylmethyl)amino}-1,4,6-trimethyl-1,4-diazacycloheptane, 6-{N-(pyridin-2-ylmethyl)-N-methylamino}-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-diazacycloheptane, 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-benzotetracyclotridecine-
 35 2,5,7,10-tetrone (6H, 11H), 5,6(4,5-di-chlorobenzo)-3,8,11,13-tetraoxo-2,2,9,9-

tetramethyl-12,12-diethyl-1,4,7,10-tetracyclotridecane, 5,6(4,5-di-chlorobenzo)-
 3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 5,6-benzo-
 3,8,11,13-tetraoxo-2,2,9,9,12,12-hexamethyl-1,4,7,10-tetracyclotridecane, 3,4,8,9-
 tetrahydro-6,6-difluoro-3,3,9,9-tetramethyl-13-nitro-1-H-1,4,8,11-
 5 benzotetracyclotridecine-2,5,7,10-tetraoxo, 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-
 1-H-1,4,8,11-benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H), 3,4,8,9-
 tetrahydrospiro-3,3,9,9-tetramethyl-6,1'-cyclopropane-1,4,8,11-
 benzotetracyclotridecine-2,5,7,10-tetraoxo, 15,15-dimethyl-5,8,13,17-tetrahydro-
 5,8,13,17-tetraazadibenzo[a,g]cyclotridecene-6,7,14,16-tetraoxo and 2,6-bis[(*N*-methyl-
 10 {*N*-(2-pyridylmethyl)}amino)methyl]pyridine.

16. The method of any one of claims 1 to 7, wherein the complex comprises a
 polydentate ligand selected from the group consisting of dimethyl 2,4-di-(2-pyridyl)-3-
 methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate,
 15 dimethyl 2,4-di-(2-pyridyl)-3-(pyridin-2-ylmethyl)-7-methyl-3,7-diaza-
 bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate, dimethyl 9,9-dihydroxy-3-methyl-2,4-di-
 (2-pyridyl)-7-(1-(*N,N*-dimethylamine)-eth-2-yl)-3,7-diaza-bicyclo[3.3.1]nonane-1,5-
 dicarboxylate, 1-(pyridin-2-ylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane, 1,4-
 bis(pyridin-2-ylmethyl)-7-methyl-1,4,7-triazacyclononane, *N*-methyl-*N*-(pyridin-2-yl-
 20 methyl)-bis(pyridin-2-yl)methylamine, *N,N*-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-
 1-aminoethane, *N,N,N',N'*-tetrakis(benzimidazol-2-ylmethyl)ethylene-1,2-diamine,
N,N,N',N'-tetrakis(pyridin-2-ylmethyl)ethylenediamine, *N*-methyl-*N,N,N'*-tris(imidazol-2-
 ylmethyl)ethylene diamine, *N*-ethyl-*N,N,N'*-tris(imidazol-2-ylmethyl)ethylene diamine,
 tris(pyridin-2-ylmethyl)amine, 6-amino-1,4-bis(pyridin-2-ylmethyl)-6-methyl-1,4-
 25 diazacycloheptane and 3,4,8,9-tetrahydro-3,3,6,6,9,9-hexamethyl-1-H-1,4,8,11-
 benzotetracyclotridecine-2,5,7,10-tetrone (6H, 11H).

17. The method of any one of claims 1 to 7, wherein the complex comprises 1,4,7-
 trimethyl-1,4,7-triazacyclononane.

18. A method of treating a substrate comprising contacting, in an aqueous medium,
 (i) the substrate (ii) an amount of a chlorine-containing chemical, which is chlorine
 dioxide; and (iii) a complex comprising one or more iron ions and one or more
 polydentate ligands, which are chelants of formulae (I), (I-B), (V), (V-B), (V-C), (VI),
 35 (VII'), (VII'-B), (IX) or (XI) as defined in claim 10.

19. The method of any one of claim 18, wherein the complex is as defined in any one of claims 11 to 14.

5 20. The method of claim 18 or claim 19, wherein the substrate is a cellulosic substrate, for example wood pulp.

21. The method of claim 18 or claim 19, which is a method of treating water, comprising contacting the water with an amount of the chlorine-containing chemical and the complex.

