(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 March 2001 (08.03.2001)

PCT

(10) International Publication Number
WO 01/16269 A1

(51) International Patent Classification[7]: C11D 3/39, D06L 3/02, C11D 17/04

(21) International Application Number: PCT/EP00/07563

(22) International Filing Date: 4 August 2000 (04.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/GB99/02878 1 September 1999 (01.09.1999) GB
0004847.0 29 February 2000 (29.02.2000) GB

(71) Applicant *(for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only)*: **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant *(for all designated States except AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, IN, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW)*: **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).

(72) Inventors: **DELROISSE, Michel, Gilbert, Jose**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **JONES, David, Andrew, Ross**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **SMITH, Richard, George**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **WELLS, John, Francis**; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agents: **ELLIOTT, Peter, William** et al.; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *With international search report.*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/16269 A1

(54) Title: METHOD OF BLEACHING STAINED FABRICS

(57) Abstract: A method for bleaching stained fabrics is provided by washing a stained fabric in an aqueous wash liquor in the presence of a wash additive that comprises a ligand that forms a transition metal complex as bleach catalyst, the complex catalysing bleaching of stains by atmospheric oxygen. The wash additive preferably comprises an iron complex comprising the ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane. One or both of the wash additive and the wash liquor are substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. The wash additive provides improved or broader stain profile bleaching.

# METHOD OF BLEACHING STAINED FABRICS

## FIELD OF INVENTION

This invention relates to a method for bleaching stained fabrics, more particularly by washing a stained fabric in an aqueous wash liquor in the presence of a wash additive that comprises an organic ligand that forms a transition metal complex as bleach catalyst. The invention further relates to the use of the ligand or complex as a wash additive for addition to an aqueous wash liquor for bleaching stains on fabrics.

## BACKGROUND OF INVENTION

EP-A-0909809 discloses a class of iron coordination complexes useful as catalysts for the bleach activation of peroxy compounds, including iron complexes comprising the ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, also referred to as MeN4Py. These catalysts are said to be useful in bleaching systems comprising a peroxy compound or a precursor thereof, such as in the washing and bleaching of substrates including laundry, dishwashing and hard surface cleaning, or for bleaching in the textile, paper and woodpulp industries, and in waste water treatment.

In our co-pending application PCT/GB99/02876, we describe methods for catalytically bleaching substrates with atmospheric oxygen in aqueous medium, using metal ligand complexes as catalytic bleaching agents. These methods are said to be particularly applicable to bleaching of laundry fabrics, suitably in detergent formulations, but also may be

used for hard surface cleaning, waste-water treatment, pulp bleaching in paper manufacture, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

However, there remains a need for improved methods of bleaching stained laundry fabrics. Thus, it would be desirable to be able to effect improved bleaching of particular stain types. It would also be desirable to be able to bleach a broader profile of stain types more effectively.

**SUMMARY OF INVENTION**

We have now found that improved or broader stain profile bleaching can be achieved in accordance with the present invention, by using a specified ligand or transition metal complex bleach catalyst as a wash additive for addition to an aqueous wash liquor for bleaching stains on fabrics.

Accordingly, in a first aspect, the present invention provides a method of bleaching fabric stains comprising washing a stained fabric in an aqueous wash liquor in the presence of a wash additive, wherein:

the wash additive comprises a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains by atmospheric oxygen; and

one or both of the wash additive and the wash liquor are substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

In a second aspect, the present invention provides the use of a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains by atmospheric oxygen, on a carrier as a wash additive for addition to an aqueous wash liquor for bleaching stains on fabrics.

Preferably, the ligand is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, and the complex is an iron complex.

We have found that certain stain types can be more effectively bleached on stained fabrics by adding the ligand or complex to a wash liquor as a wash additive. Thus, the bleaching of oily stains such as tomato stain can be improved by addition of the wash additive to the wash liquor. For stains of this type, a peroxygen bleach such as hydrogen peroxide, or a peroxy-based or -generating bleach system, may be present or absent in the wash additive, and may be present or absent in the wash liquor, but preferably is absent from the wash liquor. Bleaching of tea stains may also be improved by addition of the wash additive. For stains of this type, a peroxygen bleach such as hydrogen peroxide, or a peroxy-based or -generating bleach system, should be present in one or both of the wash additive and the wash liquor, and preferably is present in the wash additive.

In order to provide a more effective bleaching performance over a range of different stain types, it is preferred that a peroxygen bleach or a peroxy-based or -generating bleach system is present in the wash additive and is absent in the

wash liquor. It will be appreciated that once the wash additive has been added to the wash liquor, additive materials such as the ligand or complex and, if present, peroxy bleach will migrate into the wash liquor medium.

Any suitable fabric that is susceptible to stain bleaching or one that one might wish to subject to bleaching may be used. Preferably the fabric is a laundry fabric or garment. In a preferred embodiment, the method according to the present invention is carried out on laundry fabrics and the wash additive is added to the wash liquor in a conventional wash cycle.

The wash additive will comprise at least the ligand or complex in combination with any suitable carrier. The purpose of the carrier is simply to support or contain the additive active materials such as the ligand or complex and peroxy bleach, if present, and to allow delivery of the additive active materials into the wash liquor when the wash additive is added. It will be appreciated that any carrier suitable for this purpose may be used in accordance with the method of the invention.

The ligand or complex may conveniently be deposited on or impregnated into the carrier by any suitable means, for example as a liquid which is then optionally dried, or as a dry powder. Preferably, the ligand or complex is carried in or on the carrier in a composition that includes a solvent or carrier medium for the ligand or complex. The composition may take any suitable form, such as a solid,

powder, paste, gel or liquid. Preferably, the composition is in the form of a liquid.

In a particularly preferred embodiment the method according to the present invention is carried out on a laundry fabric using aqueous wash liquor. In particular, the addition of the wash additive may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More preferably, the wash additive is added in an aqueous detergent wash liquor. The ligand or complex can be delivered into the wash liquor from a carrier, which can be particulate, sheet-like or comprise a three-dimensional object. The carrier can be dispersible or soluble in the wash liquor or may remain substantially intact.

The wash additive may, for example, be presented in the form of a body from which the complex is slowly released during the whole or part of the laundry process. Such release can occur over the course of a single wash or over the course of a plurality of washes. In the latter case it is envisaged that the complex can be released from a carrier substrate used in association with the wash process, e.g. from a body placed in the dispenser drawer of a washing machine, elsewhere in the delivery system or in the drum of the washing machine. When used in the drum of the washing machine the carrier can be freely moving or fixed relative to the drum. Such fixing can be achieved by mechanical means, for example by barbs that interact with the drum wall, or employ other forces, for example a magnetic force. The modification of a washing machine to provide for means to hold and retain such a carrier is envisaged similar means

being known from the analogous art of toilet block manufacture. Freely moving carriers such as shuttles for dosage of surfactant materials and/or other detergent ingredients into the wash can comprise means for the release of the complex into the wash.

In the alternative, the wash additive can be presented in a form that is dispersed and preferably is soluble in the wash liquor. The additive can take any of the physical forms used for wash additives, including powder, granule, pellet, sheet, tablet, block, bar or other such solid form or take the form of a paste, gel or liquid. Dosage of the additive can be unitary or in a quantity determined by the user. While it is envisaged that such additives can be used in the main washing cycle, the use of them in the conditioning or drying cycle is not hereby excluded.

The present invention is not limited to those circumstances in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In these circumstances it is envisaged that the complex in the wash additive can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement which is being employed, such as a brush, bat or dolly, or from any suitable applicator.

The present invention also extends to a commercial package comprising a ligand or complex as together with instructions for its use.

The present invention also extends to use of a ligand or complex in the manufacture of a wash additive.

**DETAILED DESCRIPTION OF THE INVENTION**

The catalyst may comprise a preformed complex of a ligand and a transition metal. Alternatively, the catalyst may comprise a free ligand that complexes with a transition metal already present in the water or that complexes with a transition metal present in the substrate. The catalyst may also be included in the form of a composition of a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal, whereby the complex is formed *in situ* in the medium.

The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI.

