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A monometallic and kinetically inert complex of a ditopic open ligand as a tight polyaza cage

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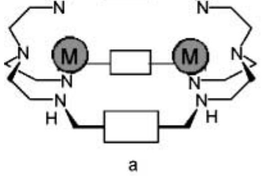
The new ligand L has been prepared by appending three 2,2′-bipyridine molecules to a tren (tris(2-aminoethyl)amine) unit. It binds a Fe^{2+} cation with its three bipyridines, imparting to it an octahedral co-ordination. The obtained $[FeL]^{2+}$ molecular cation has a closed shape, whose nature has been ascertained by X-ray diffraction studies on the complex $[Fe(HL)][PF_6]_3$. The tren unit can thus be described as one half of a bis-tren cage. The kinetic inertness of the complex between Fe^{2+} and the three bipyridines has been verified: in the pH 2–12 range the $[Fe^{II}(bipyR)_3]$ unit is stable and plays only an architectural role. According to this it has been possible to determine the protonation and complexation constants (in the presence of 1 equivalent of Cu^{2+}) of the tren fragment, which is in fact able to interact with protons and metal cations, behaving as a tight and rigid half of a bis-tren ligand. High percentages (70–100%) of the $[FeLH_n]^{(n+2)+}$ species can be found in sharp pH ranges, while, in the presence of 1 equivalent of Cu^{2+}, the metal-containing species $[FeCu(HL)]^{5+}$, $[FeCuL]^{4+}$, $[FeCuL(OH)]^{3+}$ and $[FeCuL(OH)_2]^{2+}$ exist in the pH 2–12 range, each one prevailing in distinct pH intervals, reaching high percentages (70–100%). The variation of the spectral and electrochemical properties of the $[Fe(bipyR)_3]$ fragment have been studied as a function of pH, and related with the protonation degree or complexation of the tren unit.

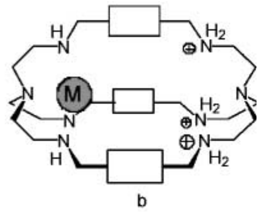
Introduction

Ditopic polyamino cages, and in particular bis-tren ligands (tren = tris(2-aminoethyl)amine) are capable of including two identical, dipositive, first-row transition metal cations (*e.g.* Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+})[1] to give $[M_2L]^{4+}$ complexes (**a**). Moreover, cascade-type complexes may eventually be formed by co-ordination of small bidentate anionic species between the two metal centres.[2] Beside, bis-tren ligands are also able to bind only one metal cation in one of their tren sites, when a 1 : 1 stoichiometry is taken into consideration. This leaves the other tren unit free to interact with different chemical species (in particular protons, to give $[MLH_n]^{(2+n)+}$ species,[1,3] see **b**, in the case of $n = 3$), sometimes imparting to it new and interesting properties.[4] However, the existence of these species is limited to a narrow pH range and they are able to reach only a low value in the % of species *vs.* pH distribution, due to the coexistence of the free metal cation, of metal-free protonated ligand and of self-assembled dimetallic species. Moreover, the possibility of having a second, different metal centre (*e.g.* M'^{2+}) co-ordinated in the available tren site is not straightforward:[5] as far as kinetically labile complexes are taken into consideration, redistribution of L between the metal centres is to be expected, and mixtures will form, which can include species like $[MLH_n]^{(2+n)+}$, $[M'LH_n]^{(2+n)+}$, $[MM'L]^{4+}$, $[M_2L]^{4+}$, $[M'_2L]^{4+}$ (and, at a higher pH value, the pertinent OH^- bridged dimetallic species), coexisting in different percentages, depending on the pH and on their formation constants.

However, the goal of obtaining, in aqueous solution, high percentages of metal/proton species and of dimetallic species containing two different metal centres can be reached through a different strategy: open, ditopic ligands can be prepared, containing a tren unit functionalized with binding fragments capable of forming kinetically inert complexes with at least one metal centre (**c**). When this monometallic complex is formed (**d**) a permanent closed shape is imparted to the tren unit, which can thus be considered as a tight cage, capable of further interactions with protons and metal cations.



a



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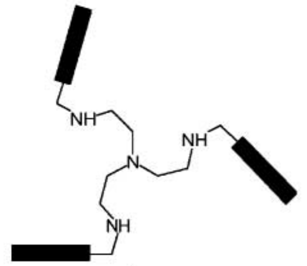
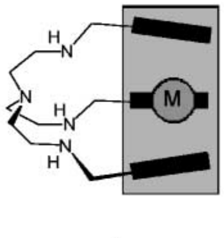


c



d

In particular, in this work three 2,2′-bipyridine (bipy) ligands have been appended to a tren molecule, giving ligand L. The bipy units have been found to bind selectively one Fe^{2+} cation, leaving a free, closed-shape tren fragment by forming the highly stable, kinetically inert octahedral complex $[FeL]^{2+}$. Potentiometric titrations in aqueous solutions demonstrated that this "iron-glued" tren cage is capable of further interactions with either protons or metal cations (Cu^{2+}), allowing us to calculate the formation constants of the pertinent species. Interestingly, on the basis of the obtained % of species *vs.* pH distribution

