CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600276

The Coordination Chemistry of $FeCl_3$ and $FeCl_2$ to Bis[2-(2,3-dihydroxyphenyl)-6-pyridylmethyl](2-pyridylmethyl)amine: Access to a Diiron(III) Compound with an Unusual Pentagonal-Bipyramidal/Square-Pyramidal Environment

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Abstract: Coordination of $FeCl_3$ to the title ligand yields a mononuclear iron(III) complex **1**, which was characterized by spectroscopic techniques and X-ray diffraction. The ligand is (κ^3-*N*) tridentate and the metal, which lies in a pseudo-octahedral environment, is bound to a phenolate group from the catechol substituent. The dichloroiron(II) complex **2** was easily obtained by metalation of the ligand with $FeCl_2$ and characterized by various spectroscopic techniques. In their cyclic voltammograms both **1** and **2** display the same reversible Fe^{II}/Fe^{III} wave at $E_{1/2} =$ 10 mV (vs. SCE). Reduction of compound **1** with Zn/Hg yields **2′**, which displays identical properties to **2**. Taken together, these findings indicate that in spite of the different oxidation state of the metal in **2**, no major geometrical/structural change is observed at the metal center with respect to **1**. The reaction of **2** with dioxygen in the absence of organic substrates proceeds extremely rapidly and yields compound **3**, which is a diiron(III) derivative whose X-ray crystal structure is also reported. The possibility of a radical-based mechanism is discussed. Compound **3** displays an unusual geometry: one iron(III) center is seven-coordinate, whereas the other lies in a square-pyramidal environment. The two iron atoms are bridged by the catecholato substituents. To the best of our knowledge, **3** is the first example of a seven-coordinate iron(III) derivative with tris(2-pyridylmethyl)amine ligands.

Keywords: dioxygen activation · iron complexes · N ligands · oxidation · radical reactions

Introduction

Tris(2-pyridylmethyl)amine-based ligands (TPAs) form one of the most widely investigated family of compounds within the class of tripodal tetraamine ligands.[1] The concept of tuning the reactivity within a series of metal complexes by substitution of the tripod skeleton, which is now well established, was formerly introduced from studies involving alkyl or simple aryl substituents.[2–4] Later on, more sophisticated ligands with non-innocent groups such as crown ethers or amido-, phenoxy-, or quinone-appended ligands, to mention only a few examples, were reported with more or less expected properties.[5–10] As a particularly salient illustration of this approach, ligands with 2,5-dimethoxyphenyl, 2,5-hydroquinone, or 2,5-quinone substituents have recently been prepared and their copper complexes studied in detail to gain insight into the mechanism by which protons can be displaced at the same time that the metal center undergoes redox modification.[11]

TPA ligands are easily accessible, and their iron complexes have been extensively used as tools to understand the chemistry at the active site of some iron proteins, thus making this series of compounds one of the most widely investigated classes of complexes for inorganic chemists involved in the field of biomimetics.[1,12–14] Iron(III) derivatives are particularly stable, easy to handle, and, among other properties, their ability to coordinate catechol derivatives

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has resulted in many studies aimed at understanding the mechanisms at the active site of intradiol dioxygenases, which are an important class of iron proteins.[15–17]

