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(54) **Title:** LAUNDRY BLEACHING AND DYE TRANSFER INHIBITING COMPOSITION

(57) **Abstract:** A bleaching composition for laundry fabrics is provided, comprising: hydrogen peroxide or a source of hydrogen peroxide; a bleach catalyst comprising a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains in the presence of peroxygen bleach or a peroxy-based or -generating bleach system; and a dye transfer inhibiting agent. The bleaching composition provides effective bleaching performance on fabric stains without unacceptable transfer of dyes between fabrics.

LAUNDRY BLEACHING AND DYE TRANSFER INHIBITING COMPOSITION

This invention relates to bleaching compositions and methods based on hydrogen peroxide or a source of hydrogen peroxide, more particularly to compositions and methods for stain bleaching of laundry fabrics.

Peroxygen bleaches are well known for their ability to remove stains from substrates. Traditionally, the substrate is subjected to hydrogen peroxide, or to substances which can generate hydroperoxyl radicals, such as inorganic or organic peroxides. Generally, these systems must be activated. One method of activation is to employ wash temperatures of 60°C or higher. However, these high temperatures often lead to inefficient cleaning, and can also cause premature damage to the substrate.

A preferred approach to generating hydroperoxyl bleach radicals is the use of inorganic peroxides coupled with organic precursor compounds. These systems are employed for many commercial laundry powders. For example, various European systems are based on tetraacetyl ethylenediamine (TAED) as the organic precursor coupled with sodium perborate or sodium percarbonate, whereas in the United States laundry bleach products are typically based on sodium nonanoyloxybenzenesulphonate (SNOBS) as the organic precursor coupled with sodium perborate.

Precursor systems are generally effective but still exhibit several disadvantages. For example, organic precursors are moderately sophisticated molecules requiring multi-step manufacturing processes resulting in high capital costs. Also, precursor systems have large formulation space requirements so that a significant proportion of a laundry powder must be devoted to the bleach components, leaving less room for other active ingredients and complicating the development of concentrated powders. Moreover, precursor systems do not bleach very efficiently in countries where consumers have wash habits entailing low dosage, short wash times, cold temperatures and low wash liquor to substrate ratios.

Alternatively, or additionally, hydrogen peroxide and peroxy systems can be activated by bleach catalysts, such as by complexes of iron and the ligand N4Py (*i.e.* N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) disclosed in WO95/34628, or the ligand Tpen (*i.e.* N, N, N', N'-tetra(pyridin-2-yl-methyl)ethylenediamine) disclosed in WO97/48787. 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, 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.

Conventional bleaching systems based on hydrogen peroxide, peroxide compounds and/or peroxyacids with bleach catalysts can provide effective bleaching performance on a variety of stain types on fabrics.

In order to prevent transfer of dyes from one fabric substrate to another fabric substrate during cleaning processes, such as in laundry detergent bleach washes, it is known and often desired to include dye transfer inhibition agents in bleaching compositions. The use of various polymers as dye transfer inhibitors (DTIs) in laundry detergent compositions and rinse conditioners has been described in the prior art. For example WO-A-0005334 discloses laundry detergents providing dye transfer inhibition benefits. Examples of well-known polymers include polyvinyl pyrrolidone (PVP), and copolymers of N-vinylpyrrolidone and N-vinylimidazole (PVPVI).

However, due to the strong catalytic bleaching activity of certain bleach catalysts in the presence of hydrogen peroxide, peroxide compounds and/or peroxyacids in the amounts necessary to ensure effective bleaching of stains, it might be expected that these catalytic bleaching systems would oxidise or otherwise interfere with the action of polymeric dye transfer inhibition agents. At the same time, the presence of dye transfer inhibition agents in these bleach systems might be expected to reduce the catalytic bleaching activity of the bleach catalysts with hydrogen peroxide, peroxide compounds and/or peroxyacids. It was therefore expected that the combination of a bleach catalyst and dye transfer inhibition agent in a peroxygen bleaching composition would result in a reduction in the catalytic activity of the catalyst or in the activity of the dye transfer inhibition agent, or both.

We have now found, surprisingly, that it is possible to provide a bleaching composition and method for stain bleaching of laundry fabrics, which can yield comparable or improved stain bleaching performance as well as comparable or improved dye transfer inhibition on fabrics, relative to conventional bleaching systems. More particularly, we have found that excellent bleaching performance together with good dye transfer inhibition can be provided by peroxygen bleaching compositions and methods, by using a bleach catalyst as defined herein in combination with a dye transfer inhibition agent and hydrogen peroxide or a source of hydrogen peroxide, as specified herein.

Accordingly, in a first aspect, the present invention provides a bleaching composition for laundry fabrics, comprising:

hydrogen peroxide or a source of hydrogen peroxide;

a bleach catalyst comprising a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains in the presence of peroxygen bleach or a peroxy-based or -generating bleach system; and

a dye transfer inhibition agent.

In a second aspect, the present invention provides a method of bleaching stains on laundry fabrics comprising contacting the stained fabric with the above bleaching composition.

We have found that the use of certain bleach catalysts, the most preferred of which is FeMeN4Py, in conjunction with a source of hydrogen peroxide, for example sodium percarbonate or sodium perborate, provides good bleaching performance on fabric stains, despite the presence of the dye transfer inhibition agent. Furthermore, we have found that the presence of the bleach catalysts, in conjuction with hydrogen peroxide or source thereof, does not adversely affect the inhibition of dye transfer between fabrics brought about by the incorporation of a dye transfer inhibition agent in the wash liquor.

Therefore, despite the excellent bleaching activity of these catalytically active systems, there is no negative influence on the dye transfer inhibiting properties afforded by dye transfer inhibition agents in these systems.

The amount of dye transfer inhibition agent in the composition according to the present invention will be from 0.01 to 10 %, preferably from 0.02 to 5 %, more preferably from 0.03 to 2 %, by weight of the composition.

The composition is preferably used in a laundry wash liquor, preferably an aqueous wash liquor. The amount of catalyst in the composition according to the present invention is sufficient to provide a concentration in the wash liquor of generally 0.05 μm to 50 mM, preferably from 0.5 μM to 100 μM, more preferably from 1 μM to 10 μM.

Any suitable dye transfer inhibition agents may be used in accordance with the present invention. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof.

Polyamine N-oxide polymers suitable for use herein contain units having the following structural formula: $R-A_X-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is an aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic group or combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups, or the N-O group can be attached to both units. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The N-O group can be represented by the following general structures: $N(O)(R')_{0-3}$, or $=N(O)(R')_{0-1}$, wherein each R' independently represents an aliphatic, aromatic, heterocyclic or alicylic group or combination thereof; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa<10, preferably pKa<7, more preferably pKa<6.

