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Square pyramidal geometry around the metal and tridentate coordination mode of the tripod in the [6-(3′-cyanophenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)amine $FeCl_2$ complex: a solid state effect†

Nasser K. Thallaj,[a] Ahmed Machkour,[a] Dominique Mandon*[a] and Richard Welter[b]

[a] *Laboratoire de Chimie Biomimétique des Métaux de Transition, UMR CNRS no 7513, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France. E-mail: mandon@chimie.u-strasbg.fr; Fax: 33-(0)390-245-001; Tel: 33-(0)390-241-537*

[b] *Laboratoire DECMET, UMR CNRS no 7513, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France*

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Metalation of the cyanophenyl mono α-substituted TPA ligand by ferrous chloride affords a stable neutral compound with spectroscopic properties in solution (molecular conductivity, UV-visible and paramagnetic ^{1}H NMR) indicating that the ligand coordinates in the tetradentate mode providing a distorted octahedral geometry around the metal. In the solid state however, the tripod acts as a tridentate ligand, and crystal structure analysis reveals a square pyramidal geometry around the metal. The substituted pyridyl arm is the dangling one, and the cyanide group seems to interact with the metal center of a neighboring molecule. Increasing the ionic strength of a solution of the compound leads to dissociation of the chloride ions from the metal, affording the bis (μ-chloro) diferrous dication, the structure of which is also reported.

Introduction

Flexibility of ligands and accessibility of small reagents to the metal centers is one of the key points in the control of the reactivity in coordination chemistry of tripodal tetraamines to transition metals.[1] It is generally believed that metal complexes with coordinatively unsaturated environment display enhanced reactivity with respect to saturated ones, all other parameters being equal. The concept of "hypodenticity", formerly termed by Constable[2] has recently been reviewed, and applies to multidentate ligands being coordinated to metals by fewer than the maximum number of donor atoms.[3] Simple ligands can coordinate either regularly (all suitably-disposed donor atoms bound) or in the "hypodentate" fashion, providing some versatility in the properties. In view of further reactivity studies, it seems thus interesting to understand the parameters that govern the coordination fashion. We previously showed that in chemistry of tris(2-pyridylmethyl)amine (TPA) ligands and derivatives, substitution at the α position of the pyridyl group can induce noticeable effects on the coordination mode of the tripod in dichloroferrous complexes: distorted octahedral or trigonal bipyramidal geometries could be found, the latter case corresponding to an increased sensitivity *versus* dioxygen.[4–6] Following our first report of structures with mono and bis α-substituted ligands, there came from Colbran *et al.* the structure of the dichloroferrous complex of the [6-(2′,5′-dimethoxyphenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)amine.[7] In this compound the tripod coordinates in the tetradentate fashion, the high spin ferrous ion lying in a distorted octahedral environment.

In order to perform further substitution on the tripodal skeleton, we synthesized a very similar compound, the [6-(3′-cyanophenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)amine (L), and carried out a complete characterization, including structural determination, on the dichloroferrous complex. Whereas all measurements in solution strongly support a tetradentate coordination mode for the tripod leading to an octahedral geometry around the metal (perfectly on line with expectations from the results of Colbran *et al.*[7]), the X-ray analysis revealed a distorted square pyramidal geometry in the solid state, the tripod acting here as a tridentate ligand. In this paper, we show that this apparent contradiction may be explained by the occurrence, within this class of monophenyl substituted tripods, of a coordination equilibrium between the two geometries (tridentate in solid state—tetradentate in solution). Attempts to modify this equilibrium by increasing the ionic strength in solution resulted in the formation of the symmetrical bis(μ-chloro) diferrous cation, the structure of which is also reported.