The transition metal complex preferably is of the general formula:

$$[M_aL_kX_n]Y_m$$

in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe (II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-

(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably from Fe(II)-(III)-(IV)-(V);

L represents the ligand, preferably N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

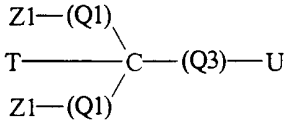
k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

Preferably, the complex is an iron complex comprising the ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane. However, it will be appreciated that the pretreatment method of the present invention may instead, or additionally, use other ligands and transition metal complexes, provided that the complex formed is capable of catalysing stain bleaching by atmospheric oxygen. Suitable classes of ligands are described below:

(A) Ligands of the general formula (IA):

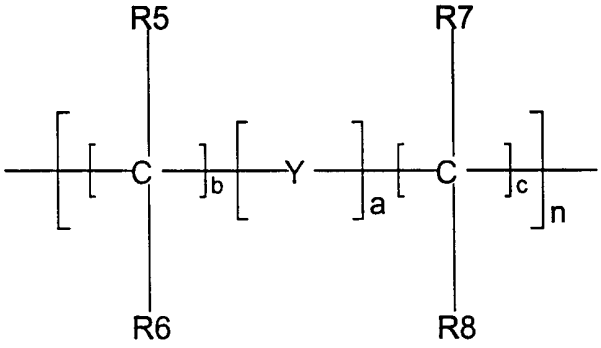



(IA)

wherein

Z1 groups independently represent a coordinating group selected from hydroxy, amino, -NHR or $-N(R)_2$ (wherein $R=C_{1-6}$-alkyl), carboxylate, amido, $-NH-C(NH)NH_2$, hydroxyphenyl, a heterocyclic ring optionally substituted by one or more functional groups E or a heteroaromatic ring optionally substituted by one or more functional groups E, the heteroaromatic ring being selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

Q1 and Q3 independently represent a group of the formula:




wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=0 or 1 (preferably n=0);

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl,

cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

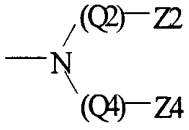
R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,

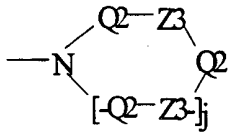
or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I;

T represents a non-coordinated group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E (preferably T= -H, -OH, methyl, methoxy or benzyl);

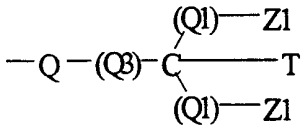
U represents either a non-coordinated group T independently defined as above or a coordinating group of the general formula (IIA), (IIIA) or (IVA):



(IIA)



(IIIA)



(IVA)

wherein

Q2 and Q4 are independently defined as for Q1 and Q3;

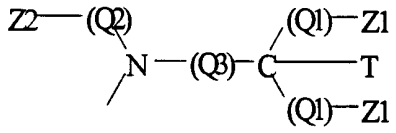
Q represents -N(T)- (wherein T is independently defined as above), or an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

Z2 is independently defined as for Z1;

Z3 groups independently represent -N(T)- (wherein T is independently defined as above);

Z4 represents a coordinating or non-coordinating group selected from hydrogen, hydroxyl, halogen, $-NH-C(NH)NH_2$, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative

group, R being optionally substituted by one or more functional groups E, or Z4 represents a group of the general formula (IIAa):



(IIAa)

and

$1 \leq j < 4$.

Preferably, Z1, Z2 and Z4 independently represent an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. More preferably, Z1, Z2 and Z4 independently represent groups selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl. Most preferred is that Z1, Z2 and Z4 each represent optionally substituted pyridin-2-yl.

The groups Z1, Z2 and Z4 if substituted, are preferably substituted by a group selected from $C_{1-4}$-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl. Preferred is that Z1, Z2 and Z4 are each substituted by a methyl group. Also, we prefer that the Z1 groups represent identical groups.

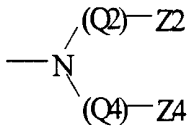
Each Q1 preferably represents a covalent bond or C1-C4-alkylene, more preferably a covalent bond, methylene or ethylene, most preferably a covalent bond.

Group Q preferably represents a covalent bond or C1-C4-alkylene, more preferably a covalent bond.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-$C_0$-$C_{20}$-alkyl, halo-$C_0$-$C_{20}$-alkyl, nitroso, formyl-$C_0$-$C_{20}$-alkyl, carboxyl-$C_0$-$C_{20}$-alkyl and esters and salts thereof, carbamoyl-$C_0$-$C_{20}$-alkyl, sulfo-$C_0$-$C_{20}$-alkyl and esters and salts thereof, sulfamoyl-$C_0$-$C_{20}$-alkyl, amino-$C_0$-$C_{20}$-alkyl, aryl-$C_0$-$C_{20}$-alkyl, $C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl, carbonyl-$C_0$-$C_6$-alkoxy, and $C_0$-$C_{20}$-alkylamide. Preferably, none of R5-R8 is linked together.

Non-coordinated group T preferably represents hydrogen, hydroxy, methyl, ethyl, benzyl, or methoxy.

In one aspect, the group U in formula (IA) represents a coordinating group of the general formula (IIA):



(IIA)

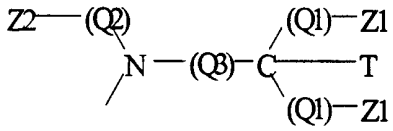
According to this aspect, it is preferred that Z2 represents an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole,

quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole, more preferably optionally substituted pyridin-2-yl or optionally substituted benzimidazol-2-yl.

It is also preferred, in this aspect, that Z4 represents an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole, more preferably optionally substituted pyridin-2-yl, or an non-coordinating group selected from hydrogen, hydroxy, alkoxy, alkyl, alkenyl, cycloalkyl, aryl, or benzyl.

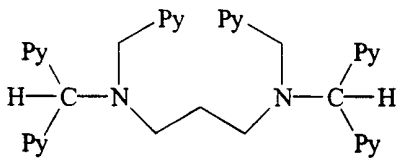
In preferred embodiments of this aspect, the ligand is selected from:
1,1-bis(pyridin-2-yl)-N-methyl-N-(pyridin-2-ylmethyl)methylamine;
1,1-bis(pyridin-2-yl)-N,N-bis(6-methyl-pyridin-2-ylmethyl)methylamine;
1,1-bis(pyridin-2-yl)-N,N-bis(5-carboxymethyl-pyridin-2-ylmethyl)methylamine;
1,1-bis(pyridin-2-yl)-1-benzyl-N,N-bis(pyridin-2-ylmethyl)methylamine; and
1,1-bis(pyridin-2yl)-N,N-bis(benzimidazol-2-ylmethyl)methylamine.

In a variant of this aspect, the group Z4 in formula (IIA) represents a group of the general formula (IIAa):



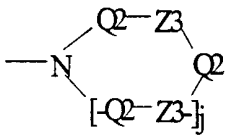
(IIAa)

In this variant, Q4 preferably represents optionally substituted alkylene, preferably $-CH_2-CHOH-CH_2-$ or $-CH_2-CH_2-CH_2-$. In a preferred embodiment of this variant, the ligand is:



wherein -Py represents pyridin-2-yl.

In another aspect, the group U in formula (IA) represents a coordinating group of the general formula (IIIA):

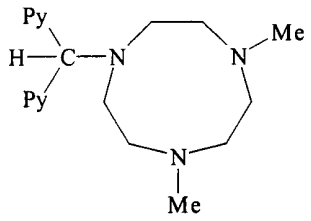


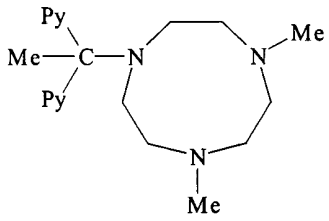
(IIIA)

wherein j is 1 or 2, preferably 1.

According to this aspect, each Q2 preferably represents $-(CH_2)_n-$ (n=2-4), and each Z3 preferably represents -N(R)- wherein R = -H or $C_{1-4}$-alkyl, preferably methyl.

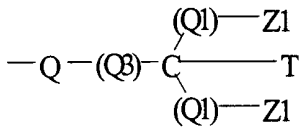
In preferred embodiments of this aspect, the ligand is selected from:




wherein -Py represents pyridin-2-yl.

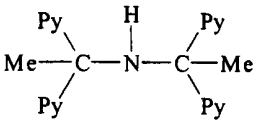
In yet another aspect, the group U in formula (IA) represents a coordinating group of the general formula (IVA):

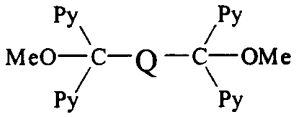


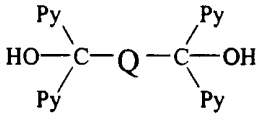

(IVA)

In this aspect, Q preferably represents -N(T)- (wherein T= -H, methyl, or benzyl) or pyridin-diyl.