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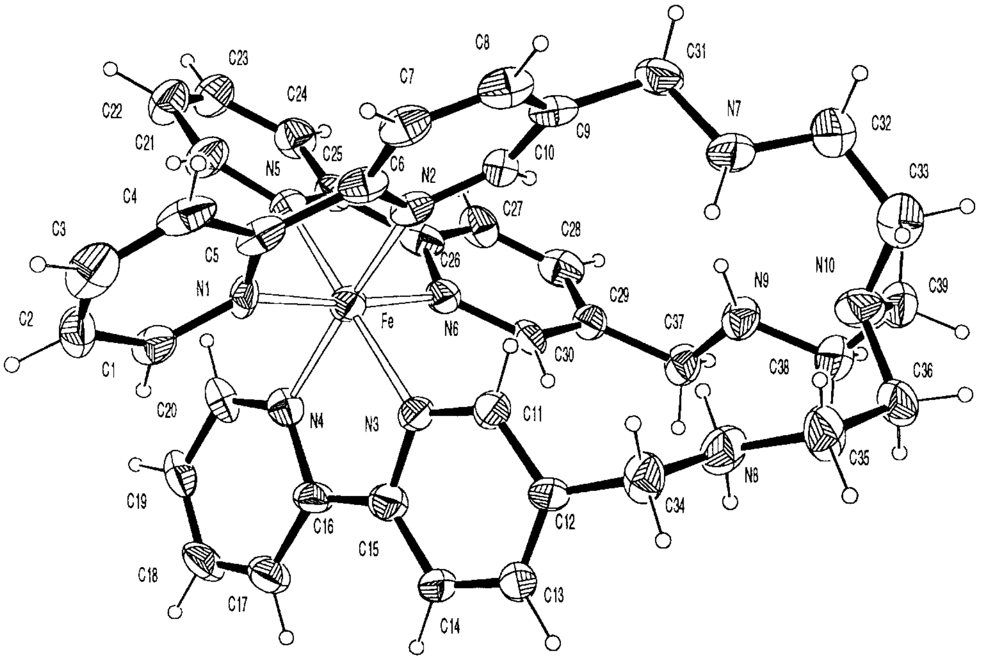
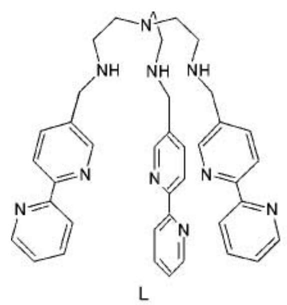


Fig. 1 An ORTEP[8] view of the molecular structure of the [Fe(HL)]$^{3+}$ complex. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses: Fe–N1 1.950(9), Fe–N2 1.944(8), Fe–N3 1.980(7), Fe–N4 1.964(7), Fe–N5 1.961(7) and Fe–N6 1.933(8); N1–Fe–N2 82.0(3), N1–Fe–N3 92.8(3), N1–Fe–N4 93.2(3), N1–Fe–N5 93.3(3), N1–Fe–N6 173.7(3), N2–Fe–N3 91.7(3), N2–Fe–N4 171.4(3), N2–Fe–N5 93.2(3), N2–Fe–N6 94.2(3), N3–Fe–N4 81.3(3), N3–Fe–N5 172.7(3), N3–Fe–N6 92.3(3), N4–Fe–N5 94.3(3), N4–Fe–N6 91.2(3), N5–Fe–N6 81.9(3) and Fe–N1–C1 127.6(7).

diagrams it is possible to select pH ranges in which each of the competing monometal–multiproton or dimetallic species is the only one existing (or by far prevailing) in solution. According to this, fixing the pH at suitable values allowed us also to evaluate the properties (*e.g.* electrochemical and spectrophotometric) of the desired species. Finally, the crystal and molecular structure of the monoprotonated closed [Fe(HL)]$^{3+}$ species has been determined and is described here.



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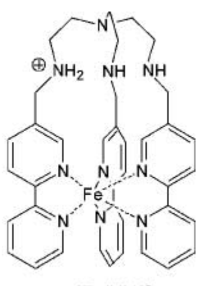

[Fe(HL)]$^{3+}$

Results and discussion

1. Synthesis and kinetic inertness of the “iron-glued” cage

Ligand L can easily be prepared from commercially available tris(2-aminoethyl)amine (tren) by NaBH$_4$ reduction of the Schiff condensation product with 5-(2,2′-bipyridine)carbaldehyde. Once available as a free base, ligand L can be made to react with Fe^{2+} by simply mixing it with the stoichiometric quantity of FeSO$_4$ in aqueous solution, obtaining the purple complex [FeL]$^{2+}$, which displays an UV-Vis band centred at 525 nm ($\varepsilon = 6800$ dm^3 mol^{-1} cm^{-1}) plus a shoulder at 490 nm ($\varepsilon = 6100$ dm^3 mol^{-1} cm^{-1}). The position of this band and its molar absorption coefficient are typical of the characteristic CT band for octahedral iron(II) complexes of the [Fe(bipy)$_3$]$^{2+}$ type.[6] Moreover, spectrophotometric titrations have been carried out on aqueous solutions of L buffered at pH 6.5 (0.1 M 2,6-dimethylpyridine–HClO$_4$ buffer), to which substoichiometric quantities of a solution of FeSO$_4$ were added: the CT band increased in intensity up to 1 equivalent of added Fe^{2+}, while only minor changes were observed on addition of a second equivalent of Fe^{2+}. A plot of A_{525} *vs.* equivalents of added Fe^{2+} was thus an ascending line, sharply changing into a plateau at 1.0 equivalent, this indicating that Fe^{2+} binds selectively to the bipy part of the ligand, forming an octahedral tris-bipy complex (the minor changes observed in the CT band on addition of the second equivalent of Fe^{2+} suggest that the excess of cation further interacts with the free tren part of the complex, perhaps causing a structural rearrangement also in the already complexed part).