Results and discussion

Ligand L, obtained as a brownish oil, was prepared by the Suzuki cross coupling route from the monobrominated precursor 2-BrTPA using the commercially available 3-cyanophenylboronic acid, following a well known procedure.[4,8,9] Metalation by ferrous chloride was performed under inert atmosphere in standard conditions and afforded $LFe^{II}Cl_2$ as a thermally stable orange solid in a quantitative yield.[5,6] In acetonitrile, the molecular electric conductivity of the complex is $\chi = 12.7$ S cm^2 mol^{-1} indicating that the complex remains neutral in solution. Its UV-visible spectrum displays maxima at

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† Electronic supplementary information (ESI) available: UV-visible and ^{1}H NMR traces of the complexes. Crystallographic information and ORTEP diagrams with complete labelling. See DOI: 10.1039/b512108f

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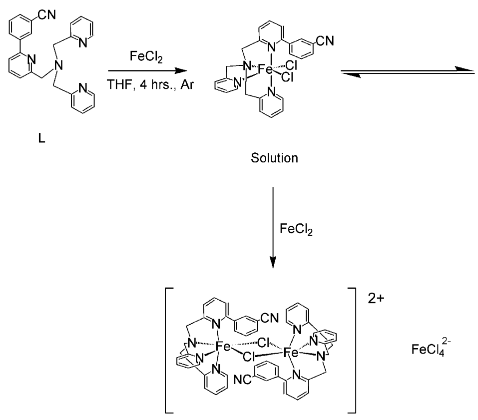

Scheme 1 Coordination chemistry of **L** to $FeCl_2$.

$\lambda = 257$ and 283 nm ($\varepsilon = 21.3 \times 10^3$ and 13.1×10^3 mmol cm^{-2} respectively) corresponding to π–π* ligand centered transitions, and a broad MLCT band at $\lambda = 392$ nm with $\varepsilon = 1.6 \times 10^3$ mmol cm^{-2}. The ^1H NMR spectrum is qualitatively similar to that already reported for 2-BrTPAFe$^{II}Cl_2$ with paramagnetically shifted signals,[5] the main difference being the presence of two signals at $\delta = 13.0$ and 10.5 ppm corresponding to the protons of the cyanophenyl substituent, broadened and slightly shifted because of their attachment to the coordinated pyridyl arm. β (β') and γ (γ') protons are very easily assigned at $\delta = 52, 42, 36, 26, 14$ and 11 ppm respectively, and their mid-intensity peak width lies within the 40 Hz $< \Delta_{1/2} <$105 Hz range (traces given in supplementary information). Taken all together, these findings indicate, as drawn on Scheme 1, that LFe$^{II}Cl_2$ is not dissociated in solution, the metal lying in a octahedral geometry with the tripod coordinated in the tetradentate fashion.[10]

Slow diffusion of diethyl ether into a solution of LFe$^{II}Cl_2$ in acetonitrile afforded crystals suitable for structural determination. Surprisingly as can be seen in Fig. 1, the crystal analysis revealed that the tripod acts as a tridentate ligand in this complex, the dangling arm being the cyanophenyl-substituted pyridine. A similar coordination mode has already been observed in dichloroferrous complexes with ligands hindered in the α position (*i.e.* di- or tris-substituted).[5,6] In the present case however, steric hindrance seems to be very limited. A careful analysis reveals that the tetragonal index value is $\tau = 0.092$, indicating that the metal center lies in a distorted square pyramidal geometry rather than a trigonal bipyramidal one.[11] This is the first example of such a geometry found within this class of compounds. Interestingly, the cyanide of the neighbour molecule lies almost vertically to the iron with a Cl–Fe–NC$_{neigh}$ angle = 172°, evoking a strongly distorted octahedral symmetry. The distance Fe–NC$_{neigh}$ however is 3.94 Å, by far too long for a bond but short enough to ensure stacking effects in the solid state. Moreover, the substituted pyridine and cyanophenyl are close to coplanearity with a dihedral angle of only 12.9°. Finally, metal to ligand distances are all consistent with a high spin state for this complex. Noteworthy is the fact that upon solubilization of the crystals, all spectroscopic data remained unchanged with respect to those detailed above.