Any polymer backbone can be used provided the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamides, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferably 1,000 to 500,000; most preferably 5,000 to 100,000. This preferred class of materials is referred to herein as "PVNO". A preferred polyamine N-oxide is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (as a class, referred to as "PVPVI") are also preferred. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000, as determined by light scattering as described in Barth, et al., Chemical Analysis, Vol. 113. "Modern Methods of Polymer Characterization") The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched. Suitable PVPVI polymers include

Sokalan(TM) HP56, available commercially from BASF, Ludwigshafen, Germany.

Also preferred as dye transfer inhibition agents are polyvinylpyrrolidone polymers ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 2000,000, and more preferably from about 5,000 to about 50,000. PVP's are disclosed for example in EP-A-262,897 and EP-A-256,696. Suitable PVP polymers include Sokalan(TM) HP50, available commercially from BASF. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

Also suitable as dye transfer inhibitiong agents are those from the class of modified polyethyleneimine polymers, as disclosed for example in WO-A-0005334. These modified polyethyleneimine polymers are water-soluble or dispersible, modified polyamines. Modified polyamines are further disclosed in US-A-4,548,744; US-A-4,597,898; US-A-4,877,896; US-A- 4,891, 160; US-A- 4,976,879; US-A-5,415,807; GB-A-1,537,288; GB-A-1,498,520; DE-A-28 29022; and JP-A-06313271.

Preferably the bleaching composition according to the present invention comprises a dye transfer inhibition agent selected from polyvinylpyrridine N-oxide (PVNO), polyvinyl pyrrolidone (PVP), polyvinyl imidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (PVPVI), copolymers thereof, and mixtures thereof.

Preferably, the bleaching composition containing the dye transfer inhibition agent is a granular composition, more preferably a particulate bleach detergent composition for laundry cleaning.

Whilst any suitable substance may incorporated in the composition to generate hydroperoxyl radicals, for example hydrogen peroxide, inorganic or organic peroxides, we prefer that the composition comprises an alkali metal percarbonate, preferably sodium percarbonate, as a source of hydrogen peroxide. Preferably, sodium percarbonate is present in an amount of from 1 to 40 % by weight, preferably from 1 to 20 % by weight, more preferably from 1 to 15 % by weight, and most preferably from 1 to 10 % by weight, of the composition.

The bleach catalyst used in the composition comprises a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains in the presence of peroxygen bleach or a peroxy-based or -generating bleach system. Suitable bleach catalysts are described further below. Preferably, the composition comprises an iron complex comprising the ligand N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane (FeMeN4Py), as bleach catalyst.

In a preferred embodiment, the composition comprises sodium percarbonate as a source of hydrogen peroxide, polyvinyl pyrrolidone (PVP) as dye transfer inhibition agent, and the bleach catalyst preferably is FeMeN4Py.

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 ligand forms a complex of the general formula (A1):

$$[M_aL_kX_n]Y_m \qquad (A1)$$

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 selected from Fe(II)-(III)-(IV)-(V);

L represents a ligand as herein defined, 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, preferably selected from O^{2-}, RBO_2^{2-}, $RCOO^-$, $RCONR^-$, OH^-, NO_3^-, NO, S^{2-}, RS^-, PO_4^{3-}, PO_3OR^{3-}, H_2O, CO_3^{2-}, HCO_3^-, ROH, $N(R)_3$, ROO^-, O_2^{2-}, O_2^-, RCN, Cl^-, Br^-, OCN^-, SCN^-, CN^-, N_3^-, F^-, I^-, RO^-, ClO_4^-, and $CF_3SO_3^-$, and more preferably selected from O^{2-}, RBO_2^{2-}, $RCOO^-$, OH^-, NO_3^-, S^{2-}, RS^-, PO_3^{4-}, H_2O, CO_3^{2-}, HCO_3^-, ROH, $N(R)_3$, Cl^- , Br^-, OCN^-, SCN^-, RCN, N_3^-, F^-, I^-, RO^-, ClO_4^-, and $CF_3SO_3^-$;

Y represents any non-coordinated counter ion, preferably selected from ClO_4^-, BR_4^-, $[MX_4]^-$, $[MX_4]^{2-}$, PF_6^-, $RCOO^-$, NO_3^-, RO^-, $N^+(R)_4$, ROO^-, O_2^{2-}, O_2^-, Cl^- , Br^-, F^-, I^-, $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^-, SCN^-, H_2O, RBO_2^{2-}, BF_4^- and BPh_4^-, and more preferably selected from ClO_4^-, BR_4^- , $[FeCl_4]^-$, PF_6^-, $RCOO^-$, NO_3^-, RO^-, $N^+(R)_4$, Cl^- , Br^-, F^-, I^-, $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^-, SCN^-, H_2O and BF_4^-;

a represents an integer from 1 to 10, preferably from 1 to 4;

k represents an integer from 1 to 10;

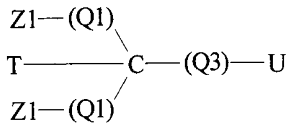
n represents an integer from 1 to 10, preferably from 1 to 4;

m represents zero or an integer from 1 to 20, preferably from 1 to 8; and

each R independently represents a group selected from hydrogen, hydroxyl, -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, wherein E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR′, $-NH_2$, -NHR′, $-N(R')_2$, $-N(R')_3^+$, -C(O)R′, -OC(O)R′, -COOH, $-COO^-$ (Na^+, K^+), -COOR′, $-C(O)NH_2$, -C(O)NHR′, $-C(O)N(R')_2$, heteroaryl, -R′, -SR′, -SH, $-P(R')_2$, $-P(O)(R')_2$, $-P(O)(OH)_2$, $-P(O)(OR')_2$, $-NO_2$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, $-S(O)_2R'$, -NHC(O)R′, and -N(R′)C(O)R′, wherein R′ represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, $-NH_3^+$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, -COOH, $-COO^-(Na^+, K^+)$, $-P(O)(OH)_2$, or $-P(O)(O^-(Na^+, K^+))_2$, and preferably each R independently represents hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C_{1-4}-alkyl.