The kinetic inertness of the low-spin, d^6 Fe^{2+} cation when co-ordinated to three bipy (or phenanthroline) ligands is well documented,[7] and in this case it has been checked by monitoring the UV-Vis spectrum of the “iron-glued” [FeL]$^{2+}$ cage both in 0.1 M HClO$_4$ and in 0.1 M NaOH. With respect to neutral solution only minor changes in the characteristic CT band were observed, which can be ascribed to the structural/electronic rearrangements due to the various degrees of protonation of the tren nitrogen atoms, as discussed in the following sections. However, significantly, the measured spectra persisted unchanged for 48 hours both in 0.1 M HClO$_4$ and in 0.1 M NaOH. Finally, solid samples of monoprotonated [Fe(HL)][PF$_6$]$_3$ can be obtained easily, in gram quantities, by treatment with an excess of NH$_4$PF$_6$, and used for further complexation, protonation or characterization of the system. Dissolution of the solid product in acetonitrile and slow diffusion of (C$_2$H$_5$)$_2$O into the solution gave crystals suitable for X-ray diffraction experiments.

2. Crystal and molecular structure of [Fe(HL)][PF$_6$]$_3$·2CH$_3$CN

The structure consists of discrete [Fe(HL)]$^{3+}$ cations, PF$_6^-$ counter ions and acetonitrile molecules of crystallization (two CH$_3$CN molecules for each [Fe(HL)][PF$_6$]$_3$ formula unit). The structure of the complex cation is illustrated in Fig. 1 together with the atomic numbering scheme.

The iron(II) ion is bound to six nitrogen atoms from three 2,2′-bipyridine ligands appended to a tren fragment which contains a proton located at the N(8) secondary nitrogen atom.

The co-ordination polyhedron of the iron atom is a slightly distorted octahedron with Fe–N distances and N–Fe–N bond angles comparable with those found in other similar octahedral iron(II) complexes reported so far.[9] The H(8a) proton located at the NH_2^+ group points toward the inside of the tren cavity at 2.46(1) Å from the bridgehead N(10) atom suggesting an intramolecular hydrogen bond with the tertiary nitrogen atom [N(8)···N(10) 2.86(1) Å and N(8)–H(8a)–N(10) 105(1)°]. Longer separations are observed between the H(8a) proton and the cage tren free NH groups N(9) [3.22(1) Å] and N(7) [3.23(1) Å].

The closed-shaped tren moiety shows a pseudo threefold symmetry axis passing through the N(10) bridgehead nitrogen. The N···N distances separating the tertiary nitrogen from the protonated and unprotonated secondary nitrogen atoms are very similar to each other [2.86(1) and 2.89(1) Å for N(7), N(8) and N(9)]. On the contrary, significant differences are observed in the distances between the NH_2^+ group and the two free NH groups [3.94(1) and 3.97(1) Å for N(9) and N(7) respectively] shorter by 0.08–0.11 Å than the separation N(7)···N(9) [4.05(1) Å] found for the two unprotonated nitrogens. This could be attributed to the proton at N(8) oriented toward the inside of the cage tren cavity, which is almost aligned with the lone pair direction of the bridgehead N(10) nitrogen, thus playing a double role: an intramolecular hydrogen bond [N(8)–H(8a)···N(10)] and simultaneously two weaker long-range attractive interactions with N(7) and N(9).