In preferred embodiments of this aspect, the ligand is selected from:

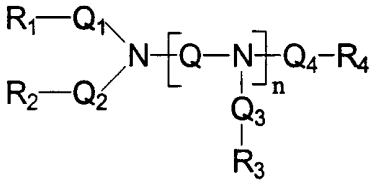






wherein -Py represents pyridin-2-yl, and -Q- represents pyridin-2,6-diyl.

(B) Ligands of the general formula (IB):



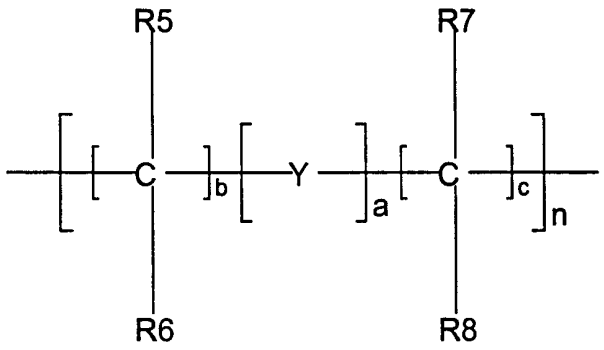
(IB)

wherein

n = 1 or 2, whereby if n = 2, then each $-Q_3-R_3$ group is independently defined;

$R_1$, $R_2$, $R_3$, $R_4$ independently represent a group selected from hydrogen, hydroxyl, halogen, $-NH-C(NH)NH_2$, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

$Q_1$, $Q_2$, $Q_3$, $Q_4$ and Q independently represent a group of the formula:




wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6

together with R7, represent $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I,

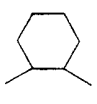
provided that at least two of $R_1$, $R_2$, $R_3$, $R_4$ comprise coordinating heteroatoms and no more than six heteroatoms are coordinated to the same transition metal atom.

At least two, and preferably at least three, of $R_1$, $R_2$, $R_3$, $R_4$ independently represent a group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

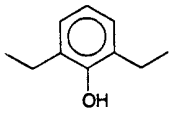
Preferably, substituents for groups $R_1$, $R_2$, $R_3$, $R_4$, when representing a heterocyclic or heteroaromatic ring, are selected from $C_{1-4}$-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

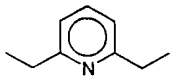
The groups $Q_1$, $Q_2$, $Q_3$, $Q_4$ preferably independently represent a group selected from -$CH_2$- and -$CH_2CH_2$-.

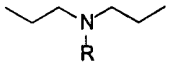
Group Q is preferably a group selected from -$(CH_2)_{2-4}$-, -$CH_2CH(OH)CH_2$-,



optionally substituted by methyl or ethyl,



, 

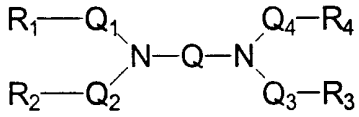
, and 


wherein R represents -H or $C_{1-4}$-alkyl.

Preferably, $Q_1$, $Q_2$, $Q_3$, $Q_4$ are defined such that a=b=0, c=1 and n=1, and Q is defined such that a=b=0, c=2 and n=1.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-$C_0$-$C_{20}$-alkyl, halo-$C_0$-$C_{20}$-alkyl, nitroso, formyl-$C_0$-$C_{20}$-alkyl, carboxyl-$C_0$-$C_{20}$-alkyl and esters and salts thereof, carbamoyl-$C_0$-$C_{20}$-alkyl, sulfo-$C_0$-$C_{20}$-alkyl and esters and salts thereof, sulfamoyl-$C_0$-$C_{20}$-alkyl, amino-$C_0$-$C_{20}$-alkyl, aryl-$C_0$-$C_{20}$-alkyl, $C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl, carbonyl-$C_0$-$C_6$-alkoxy, and $C_0$-$C_{20}$-alkylamide. Preferably, none of R5-R8 is linked together.

In a preferred aspect, the ligand is of the general formula (IIB):




(IIB)

wherein

$Q_1$, $Q_2$, $Q_3$, $Q_4$ are defined such that a=b=0, c=1 or 2 and n=1;

Q is defined such that a=b=0, c=2,3 or 4 and n=1; and

$R_1$, $R_2$, $R_3$, $R_4$, R7, R8 are independently defined as for formula (I).

Preferred classes of ligands according to this aspect, as represented by formula (IIB) above, are as follows:

(i) ligands of the general formula (IIB) wherein:

$R_1$, $R_2$, $R_3$, $R_4$ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1;

$R_1$, $R_2$, $R_3$, $R_4$ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

(ii) ligands of the general formula (IIB) wherein:

$R_1$, $R_2$, $R_3$ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

$R_4$ represents a group selected from hydrogen, $C_{1-20}$ optionally substituted alkyl, $C_{1-20}$ optionally substituted arylalkyl, aryl, and $C_{1-20}$ optionally substituted $NR_3^+$ (wherein R=$C_{1-8}$-alkyl).

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1;

$R_1$, $R_2$, $R_3$ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

$R_4$ represents a group selected from hydrogen, $C_{1-10}$ optionally substituted alkyl, $C_{1-5}$-furanyl, $C_{1-5}$ optionally substituted benzylalkyl, benzyl, $C_{1-5}$ optionally substituted alkoxy, and $C_{1-20}$ optionally substituted $N^+Me_3$.

(iii) ligands of the general formula (IIB) wherein:

$R_1$, $R_4$ each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

$R_2$, $R_3$ each independently represent a group selected from hydrogen, $C_{1-20}$ optionally substituted alkyl, $C_{1-20}$ optionally substituted arylalkyl, aryl, and $C_{1-20}$ optionally substituted $NR_3^+$ (wherein R=$C_{1-8}$-alkyl).

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1;

$R_1$, $R_4$ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

$R_2$, $R_3$ each independently represent a group selected from hydrogen, $C_{1-10}$ optionally substituted alkyl, $C_{1-5}$-furanyl, $C_{1-5}$ optionally substituted benzylalkyl, benzyl, $C_{1-5}$ optionally substituted alkoxy, and $C_{1-20}$ optionally substituted $N^+Me_3$.

Examples of preferred ligands in their simplest forms are:

N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-trimethylammoniumpropyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N-(2-hydroxyethylene)-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N,N,N',N'-tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine;
N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine;
N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine;

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'(2'-methoxy-ethyl-1)-ethylenediamine;
N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine;
N-(furan-2-yl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine;

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

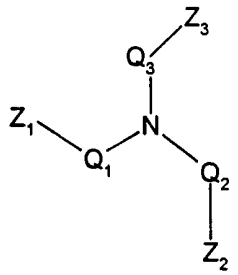
N-methyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and
N-(2-methoxyethyl)-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

More preferred ligands are:
N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and
N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

(C) Ligands of the general formula (IC):

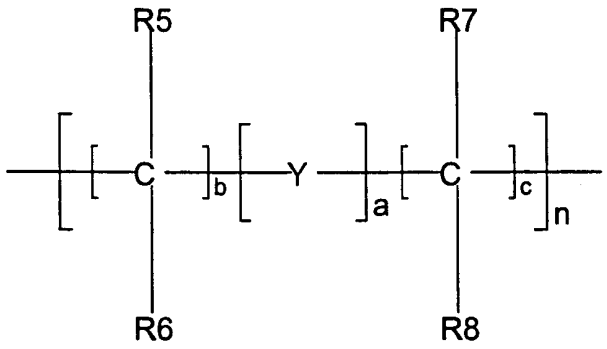



(IC)

wherein

$Z_1$, $Z_2$ and $Z_3$ independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole;

$Q_1$, $Q_2$, and $Q_3$ independently represent a group of the formula:




wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E; and

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I.

$Z_1$, $Z_2$ and $Z_3$ each represent a coordinating group, preferably selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl. Preferably, $Z_1$, $Z_2$ and $Z_3$ each represent optionally substituted pyridin-2-yl.

Optional substituents for the groups $Z_1$, $Z_2$ and $Z_3$ are preferably selected from $C_{1-4}$-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl, preferably methyl.

Also preferred is that $Q_1$, $Q_2$ and $Q_3$ are defined such that a=b=0, c=1 or 2, and n=1.