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 present invention may instead, or additionally, use other ligands and transition metal complexes, provided that the complex formed is capable of catalysing stain bleaching in the presence of peroxygen bleach or a peroxy-based or -generating bleach system. Suitable classes of ligands are described below:

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

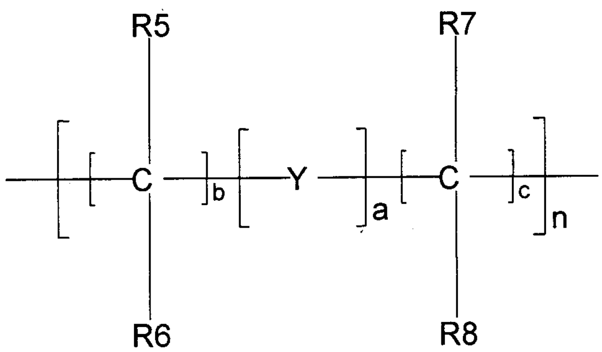


(IA)

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;

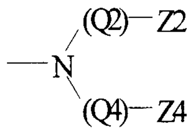
R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

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

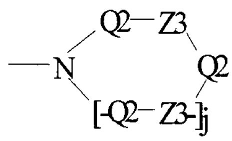
or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C_{1-6}-alkylene optionally substituted by C_{1-4}-alkyl, -F, -Cl, -Br or -I;

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);

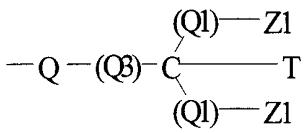
U represents either a non-coordinated group T independently defined as above or a coordinating group of the general formula (IIA), (IIIA) or (IVA):



(IIA)



(IIIA)



(IVA)

wherein

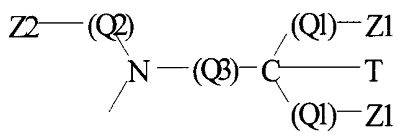
Q2 and Q4 are independently defined as for Q1 and Q3;

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.

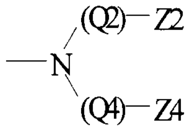
Each Q1 preferably represents a covalent bond or C1-C4-alkylene, more preferably a covalent bond, methylene or ethylene, most preferably a covalent bond.

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.

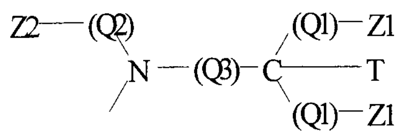
In preferred embodiments of this aspect, the ligand is selected from:

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;

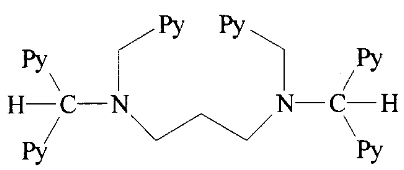
1,1-bis(pyridin-2-yl)-N,N-bis(5-carboxymethyl-pyridin-2-ylmethyl)methylamine;
1,1-bis(pyridin-2-yl)-1-benzyl-N,N-bis(pyridin-2-ylmethyl)methylamine; and
1,1-bis(pyridin-2yl)-N,N-bis(benzimidazol-2-ylmethyl)methylamine.

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



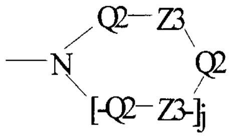
(IIAa)

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):

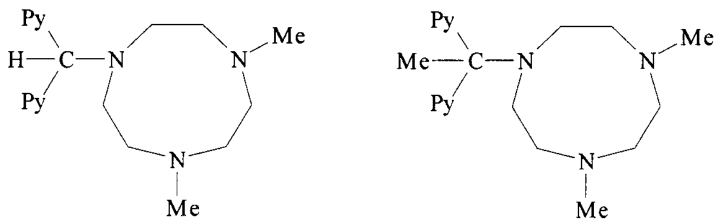


(IIIA)

wherein j is 1 or 2, preferably 1.

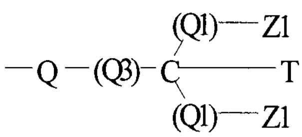
According to this aspect, each Q2 preferably represents -$(CH_2)_n$- (n=2-4), and each Z3 preferably represents -N(R)- wherein R = -H or C_{1-4}-alkyl, preferably methyl.

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



wherein -Py represents pyridin-2-yl.

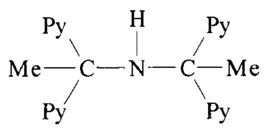
In yet another aspect, the group U in formula (IA) represents a coordinating group of the general formula (IVA):

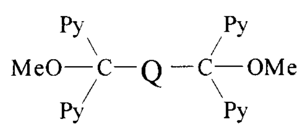


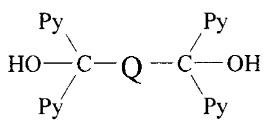
(IVA)

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:

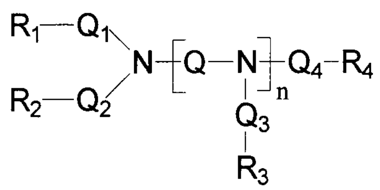






wherein -Py represents pyridin-2-yl, and -Q- represents pyridin-2,6-diyl.

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



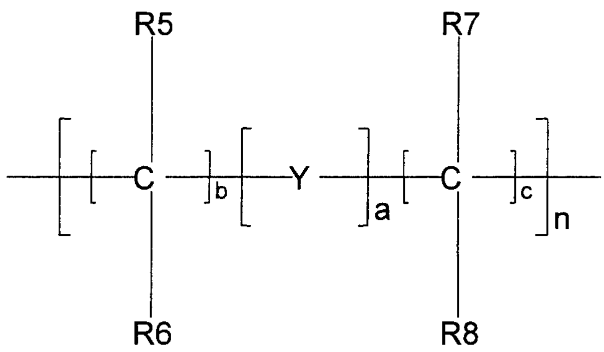
(IB)

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,

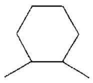
provided that at least two of R_1, R_2, R_3, R_4 comprise coordinating heteroatoms and no more than six heteroatoms are coordinated to the same transition metal atom.

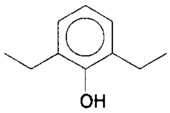
At least two, and preferably at least three, of R_1, R_2, R_3, R_4 independently represent a group selected from carboxylate, amido, $-NH-C(NH)NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine,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

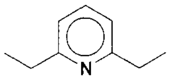
Preferably, substituents for groups R_1, R_2, R_3, R_4, when representing a heterocyclic or heteroaromatic ring, are selected from C_{1-4}-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

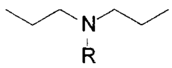
The groups Q_1, Q_2, Q_3, Q_4 preferably independently represent a group selected from $-CH_2-$ and $-CH_2CH_2-$.