Hydrogen bonds involving the H(8b) hydrogen from the NH_2^+ group of the cationic complexes and the F(33) atom from hexafluorophosphate anions [N(8)···F(33) 2.98(1), H(8b)···F(33) 2.25(1) Å and N(8)–H(8b)–F(33) 132(1)°] determine the crystal packing. The space inside the intramolecular cavity of the tren fragment can also accommodate a Cu^{2+} metal ion. This is supported by the N(bridgehead nitrogen)···N(secondary amino group) and N(secondary nitrogen)···N(secondary nitrogen) distances found in the literature for bis-tren dimetallic cryptates. The reported distances are respectively 2.81–2.87 and 3.47–3.85 Å in a μ-carbonato-dicopper(II) cryptate in which the two tren fragments are joined by *m*-xylyl spacers,[3b] 2.76–2.86 and 3.40–3.90 Å in a μ-OH dicopper(II) macrobicyclic complex in which diethylene ether groups join the two tren moieties,[10] 2.81–2.88 and 3.64–3.79 Å in a μ-OH dicopper cryptate containing 2,5-furan dimethyl spacers which join the two tren moieties,[1f] 2.76–2.83 and 3.45–3.93 Å in a μ-cyanato- and 2.70–2.76 and 3.33–3.87 Å in a μ-azido dicopper(II) cryptate in which the two tren fragments are joined by *p*-xylyl spacers[2e] and 2.81–2.92 and 3.46–4.08 Å in a μ-imidazolato copper–zinc crypate in which the *p*-xylyl spacers join the two tren units.[5] On the other hand, the distances N(bridgehead nitrogen)···N(secondary amino group) [3.75–3.80 Å] and N(secondary nitrogen)···N(secondary nitrogen) [5.91–6.85 Å] found in an empty, fully protonated bis-tren cryptand[3b] with *m*-xylyl spacers are significantly longer than the corresponding values observed in our complex. However, these relevant differences could be due both to the conformational rearrangement of the macrocyclic ligand when co-ordinating to the metal ions and to the octaprotonation of the ligand, whose protons all point toward the outside of the spherical internal cavity to form hydrogen bonds with the counter anions.

3. Protonation processes in $[FeL]^{2+}$

As already pointed out, the presence of the inert iron(II) cation in the bipy part of ligand L closes it, imparting to the tren unit the conformation of a tight cage. The binding tendencies of this particular kind of cage can be studied with conventional methods, considering the $Fe(bipyR)_3$ unit as a fixed fragment, playing only an architectural role. In particular, potentiometric titration experiments with standard base have been carried out on solutions containing $[Fe(HL)][PF_6]_3$ plus an excess of perchloric acid, which allowed us to determine the presence of three proton-containing species ($[Fe(HL)]^{3+}$, $[Fe(H_2L)]^{4+}$, $[Fe(H_3L)]^{5+}$) beside the non-protonated $[FeL]^{2+}$ species. The relative protonation constants were calculated and the % of species *vs.* pH distribution diagram drawn (Fig. 2).

Table 1 Stepwise protonation constants (logarithmic values) of $[FeL]^{2+}$, tren and *m*-xylyl bis-tren. In the case of $[FeL]^{2+}$ the reported values bear a ±0.01 uncertainty

Protonation step	$[FeL]^{2+}$	tren[a]	*m*-xylyl bis-tren[b]
1	8.90	10.15	9.92
2	7.48	9.45	9.26
3	5.69	8.43	8.75
4			7.67
5			7.16
6			6.59

[a] Values taken from reference 11, 0.1 mol dm^{-3} KCl as medium. [b] Values taken from reference 3(*b*), 0.1 mol dm^{-3} KNO_3 as medium.

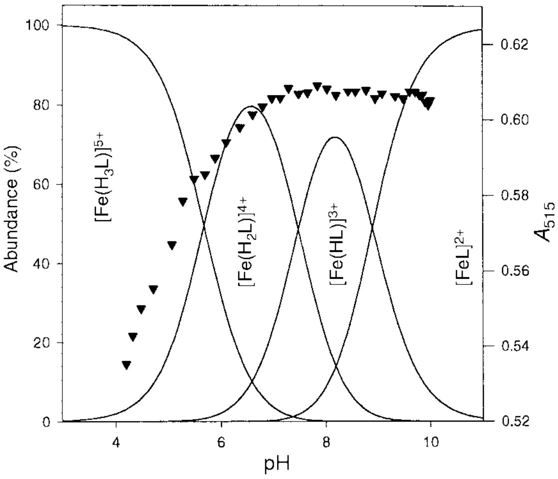

Fig. 2 Distribution diagram (% of species *vs.* pH) for the species $[FeLH_n]^{(2+n)+}$. Black triangles describe the profile of the absorbance of the $Fe^{II}(bipyR)_3$ chromophore (at 515 nm) *vs.* pH.

For comparison the calculated stepwise protonation constants are listed in Table 1 together with the three stepwise protonation constants for tren[11] and the six stepwise protonation constants for a bis-tren ligand[3b] in which the two tren fragments are linked by 1,3-xylyl spacers.† The first protonation constant for $[FeL]^{2+}$ is significantly lower than for both plain and bis-tren (1.25 and 1.02 log units, respectively). This may reflect the unfavourable electrostatic effect on the protonation process exerted by the proximate Fe^{2+} cation. However, electrochemical studies (see below) suggest that repulsive electrostatic interactions between the $Fe^{II}(bipy)_3$ moiety and the protonated tren unit are only weak. The hypothesis that the non-bonding nitrogen electron pairs are particularly hindered can then be put forward, supported by the observation that, in the molecular structure of $[Fe(HL)]^{3+}$, the remaining free electron pairs are all *endo* with respect to the tren cavity and the same can reasonably be imagined, before protonation, for the electron pair of the NH_2^+ group. As regards the second protonation constant for $[FeL]^{2+}$, the difference is even more remarkable with respect to tren (1.97 log units lower), this reflecting either the closed nature of the iron-containing cage (which is not able to unfold and arrange the two positive charges at such a distance as can be expected in plain tren) or the interactions between the first proton and the N lone pairs inside the cage (as the molecular