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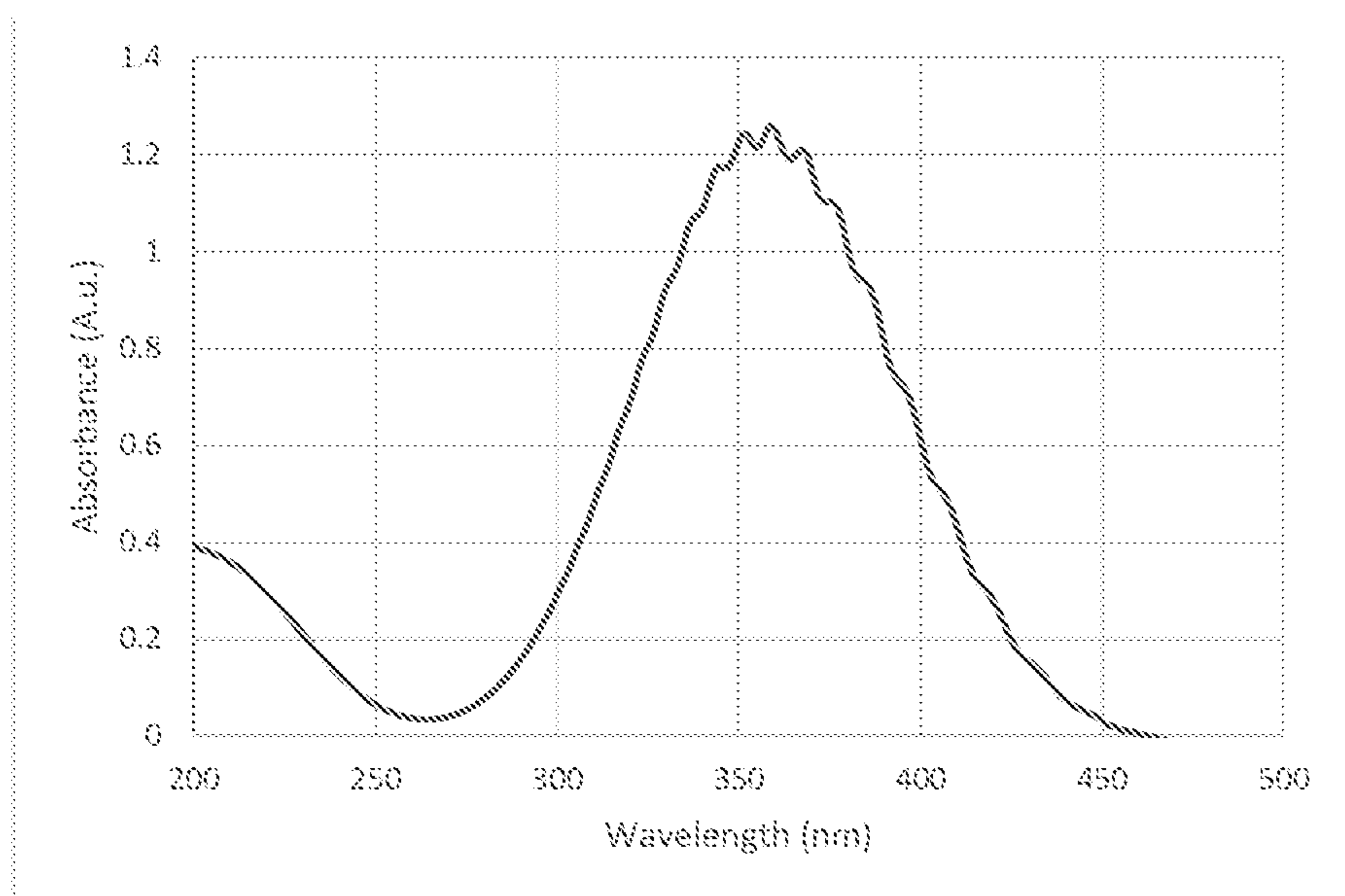
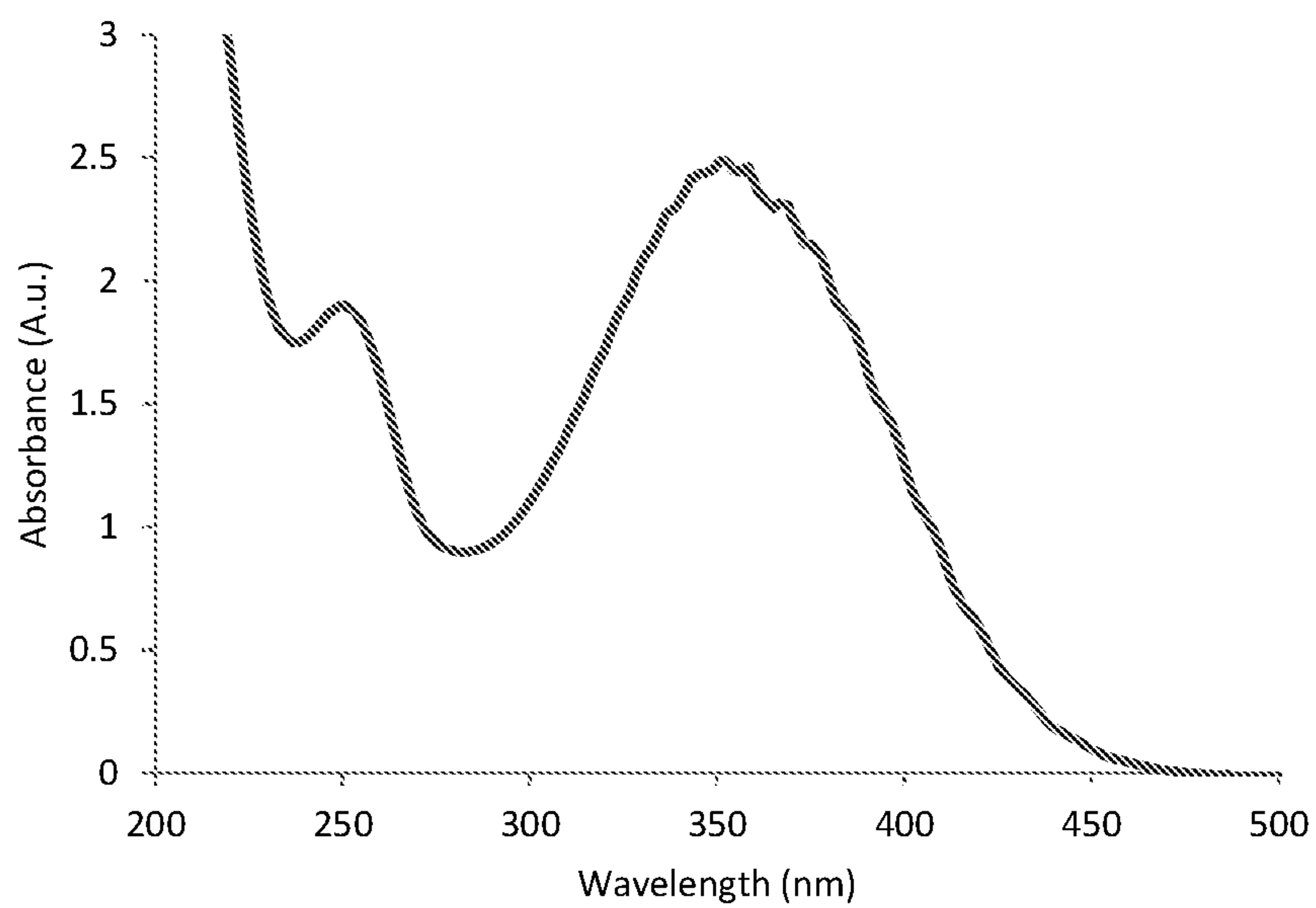
22. The method of any one of claims 18 to 21, wherein the aqueous medium comprises between about 0.1 and about 5 μ M of the complex.