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

 optionally substituted by methyl or ethyl,



, 

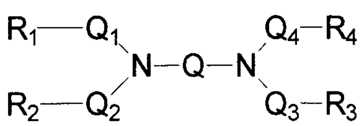
, and 

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;

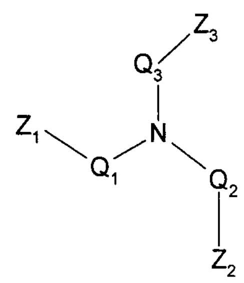
N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylen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

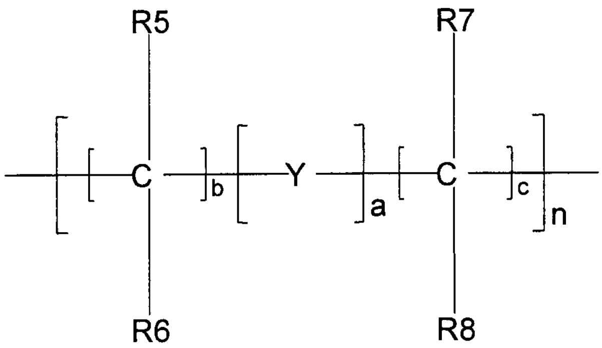


(IC)

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.

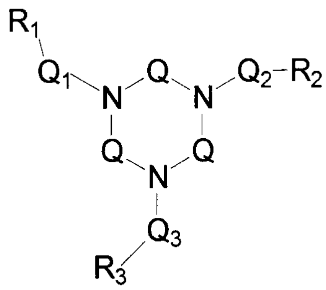
Also preferred is that Q_1, Q_2 and Q_3 are defined such that a=b=0, c=1 or 2, and n=1.

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):



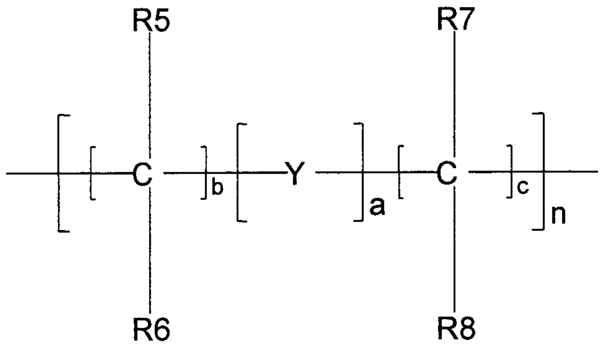
(ID)

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.

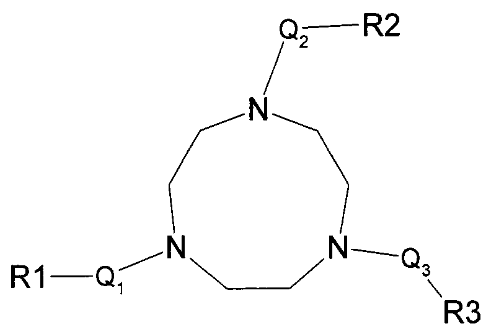
Preferably, substituents for groups R_1, R_2, R_3, when representing a heterocyclic or heteroaromatic ring, are selected from C_{1-4}-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

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

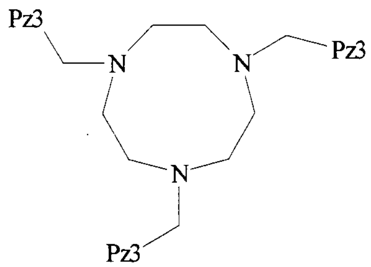
one of R1, R2, R3 represents a group selected from hydrogen, C_{1-20} optionally substituted alkyl, C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein R=C_{1-8}-alkyl).

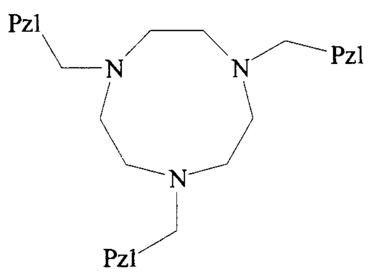
In this class, we prefer that:

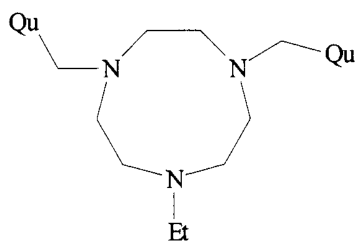
two of R1, R2, R3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

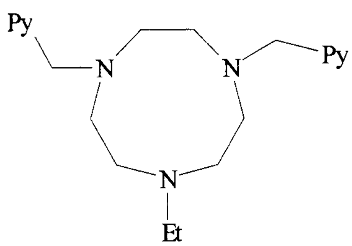
one of R1, R2, R3 represents a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5}-furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted $N^{+}Me_3$.

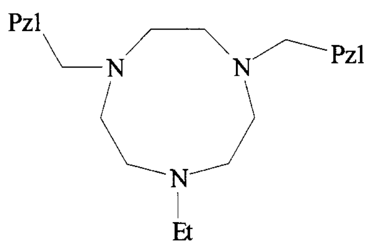
In especially preferred embodiments, the ligand is selected from:











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):

$$T1-[-\underset{R1}{\overset{|}{N}}-(Q1)_r-]_s-\underset{R2}{\overset{|}{N}}-(Q2)_g-T2$$

(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:

$$-[-\underset{R7}{\overset{R6}{C}}-]_d-[-Y1-]_e-[-\underset{R9}{\overset{R8}{C}}-]_f-$$

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

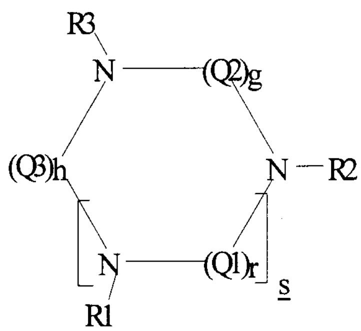
T1 and T2 may together (-T2-T1-) represent a covalent bond linkage when s>1 and g>0;

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.

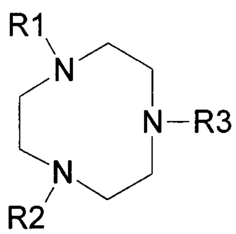
In a first variant according to formula (IE), the groups T1 and T2 together form a single bond linkage and s>1, according to general formula (IIE):

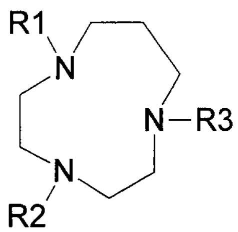


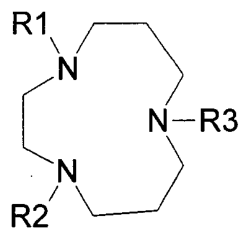
(IIE)

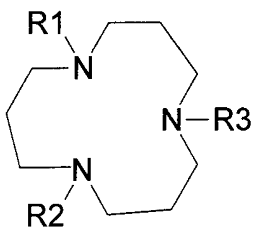
wherein R3 independently represents a group as defined for R1-R9; Q3 independently represents a group as defined for Q1, Q2; h represents zero or an integer from 1 to 6; and $\underline{s}$=s-1.