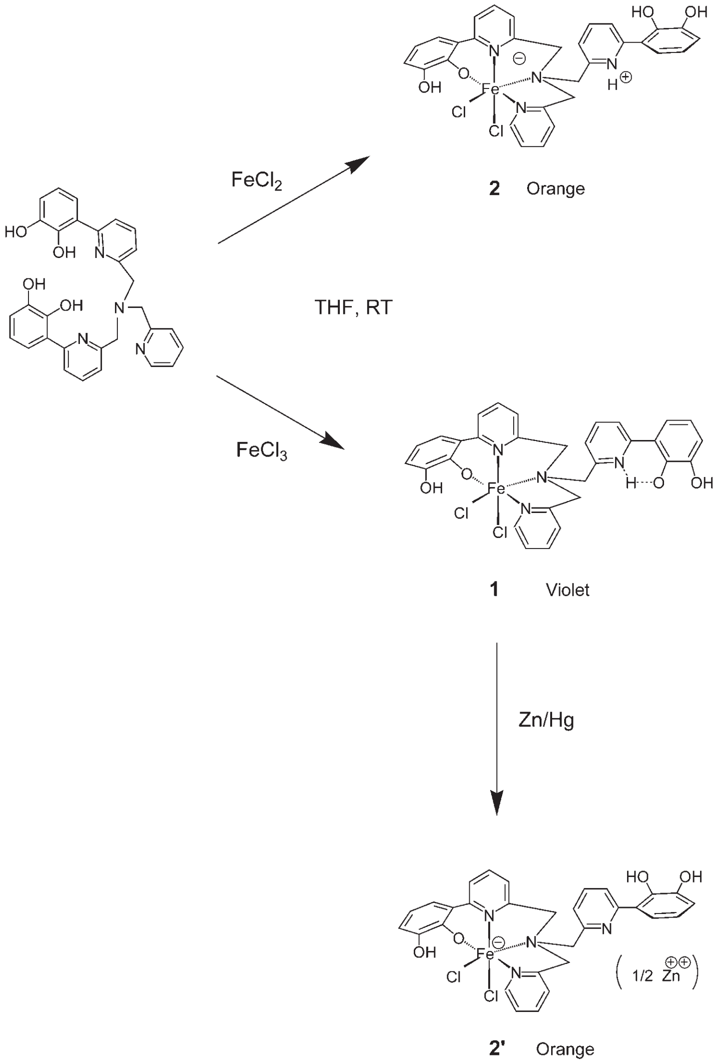
Catechol fragments form stable complexes with iron and are also involved in iron uptake and transport by siderophores.[18] Catechols, and phenolates in general, are considered as "hard ligands" and therefore would stabilize iron in the iron(III) state, whereas nitrogen-containing ligands are "soft" and would stabilize the iron(II) state. Following these principles, an elegant example of redox-driven translocation of iron in a bicompartmental ligand has already been described.[19]

We have been involved in the chemistry of stable iron(II) derivatives with various substituted aminomethylpyridyl-containing ligands, and have reported that some of them exhibit an interesting reactivity towards dioxygen.[20–22] As an extension of our work with substituted TPA derivatives, we decided to prepare a ligand with two very different coordination sites, namely bis[2-(2,3-dihydroxyphenyl)-6-pyridylmethyl](2-pyridylmethyl)amine (BCATTPA), whose structure is shown in Scheme 1, and embarked upon an investigation of the coordination chemistry of this ligand with iron(III) and iron(II) chloride.

Rather unexpectedly, coordination of iron(III) to this ligand occurs through the nitrogen-containing site, as confirmed by X-ray diffraction analysis of the complex. The dichloroiron(II) complex displays a similar geometry, and can be synthesized either by metalation of the ligand with iron(II) chloride or chemical reduction of the iron(III) derivative. This complex is extremely oxygen sensitive and in the absence of substrate yields a dinuclear compound with a very unusual structure: two metals bridged by phenoxo groups lie in seven- and five-coordinate environments, respectively. To the best of our knowledge, this is the first example of a seven-coordinate iron(III) derivative in the field of tris(2-pyridylmethyl)amine ligands. We report here the coordination chemistry of this new ligand and the preparation and structural characterization of an original diiron complex.

Results and Discussion

Preparation of the ligands: This is straightforward and follows a procedure involving a Suzuki-type cross-coupling reaction between a boronic acid and aryl halide.[4] Although condensation from simple pyridyl-based precursors of the ligands may be carried out,[5,23] we started directly with the preformed Br2TPA tripod, for convenience, and treated it with 2,3-dimethoxyphenylboronic acid. The tetramethoxy derivative BDMPTPA obtained was then treated with BBr_3 to yield the catechol-containing ligand BCATTPA. Note that the BBr_3/ligand ratio should not be too high (typically 6–7/1) in order to minimize side reactions between the Lewis acid and the nitrogen-containing base. We obtained the ligand as a crystalline material with typical yields of 55 to 60%.



Scheme 1. Mononuclear iron(II) and iron(III) complexes of BCATTPA described in this work.

Metalation of BCATTPA with $FeCl_3$: Metalation of the catechol ligand in the absence of a base was expected to occur due to the vicinity of the nitrogen of the pyridyl group with the proton of the hydroxy function. This reaction actually worked very well, and treatment of anhydrous $FeCl_3$ with one equivalent of the ligand in THF or CH_3CN yielded a dark violet solution. Once the reaction was complete, workup was carried out without the need for any particular precautions and the compound was obtained as a thermally and oxygen stable solid.