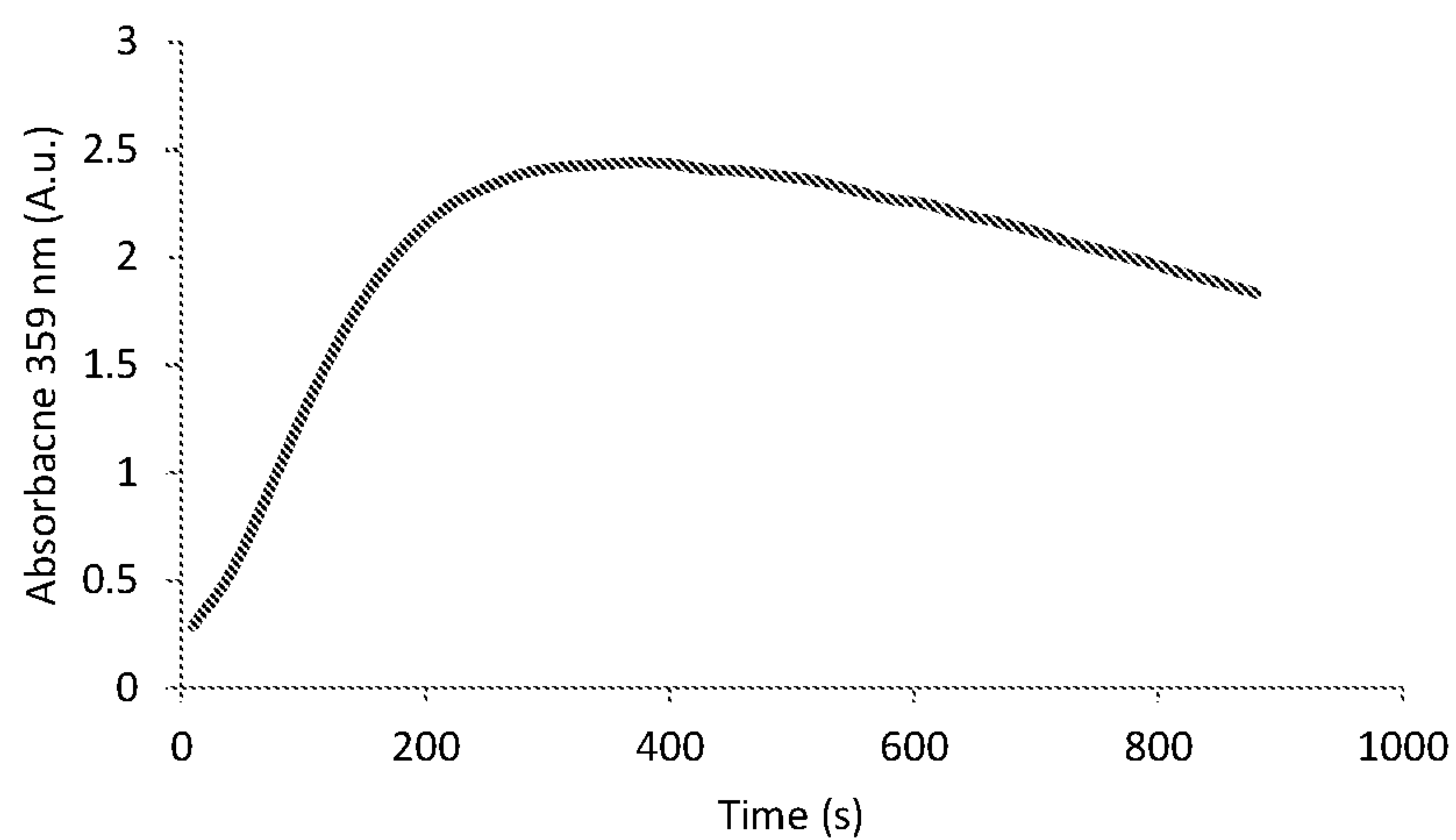
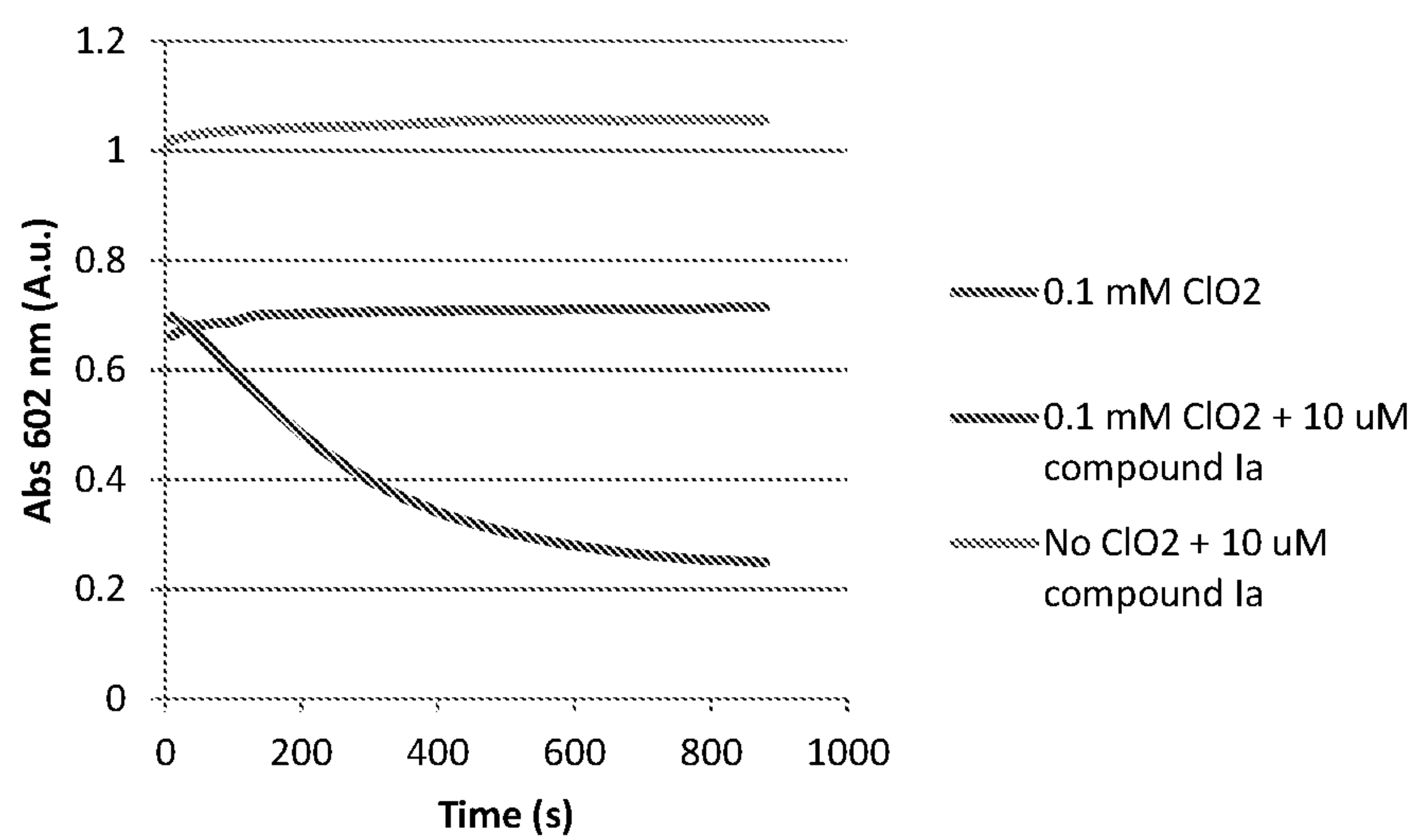
15 23. An aqueous medium comprising a chlorine-containing chemical, which is a chlorite salt, and a complex of one or more iron ions and one or more polydentate ligands, which are chelants that contain at least three nitrogen atoms, with the proviso that the complex does not comprise a porphyrin ligand.

20 24. An aqueous medium comprising a chlorine-containing chemical, which is chlorine dioxide, and a complex comprising one or more iron ions and one or more polydentate ligands, which are chelants of formulae (I), (I-B), (V), (V-B), (V-C), (VI), (VII'), (VII'-B), (IX) or (XI) as defined in claim 10.

25 25. A kit comprising a chlorite salt and, separately, a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the one or more polydentate ligands are not porphyrin ligands.

30 26. A composition comprising a chlorite salt and a complex of one or more iron ions and one or more polydentate ligands, which are chelants capable of chelating at least one iron ion through at least three nitrogen atoms, with the proviso that the one or more polydentate ligands are not porphyrin ligands.

**Fig. 1****Fig. 2**

**Fig. 3****Fig. 4**