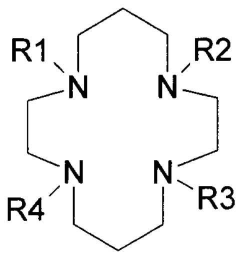
In a first embodiment of the first variant, in general formula (IIE), $\underline{s}$=1, 2 or 3; r=g=h=1; d=2 or 3; e=f=0; R6=R7=H, preferably such that the ligand has a general formula selected from:

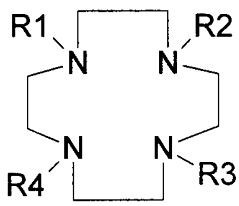


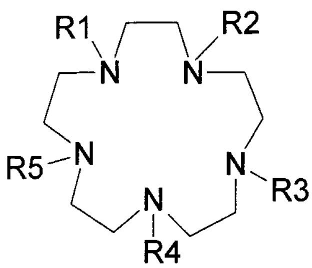






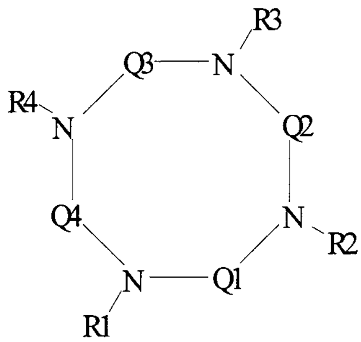






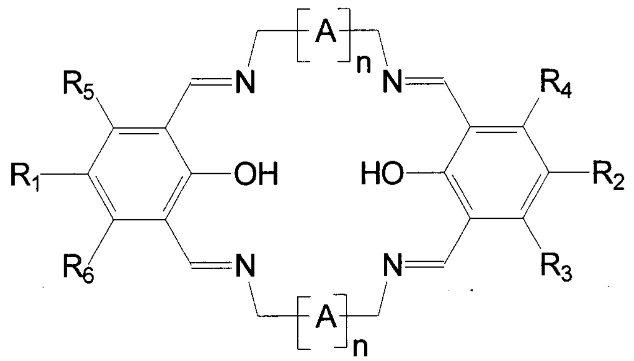
In these preferred examples, R1, R2, R3 and R4 are preferably independently selected from -H, alkyl, aryl, heteroaryl, and/or one of R1-R4 represents a bridging group bound to another moiety of the same general formula and/or two or more of R1-R4 together represent a bridging group linking N atoms in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

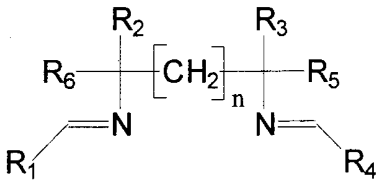
Preferably, R1-R6 represent hydrogen, n=1 and A= $-CH_2-$, $-CHOH-$, $-CH_2N(R)CH_2-$ or $-CH_2CH_2N(R)CH_2CH_2-$ wherein R represents hydrogen or alkyl, more preferably A= $-CH_2-$, $-CHOH-$ or $-CH_2CH_2NHCH_2CH_2-$.

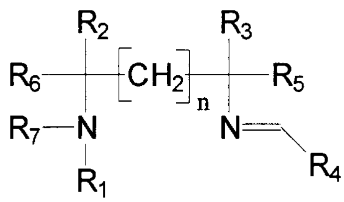
In a second variant according to formula (IE), T1 and T2 independently represent groups R4, R5 as defined for R1-R9, according to the general formula (IIIE):

$$\mathrm{R4}-[-\underset{\mathrm{R1}}{\underset{|}{\mathrm{N}}}-(\mathrm{Q1})_r-]_s-\underset{\mathrm{R2}}{\underset{|}{\mathrm{N}}}-(\mathrm{Q2})_g-\mathrm{R5}$$

(IIIE)

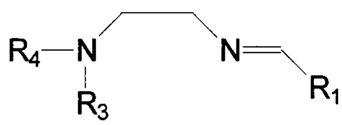
In a first embodiment of the second variant, in general formula (IIIE), s=1; r=1; g=0; d=f=1; e=0-4; Y1= $-CH_2-$; and R1 together with R4, and/or R2 together with R5, independently represent =CH-R10, wherein R10 is as defined for R1-R9. In one example, R2 together with R5 represents =CH-R10, with R1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





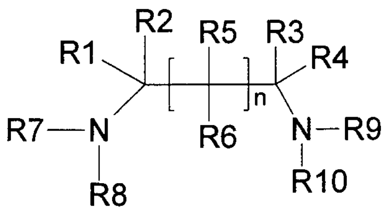
wherein n = 0-4.

Preferably, the ligand is selected from:



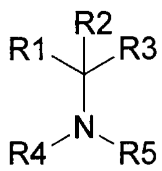
wherein R1and R2 are selected from optionally substituted phenols, heteroaryl-C_0-C_{20}-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, heteroaryl-C_0-C_{20}-alkyls, alkylaryl, aminoalkyl, alkoxy, more preferably R1 and R2 being selected from optionally substituted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



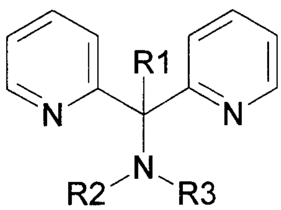
The groups R1, R2, R3, R4, R5 in this formula are preferably -H or C_0-C_{20}-alkyl, n=0 or 1, R6 is -H, alkyl, -OH or -SH, and R7, R8, R9, R10 are preferably each independently selected from -H, C_0-C_{20}-alkyl, heteroaryl-C_0-C_{20}-alkyl, alkoxy-C_0-C_8-alkyl and amino-C_0-C_{20}-alkyl.

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:



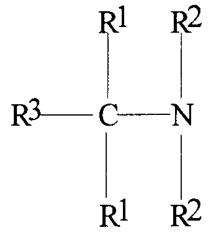
This class of ligand is particularly preferred according to the invention.

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 $-R^3-V$, 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 0.05μM to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 0.5 μM to 100 μM, more preferably from 1 μM to 10 μM.

Preferably, the composition provides 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.

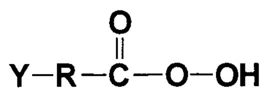
According to the present invention, the composition contains a peroxygen bleach or a peroxy-based or -generating system. The peroxy bleach may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali 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.

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.

Generally, the composition can be suitably formulated to contain from 1 to 40 %, preferably from 1 to 20 %, more preferably from 1 to 15 %, and most preferably from 1 to 10 % by weight of the composition, 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.