The UV/Vis spectrum of this complex is shown in Figure 1 and reveals a broad band at $\lambda_4 = 617$ nm ($\varepsilon_4 = 0.82 \times 10^3$ mmol cm^2), which we assigned to a LMCT phenolate→Fe^{III} transition. This transition is responsible for the dark color of the complex. In general, complexes with iron(III) chloride coordinated to pyridyl-containing tripods exhibit a moderately intense LMCT Cl→Fe^{III} absorption in the region 360–390 nm.[24,25] In the present case, a shoulder is observed at $\lambda_3 = 354$ nm. Although it lacks a well-defined

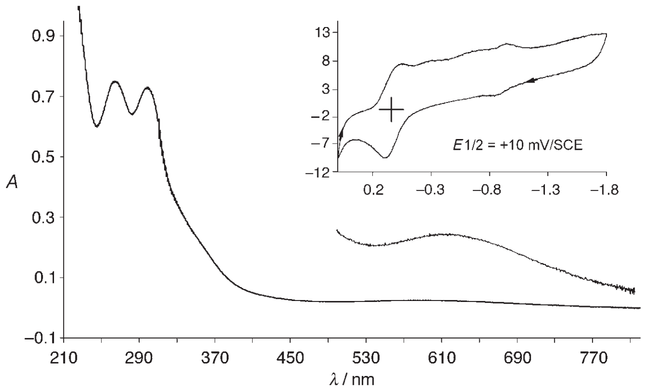


Figure 1. UV/Vis spectrum of [(BCATTPA)Fe^{III}Cl$_2$] (**1**) in CH$_3$CN at room temperature. Inset: cyclic voltammogram of the same compound in CH$_3$CN (0.1 M (TBA)PF$_6$, 200 mV s^{-1}, scan to negative values).

pattern, this signal might be this expected LMCT band, thus suggesting that the tripod is indeed involved in coordination to the iron, as outlined in Scheme 1. Finally, two other ligand-based absorptions are observed at $\lambda_2 = 297$ and 263 nm ($\varepsilon_2 = 13.01$ and 13.67×10^3 mmol cm^2, respectively).

We have previously reported ^{1}H NMR spectroscopic data for trichloroiron(III) complexes with substituted TPA ligands.[24] The resonances in the paramagnetic region are generally extremely broad for high-spin iron(III) derivatives. In the present case, only two extremely weak and poorly defined signals were detected at around $\delta = 95$ and 60 ppm. Broadened signals, which might be due to the uncoordinated part of the ligand, were also observed in the diamagnetic region. The spectrum is given in the Supporting Information.

Single crystals of [(BCATTPA)Fe^{III}Cl$_2$]·Et$_2$O (**1**·Et$_2$O) could be obtained by layering an acetonitrile solution of **1** with dry diethyl ether. An ORTEP diagram of **1** is displayed in Figure 2, in which it can clearly be seen that the metal is coordinated to the nitrogen atoms of the ligand. The nitrogen-containing tripod coordinates in a tridentate fashion (κ^3-*N*), with one substituted pyridyl unit remaining remote from the coordination center. The coordination environment is completed by two chloride ligands from the starting metal salt and one phenolato group from a singly deprotonated substituent of one coordinated pyridine. The metal lies in a distorted octahedral environment. All the N−Fe distances are longer than 2.1 Å, in line with a high-spin state for the metal. The O1−Fe distance (1.870 Å) is short and is consistent with an anionic bond between a deprotonated phenol and the iron(III) center. The chloride to iron distances lie in the expected range (Cl1−Fe 3.358 and Cl2−Fe 2.309 Å). It is noteworthy that the HO3 proton interacts with the N4 nitrogen of the vicinal pyridine, the corresponding distance being only 1.835 Å. As a consequence, the aromatic rings in the uncoordinated pyridine are almost co-planar.

The ν_{OH} vibration is observed at 3412 cm^{-1} in the IR spectrum, a value perfectly in line with the presence of a bound hydroxy group.