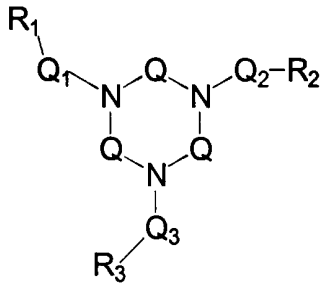
Preferably, each $Q_1$, $Q_2$ and $Q_3$ independently represent $C_{1-4}$-alkylene, more preferably a group selected from $-CH_2-$ and $-CH_2CH_2-$.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-$C_0$-$C_{20}$-alkyl, halo-$C_0$-$C_{20}$-alkyl, nitroso, formyl-$C_0$-$C_{20}$-alkyl, carboxyl-$C_0$-$C_{20}$-alkyl and esters and salts thereof, carbamoyl-$C_0$-$C_{20}$-alkyl, sulfo-$C_0$-$C_{20}$-alkyl and esters and salts thereof, sulfamoyl-$C_0$-$C_{20}$-alkyl, amino-$C_0$-$C_{20}$-alkyl, aryl-$C_0$-$C_{20}$-alkyl, $C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl, carbonyl-$C_0$-$C_6$-alkoxy, and $C_0$-$C_{20}$-alkylamide. Preferably, none of R5-R8 is linked together.

Preferably, the ligand is selected from tris(pyridin-2-ylmethyl)amine, tris(3-methyl-pyridin-2-ylmethyl)amine,

tris(5-methyl-pyridin-2-ylmethyl)amine, and tris(6-methyl-pyridin-2-ylmethyl)amine.

(D) Ligands of the general formula (ID):



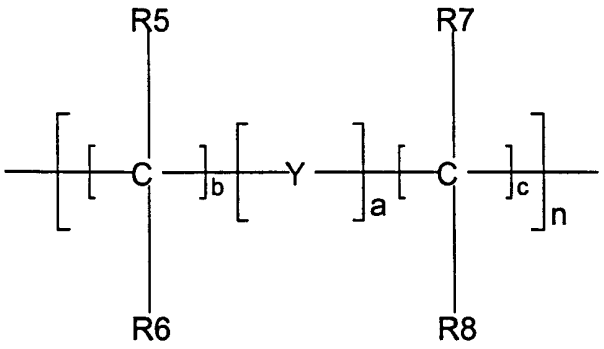
(ID)

wherein

$R_1$, $R_2$, and $R_3$ independently represent a group selected from hydrogen, hydroxyl, halogen, -NH-C(NH)$NH_2$, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E;

Q independently represent a group selected from $C_{2-3}$-alkylene optionally substituted by H, benzyl or $C_{1-8}$-alkyl;

$Q_1$, $Q_2$ and $Q_3$ independently represent a group of the formula:




wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E; and

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I,

provided that at least one, preferably at least two, of $R_1$, $R_2$ and $R_3$ is a coordinating group.

At least two, and preferably at least three, of $R_1$, $R_2$ and $R_3$ independently represent a group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole. Preferably, at least two of $R_1$, $R_2$, $R_3$ each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

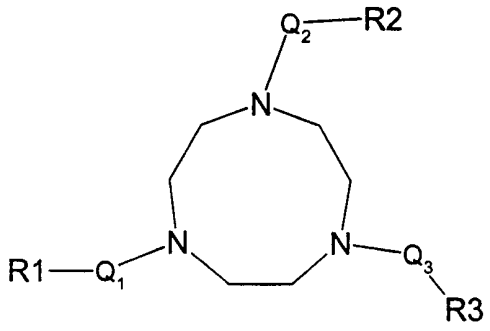
Preferably, substituents for groups $R_1$, $R_2$, $R_3$, when representing a heterocyclic or heteroaromatic ring, are selected from $C_{1-4}$-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

Preferably, $Q_1$, $Q_2$ and $Q_3$ are defined such that a=b=0, c=1,2,3 or 4 and n=1. Preferably, the groups $Q_1$, $Q_2$ and $Q_3$ independently represent a group selected from -$CH_2$- and -$CH_2CH_2$-.

Group Q is preferably a group selected from -$CH_2CH_2$- and -$CH_2CH_2CH_2$-.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-$C_0$-$C_{20}$-alkyl, halo-$C_0$-$C_{20}$-alkyl, nitroso, formyl-$C_0$-$C_{20}$-alkyl, carboxyl-$C_0$-$C_{20}$-alkyl and esters and salts thereof, carbamoyl-$C_0$-$C_{20}$-alkyl, sulfo-$C_0$-$C_{20}$-alkyl and esters and salts thereof, sulfamoyl-$C_0$-$C_{20}$-alkyl, amino-$C_0$-$C_{20}$-alkyl, aryl-$C_0$-$C_{20}$-alkyl, $C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl, carbonyl-$C_0$-$C_6$-alkoxy, and $C_0$-$C_{20}$-alkylamide. Preferably, none of R5-R8 is linked together.

In a preferred aspect, the ligand is of the general formula (IID):




(IID)

wherein R1, R2, R3 are as defined previously for $R_1$, $R_2$, $R_3$, and $Q_1$, $Q_2$, $Q_3$ are as defined previously.

Preferred classes of ligands according to this preferred aspect, as represented by formula (IID) above, are as follows:

(i) ligands of the general formula (IID) wherein:

R1, R2, R3 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$,

hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

In this class, we prefer that:

R1, R2, R3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

(ii) ligands of the general formula (IID) wherein:

two of R1, R2, R3 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)$NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

one of R1, R2, R3 represents a group selected from hydrogen, $C_{1-20}$ optionally substituted alkyl, $C_{1-20}$ optionally substituted arylalkyl, aryl, and $C_{1-20}$ optionally substituted $NR_3^+$ (wherein R=$C_{1-8}$-alkyl).

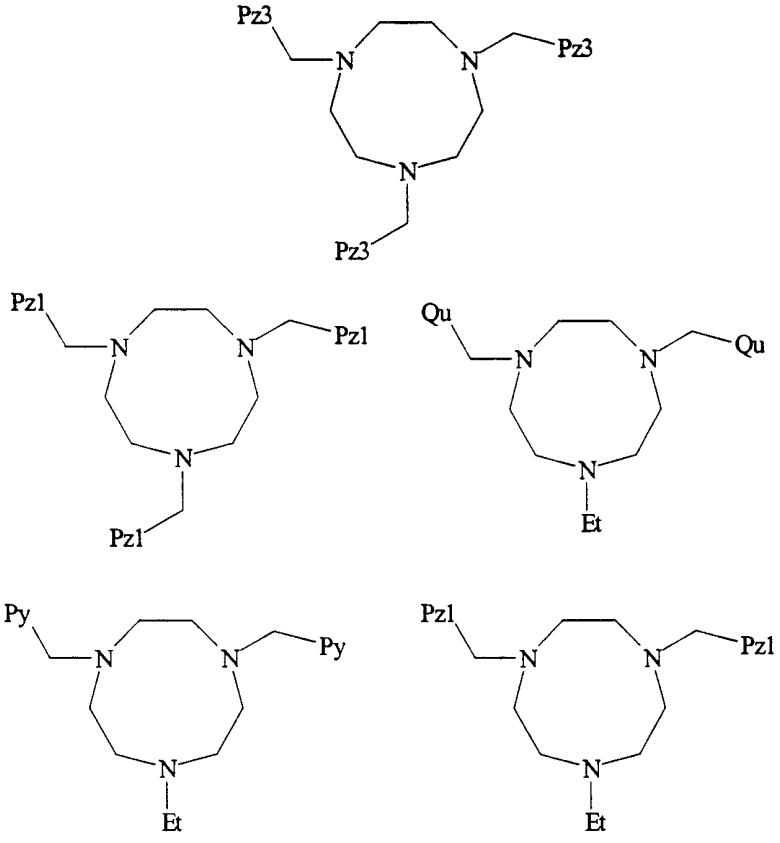
In this class, we prefer that:

two of R1, R2, R3 each independently represent a coordinating group selected from optionally substituted

pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

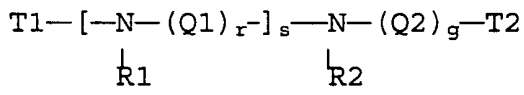
one of R1, R2, R3 represents a group selected from hydrogen, $C_{1-10}$ optionally substituted alkyl, $C_{1-5}$-furanyl, $C_{1-5}$ optionally substituted benzylalkyl, benzyl, $C_{1-5}$ optionally substituted alkoxy, and $C_{1-20}$ optionally substituted $N^{+}Me_3$.

In especially preferred embodiments, the ligand is selected from:




wherein -Et represents ethyl, -Py represents pyridin-2-yl, Pz3 represents pyrazol-3-yl, Pz1 represents pyrazol-1-yl, and Qu represents quinolin-2-yl.