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† Although protonation data are available for other bis-tren cages,[1a,3b] the considered molecule has been chosen due to the "benzyl-like" nature of the substituent on the secondary amino groups of tren in our compound.

structure has indicated). Comparison with the chosen bis-tren ligand should be made not with its second protonation constant (as the second proton goes in the second, neutral tren compartment), but with its third protonation constant, which corresponds to a N atom belonging to a tren fragment already bearing a NH_2^+ group. In this case, a 1.27 log units difference is observed which, again, reflects the more unfavourable energetics found when adding a proton to the closed-shaped, three-plus charged $[Fe(HL)]^{3+}$ instead of the two-plus bis-tren cage, which keeps a higher degree of elasticity (see also discussion in section 2 about the octaprotonated bis-tren cage[3b]). Finally, the third protonation constant for the iron cage ($H^+ + [Fe(H_2L)]^{4+} \rightleftharpoons [Fe(H_3L)]^{5+}$) is 2.74 log units lower than for tren and 1.47 log units lower than the fifth protonation constant for the bis-tren cage (this latter case corresponding to the addition of a proton on a doubly protonated tren unit, belonging to a molecule bearing an overall charge of plus four). Again, these huge differences point towards a particular rigidity and tightness of the "iron-glued" cage, even with respect to the bis-tren cage system which, in the comparable protonation step, interestingly bears the same overall charge as $[Fe(H_2L)]^{4+}$.‡ From the distribution diagram (% of species *vs.* pH, Fig. 2) it can be seen that, in selected pH ranges, only one of the possible species prevails in solution. In particular, $[Fe(H_3L)]^{5+}$ reaches over 95% under pH 4.4, $[Fe(H_2L)]^{4+}$ is more than 75% in the $6.3 < pH < 6.9$ range (reaching 80% at pH 6.75), $[Fe(HL)]^{3+}$ is more than 70% in the $8.0 < pH < 8.35$ range (reaching 73% at pH 8.2). On the other hand, when pH is higher than 10, $[FeL]^{2+}$ becomes the only species existing in solution (*i.e.* > 95%). Literature reports for bis-tren ligands (in the presence of 1 equivalent of metal cations) give a maximum of ≈48, ≈30 and ≈18% for $[Cu(H_3L)]^{5+}$, $[Cu(H_2L)]^{3+}$ and $[Cu(HL)]^{3+}$, respectively, in the case of a $(CH_2)_2O(CH_2)_2$ connected bis-tren ligand[12] and of ≈70, ≈45 and ≈30%, respectively, in the case of a $(CH_2)_5$ connected bis-tren ligand.[12] It is of interest that, with $[FeL]^{2+}$, monometal–multiproton cage species exist in high percentages over significant pH ranges, as this allows one to isolate the single species and, in principle, to study with a reasonable approximation their properties (*i.e.* not those of a mixture of species). According to this, the $Fe(bipyR)_3$ fragment has been used as a "spectator" on varying the degree of protonation of the tren unit. Coupled potentiometric/spectrophotometric titrations showed a variation in the $Fe(bipyR)_3$ CT band as a function of pH: on going from acidic to basic solutions it increases in intensity, shifting to shorter wavelengths (λ_{max} goes from 525 to 515 nm). When compared to the % of species *vs.* pH curves, the A_{525} *vs.* pH profile (full triangles in Fig. 2) shows that the spectral change is due only to the transformation of $[Fe(H_3L)]^{5+}$ into $[Fe(H_2L)]^{4+}$, as it superimposes on the ascending part of the curve pertinent to the formation of $[Fe(H_2L)]^{4+}$. This could be due to a structural rearrangement in the $Fe(bipyR)_3$ fragment caused by the release of a proton from the tren nitrogens, indicating that the repulsion between the three charged nitrogens in the tight tren cage induces serious deformations also in the connected iron complex. Further addition of base does not result in other significant variations of absorbance, suggesting that no structural rearrangements take place when one or two more protons are released.

Table 2 Formation constants (logarithmic values) for the system $[FeL]^{2+}:Cu^{2+}$ (1 : 1 molar ratio). The reported values bear a ±0.02 uncertainty

Equilibrium	log *K*
$[FeL]^{2+} + H^+ + Cu^{2+} \rightleftharpoons [FeCu(HL)]^{5+}$	15.75
$[FeL]^{2+} + Cu^{2+} \rightleftharpoons [FeCuL]^{4+}$	9.06
$[FeL]^{2+} + Cu^{2+} + H_2O \rightleftharpoons [FeCuL(OH)]^{3+} + H^+$	0.04
$[FeL]^{2+} + Cu^{2+} + 2H_2O \rightleftharpoons [FeCuL(OH)_2]^{2+} + 2H^+$	−10.31

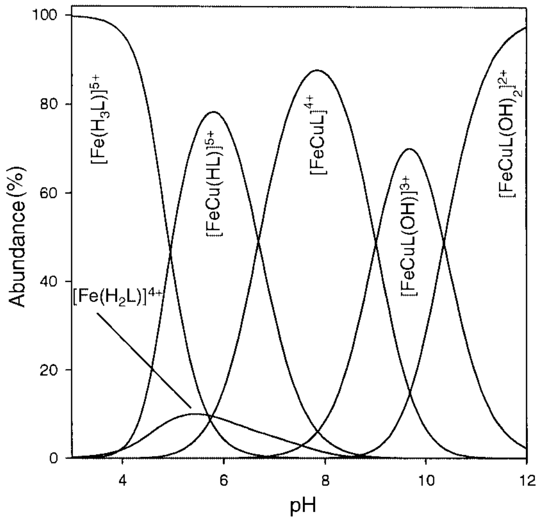

Fig. 3 Distribution diagram (% of species *vs.* pH) for the system $[FeL]^{2+}:Cu^{2+}$ (1 : 1 molar ratio).