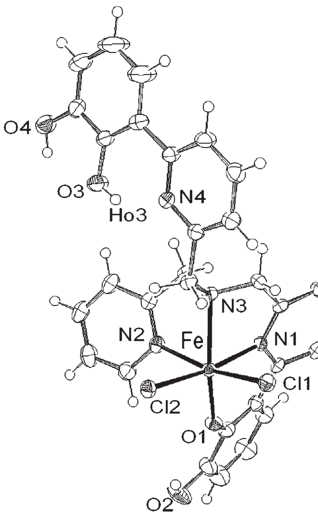


Figure 2. Structure of [(BCATTPA)Fe^{III}Cl$_2$] (**1**; ORTEP diagram showing a partial numbering scheme). Selected bond lengths [Å] and angles [°]: Fe−O1 1.870(3), Fe−N1 2.164(3), Fe−N2 2.182(3), Fe−N3 2.259(3), Fe−Cl2 2.3093(13), Fe−Cl1 2.3581(12), Ho3−N4: 1.835(4); O1-Fe-N1 87.17(12), O1-Fe-N2 92.50(13), N1-Fe-N2 91.25(13), O1-Fe-N3 157.87(13), N1-Fe-N3 74.23(12), N2-Fe-N3 76.36(13), O1-Fe-Cl2 99.41(9), N1-Fe-Cl2 172.47(9), N2-Fe-Cl2 84.85(10), N3-Fe-Cl2 98.56(9), O1-Fe-Cl1 99.61(10), N1-Fe-Cl1 88.50(9), N2-Fe-Cl1 167.86(10), N3-Fe-Cl1 91.92(9). The ellipsoids enclose 50 % of the electronic density.

To understand any further reactivity studies, the question of whether the structure is retained in solution must be considered. Within the dichloroiron(II) series of complexes with this kind of ligand, this point can be addressed by combining NMR, UV/Vis and molecular conductivity data.[20,21,26,27] In the present case, however, the ^{1}H NMR spectrum is uninformative, and one has to rely on UV/Vis and electrochemical techniques. The molecular conductivity ($\Lambda = 39$ S cm^2 mol^{-1}) was measured in CH$_3$CN, and its value indicates that the complex remains undissociated in solution. This observation strongly suggests that the geometry of **1** is retained in solution.

Cyclic voltammetry experiments were carried out within the range expected for reduction of iron(III) to iron(II). As shown in Figure 1, a reversible wave is observed at $E_{1/2} =$ 10 mV (vs. SCE). This suggests that no major structural change is observed upon reduction of compound **1**.

Metalation of BCATTPA with FeCl$_2$: This reaction was carried out following previously reported methods, under strictly anaerobic conditions, in THF or CH$_3$CN. Iron(II) chloride reacts immediately with the ligand to produce an intense orange color. The compound formed (**2**) is one of the most oxygen-sensitive dichloroiron(II) complexes that we have ever come across within the series of complexes of substituted TPA ligands—it becomes dark violet within a fraction of a second upon exposure to air, even in the solid state. Unfortunately, we have not yet been able to isolate crystals suitable for an X-ray diffraction analysis, therefore the structure of **2** shown in Scheme 1 is based on spectroscopic data only.

The UV/Vis spectrum (Figure 3) contains, together with the ligand-centered transitions observed at $\lambda_1 = 260$ and 290 nm ($\varepsilon_2 = 11.72\times10^3$ mmol cm^2 and 13.05×10^3 mmol cm^2, respectively), two absorptions at $\lambda = 355$ and 446 nm ($\varepsilon = 2.98\times10^3$ mmol cm^2 and 0.72×10^3 mmol cm^2, respectively).

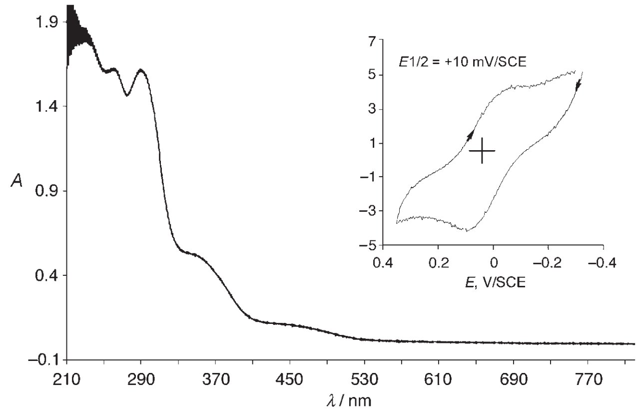


Figure 3. UV/Vis spectrum of [(BCATTPA)Fe^{II}Cl$_2$] (**2**) in CH$_3$CN at room temperature. Inset: cyclic voltammogram of the same compound in CH$_3$CN (0.1 M (TBA)PF$_6$, 200 mV s^{-1}, scan to positive values).

Both the wavelength and intensity features of the absorption at 446 nm strongly suggest that it corresponds to a MLCT Fe$^{II}\rightarrow$N$_{(py)}$ transition for which the ligand coordinates in a so-called "hypodentate" mode, that is, in a tridentate (κ^3-*N*) fashion.[20,28] The absorption at 355 nm is absent from the spectrum of any other simple dichloroiron(II) complex reported in the literature, such as [(TPA)FeCl$_2$] for instance, and is therefore assigned to a LMCT phenolate→Fe^{II} transition, thereby indicating that, as is the case for **1**, the catechol coordinates to the metal.