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 peracid precursor TAED is particularly preferred.

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

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

The composition 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 composition 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 composition 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 composition 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 composition 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 composition 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.

When using a hydrogen peroxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Of the additives, transition metal sequestrants such as EDTA and the phosphonic acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate)-EDTMP- are of special importance, as not only do they improve the stability of the catalyst/H_2O_2 system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above. Other suitable transition metal sequestrants are known and can be chosen by those skilled in the art, for example aminocarboxylates, aminophosphonates, and polyfunctionally substituted aromatic chelating agents, as disclosed further in WO-A-98/39406. If present, the sequestrants are generally present in amounts of 0.001 to 15%, more preferably 0.01 to 3.0%, by weight of the composition.

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: linear and branched C1-C8-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-propylidene; 1,2-propylene; 1,3-propylene; 2,2-propylidene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,3-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; cyclopentan-1,2-diyl; and cyclopentan-1,3-diyl,

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

arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphtalenylene; 1,3-naphtalenylene; 1,4-naphtalenylene; 2,3-naphtalenylene; 1-hydroxy-2,3-phenylene; 1-hydroxy-2,4-phenylene; 1-hydroxy-2,5-phenylene; and 1-hydroxy-2,6-phenylene,

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, wherein the heteroaryl may be connected to the compound via any atom in the ring of the selected heteroaryl,

heteroarylene: selected from the group consisting of: pyridindiyl; quinolindiyl; pyrazodiyl; pyrazoldiyl; triazolediyl; pyrazindiyl; and imidazolediyl, wherein the heteroarylene acts as a bridge in the compound via any atom in the ring of the selected heteroarylene, more specifically preferred are: 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; 1,4-piperazinyl; tetrahydrothiophenyl; tetrahydrofuranyl; 1,4,7-triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4-diaza-7-thia-cyclononanyl; 1,4-diaza-7-oxa-cyclononanyl; 1,4,7,10-tetraazacyclododecanyl; 1,4-dioxanyl; 1,4,7-trithia-cyclononanyl; tetrahydropyranyl; and oxazolidinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl,

heterocycloalkylene: selected from the group consisting of: piperidin-1,2-ylene; piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,5-ylene; 1,4-piperazin-2,6-ylene; 1,4-piperazin-1,2-ylene; 1,4-piperazin-1,3-ylene; 1,4-piperazin-1,4-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrothiophen-2,3-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; tetrahydrofuran-2,3-ylene; pyrrolidin-2,5-ylene; pyrrolidin-3,4-ylene; pyrrolidin-2,3-ylene; pyrrolidin-1,2-ylene; pyrrolidin-1,3-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,9-ylene; 1,4,7-triazacyclonon-3,8-ylene; 1,4,7-

triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene; 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,5-ylene; 1,4,8,11-tetraazacyclotetradec-1,2-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-1,2-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,3-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,2-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,2-ylidene; 1,4-diaza-7-thia-cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-1,2-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-cyclonon-6,8-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-1,2-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-diaza-7-oxa-cyclonon-6,8-ylene; 1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,3-ylene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,3-ylene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; tetrahydropyran-2,2-ylidene; 1,4,7-trithia-cyclonon-2,3-ylene; 1,4,7-trithia-cyclonon-2,9-ylene; and 1,4,7-trithia-cyclonon-2,2-ylidene,

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,

sulfonate: 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,

sulfate: 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,

sulfone: the group $-S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give sulfonamide) 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: linear and branched C1-C6-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; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; and cyclopentan-1,2-diyl,

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

arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphtalenylene; 1,4-naphtalenylene; 2,3-naphtalenylene and 1-hydroxy-2,6-phenylene,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl, wherein the heteroaryl may be connected to the compound via any atom in the ring of the selected heteroaryl,

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; piperidinyl; 1,4-piperazinyl; tetrahydrofuranyl; 1,4,7-triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4,7,10-tetraazacyclododecanyl; and piperazinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl,

heterocycloalkylene: selected from the group consisting of: piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,6-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; pyrrolidin-2,5-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene; 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4-diaza-7-thia-cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-

thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene;1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; and tetrahydropyran-2,2-ylidene,

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,

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

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

sulfone: 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 present invention will now be further illustrated by the following non-limiting examples:

EXAMPLES

(i) Preparation of MeN4Py ligand

N, N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, MeN4Py, was prepared according to the procedure found in EP 0 909 809 A.

(ii) Synthesis of the complex $FeMeN4PyCl_2$ (complex 1)

MeN4Py ligand (33.7 g; 88.5 mmoles) was dissolved in 500ml dry methanol. Small portions of $FeCl_2.4H_2O$ (0.95 eq; 16.7g;

84.0 mmoles) were added, yielding a clear red solution. After addition, the solution was stirred for 30 minutes at room temperature, after which the methanol was removed. The dry solid was ground and 150 ml of ethylacetate was added and the mixture was stirred until a fine red powder was obtained. This powder was washed twice with ethyl acetate, dried in the air and further dried under vacuum (40 oC). El. Anal. Calc. for [Fe(MeN4py)Cl]Cl.2H_2O: C 53.03; H 5.16; N 12.89; Cl 13.07; Fe 10.01%. Found C 52.29/ 52.03; H 5.05/5.03; N 12.55/12.61; Cl: 12.73/12.69; Fe: 10.06/10.01%.

Complex 2: [(N4Py)FeCl]Cl
Complex 2 was synthesised according to the procedure as described for the analogous MeN4py complex using now N4py (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminomethane) as ligand (see above). The N4py ligand has been prepared as described in WO-A-9534628.

Complex 3 [(N3pyMe)Fe(CH_3CN)$_2$](ClO_4)$_2$
(N3pyMe = 1,1-bis(pyridin-2-yl)-N-methyl-N-(pyridin-2-ylmethyl)methylamine
This compound has been synthesised as described elsewhere (WO0060044).

Complex 4: [Fe(L1)]Cl]PF_6
(L1=N-Methyl-N,N',N'-tris(3-methylpyridin-2ylmethyl)ethylenediamine).This compound has been synthesised as described in WO0027976.

Complex 5: [Fe(N-Methyl-N,N',N'-tris(pyridin-2ylmethyl)ethylenediamine]Cl]PF_6

N-methyl-,N,N'N'-tris(pyridin-2ylmethyl)ethane-diamine (trispicen-NMe). This ligand was prepared according to a modified procedure described by Bernal et al in J. Chem. Soc., Dalton Trans, 22, 3667 (1995).