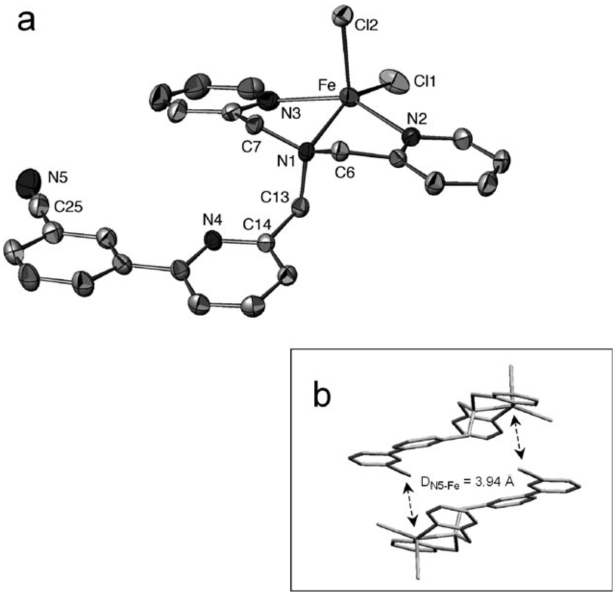

Fig. 1 a): ATOMS[16] view of LFe$^{II}Cl_2$. Selected bond lengths (Å) and angles (°): Fe–N1, 2.259(2); Fe–N2, 2.130(2); Fe–N3, 2.159(3); Fe–Cl1, 2.303(1); Fe–Cl2, 2.343(1); N2–Fe–N3, 146.05(9); N1–Fe–Cl1, 151.58(7); Cl2–Fe–Cl1, 108.50(4). b): Stacking effects between two adjacent molecules showing the distance between the nitrile and the iron atom of an adjacent complex.

The structure of some dichloroferrous complexes with substituted TPA ligands in which the tripods coordinate in tridentate mode have already been reported.[5,6] In general, the τ values lie in between 0.8 to 0.6, on line with a (albeit more or less distorted) trigonal bipyramidal geometry. The difference with the present case (square pyramidal geometry) lies in the fact that in none of the other reported structures could be found any kind of intermolecular interaction. We believe that for LFe$^{II}Cl_2$ in the solid state, the position of the nitrile substituent is not innocent, *i.e.* it is fixed and stabilized by stacking interaction with the metal of the neighbouring molecule in the unit cell. As a consequence, the geometry moves towards square pyramidal.

Dichloroferrous complexes with "hypodentate" coordination of the tripod generally display weak MLCT transitions in UV-visible spectroscopy. Sometimes these transitions are even not detectable.[5,6,10] When detected, their molecular extinction coefficient value lie close to half of the values of those measured for normal coordination mode.[5] We measured the UV-visible spectrum of LFe$^{II}Cl_2$ in solution in a standard way, then within the same cell let the solvent evaporate until an orange-yellow film could be obtained. We thus performed a new measurement on the film. The result is spectacular and displayed in Fig. 2. We noticed the disappearance of the well defined absorption observed in solution at $\lambda = 392$ nm, and detected only a broad and very weak plateau between 400 and 480 nm on the film sample with an intensity decreased by 50–60%, strongly supporting tridentate coordination of the ligand in the solid state.

Upon solubilization of the film, and after allowing the solution to stand for five minutes, the spectrum of LFe$^{II}Cl_2$

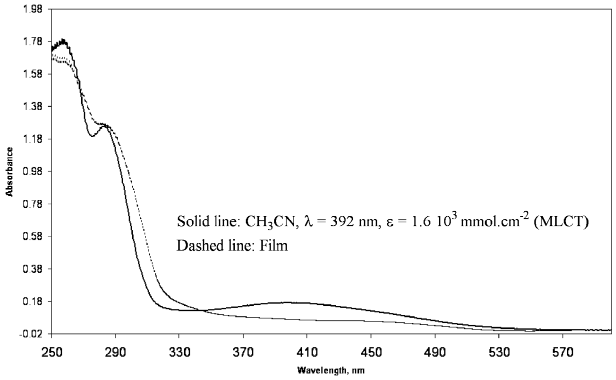

Fig. 2 UV-visible spectrum of LFe$^{II}Cl_2$. Two traces from the same cell, before and after solvent evaporation and vacuum drying. The solid line stands for the spectrum in a CH_3CN solution at 295 K. The dashed line has been obtained from the film obtained upon evaporation of the solvent.