Unlike the iron(III) derivative, paramagnetically shifted signals appear in the ^{1}H NMR spectrum of **2**. Relatively sharp signals with full widths at half-height (FWHHs) of between 120 and 150 Hz are observed at $\delta = 47$, 46, and 18 ppm, reminiscent of coordinated β-β′ pyridyl protons in an octahedral geometry.[20] Other broad resonances with FWHHs of more than 300 Hz are observed at $\delta = 127$, 50, 35, 20, and −7 ppm. The presence of moderately broadened signals in the diamagnetic region supports the "hypodentate" coordination of the ligand; these resonances are assigned to protons belonging to the uncoordinated arm of the ligand. The ^{1}H NMR spectrum is given in the Supporting Information.

The molecular conductivity ($\Lambda = 107$ S cm^2 mol^{-1}) was measured in CH$_3$CN and its value indicates an ionic behavior in solution, in line with the presence of a singly charged species.[29] The cyclic voltammetric behavior was also investigated and, interestingly, the same wave as already seen with the iron(III) compound **1** was observed ($E_{1/2} = 10$ mV vs. SCE; Figure 3).

To summarize, we have observed: i) coordination of the ligand in a tridentate (κ^3-*N*) fashion by nitrogen atoms along with at least one phenolate, ii) a very likely octahedral geometry around the metal, iii) an ionic character of the compound, and iv) an identical Fe^{II}/Fe^{III} redox wave to that obtained with compound **1**. When viewed together, these observations do not leave many possibilities for a structure different to that drawn in Scheme 1, that is, two coordinated chloride anions and one phenolate from a catechol-substituted pyridine for a ligand coordinated in a "hypodentate" mode. Elemental analysis was expected to confirm this structure by direct fit of the percentages with those calculated. However, the extreme sensitivity of **2** to oxygen impeded any satisfactory result. However, we were at least able to see that the Cl/Fe molar ratio (2.0) indicates that two chloride ligands per iron atom are indeed present in the complex.

Reduction of [(BCATTPA)FeCl$_3$] with Zn/Hg: indirect characterization of 2: Because of the identical nature of the electrochemical data for **1** and **2**, we decided to reduce **1** with zinc amalgam, as shown in Scheme 1. The reaction was carried out under rigorously anaerobic conditions in CH$_3$CN or THF, and the medium, which was dark violet at the beginning, turned bright orange within a few tens of minutes. Filtration and precipitation afforded an orange solid whose ^{1}H NMR and UV/Vis spectroscopic data were identical to those obtained for an authentic sample of **2**. Obviously, going from the neutral molecule **3** to the charged compound **2′** requires the presence of a countercation. In this case it is likely to be zinc. The metal center is, however, unaffected by this cation. We therefore strongly believe that the structure of **2** drawn in Scheme 1 is the correct one.

Oxygenation of [(BCATTPA)FeCl$_2$]: As already mentioned above, **2** is extremely sensitive to dioxygen, even in the solid state, where the orange solid turns dark within a second. In solution this oxygenation reaction can be monitored by UV/Vis spectroscopy upon lowering the temperature to 263 K, as shown in Figure 4. The reaction is complete within one hour at this temperature, and no intermediate species could be detected.

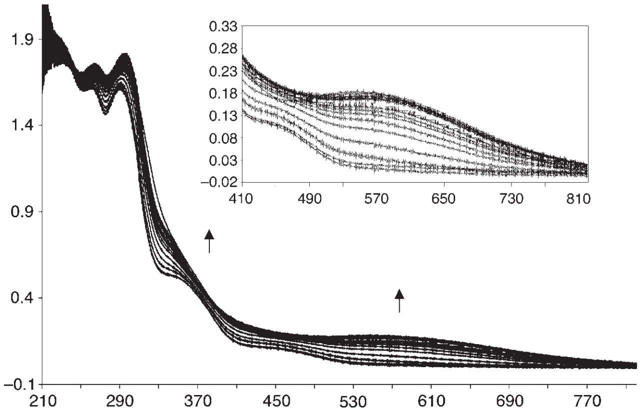


Figure 4. UV/Vis spectral changes observed upon oxygenation of [(BCATTPA)Fe^{II}Cl$_2$] (**2**) at 263 K in acetonitrile solution (one trace every five minutes for 75 minutes).