(E) Ligands of the general formula (IE):



(IE)

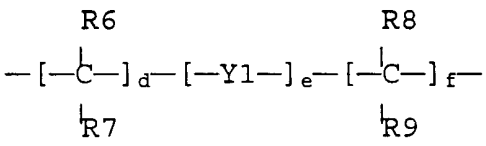
wherein

g represents zero or an integer from 1 to 6;

r represents an integer from 1 to 6;

s represents zero or an integer from 1 to 6;

Q1 and Q2 independently represent a group of the formula:



wherein

$5 \geq d+e+f \geq 1$; d=0-5; e=0-5; f=0-5;

each Y1 independently represents a group selected from -O-, -S-, -SO-, -$SO_2$-, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

if s>1, each -[-N(R1)-$(Q1)_r$-]- group is independently defined;

R1, R2, R6, R7, R8, R9 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R6 together with R7, or R8 together with R9, or both, represent oxygen,

or R6 together with R8 and/or independently R7 together with R9, or R6 together with R9 and/or independently R7 together with R8, represent $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I;

or one of R1-R9 is a bridging group bound to another moiety of the same general formula;

T1 and T2 independently represent groups R4 and R5, wherein R4 and R5 are as defined for R1-R9, and if g=0 and s>0, R1 together with R4, and/or R2 together with R5, may optionally independently represent =CH-R10, wherein R10 is as defined for R1-R9, or

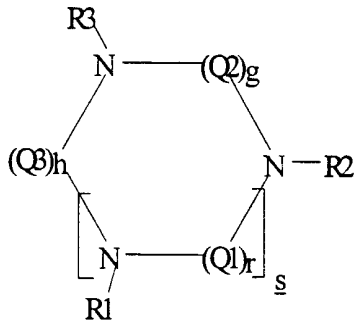
T1 and T2 may together (-T2-T1-) represent a covalent bond linkage when s>1 and g>0;

if T1 and T2 together represent a single bond linkage, Q1 and/or Q2 may independently represent a group of the formula: $=CH-[-Y1-]_e-CH=$ provided R1 and/or R2 are absent, and R1 and/or R2 may be absent provided Q1 and/or Q2 independently represent a group of the formula: $=CH-[-Y1-]_e-CH=$.

The groups R1-R9 are preferably independently selected from -H, hydroxy-$C_0$-$C_{20}$-alkyl, halo-$C_0$-$C_{20}$-alkyl, nitroso, formyl-$C_0$-$C_{20}$-alkyl, carboxyl-$C_0$-$C_{20}$-alkyl and esters and salts thereof, carbamoyl-$C_0$-$C_{20}$-alkyl, sulpho-$C_0$-$C_{20}$-alkyl and esters and salts thereof, sulphamoyl-$C_0$-$C_{20}$-alkyl, amino-$C_0$-$C_{20}$-alkyl, aryl-$C_0$-$C_{20}$-alkyl, heteroaryl-$C_0$-$C_{20}$-alkyl, $C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl, carbonyl-$C_0$-$C_6$-alkoxy, and aryl-$C_0$-$C_6$-alkyl and $C_0$-$C_{20}$-alkylamide.

One of R1-R9 may be a bridging group which links the ligand moiety to a second ligand moiety of preferably the same general structure. In this case the bridging group is independently defined according to the formula for Q1, Q2, preferably being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge, more preferably $C_{1-6}$-alkylene optionally substituted by $C_{1-4}$-alkyl, -F, -Cl, -Br or -I.

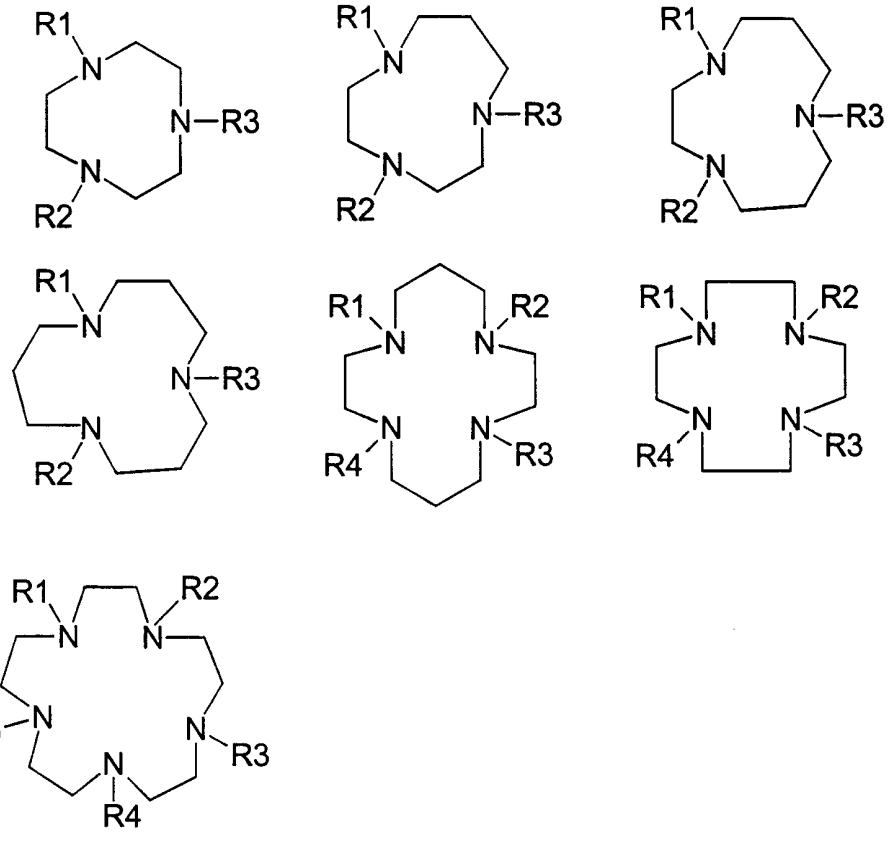
In a first variant according to formula (IE), the groups T1 and T2 together form a single bond linkage and s>1, according to general formula (IIE):




(IIE)

wherein R3 independently represents a group as defined for R1-R9; Q3 independently represents a group as defined for Q1, Q2; h represents zero or an integer from 1 to 6; and s=s-1.

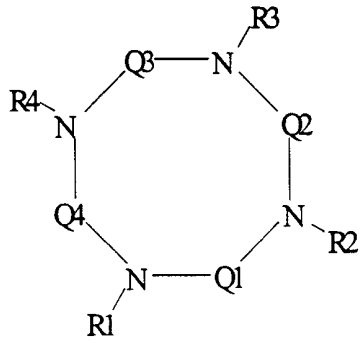
In a first embodiment of the first variant, in general formula (IIE), s=1, 2 or 3; r=g=h=1; d=2 or 3; e=f=0; R6=R7=H, preferably such that the ligand has a general formula selected from:



In these preferred examples, R1, R2, R3 and R4 are preferably independently selected from -H, alkyl, aryl, heteroaryl, and/or one of R1-R4 represents a bridging group bound to another moiety of the same general formula and/or two or more of R1-R4 together represent a bridging group

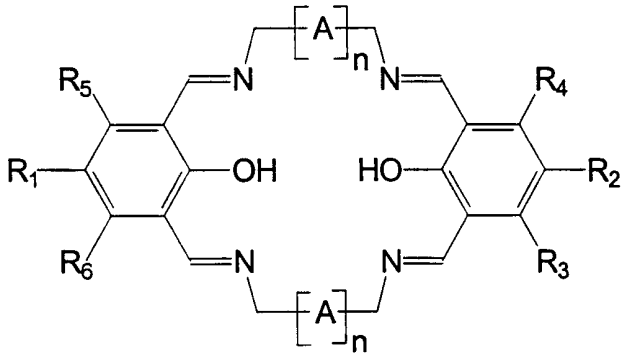
linking N atoms in the same moiety, with the bridging group being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge, preferably heteroarylene. More preferably, R1, R2, R3 and R4 are independently selected from -H, methyl, ethyl, isopropyl, nitrogen-containing heteroaryl, or a bridging group bound to another moiety of the same general formula or linking N atoms in the same moiety with the bridging group being alkylene or hydroxy-alkylene.

In a second embodiment of the first variant, in general formula (IIE), s=2 and r=g=h=1, according to the general formula:




In this second embodiment, preferably R1-R4 are absent; both Q1 and Q3 represent $=CH-[-Y1-]_e-CH=$ ; and both Q2 and Q4 represent $-CH_2-[-Y1-]_n-CH_2-$.

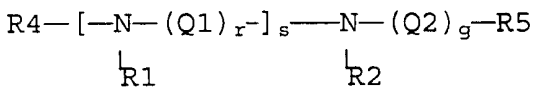
Thus, preferably the ligand has the general formula:



wherein A represents optionally substituted alkylene optionally interrupted by a heteroatom; and n is zero or an integer from 1 to 5.