could be qualitatively obtained, thus indicating that the process of coordination change of the ligand is reversible.[12]

Upon addition of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) to the solution of LFe^{II}Cl$_2$, the colour turned to bright yellow and significant changes were observed in the UV-visible spectrum with the disappearance of the 392 nm absorption and the presence of a new band at $\lambda = 363$ nm ($\varepsilon = 2.6 \times 10^3$ mmol cm^{-2}). The ^{1}H NMR spectrum displayed paramagnetically shifted signals in the range 130–10 ppm, consistent with the presence of an octahedral geometry around the iron (traces are given in the supplementary information†). Attempts to obtained single crystals from the solution failed. However, keeping in mind that in some cases, the use of an excess of metal salt can induce crystallization by formation of the FeCl$_4^{2-}$ anion,[13,14] TBAPF$_6$ was replaced by FeCl$_2$, and this yielded crystals suitable for structural analysis. We checked that all spectroscopic data remained unaffected whether TBAPF$_6$ or FeCl$_2$ was added. We also checked that on a preparative scale, the formation of this species can by achieved by metalation of L with at least two equivalents of FeCl$_2$.

Single crystals were obtained by slow diffusion of diethyl ether in an acetonitrile solution. The crystal analysis revealed the presence of the bis(μ-chloro) diferrous cation [LFe(Cl)$_2$-FeL]$^{2+}$, with FeCl$_4^{2-}$as counter anion. This structure, displayed in Fig. 3, is not unusual, and is similar to those previously reported in the chemistry of various tripods.[6,13,15] The ligand coordinates in the tetradentate mode and each iron atom adopts a distorted octahedral environment. Basically, all the distances and angles lie in the expected range for diferrous high-spin derivatives. In this structure, the presence of the FeCl$_4^{2-}$ anion impedes close contact within adjacent molecules. The cyanide of the phenyl substituent is completely free and does not seem to interact with any adjacent atom. The dihedral angle between the substituted pyridine and the cyanophenyl is close to 44.0°, closer to the expected value for a biphenyl unit.

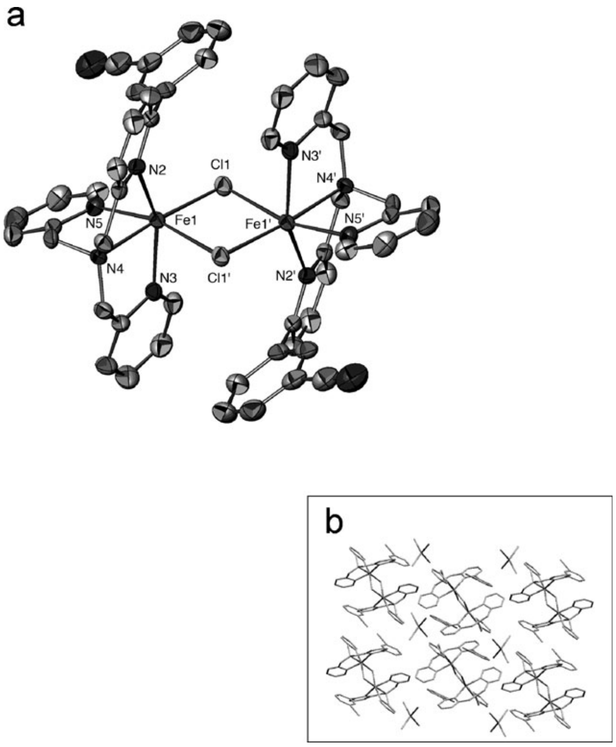

Fig. 3 a): ATOMS[16] view of [LFe^{II}Cl]$_2^{2+}$, FeCl$_4^{2-}$. The anion and solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–N2, 2.229(3); Fe1–N3 2.202(3); Fe1–N4, 2.183(3); Fe1–N5, 2.187(3); Fe1–Cl1, 2.3308(9); Fe1–Cl1′, 2.6643(12); Fe1–Fe1, 3.585; Cl1–Fe–Cl1′, 88.53(4); N3–Fe1–N2, 153.55(10). Symmetry operator: $-x + 1/2$, $-y + 1/2$, $-z$. b): Stacking within the unit cell.