The most striking feature is the progressive appearance of a new broad absorption centered at $\lambda_3=590$ nm ($\varepsilon_3=1.10\times10^3$ mmol cm^2). This absorption is slightly blue shifted and more intense than that observed for compound **1**, but can also be assigned to a LMCT phenolate→Fe^{III} transition. The ligand-centered bands are also slightly red shifted to $\lambda_1=266$ nm and $\lambda_2=300$ nm ($\varepsilon_1=12.67\times10^3$ mmol cm^2 and $\varepsilon_2=14.64\times10^3$ mmol cm^2, respectively).

On a preparative scale, a black solid was obtained upon addition of diethyl ether to the oxygenated medium. The ^{1}H NMR spectrum of this compound displays no obvious signals in the paramagnetic region. Unlike **1**, nothing suggesting that any uncoordinated fragment is present could be detected—only two broad and unresolved resonances were observed at $\delta=3$ and 1 ppm. The ^{1}H NMR spectrum is given in the Supporting Information section.

An X-ray diffraction analysis study showed that the reaction product (**3**) is a dinuclear species, as shown in Scheme 2.

Slow evaporation of the solvent from an acetonitrile solution of **3** afforded single crystals. An ORTEP diagram of the complex is shown in Figure 5 and the main geometrical features are detailed in Figure 6.

The molecular structure of compound **3** reveals the presence of two iron atoms for each ligand. Fe2 lies in an unusual seven-coordinate environment, with the tripod coordinating in a (κ^4-*N)* mode; one chloride ligand coordinates *trans* to a pyridine, and two bridging phenolates from the catechol substituents complete the coordination sphere. All Fe2−N distances are above 2.2 Å, with a maximum for the two equatorial pyridines (Fe2−N1 2.503, Fe2−N4 2.477 Å). The Fe–catecholato distances (Fe2−O2 2.066, Fe2−O3 2.024 Å) are consistent with the values expected for a bridging phenolate. The angles between two adjacent atoms in the equatorial plane do not differ much from the ideal value of 72°, with a minimum for N2-Fe2-N4 (68.06°) and a maximum for O2-Fe2-N1 (74.11°). The axial angle is defined by N3-Fe2-Cl2 (168.82°).

On the other hand, Fe1 lies in a severely distorted square-pyramidal environment with two long catechol–Fe bonds (Fe1−O2 2.057, Fe1−O3 2.029 Å), two short ones (Fe1−O1 1.887, Fe1−O4 1.906 Å), and an Fe1−Cl1 distance of 2.2407 Å. The distance between the two metal centers is 3.281 Å.

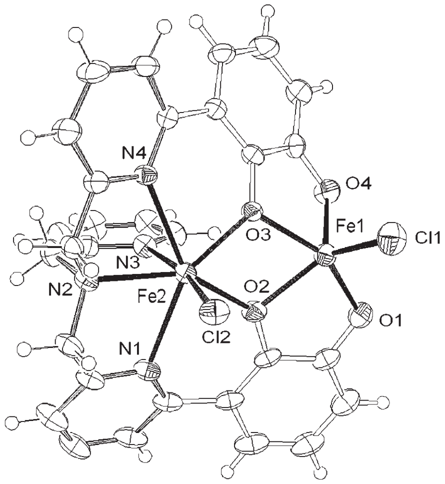
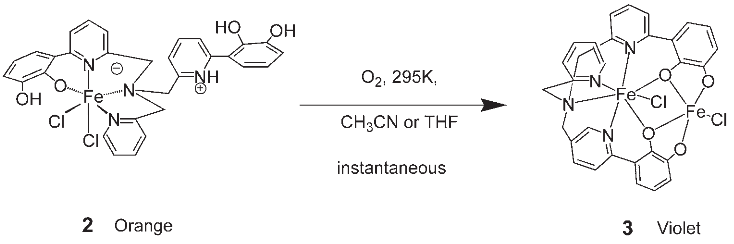


Figure 5. Structure of [(BCATTPA)Fe$^{III}_2$Cl$_2$] (**3**; ORTEP diagram showing a partial numbering scheme). Selected bond lengths [Å]: Fe2−N1 2.503(4), Fe2−N2 2.246(4), Fe2−N4 2.477(4), Fe2−O3 2.024(3), Fe2−O2 2.066(3), Fe2−Cl2 2.2781(13), Fe2−N3 2.103(4), Fe1−O2 2.057(3), Fe1−O3 2.029(3), Fe1−O4 1.906(3), Fe1−O1 1.887(3), Fe1−Cl1 2.2407(15), Fe1−Fe2 3.281(4). The ellipsoids enclose 50% of the electronic density.