First N,N'-bis(pyridin-2ylmethyl)-ethanediamine (bispicen) was synthesised by the following procedure. Ethylenediamine (26 ml, 0.38 mol) was dissolved in 200 ml dry methanol. To this mixture 74 ml (0.76 mol) pyridincarboxaldehyde was added. The mixture was refluxed for 2 h, after which the mixture was left to cool to RT and in small portions 40 g of $NaBH_4$ was added. The mixture was subsequently stirred for 16 h at RT. The methanol was evaporated and 500 ml of water was added. The aqueous mixture was extracted in three portions of dichloromethane (100 ml) and the dichloromethane solution was dried over sodium sulfate, filtered off and the solvent was removed. The dark oil containing N, N'-bis(pyridin-2ylmethyl)-ethanediamine (73.7 g; 81%) was analysed by NMR and used without further purification. ^{1}H-nmr ($CDCl_3$): δ 2.20 (br, NH); 2.78 (s, 4H); 3.85 (s, 4H); 7.00-7.40 (m, 4H); 7.58 (m, 2H); 8.45 (m, 2H).

In the second step the aminal of bispicen with 2-pyridincarboxaldehyde was synthesised. 73,7 g of the unpurified bispicen material (see above) was under argon dissolved in 750 ml of dry diethyether (distilled over P_2O_5. To this solution 32.8 of 2-pyridincarboxaldehyde was added, the reaction mixture was stirred and cooled in an ice/water bath. After 20 min a white precipitate was formed that was filtered off (P4-glass filter) and dried with dry ether. The yield was 66.6 g (66%) and was used without further purification. ^{1}H-nmr ($CDCl_3$): δ 2.75 (m, 2H); 3.13 (m, 2H); 3.65 (d, 2H); 4.93 (d, 2H); 4.23 (s, 1H); 7.00-7.90 (m, 9H); 8.43 (m, 3H).

In the third step the desired ligand was obtained (N, N, N'-tris(pyridin-2ylmethyl)ethane-diamine - trispicen-NH). The aminal (45.0 g; 0.135 mol), obtained as described as above, was dissolved in 1.2 l of dry methanol (distilled over Mg), and to this mixture 8.61 g (0.137 mol) of $NaBCNH_3$ was added in small portions. Subsequently 21 ml of trifluoroacetic acid was added dropwise in the solution. The mixture was stirred for 16 h at RT and subsequently 1.05 L of 5N NaOH was added and the mixture was stirred for 6 h. Extraction with dichloromethane yielded after drying, filtration and removal of the solvent a yellow oil as product (42.7 g , 0.128 mol; 95%. ^{1}H-nmr ($CDCl_3$): δ 2.15 (br, NH); 2.75 (s, 4H); 3.80 (s, 4H); 3.82(s, 2H); 7.0-7.8 (m, 3H); 7.45-7.70 (m, 6H); 8.40-8.60 (m, 3H). ^{13}C-nmr ($CDCl_3$): δ 53.9 (t); 54.7 (t); 60.4 (t); 121.7 (d); 121.9 (d); 122.1 (d); 123.0 (d); 136.3 (d); 136.4 (d); 148.9 (d); 149.1 (d); 159.3 (s); 159.6 (s).

The desired ligand was obtained by the following procedure: trispicen-NH (10g, 30 mmol) was dissolved in 25 ml formic acid and 10 ml water. To this mixture 36 % formaldehyde solution was added (16 ml, 90 mmol) and the mixture was warmed up till 90 °C for 3 h. Formic acid was evaporated and the 2.5 N NaOH solution was added until the pH was higher than 9. Extraction by dichloromethane and drying over sodium sulfate, filtration of the solution and subsequently drying yielded a dark-coloured oil (8.85g). The oil was purified over a alumina column (elutant: ethyl acetate/ hexane/ triethylamine 9:10:1). Yield 7,05g pale yellow oil (20,3mmoles; 68%). ^{1}H-nmr ($CDCl_3$): δ 2.18 (s, 3H); 2.65 (m, 2H); 2.75 (m, 2H); 3.60 (s; 2H); 3.83 (s; 4H); 7.10 (m, 3H); 7.3-7.6 (m, 6H); 8.5 (d, 3H).

The iron complex 5 has been synthesised as follows: TrispicenNMe (6.0 g; 17.3 mmoles) was dissolved in 15 ml methanol/water 1/1 v/v) and was heated till 50 °C. $FeCl_2.4H_2O$ 3,43g; 17.0 mmoles), dissolved in 20 ml water/methanol 1/1), was added. The dark solution was stirred for 20 min at 50 °C. Subsequently 3.17 g (17 mmol) of KPF_6 dissolved in 10 ml water, was added and the solution was stirred for 15 h to yield a yellow precipitation. The solid was filtered off, wasged with methanol/water 1/1, v/v) and ethyl acetate. Drying yielded 8.25 g of a pale-yellow powder.

Complex 6: [(tpen)Fe]$(ClO_4)_2$
(tpen=tetrakis(pyridin-2-ylmethyl)ethylenediamine)
This compound was prepared according to the procedure found in H. Toftlund et al., J. Am. Chem. Soc., 112, 6814 (1990).

Complex 7: [Fe(1-[di(2-pyridinyl)methyl]-4,7-dimethyl-1,4,7-triazacyclonane)(CH_3CN)](ClO_4)$_2$
This compound was made as described in WO006004.

Experiments were conducted to investigate bleaching performance of the bleach catalysts and one free ligand in a formulation containing dye transfer inhibition agent (0.6%

PVP) on tomato stain, and dye transfer inhibition by PVP in the presence of the bleach catalysts or ligand.

Formulation A:

Na-LAS:	8.7%
Nonionic 7EO, branched:	4.6 %
Nonionic 3EO, branched:	2.4 %
Soap:	1.1 %
Zeolite A24 (anhydrous)	29.6 %
Na-citrate 2 aq:	3.5 %
SCMC - sodium carboxymethylcellulose(68%)	0.5 %
Moistures, salts, NDOM	4.8 %
PVP: K-15 solution, ISP technologies, Inc .	0.6 %

Stain: tomato-soya sauce oil stain

Dyes:

1. CDB-RF (Direct Blue monitor): 1% Solophenyl Blue GL (ex CIBA) on cotton; resin and cationic finish.
2. CDG-RF (Direct Green monitor)-: 1.5 % Solophenyl Green GL = Direct Green 26 (ex CIBA) on cotton; resin finish.
3. 0.01CD, 1% Solophenyl Red 3BL, Direct Red 80 on woven cotton.