Conclusion

In conclusion, whereas a clear-cut situation is observed in coordination chemistry of simple phenyl-α-substituted tripods to FeCl$_2$, the presence of a cyanophenyl substituent on the tripod seems to induce a coordination equilibrium. In solution the general behaviour as previously observed for monosubstituted tripods is observed with an octahedral geometry and a tetradentate coordination mode of the ligand. In the solid state, the tridentate coordination mode leading to the unexpected square pyramidal geometry does occur, presumably through stacking or intermolecular effects. The structure can be described as an "aggregation of two neutral monomers" through the nitrile substituent of the ligand, that is no longer possible upon dissociation and use of big anions, the regular dinuclear complex being thus obtained. Effects on this equilibrium on the kinetics of ligation of dioxygen are currently under investigation.

Experimental

^{1}H NMR data were recorded in CD$_3$CN (CDCl$_3$ for the ligand) at ambient temperature on a Bruker AC 300 spectrometer at 300.1300 MHz using the residual signal of CD$_2$HCN (CHCl$_3$) as a reference for calibration.

The UV-vis spectra were recorded on a Varian Cary 05 E UV-Vis NIR spectrophotometer.

Conductivity measurements were carried out under argon at 20 °C with a CDM 210 Radiometer Copenhagen Conductivity Meter, using a Tacussel CDC745-9 electrode.

Elemental analyses were carried out by the Service Central d'Analyses du CNRS in Vernaison, France.

Synthesis of [6-(3′-cyanophenyl)-2-pyridylmethyl] bis(2-pyridylmethyl)amine (L)

2-BrTPA was prepared according to already published procedures.[5]

To 800 mg (2.17 mmol) of 2-BrTPA in solution in 100 ml of degassed toluene was added a stoichiometric amount of the commercially available (Aldrich) 3-cyano phenyl boronic acid suspended in 10 ml of degassed methanol. 7.2 ml of a 0.1 M solution of Na$_2$CO$_3$ were added, together with 140 mg of [Pd(PPh$_3$)$_4$)]. The mixture, kept under an argon atmosphere was heated to reflux and stirred for 25 hours.

Following this, the solution was evaporated to dryness, taken up in CH$_2$Cl$_2$ and washed several times with aqueous Na$_2$CO$_3$, then water. After drying over magnesium sulfate, the organic phase was concentrated. Addition of pentane resulted in separation of a brown residue. The residue was dissolved in CH$_2$Cl$_2$, and the separation procedure repeated. The brown oil thus obtained turned out to be the clean ligand (750 mg, 1.92 mmol, 88%). The mother solutions contained detectable amounts of the starting 2-BrTPA.

Elemental analysis. L (C$_{25}$H$_{21}$N$_5$. 391): calcd%: C 76.72, H 5.37. Found%: 76. 69, H 5.20.

^{1}H NMR. CDCl$_3$, δ ppm/solvent (7.26): 8.50 (d, 2H, α-pyridyl), 8.35 (m, 1H), 8.22 (d, 1H), 7.93–7.40 (m, 9H), 7.05 (m, 2H), 3.94 (s, 2H, CH$_2$), 3.88 (s, 4H, CH$_2$).

Characterization of LFeCl$_2$

Preparation of the complex. This was achieved following already published procedures outlined in refs. 5 and 6.

Elemental analysis. LFeCl$_2$ (C$_{25}$H$_{21}$N$_5$FeCl$_2$. 518): calcd%: C 57.91, H 4.05. Found%: 57.85, H 3.75.

UV-Visible spectrum. CH$_3$CN, R.T, λ, nm (ε, 10^3 mmol^{-1} cm^2): 257(21.30), 282(13.06), 400(1.65).