Scheme 2. Oxygenation of [(BCATTPA)FeCl$_2$] (**2**).

The present work reports some preliminary coordination chemistry of FeCl$_3$ and FeCl$_2$ with a ligand that contains two different coordination sites. We expected that the presence of two catechol moieties and nitrogen-containing bases within the same ligand would allow coordination of the metal to the "hard" catechol site and leave the tripod free (or at least protonated, with the nitrogen atoms acting as bases). However, a "normal" coordination of the TPA tripod was observed, although with one chloride ion being replaced by a phenolato group from the substituent. The structure of **1** in the solid state indicates that the ligand coordinates in a tridentate (κ^3-*N*) fashion, with a dangling substituted pyridine. This coordination mode is now well established in the chemistry of substituted TPA ligands and obviously reflects a gain in stability with respect to a more sterically hindered environment.[12,24,30] The ^{1}H NMR spectra of the FeCl$_3$ complexes generally display broad and unresolved signals in the paramagnetic region.[24,25] Complex **1**, with an almost silent trace, is no exception to this rule. Uncoordinated substituents of the tripod can, however, be observed as broadened resonances in the diamagnetic region, thus indicating that the geometry is retained in solution. The very low value for the molecular conductivity also supports this. Electrochemical studies carried out on FeCl$_3$ and FeCl$_2$ complexes of simple TPA derivatives generally display an Fe^{III}/Fe^{II} wave at markedly positive values.[25,31] The presence of an anionic ligand can significantly lower the corresponding potential, with consequences for the reactivity towards dioxygen, for instance. In the

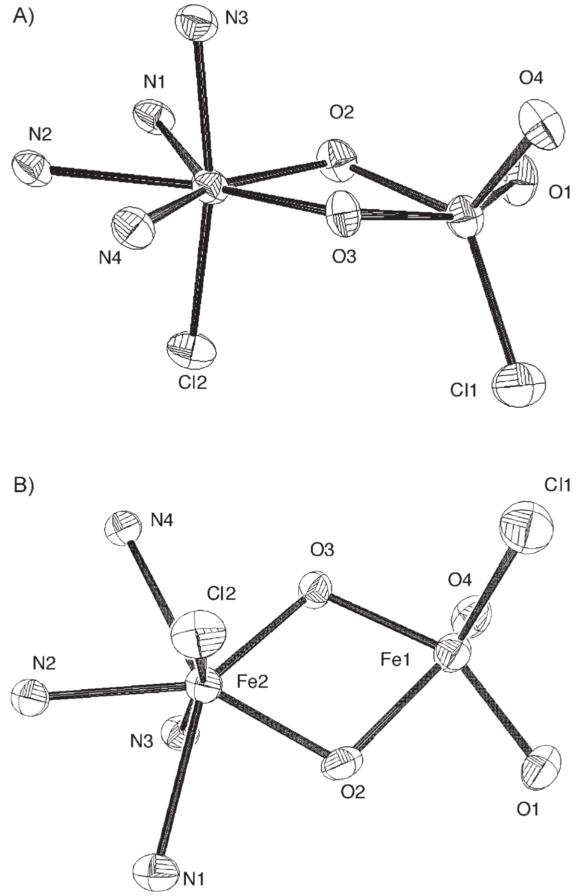


Figure 6. Side (A) and bottom (B) views of the coordination environment in [(BCATTPA)$Fe^{III}_2Cl_2$] (**3**). Selected bond angles [°]: N3-Fe2-Cl2 168.82(11), N1-Fe2-N2 72.00(14), N2-Fe2-N4 68.06(14), N4-Fe2-O3 73.01(14), O3-Fe2-O2 71.93(12), O2-Fe2-N1 74.11(14), O2-Fe1-O3 72.03(12), O3-Fe1-O4 83.21(13), O4-Fe1-O1 103.09(15), O1-Fe1-O2 81.33(14), Cl1-Fe1-O2 129.89(10), Cl1-Fe1-O3 99.59(9), Cl1-Fe1-O4 110.00(12), Cl1-Fe1-O1 103.30(12).

