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MANUFACTURE OF NEW COLORING MATTERS

Maurice Arthur Thorold Rogers, Blackley, Manchester, England, assignor to Imperial Chemical Industries Limited, a corporation of Great Britain

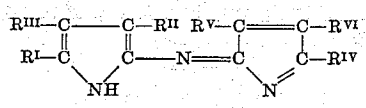
No Drawing. Application July 9, 1943, Serial No. 494,120. In Great Britain July 13, 1942

3 Claims. (Cl. 260—313)

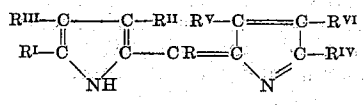
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The present invention relates to the manufacture of new coloring matters.

In British application No. 16,276/41, and in copending application Serial No. 457,228, filed September 3, 1942, now U. S. Patent 2,382,914, there are described tetraaryl-aza-dipyrromethines of formula

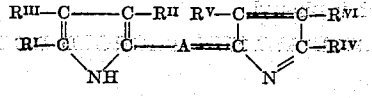


and in copending application No. 494,126, filed July 9, 1943, there are described tetraaryldipyrromonomethines of formula



where R^I, R^{II}, R^{IV} and R^V stand for aryl radicals, for example of the benzene or naphthalene series, substituted or not, the same or different, where R^{III} and R^{VI} each stand for hydrogen or for a non-reactive substituent, the same or different, for example, an aryl-, alkyl-, alkylamino-, benzylideneamino- or acylamino- radical, and where R stands for hydrogen or an alkyl-, aralkyl or aryl-radical, or for a heterocyclic residue.

The present invention is directed to the production of metal complexes from these compounds that is to say, from compounds of the formula



where R^I, R^{II}, R^{III}, R^{IV}, R^V and R^{VI} have the significance given above, and where A stands for nitrogen or for the group CR, R being, as before, hydrogen or an alkyl-, aralkyl- or aryl-radical, or a heterocyclic residue.

According to the invention the metal complexes are manufactured by a process which comprises bringing into reaction with each other a compound of the general formula given above and a metal of the group consisting of copper, zinc, nickel, cobalt, chromium and cadmium.

Suitable compounds of the formula given above include 2:2′:4:4′-tetraphenyl-aza-dipyrromethine, 2:2′:4:4′-tetraphenyl - aza - dipyrromethine disulphonic acid, 2:2′-diphenyl-4:4′-di-(p-methoxyphenyl)-aza-dipyrromethine, 2:2′:4:4′-tetraphenyldipyrromonomethine, 2:2′:4-triphenyl-4′-(p - methoxyphenyl) - dipyrromonomethine and

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2:2′:4:4′ - tetraphenyl-meso-phenyl-dipyrromonomethine.

The metal complexes may be formed by using the metals themselves, for example in a finely divided form, or by using salts, for example the acetates, sulphates, chlorides, phosphates or double salts such as dichromates. Good results have been obtained with, for example, copper acetate, copper sulphate, zinc acetate, chromium fluoride, cobalt sulphate, cobalt acetate, and nickel acetate.

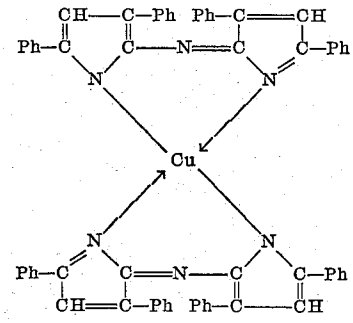
The reaction may be carried out by heating the reagents by themselves or in the presence of a solvent for one or both.

Alternatively, when metal complexes are to be made from water-soluble derivatives of tetraaryl-aza-dipyrromethines or tetraaryldipyrromonomethines, for example, their sulphonic acid derivatives which are described in copending application Serial No. 482,479, filed April 9, 1943, now U. S. Patent 2,382,917, or the salts of their amino-derivatives, they may be made by treating dyeings of these water-soluble compounds, for example on wool, with aqueous solutions of the metal salts. In this way, the metal complexes are formed on the fibre.

The invention is illustrated but not limited by the following examples, in which the parts are expressed by weight.