Electrochemical (differential pulse voltammetry, DPV) experiments were carried out in 0.1 M $NaClO_4$, starting from a solution made acidic with an excess of $HClO_4$ and adding standard NaOH. At any pH, only one semireversible wave was found in the examined range ($0 < E < 1.5$ V *vs.* NHE), corresponding to the monoelectronic oxidation of the co-ordinated iron cation. The signal was centred at $E_{\frac{1}{2}} = 1195$ mV *vs.* NHE at pH = 2.5 and it slightly shifted towards less positive values when moving to higher pH values. An $E_{\frac{1}{2}}$ value of 1150 mV *vs.* NHE was reached at pH 7.5 and further addition of base did not result in any further change. The obtained values are to be compared with the $E_{\frac{1}{2}}$ value of 1110 mV *vs* NHE reported for the $[Fe(bipy)_3]^{3+}$–$[Fe(bipy)_3]^{2+}$ couple:[13] the presence of protonated amino groups in the tren unit affects only slightly the oxidation potential of the iron centre. In particular, while some difference is observed on going from $[Fe(H_3L)]^{5+}$ to $[Fe(H_2L)]^{4+}$, the release of two more protons does not affect the redox process on the iron centre. Considering also what is observed in the course of spectrophotometric titrations, it may be suggested that the 50 mV redox potential shift is due either to the decrease of a slightly unfavourable electrostatic effect, or to some serious rearrangement involving the whole molecule (and thus also the $Fe(bipyR)_3$ fragment) when passing from a three- to a two-protonated tren subunit.

4. $[FeL]^{2+}$ as a ligand for Cu^{2+}

Also the binding properties of the iron cage $[FeL]^{2+}$ towards Cu^{2+} have been examined in aqueous solution by means of potentiometric titrations (addition of standard base to solutions containing equimolar quantities of copper perchlorate and $[Fe(HL)]^{3+}$, plus excess of acid). Four bimetallic, copper-containing species have been singled out and the pertinent formation constants calculated (see Table 2), from which a distribution diagram (% of species *vs.* pH, Fig. 3) has been drawn.

The expected bimetallic species $[FeCuL]^{4+}$ is prevalent in the $6.6 < pH < 8.9$ range, reaching ≈90% at pH 7.9. Its formation

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‡ It is also possible to compare the protonation constants found for our compound also with those reported for the bis-tren ligand, but in the presence of 1 equivalent of Cu^{2+} and Co^{2+}. Three steps are reported, relative to protonation of the free tren unit which bears a closed, plus-two charged, complexed tren unit: even if still higher than for $[FeL]^{2+}$, the values of the stepwise protonation constants are closer to those of our compound (for steps 1, 2 and 3 log *K* values of 8.65, 7.29, 6.23 and 9.10, 8.07, 6.38 are reported in the cases of Cu^{2+} and Co^{2+}, respectively[3b]), indicating an increased rigidity of the mono-complexed bis-tren molecule, probably due to the geometric co-ordination requirements of the metal centre, which imposes an *endo* configuration also on the free tren unit.

constant can be compared with that found for the equilibrium tren + $Cu^{2+} \rightleftharpoons [Cu(tren)]^{2+}$ (log $K = 18.50$[3b]), which reflects the dramatically reduced binding tendencies of the tren unit in $[FeL]^{2+}$. Comparison can be made also with literature reports of the complexation constant of the second copper cation in bis-tren ligands, *i.e.* for the constant relative to the equilibrium $[(bis\text{-}tren)Cu]^{2+} + Cu^{2+} \rightleftharpoons [(bis\text{-}tren)Cu_2]^{4+}$; log *K* values of 9.41,[3b] 10.73[3a] and 13.37[3b] have been found for *m*-xylyl, $(CH_2)_2O(CH_2)_2$ and $(CH_2)_5$ connected bis-tren ligands, respectively. The much lower value found for our system suggests either that complexation inside the tren unit is made less favourable by the tight nature and by the dipositive charge of the $[FeL]^{2+}$ cage or that complexation of the Cu^{2+} cation by the tren unit takes place not inside it, but outside, thanks to an energetically expensive rearrangement of the tren backbone, so that only some of the nitrogen groups can bind an external Cu^{2+} cation. This hypothesis is strongly supported by the existence in solution of the $[FeCu(HL)]^{5+}$ species, in which a nitrogen group is protonated while Cu^{2+} is co-ordinated, and by the existence of the $[FeCuL(OH)_2]^{2+}$ species, in which two hydroxide anions bind Cu^{2+} while it is co-ordinated to tren. Both species contrast with the five co-ordinated, trigonal bipyramidal nature of the typical Cu–tren complexes, while their existence is quite reasonable in terms of a partial co-ordination to Cu^{2+} of the tren unit in $[FeL]^{2+}$, *e.g.* through a $NHCH_2CH_2N(R)CH_2CH_2NH$ fragment. A comment should be made also on the nature of the OH-containing $[FeCuL(OH)]^{3+}$ and $[FeCuL(OH)_2]^{2+}$ species: the proximity of the Cu^{2+} and Fe^{2+} cations could suggest that they are intramolecular hydroxo-bridged species. However, co-ordination of an OH^- anion to the octahedral, co-ordinatively saturated Fe^{2+} cation would require a dramatic change in its co-ordination sphere, with one of the bipyridine nitrogen atoms leaving its place to one or two OH^-. This is very unlikely for a kinetically inert complex such as $Fe(bipy)_3$ and, moreover, it would seriously affect its peculiar visible spectrum. However, no dramatic changes in the CT visible band are observed for the system $[FeL]^{2+}/Cu^{2+}$ in the pH 8–12 range, showing that OH^- groups co-ordinate, as expected, only to the Cu^{2+} cation.