Solid state: LFe^{II}Cl$_2$ was dissolved in CH$_3$CN under argon. A first spectrum was recorded, displayed as the solid line in Fig. 2. Then, the solvent was evaporated by smoothly fluxing argon at the top of the cell, avoiding any turbulence. Over 30 minutes, a film was formed. The spectrum was recorded, and at that time displayed only a moderately decreased intensity and broadening of the 392 nm absorption. The UV-vis cell was placed under vacuum overnight, and the trace finally obtained is the one displayed as a dashed line in Fig. 2.

Molecular electric conductivity. CH$_3$CN, R.T. C = 3.0 mmol l^{-1}, $\chi = 12.7$ S cm^2 mol^{-1}.

^{1}H NMR. CD$_3$CN, δ ppm/solvent, ($\Delta_{1/2}$, Hz): 127(1550), α; 77(1650), 46(1140), 38 (broad, bottom), C$\underline{H}_2$; 52.4(50), 42.4(41), 36.6(64), 26.5(105), β and β'; 14.5(34), 11.6(23), γ and γ'; 13.0(54), 10.5(35) cyanophenyl protons.

Crystal structure for LFe^{II}Cl$_2$. Monoclinic, space group $P2_1/c$, $a = 10.981(5)$ Å, $b = 12.583(5)$ Å, $c = 17.066(5)$ Å, $\beta = 97.946(5)°$, $V = 2335.4(16)$ Å^3, temperature = 173(2) K, $Z = 4$, $D_{\text{calc.}} = 1.474$, $\mu = 0.898$ mm^{-1}, reflection collected = 6781, independent reflections ($I > 2\sigma(I)$) = 4054, ($R_{\text{int}} = 0.031$), $R_1 = 0.0499$, wR_2 (all data) = 0.1204, GooF = 0.853. CCDC 274995. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512108f

Characterization of [LFeCl]$_2$ [FeCl$_4$]

Preparation of the complex. Two CH$_3$CN solutions of FeCl$_2$ (25 mg) and LFeCl$_2$ (80 mg) were mixed under strict anaerobic conditions. The medium turned bright yellow, and was stirred for two hours. Overlaying the solution with dry and degassed diethyl ether resulted in the bulk formation of microcrystals. The supernatant was sucked out and the solid (75 mg) was dried under vacuum.

Elemental analysis. [LFeCl]$_2$ [FeCl$_4$]. Et$_2$O: (C$_{54}$H$_{52}$N$_{10}$O-Fe$_3$Cl$_6$. 1237): calcd%: C 52.38, H 4.20. Found%: 51.97, H 3.75.

UV-Visible spectrum. CH$_3$CN, R.T, λ, nm (ε, 10^3 mmol^{-1} cm^2): 261 (13.27), 284 (8.22) 363 (2.60).

^{1}H NMR. CD$_3$CN, δ ppm/solvent, ($\Delta_{1/2}$, Hz): 131(1000), α; 76(740), 67(780), 47(broad, bottom), C$\underline{H}_2$; 55.4(71), 47.4(70), 46.9(70), 37.8(107); 14.6 (53), β, β', γ and γ'; 6.11(59) and diamagnetic area: cyanophenyl protons.

Crystal structure for [LFeCl]$_2$ [FeCl$_4$] Et$_2$O. Monoclinic, space group $C2/c$, $a = 21.396(5)$ Å, $b = 11.286(5)$ Å, $c = 22.693(5)$ Å, $\beta = 90.656(5)°$, $V = 5479(3)$ Å^3, temperature = 173(2) K, $Z = 4$, $D_{\text{calc.}} = 1.500$, $\mu = 1.126$ mm^{-1}, reflection collected = 10664, independent reflections ($I > 2\sigma(I)$) = 4138, ($R_{\text{int}} = 0.054$), $R_1 = 0.0503$, wR_2 (all data) = 0.1387, GooF = 1.067. CCDC 274996. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512108f

Acknowledgements

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