Example I

1 part of 2:2′:4:4′-tetraphenyl-aza-dipyrromethine, 0.5 part of copper acetate and 50 parts of butanol are boiled together for 1 hour, and the coppery brown crystalline material which forms is collected by filtration. The product analyses for $C_{64}H_{44}N_6Cu$, and has the probable formula:



It is sparingly soluble in nitrobenzene, dioxan, pyridine and dimethylformamide forming solutions which are blue in color.

In a similar manner, cobalt, nickel and zinc acetates yield the corresponding complexes.

Example II

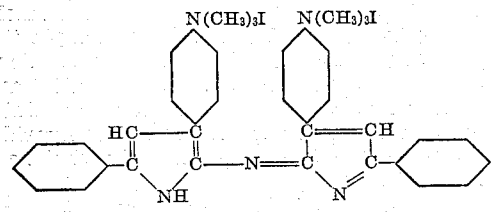
In place of the aza methine in Example I there is used 1 part of 2:2':4:4'-tetraphenyldipyrromonomethine. The copper complex forms coppery brown platelets, which are crystallised from a mixture of pyridine and methyl alcohol in the form of platelets. The product analyses for $C_{66}H_{46}N_4Cu$ and is believed to have a structure similar to that assigned to the product of Example I.

Example III

The disulphonic acid derivative of 2:2':4:4'-tetraphenyl-aza-dipyrromethine is dyed on to wool from an acid dyebath. The dyed wool so obtained is heated in a ½% aqueous solution of copper sulphate for 1 hour at 80–90° C. The color of the dyeing changes from a reddish-blue to a greener color as the copper complex is formed.

Example IV

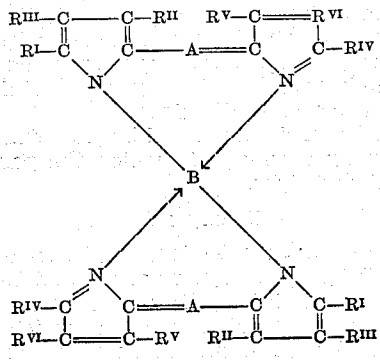
A compound of the formula



made by interacting 2:2'-diphenyl-4:4'-(p-dimethyl-aminophenyl)-aza-dipyrromethine with methyl iodide is dyed on to wool from a neutral dyebath. The greenish blue dyeing so obtained is heated in a 1% aqueous solution of copper acetate. The color of the dyeing changes to a reddish blue as the copper complex is formed.

I claim:

1. Metal complexes of the formula:

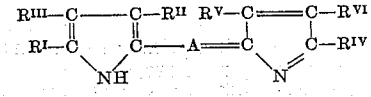


where R^I, R^{II}, R^{IV}, and R^V stand for aryl radicals, R^{III} and R^{VI} each are a member of the group consisting of hydrogen, aryl-, alkyl-, alkylamino-, benzylideneamino-, and acylamino- radicals, A is a member of the group consisting of nitrogen and the group



wherein R is a member of the group consisting of hydrogen, alkyl-, aralkyl-, aryl-, and heterocyclic radicals; and B is a metal of the group consisting of copper, zinc, nickel, cobalt, chromium, and cadmium.

2. Process for the manufacture of metal complexes which comprises bringing into reaction with each other a compound of the general formula:

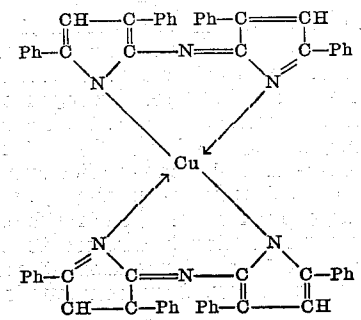


where R^I, R^{II}, R^{IV}, and R^V stand for aryl radicals, R^{III} and R^{VI} each are a member of the group consisting of hydrogen, aryl-, alkyl-, alkylamino-, benzylideneamino-, and acylamino- radicals, A is a member of the group consisting of nitrogen and the group



wherein R is a member of the group consisting of hydrogen, alkyl-, aralkyl-, aryl-, and heterocyclic radicals, with a member taken from the group consisting of copper, zinc, nickel, cobalt, chromium, and cadmium and their salts.

3. The compound of the formula:



where Ph is phenyl.

MAURICE ARTHUR THOROLD ROGERS.