5 g/l of formulation A was added to 1 litre water (16 ^{0}FH) containing (stock solution), with optionally 0.6 % of PVP solution. To each solution (25 mL) optionally 10 µM of FeMeN4Py.Cl2 was added, and/or 5 mM of hydrogen peroxide, according to the set-up shown in Table 1 below (using CFG-RF and CDB-RF monitors).

In the second series of experiments, 0.01CD monitor was used to assess the dye transfer inhibition effects with various compounds in the presence of hydrogen peroxide (10mM). For this series of experiments 3 g/l of formulation A was used. The set-up and results are shown in Table 2.

Bottles tests were done (25 mL solution), each bottle containing one piece of white cotton (4 x 4 cm; redeposition cloth) and two pieces of the coloured cloth (4x4 cm; CDG-RF and CDB-RG, respectively). In a separate series of tests, tomato stained cloth (1 cloth of 4 x 4 cm) was added in the bottle, with no dyed cloths present.

The cloths were washed for 30 min at 40 °C. After the wash, the cloths were rinsed with water and subsequently dried, and the change in reflectance at 460 nm was measured immediately after drying on a Minolta CM-3700d spectrophotometer including a UV-Vis filter before and after treatment.

The difference in ΔR between both reflectance values gives a measure of the bleaching performance of the system on the stain, i.e. a higher ΔR value corresponds to an improved bleaching performance. On the other hand, a higher ΔR value for the redeposition cloths indicates more dye transfer (for CDB-RF, CDG-RF and 0.01CD).

The results for bleaching performance and dye transfer inhibition are shown in Table1 and table 2 below:

Table 1

Experiment	0.6 % PVP	5 mM H2O2	10 μM $FeMeN4PyCl_2$	ΔR (Tomato stain)	ΔR redep CDB-RF	ΔR redep CDG-RF
1	-	-	-	12	7	31
2	+	-	-	11	0.5	8
3	-	+	-	10	7	31
4	+	+	-	10	0.5	7
5	-	+	+	41	7	27
6	+	+	+	40	0.7	7

Table 2

Experiment	0.6 % PVP	10 mM H2O2	Compound	ΔR (Tomato stain)	ΔR redep 0.01CD
1	-	-	-	15/18	28
2	+	-	-	14/16	18
1	-	+	-	14/15	29
2	+	+	-	14/14	20
3	-	+	10 μM **2**	19/21	28
4	+	+	10 μM **2**	21/25	20
5	-	+	10 μM **3**	17/18	29
6	+	+	10 μM **3**	17/18	22
9	-	+	10 μM **4**	36/42	31
10	+	+	10 μM **4**	37/42	18
11	-	+	10 μM **5**	16/19	28

12	+	+	10 μM **5**	15/17	18
13	−	+	10 μM **6**	15/17	31
14	+	+	10 μM **6**	14/16	22
15	−	+	10 μM **7**	27/35	28
16	+	+	10 μM **7**	28/35	18
17	−	+	20 μM **L1**	19/22	29
18	+	+	20 μM **L1**	22/24	20

From the results in Table 1 and 2, it may be seen that:

- The compounds give significant bleaching of tomato stain in the presence of hydrogen peroxide, in the absence and presence of PVP. Thus the catalytic activity is fully retained even in the presence of a dye transfer inhibition agent.
- PVP shows dye transfer inhibition without and with the compounds. Thus the effectiveness of the dye transfer inhibition agent is fully retained even in the presence of the iron bleaching catalysts or free ligand.

CLAIMS:

1. A bleaching composition for laundry fabrics, comprising:

hydrogen peroxide or a source of hydrogen peroxide;

a bleach catalyst comprising a ligand which forms a complex with a transition metal, the complex catalysing bleaching of stains in the presence of peroxygen bleach or a peroxy-based or -generating bleach system; and

a dye transfer inhibiting agent.

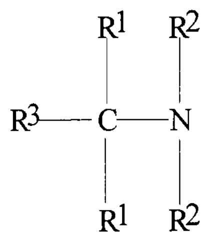
2. A bleaching composition according to claim 1, wherein the amount of dye transfer inhibiting agent is from 0.02 to 5 %, preferably from 0.03 to 3 %, by weight of the composition.

3. A bleaching composition according to claim 1, wherein the dye transfer inhibiting agent is selected from polyvinylpyrridine N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (PVPVI), modified polyethyleneimine polymer and copolymers thereof, and mixtures thereof.

4. A bleaching composition according to any preceding claim, wherein the source of hydrogen peroxide comprises sodium percarbonate or sodium perborate, preferably sodium percarbonate.

5. A bleaching composition according to any preceding claim in a wash liquor, wherein the amount of catalyst is from 0.05 μM to 50 mM, preferably from 1 μM to 100 μM.

6. A bleaching composition according to any preceding claim, wherein the catalyst comprises 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.

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

8. A bleaching composition 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.

9. A bleaching composition according to any preceding claim, wherein the composition provides a pH value in the

range from pH 6 to 11, preferably in the range from pH 8 to 10, in aqueous medium.

10. A bleaching composition according to any preceding claim, wherein the composition further comprises a surfactant.

11. A bleaching composition according to claim 10, wherein the composition further comprises a builder.

12. A bleaching composition according to any of claims 1 to 11, wherein the catalyst comprises a preformed complex of the ligand and a transition metal.

13. A bleaching composition according to any of claims 1 to 11, wherein the composition comprises free ligand that complexes with a transition metal present in the water.

14. A bleaching composition according to any of claims 1 to 11, wherein the composition comprises a free ligand that complexes with a transition metal present in the substrate.

15. A bleaching composition according to any of claims 1 to 11, wherein the composition comprises free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

16. A method of bleaching stains on laundry fabrics comprising contacting the stained fabric, in a wash liquor, with a bleaching composition as defined in any of claims 1 to 15.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/00408

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39 C11D3/37

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 478 489 A (FREDJ ABDENNACEUR ET AL) 26 December 1995 (1995-12-26) claims 1-4,6,8-15 ---	1-3, 9-12,16 4
X A	EP 0 902 083 A (CIBA GEIGY AG) 17 March 1999 (1999-03-17) paragraphs '0015!-'0034! claims 1,15-21 ---	1-3,5,8, 10-12,16 4
X	EP 0 688 859 A (PROCTER & GAMBLE) 27 December 1995 (1995-12-27) claims 1,2,10-12; examples I,IV ---	1-5, 8-12,16
A	WO 95 34628 A (UNILEVER) 21 December 1995 (1995-12-21) cited in the application the whole document --- -/--	1,4-12, 16

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 July 2001	16/07/2001

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/00408

C.(Continuation) 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) 21 April 1999 (1999-04-21) cited in the application the whole document	1,4-12, 16

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

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International Application No
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