The co-ordination of Cu^{2+} to the $[FeL]^{2+}$ cage can be followed also by means of spectrophotometric titrations. In a solution buffered with morpholine/$HClO_4$ at pH 7.9 (at which $[FeCuL]^{4+}$ reaches its maximum % value), addition of substoichiometric quantities of copper perchlorate to $[FeL]^{2+}$ caused a shift of the CT maximum to lower wavelengths; λ_{max} was found to reach a minimum value of 508 nm and A_{508} *vs.* equivalents of added copper showed a clear stop at 1 equivalent.

Finally, electrochemical titrations with $Cu(ClO_4)_2$ were performed on aqueous solutions containing $[Fe(HL)][PF_6]_3$ whose pH was regulated to 8.0 with microadditions of standard NaOH. Addition of substoichiometric quantities of Cu^{2+} caused the Fe^{II} to Fe^{III} oxidation wave to shift to higher potential, and a final value of 1215 mV *vs.* NHE was found after the addition of 1 equivalent or more of copper perchlorate. The observed small shift (+65 mV) fits well with what was found in the case of protonation, and suggests again that the variation in the oxidation potential of the $Fe(bipy)_3$ core is probably connected to a rearrangement of the whole molecule than to an unfavourable electrostatic effect.

Experimental

Physical measurements

The NMR spectra were recorded on a Bruker AMX 400 instrument, mass spectra (ESI) on a Finnigan TSQ 700 instrument, UV-VIS absorption spectra with a Hewlett-Packard HP8453 diode array spectrophotometer or a Perkin-Elmer λ 16 spectrophotometer and IR spectra (NaCl cells, Nujol mull) with a Mattson 5000 FT-IR instrument.

Synthesis

5-(2,2′-Bipyridine)carbaldehyde was prepared according to a described procedure.[14] All the other reagents were commercially available and used without further purification.

Ligand L. 0.11 g (0.75 mmol) of tris(2-aminoethyl)amine, tren, was dissolved in 15 cm^3 CH_3OH and allowed to react with 0.40 g (2.25 mmol) of 5-(2,2′-bipyridine)carbaldehyde at room temperature, under a nitrogen atmosphere. After 24 hours a precipitate of the tris-imino derivative was obtained, which was filtered off and characterized only through IR and ^1H NMR spectroscopy (IR: 1655, C=N stretch; 1590, 1588, 1580 cm^{-1}, C=C stretch. NMR ($CDCl_3$) δ 8.78, 3H, s, N=C*H*; 8.62, 3H, dd + 8.35, 6H, m + 8.24, 3H, s + 8.14, 3H, dd + 7.74, 3H, dt + 7.27, 3H, dt, hydrogens of the bipy rings; 3.75, 6H, t, CH_2N=CH; 2.97, 6H, t, CH_2CH_2N=CH). A 0.3 g sample of this product was dissolved in 30 cm^3 of boiling ethanol and reduced with an excess of $NaBH_4$ (1.0 g), which was added in small portions to avoid excessive foaming. The obtained solution was further heated at reflux temperature for 2 hours, then the solvent was removed on a rotary evaporator. The solid residue was dissolved in 20 cm^3 water and extracted with CH_2Cl_2 (5 × 20 cm^3). The gathered organic phases were dried over Na_2SO_4, then the solvent was removed on a rotary evaporator to obtain the product as a waxy solid, in 80% yield. IR: 1590, 1587, 1578 cm^{-1}, C=C stretch of the bipy rings. NMR ($CDCl_3$): δ 8.6, 6H, m + 8.2, 6H, m + 7.7, 6H, m + 7.21, 3H, dt, hydrogens of the bipy rings; 3.70, 6H, s, bipy-CH_2NH; 2.55, 6H, t + 2.70, 6H, t, CH_2CH_2NH + CH_2CH_2NH).