Preferably, R1-R6 represent hydrogen, n=1 and A= $-CH_2-$, $-CHOH-$, $-CH_2N(R)CH_2-$ or $-CH_2CH_2N(R)CH_2CH_2-$ wherein R represents hydrogen or alkyl, more preferably A= $-CH_2-$, $-CHOH-$ or $-CH_2CH_2NHCH_2CH_2-$.

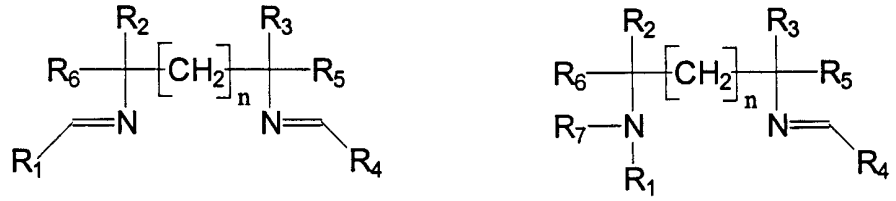
In a second variant according to formula (IE), T1 and T2 independently represent groups R4, R5 as defined for R1-R9, according to the general formula (IIIE):



(IIIE)

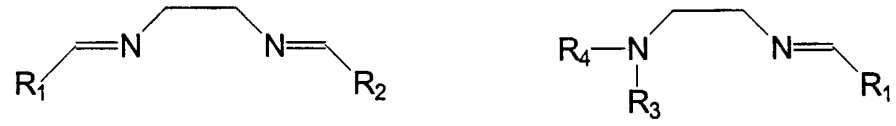
In a first embodiment of the second variant, in general formula (IIIE), s=1; r=1; g=0; d=f=1; e=0-4; Y1= $-CH_2-$ ; and R1 together with R4, and/or R2 together with R5, independently represent =CH-R10, wherein R10 is as defined for R1-R9. In one example, R2 together with R5 represents =CH-R10, with R1 and R4 being two separate groups.

Alternatively, both R1 together with R4, and R2 together with R5 may independently represent =CH-R10. Thus, preferred ligands may for example have a structure selected from:



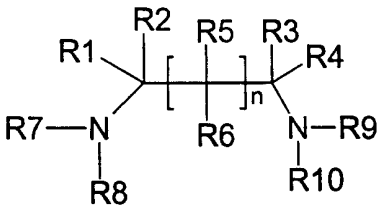
wherein n = 0-4.

Preferably, the ligand is selected from:



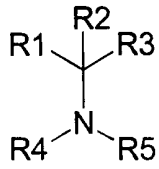
wherein R1and R2 are selected from optionally substituted phenols, heteroaryl-$C_0$-$C_{20}$-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, heteroaryl-$C_0$-$C_{20}$-alkyls, alkylaryl, aminoalkyl, alkoxy, more preferably R1 and R2 being selected from optionally substituted phenols, heteroaryl-$C_0$-$C_2$-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, nitrogen-heteroaryl-$C_0$-$C_2$-alkyls.

In a second embodiment of the second variant, in general formula (IIIE), s=1; r=1; g=0; d=f=1; e=1-4; Y1= -C(R')(R''), wherein R' and R'' are independently as defined for R1-R9. Preferably, the ligand has the general formula:



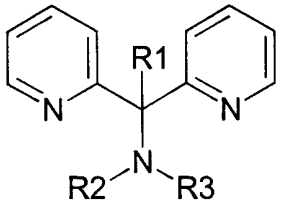

The groups R1, R2, R3, R4, R5 in this formula are preferably -H or $C_0$-$C_{20}$-alkyl, n=0 or 1, R6 is -H, alkyl, -OH or -SH, and R7, R8, R9, R10 are preferably each independently selected from -H, $C_0$-$C_{20}$-alkyl, heteroaryl-$C_0$-$C_{20}$-alkyl, alkoxy-$C_0$-$C_8$-alkyl and amino-$C_0$-$C_{20}$-alkyl.

In a third embodiment of the second variant, in general formula (IIIE), s=0; g=1; d=e=0; f=1-4. Preferably, the ligand has the general formula:



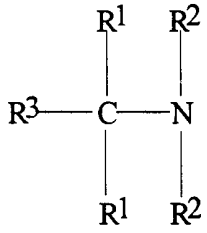

This class of ligand is particularly preferred according to the invention.

More preferably, the ligand has the general formula:



wherein R1, R2, R3 are as defined for R2, R4, R5.

In a fourth embodiment of the second variant, the ligand is a pentadentate ligand of the general formula (IVE):



(IVE)

wherein

each $R^1$ , $R^2$ independently represents $-R^4-R^5$,

$R^3$ represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or $-R^4-R^5$,

each $R^4$ independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and

each $R^5$ independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

Ligands of the class represented by general formula (IVE) are also particularly preferred according to the invention. The ligand having the general formula (IVE), as defined above, is a pentadentate ligand. By 'pentadentate' herein is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex.

In formula (IVE), one coordinating hetero atom is provided by the nitrogen atom in the methylamine backbone, and preferably one coordinating hetero atom is contained in each of the four $R^1$ and $R^2$ side groups. Preferably, all the coordinating hetero atoms are nitrogen atoms.

The ligand of formula (IVE) preferably comprises at least two substituted or unsubstituted heteroaryl groups in the four side groups. The heteroaryl group is preferably a pyridin-2-yl group and, if substituted, preferably a methyl- or ethyl-substituted pyridin-2-yl group. More preferably, the heteroaryl group is an unsubstituted pyridin-2-yl group. Preferably, the heteroaryl group is linked to methylamine, and preferably to the N atom thereof, *via* a methylene group. Preferably, the ligand of formula (IVE) contains at least one optionally substituted amino-alkyl side group, more preferably two amino-ethyl side groups, in particular 2-(N-alkyl)amino-ethyl or 2-(N,N-dialkyl)amino-ethyl.

Thus, in formula (IVE) preferably $R^1$ represents pyridin-2-yl or $R^2$ represents pyridin-2-yl-methyl. Preferably $R^2$ or $R^1$ represents 2-amino-ethyl, 2-(N-(m)ethyl)amino-ethyl or 2-(N,N-di(m)ethyl)amino-ethyl. If substituted, $R^5$ preferably represents 3-methyl pyridin-2-yl. $R^3$ preferably represents hydrogen, benzyl or methyl.

Examples of preferred ligands of formula (IVE) in their simplest forms are:

(i) pyridin-2-yl containing ligands such as: N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine;

N,N-bis(pyrazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
N,N-bis(imidazol-2-yl-methyl)-bis(pyridin-2-yl)methylamine;
N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
N,N-bis(pyridin-2-yl-methyl)-bis(pyrazol-1-yl)methylamine;
N,N-bis(pyridin-2-yl-methyl)-bis(imidazol-2-yl)methylamine;
N,N-bis(pyridin-2-yl-methyl)-bis(1,2,4-triazol-1-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-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-2-phenyl-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-1-aminoethane;

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-2-phenyl-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
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)-1-aminohexane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(4-sulphonic acid-phenyl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-2-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-3-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-4-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-4-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-3-yl)-1-aminoethane;
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-2-yl)-1-aminoethane;

(ii) 2-amino-ethyl containing ligands such as:
N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;

N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;
N,N-bis(2-(N-alkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;
N,N-bis(2-(N-alkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;
N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;
N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;
N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;
N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;
N,N-bis(pyridin-2-yl-methyl)-bis(2-amino-ethyl)methylamine;
N,N-bis(pyrazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine;
N,N-bis(imidazol-2-yl-methyl)-bis(2-amino-ethyl)methylamine;
N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine.

More preferred ligands are:
N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, hereafter referred to as N4Py.
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, hereafter referred to as MeN4Py,
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, hereafter referred to as BzN4Py.

In a fifth embodiment of the second variant, the ligand represents a pentadentate or hexadentate ligand of general formula (VE):

$R^1R^1N\text{-}W\text{-}NR^1R^2$

(VE)

wherein

each $R^1$ independently represents $-R^3\text{-}V$, in which $R^3$ represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and V represents an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

W represents an optionally substituted alkylene bridging group selected from $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2-C_6H_4-CH_2-$, $-CH_2-C_6H_{10}-CH_2-$, and $-CH_2-C_{10}H_6-CH_2-$; and

$R^2$ represents a group selected from $R^1$, and alkyl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and $N^+(R^4)_3$, wherein $R^4$ is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

The ligand having the general formula (VE), as defined above, is a pentadentate ligand or, if $R^1=R^2$, can be a hexadentate ligand. As mentioned above, by 'pentadentate' is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex. Similarly, by 'hexadentate' is meant that six hetero atoms can in principle coordinate to

the metal M ion. However, in this case it is believed that one of the arms will not be bound in the complex, so that the hexadentate ligand will be penta coordinating.