Complex $[Fe(HL)][PF_6]_3\cdot 2H_2O$. 0.27 g (0.4 mmol) of ligand L was dissolved in 10 cm^3 water and treated with 0.11 g (0.4 mmol) of $FeSO_4\cdot 7H_2O$, dissolved in 8 cm^3 water. The obtained purple solution was heated at its boiling temperature for 30 minutes, then cooled to room temperature and treated with 0.3 g of NH_4PF_6, which caused the precipitation of the product as a purple solid (40% yield). Calc. for $C_{39}H_{47}F_{18}FeN_{10}O_2P_3$, $[Fe(HL)][PF_6]_3\cdot 2H_2O$: C, 39.76; H, 3.99; N, 11.88%. Found: C, 39.85; H, 3.98; N, 11.79%. ^1H NMR (D_2O): δ 8.58, d, 3H + 8.54, d, 3H + 8.17, dt, 3H + 8.08, dd, 3H + 7.60, d, 1H + 7.48, dt, 1H + 7.22, s, 1H, H of the bipy rings; 3.9–2.8, m, 18H, $CH_2CH_2NHCH_2$–bipy. Mass (ESI): *m*/*z* 705 ($[LFe - H]^+$).

Crystals suitable for X-ray diffraction experiments were obtained by slow diffusion of diethyl ether in an acetonitrile solution of $[Fe(HL)][PF_6]_3\cdot 2H_2O$. The crystalline product precipitated as $[Fe(HL)][PF_6]_3\cdot 2CH_3CN$.

Potentiometric titrations

Potentiometric titrations were performed in aqueous solutions (50 cm^3, made 0.1 M in sodium perchlorate) containing $[Fe(HL)]^{3+}$ (10^{-3}–5×10^{-4} M) plus an excess of standard perchloric acid (protonation constants) or plus an equimolar quantity of Cu^{2+} perchlorate and an excess of perchloric acid (complexation constants), by addition of standard aqueous NaOH, under a nitrogen atmosphere, in a cell thermostatted at 25 °C. In each titration 60–70 points were recorded. The potentiometric data were refined using the HYPERQUAD package,[15] which minimizes a least squares function. The fit between calculated and experimental emf data was evaluated through the σ and χ^2 parameters,[16] whose values, in each treatment, were found to be 1(±0.1) and <8%, respectively. The calculated log *K* and pK_a values, which are reported in the text, bear an uncertainty lower than ±0.02.

Spectrophotometric titrations

Coupled pH-metric and spectrophotometric titrations were performed in aqueous solutions made 0.1 M in sodium

Table 3 Crystallographic data and processing parameters for [Fe(HL)][PF$_6$]$_3$·2CH$_3$CN

Formula	$C_{43}H_{48}F_{18}FeN_{11}P_3$
Crystal system	Monoclinic
Space group	$P2_1/n$
T/K	295
a/Å	15.005(5)
b/Å	12.600(5)
c/Å	27.920(5)
β/°	98.30(2)
V/Å^3	5223(2)
Z	4
D_{calc}/g cm^{-3}	1.538
F(000)	2464
μ(Mo-Kα)/cm^{-1}	4.89
Reflections collected	6961
Independent reflections	6424 ($R_{int} = 0.05$)
Final $R1$, $wR2$ ($I > 4\sigma(I)$)	0.057, 0.132
All data	0.226, 0.159

perchlorate. 30–50 cm^3 Volumes were employed, with samples in the 1×10^{-3}–5×10^{-4} M concentration range. Solutions, in which the pH-reading electrode was dipped, were kept under a nitrogen atmosphere and thermostatted at 25 °C. After each base addition, 2.5–3.0 cm^3 solution samples were quickly transferred to a quartz cuvette and, after measuring the spectrum, then returned to the bulk solution.

Electrochemistry

Electrochemical measurements (DPV) were performed with a P.A.R. 273 potentiostat/galvanostat, under the control of a PC, with dedicated software. In a typical experiment, 10^{-3} mol dm^{-3} electroactive species was employed, in aqueous solutions made 0.1 M in $NaClO_4$. The pH of the solution was monitored through a glass electrode dipped in the electrochemical cell, and during coupled pH-metric and electrochemical titrations it was made to vary with microadditions of standard NaOH or $HClO_4$. A carbon paste electrode was used as the working electrode, a SCE as the reference and a platinum foil as the counter electrode.

Crystal structure determination

X-Ray intensity data were collected on a Siemens A.E.D. three-circle diffractometer. Crystal data, details of the data collection and structure refinement are given in Table 3. Data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by direct methods using SIR 92.[17] Two solvent acetonitrile molecules have been found in the lattice. The structure was refined on F_o^2 using SHELXL 96.[18] The hydrogen atoms were calculated and refined "riding" on their parent atoms except those at the protonated and unprotonated amine which were found in the ΔF map but refined with geometrical constraints. Geometrical parameters were calculated by PARST.[19] The plot of the molecule was obtained by ORTEP 3 included in the WinGX suite.[8]

CCDC reference number 186/1860.

See http://www.rsc.org/suppdata/dt/a9/a909756b/ for crystallographic files in .cif format.

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