In the formula (VE), two hetero atoms are linked by the bridging group W and one coordinating hetero atom is contained in each of the three $R^1$ groups. Preferably, the coordinating hetero atoms are nitrogen atoms.

The ligand of formula (VE) comprises at least one optionally substituted heteroaryl group in each of the three $R^1$ groups. Preferably, the heteroaryl group is a pyridin-2-yl group, in particular a methyl- or ethyl-substituted pyridin-2-yl group. The heteroaryl group is linked to an N atom in formula (VE), preferably *via* an alkylene group, more preferably a methylene group. Most preferably, the heteroaryl group is a 3-methyl-pyridin-2-yl group linked to an N atom *via* methylene.

The group $R^2$ in formula (VE) is a substituted or unsubstituted alkyl, aryl or arylalkyl group, or a group $R^1$. However, preferably $R^2$ is different from each of the groups $R^1$ in the formula above. Preferably, $R^2$ is methyl, ethyl, benzyl, 2-hydroxyethyl or 2-methoxyethyl. More preferably, $R^2$ is methyl or ethyl.

The bridging group W may be a substituted or unsubstituted alkylene group selected from $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH-{}_2CH_2-$, $-CH_2-C_6H_4-CH_2-$, $-CH_2-C_6H_{10}-CH_2-$, and $-CH_2-C_{10}H_6-CH_2-$ (wherein $-C_6H_4-$, $-C_6H_{10}-$, $-C_{10}H_6-$ can be *ortho*-, *para*-, or *meta*-$C_6H_4-$, $-C_6H_{10}-$, $-C_{10}H_6-$). Preferably, the bridging group

W is an ethylene or 1,4-butylene group, more preferably an ethylene group.

Preferably, V represents substituted pyridin-2-yl, especially methyl-substituted or ethyl-substituted pyridin-2-yl, and most preferably V represents 3-methyl pyridin-2-yl.

(F) Ligands of the classes disclosed in WO-A-98/39098 and WO-A-98/39406.

The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as $RCOO^-$, $BPh_4^-$, $ClO_4^-$, $BF_4^-$, $PF_6^-$, $RSO_3^-$, $RSO_4^-$, $SO_4^{2-}$, $NO_3^-$, $F^-$, $Cl^-$, $Br^-$, or $I^-$, with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from $R^7COO^-$, $ClO_4^-$, $BF_4^-$, $PF_6^-$, $RSO_3^-$ (in particular $CF_3SO_3^-$), $RSO_4^-$, $SO_4^{2-}$, $NO_3^-$, $F^-$, $Cl^-$, $Br^-$, and $I^-$, wherein R represents hydrogen or optionally substituted phenyl, naphthyl or $C_1$-$C_4$ alkyl.

It will be appreciated that the complex (A1) can be formed by any appropriate means, including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A1) under conditions of

storage or use. Preferably, the complex is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as $FeSO_4$ can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active complex. Thus, for example, the composition may formed from a mixture of the ligand L and a metal salt $MX_n$ in which preferably n=1-5, more preferably 1-3. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according the formula (A1).

In typical washing compositions the level of the catalyst is such that the in-use level is from 1$\mu$M to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 10 to 100 $\mu$M.

Preferably, the wash liquor has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more

preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

In the context of the present invention bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with a substrate. However, it is envisaged that the present invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate. Furthermore, in the context of the present invention bleaching is to be understood as being restricted to any bleaching mechanism or process that does not require the presence of light or activation by light. Thus, photobleaching compositions and processes relying on the use of photobleach catalysts or photobleach activators and the presence of light are excluded from the present invention.

According to the present invention, both of the wash additive and the wash liquor may be substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, whereby the catalytic bleaching by atmospheric oxygen or air will predominate. However, in this case it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in the composition, if desired. Therefore, by "substantially devoid of peroxygen bleach or peroxy-based or -generating bleach systems" is meant that the composition contains from 0 to 50 %, preferably from 0 to 10 %, more preferably from 0 to 5 %, and optimally from 0 to 2 % by molar weight on an

oxygen basis, of peroxygen bleach or peroxy-based or -generating bleach systems. Preferably, however, the composition will be wholly devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

Thus, at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of the stain substrate is effected by oxygen sourced from the air.

According to the present invention, preferably the wash additive liquor contains a peroxygen bleach or a peroxy-based or -generating system. The peroxy bleach may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

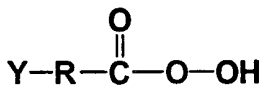
Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 5-35 % by weight, preferably from 10-25 % by weight.

Another suitable hydrogen peroxide generating system is a combination of a $C_1$-$C_4$ alkanol oxidase and a $C_1$-$C_4$ alkanol,

especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO-A-9507972, which is incorporated herein by reference.

Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



wherein R is an alkyl- or alkylidene- or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or COOOH group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-a-naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxylauric acid, peroxystearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and

(iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

(iv) 1,12-diperoxydodecanedioic acid (DPDA);

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-dioic acid; and

(viii) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 4-8 % by weight.

All these peroxy compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal.

Generally, the wash additive composition can be suitably formulated to contain from 2 to 35%, preferably from 5 to 25% by weight, of the peroxy bleaching agent.

Peroxyacid bleach precursors are known and amply described in literature, such as in GB-A-836988; GB-A-864,798; GB-A-907,356; GB-A-1,003,310 and GB-A-1,519,351; DE-A-3,337,921; EP-A-0,185,522; EP-A-0,174,132; EP-A-0,120,591; and US-A-1,246,339; US-A-3,332,882; US-A-4,128,494; US-A-4,412,934 and US-A-4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted

peroxyacid precursors as disclosed in US-A-4,751,015 and US-A-4,397,757, in EP-A-0,284,292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:
2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride - (SPCC);
N-octyl,N,N-dimethyl-$N_{10}$-carbophenoxy decyl ammonium chloride - (ODC);
3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520; EP-A-458,396 and EP-A-464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, although some may be more preferred than others.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoloxy benzoate; 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride (SPCC);

trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

The precursors may be used in an amount of up to 12 %, preferably from 2-10 % by weight, of the wash additive composition.

The method of the present invention has particular application in detergent bleaching, especially for laundry cleaning. Accordingly, the method preferably uses a wash liquor that contains a surface-active material, optionally together with detergency builder.

Optionally, the wash additive may also include a surface-active material, optionally together with detergency builder. The wash additive may contain a surface-active material in an amount, for example, of from 10 to 50% by weight.

The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and

sulphonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl groups. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher ($C_8$-$C_{18}$) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl ($C_9$-$C_{20}$) benzene sulphonates, particularly sodium linear secondary alkyl ($C_{10}$-$C_{15}$) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher ($C_9$-$C_{18}$) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins ($C_8$-$C_{20}$) with sodium bisulphite and those derived by reacting paraffins with $SO_2$ and $Cl_2$ and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium ($C_7$-$C_{12}$) dialkyl sulphosuccinates; and olefin sulphonates, which term is used to describe material made by reacting olefins, particularly ($C_{10}$-$C_{20}$) alpha-olefins, with $SO_3$ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium ($C_{10}$-$C_{15}$) alkylbenzene sulphonates, and sodium ($C_{16}$-$C_{18}$) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl ($C_6$-$C_{22}$) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic ($C_8$-$C_{18}$) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

The wash additive will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is free from $C_{16}$-$C_{12}$ fatty acid soaps.

The wash additive may also contain a detergency builder, for example in an amount of from about 5 to 80 % by weight, preferably from about 10 to 60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

In particular, the wash additive or wash liquor may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and

water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

It is preferred that the wash additive contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Apart from the components already mentioned, the wash additive or wash liquor can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as EDTMP (ethylene diamine

tetra(methylene phosphonate)) may also be included, in addition to the catalyst ligand specified, for example to improve the stability sensitive ingredients such as enzymes, fluorescent agents and perfumes, but provided the composition remains bleaching effective. However, the was additive containing the catalyst, is preferably substantially, and more preferably completely, devoid of transition metal sequestrants (other than the catalyst ligand).

Throughout the description and claims generic groups have been used, for example alkyl, alkoxy, aryl. Unless otherwise specified the following are preferred group restrictions that may be applied to generic groups found within compounds disclosed herein:

alkyl: C1-C6-alkyl,

alkenyl: C2-C6-alkenyl,

cycloalkyl: C3-C8-cycloalkyl,

alkoxy: C1-C6-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylene; 1,2-propylene; 1,3-propylene; 2,2-propylene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; and 1,4-butylene,

aryl: selected from homoaromatic compounds having a molecular weight under 300,

arylene: selected from the group consisting of: 1,2-benzene; 1,3-benzene; 1,4-benzene; 1,2-naphthalene; 1,3-naphthalene; 1,4-naphthalene; 2,3-naphthalene; phenol-2,3-diyl; phenol-2,4-diyl; phenol-2,5-diyl; and phenol-2,-6-diyl,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; pyrazinyl; triazolyl, pyridazinyl; 1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl; imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl; oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl,

heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,5-diyl; pyridin-2,6-diyl; pyridin-3,4-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; quinolin-2,8-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-1,3-diyl; pyrazol-3,5-diyl; triazole-3,5-diyl; triazole-1,3-diyl; pyrazin-2,5-diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of: pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl; piperazinyl; hexamethylene imine; and oxazolidinyl,

amine: the group $-N(R)_2$ wherein each R is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R are C1-C6-alkyl both R together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

halogen: selected from the group consisting of: F; Cl; Br and I,

sulphonate: the group $-S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

sulphate: the group $-OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

sulphone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give sulphonamide) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

carboxylate derivative: the group -C(O)OR, wherein R is selected from: hydrogen, C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5, Li; Na; K; Cs; Mg; and Ca,

carbonyl derivative: the group -C(O)R, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give amide) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -

NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

phosphonate: the group $-P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphate: the group $-OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphine: the group $-P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5,

phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5; and amine (to give phosphonamidate) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.

Unless otherwise specified the following are more preferred group restrictions that may be applied to groups found within compounds disclosed herein:

alkyl: C1-C4-alkyl,

alkenyl: C3-C6-alkenyl,

cycloalkyl: C6-C8-cycloalkyl,

alkoxy: C1-C4-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,2-ethylene; 1,3-propylene; butan-2-ol-1,4-diyl; and 1,4-butylene,

aryl: selected from group consisting of: phenyl; biphenyl, naphthalenyl; anthracenyl; and phenanthrenyl,

arylene: selected from the group consisting of: 1,2-benzene, 1,3-benzene, 1,4-benzene, 1,2-naphthalene, 1,4-naphthalene, 2,3-naphthalene and phenol-2,6-diyl,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl,

heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,6-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-3,5-diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of: pyrrolidinyl; morpholinyl; piperidinyl; and piperazinyl,

amine: the group $-N(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

halogen: selected from the group consisting of: F and Cl,

sulphonate: the group $-S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

sulphate: the group $-OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

sulphone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

carboxylate derivative: the group -C(O)OR, wherein R is selected from hydrogen; Na; K; Mg; Ca; C1-C6-alkyl; and benzyl,

carbonyl derivative: the group: -C(O)R, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

phosphonate: the group $-P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl, benzyl; Na; K; Mg; and Ca,

phosphate: the group $-OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

phosphine: the group $-P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

phosphine oxide: the group $-P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

The invention will now be further illustrated by way of the following non-limiting example:

EXAMPLE

In the following FeMeN4Py was obtained according to the procedure found in EP-A-0909809 A.

The effect of incorporating the iron complex FeMeN4Py as catalyst into a mainwash via cloth impregnated with the catalyst was tested on tea stains and tomato stains, as follows:

An aqueous solution of catalyst was applied to pieces of cotton and allowed to dry overnight. The concentration was such that addition of one piece to the mainwash would

provide a maximum concentration of 10 μM in the wash liquor. Washes were carried out using 3.5 g/l detergent base (post-dosed with 0.5 % Dequest 2047 and 10 % $Na_2CO_3$) in 4° FH (2:1 $Ca^{2+}$:$Mg^{+}$) water at 25 °C in a tergotometer (80 opm). Catalyst cloths and peroxide (added as 15 % perborate monohydrate on base) were added as required.

The detergent base powder composition is given below:

| Component | Parts by weight |
|---|---|
| LAS (linear alkylbenzene sulfonate) | 28 |
| Sodium sulphate | 10.258 |
| STP | 28 |
| Alkaline silicate | 9.9778 |
| Fluorescer | 0.24 |
| EDTA | 0.009 |
| SCMC (Na carboxymethylcellulose) | 1.12 |
| Water | 10.222 |
| TOTAL | 87.627 |

$\Delta E_{aw}$ (aw = after wash) values were measured as follows:

After the wash, the cloths were rinsed with water and subsequently dried at ambient temperature in the dark and the change in colour was measured after leaving the cloths for 24 h in the dark with an Ultrascan XE spectrophotometer (ex Hunterlab). The change in colour (including bleaching) is expressed as the $\Delta E_{aw}$ value relative to clean white cotton. The measured colour difference ($\Delta E_{aw}$) between the

washed cloth and the clean white cotton cloth is defined as follows:

$$\Delta E_{aw} = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

wherein $\Delta L$ is a measure for the difference in darkness between the washed and clean white cloth; $\Delta a$ and $\Delta b$ are measures for the difference in redness and yellowness respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric colour terms, supplement no 2 to CIE Publication, no 15, Colormetry, Bureau Central de la CIE, Paris 1978.

The results are shown in the following table.

Table 1. Iron complex FeMeN4Py in the mainwash - incorporation via a cloth impregnated with catalyst

| | Eaw | |
|---|---|---|
| | Tea | Pomarola |
| Blank | 20.9 | 14.4 |
| Perox | 19.9 | 14.6 |
| Cat | 21.1 | 3.1 |
| Cat/perox | 18.2 | 1.7 |

**CLAIMS:**

1. A method of bleaching fabric stains comprising washing a stained fabric in an aqueous wash liquor in the presence of a wash additive, wherein:

the wash additive comprises a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains by atmospheric oxygen; and

one or both of the wash additive and the wash liquor are substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

2. A method according to claim 1 wherein one of the wash additive and the wash liquor comprises peroxygen bleach or a peroxy-based or -generating bleach system, preferably hydrogen peroxide, and the other of the pretreatment liquid and the wash liquor is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

3. A method according to claim 2 wherein the wash additive comprises the peroxygen bleach or peroxy-based or -generating bleach system.

4. A method according to claim 1 or claim 2 wherein the wash additive is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

5. A method according to any preceding claim wherein the wash additive comprises the complex on a carrier.

6. A method according to claim 5 wherein the carrier is a cloth impregnated with the complex.

7. A method according to any preceding claim wherein the ligand forms a complex of the general formula:

$$[M_aL_kX_n]Y_m$$

in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe (II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably from Fe (II)-(III)-(IV)-(V);

L represents the ligand, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

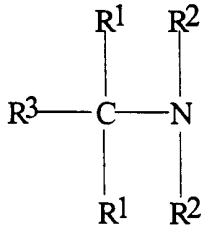
a represents an integer from 1 to 10;

k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

8. A method according to any preceding claim wherein the ligand is a pentadentate ligand of the general formula (IVE):



(IVE)

wherein

each $R^1$ , $R^2$ independently represents $-R^4-R^5$,

$R^3$ represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or $-R^4-R^5$,

each $R^4$ independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and

each $R^5$ independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

9. A method according to any preceding claim wherein the ligand is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane.

10. A method according to any of claims 1 to 9, wherein the pretreatment composition comprises a preformed complex of the ligand and the transition metal.

11. A method according to any of claims 1 to 10, wherein the pretreatment composition comprises free ligand that complexes with transition metal present in the wash liquor.

12. A method according to any of claims 1 to 10, wherein the pretreatment composition comprises free ligand that complexes with transition metal present in the stain.

13. A method according to any of claims 1 to 10, wherein the pretreatment composition comprises free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

# INTERNATIONAL SEARCH REPORT

Interr. nal Application No
PCT/EP 00/07563

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39 D06L3/02 C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | EP 0 909 809 A (UNILEVER)<br>21 April 1999 (1999-04-21)<br>claims 1-7; examples 1,3-5 | 1,7-10 |
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| P,A | WO 00 12667 A (UNILEVER)<br>9 March 2000 (2000-03-09)<br>cited in the application<br>page 18, line 7 -page 20, line 12<br>examples 1,7,8 | 1-4,7-10 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 27 November 2000 | 04/12/2000 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Bertran Nadal, J |

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# INTERNATIONAL SEARCH REPORT

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