present case the redox wave is reversible, and the value of 10 mV (vs. SCE) that we observe, although still positive, is not too far from the value of −38 mV found for [Fe(BPG)Cl_2], another complex in which a carboxylate substituent binds to the metal with a di(pyridylmethyl)amine environment.[25]

Unlike $FeCl_3$, coordination of $FeCl_2$ to the nitrogen-containing part of the ligand was expected. In addition to the common spectroscopic features observed for dichloroiron(II) complexes with simple TPA ligands, complex **2** displays additional patterns (LMCT absorption in the UV/Vis spectrum; ^1H NMR spectrum) that indicate that a phenolate is coordinated, leaving one substituted pyridyl arm uncoordinated, with the metal center lying in an pseudo-octahedral environment. The molecular conductivity value indicates that **2** is a charged molecule, in line with our expectation of coordination of two chloride anions and a phenolate. This requires a pyridyl unit to be protonated, as drawn in Scheme 1. At this point we needed a structural confirmation. The fact that **1** and **2** exhibit an identical reversible cyclic voltammogram in the potential range corresponding to the Fe^{II}/Fe^{III} couple led us to suspect that their coordination environments might be similar, at least at the metal center. Confirmation of this hypothesis came from reduction of **1** with Zn/Hg, as complex **2′** was obtained.

With respect to activation of dioxygen, those mononuclear iron(II) TPA derivatives that have been found to react rapidly with dioxygen are either complexes in which the metal is coordinated to a noninnocent ligand or derivatives with a coordinatively unsaturated environment at the metal.[2,20,21,30] An iron(II)–TPA complex in which a thiolate is coordinated to the metal has been found to react rapidly with dioxygen.[32] The redox potential for this complex is not available, but as it is a cationic species the value is likely to be positive. In fact, the metal ion is coordinatively unsaturated, and the spectroscopic detection of an intermediate led the authors to postulate a mechanism similar to that published a long time ago in the chemistry of porphyrins.[33] Subsequently, we reported the formation of μ-oxo dimers by reaction of dioxygen with dichloroiron(II) complexes. The fact that all complexes exhibit a positive Fe^{II}/Fe^{III} couple, which makes outer sphere reduction of dioxygen unlikely, is noteworthy.[21,31] A mechanism similar to that occurring within the chemistry of porphyrins was also postulated. In our hands, complex **2** is certainly the one that is the most difficult to handle in the TPA series—it becomes dark immediately, even in the solid state. This is probably due to the anionic character of the metal center in **2**, which actually decreases the redox potential of the Fe^{II}/Fe^{III} couple. No intermediate is detected, and we measure a redox couple close to zero. The potential of the first reduction of molecular dioxygen is negative ($E° = -0.73$ V vs. SCE in DMSO), although this value is extremely dependant on the conditions, especially organic solvents with different dielectric constants and/or the presence or not of protons, and can be shifted to less negative values.[34,35] In our case, we have no spectroscopic evidence that dioxygen coordinates and cannot argue this point, although we believe that the low potential of the metal center, together with the presence of accessible protons from the catechol, might induce reduction of dioxygen to superoxide. Superoxide is known to react with metal salts, sometimes leading to the formation of metal peroxides.[35,36] In the chemistry of metalloporphyrins, the presence of amido residues close to the coordination center can even stabilize such complexes.[37] In the present case, catechols definitely provide acidic protons that would react with the superoxide ion. As a consequence, the free hydroxy group of the ligand is likely to be deprotonated, yielding the highly reactive $HO_2\cdot$ radical and leaving no chance for any putative intermediate to be detected.

Formation of **3** from **2** requires either decoordination or decomposition of one ligand. In any case, the reaction is very fast and is perfectly reproducible, the amount of oxidized material recovered being constant over a series of more than ten experiments. Analysis of the work-up solvents showed that no BCATTPA was present, only decomposition products. Whereas free ligand could be recovered by oxygenation of the iron(II) complex in the fluorinated TPA series,[21] the present result suggests that the formation of the final species proceeds via a different mechanism, and supports the formation of the reactive $HO_2^{\cdot}$ radical. In general, μ-oxo dinuclear complexes are obtained upon reaction of dichloroiron(II) species with molecular dioxygen or organic peroxides.[21,38] The present situation, however, is different: because of the presence of protons and radicals, the oxygenation conditions are more drastic and lead to some ligand decomposition. As a consequence, free iron(III) is generated and is trapped by the catechol substituents.

Only a few examples can be found in literature where the metal in iron(III) complexes lies in a seven-coordinate environment. In most of these cases, the ligands are potentially penta- or even heptadentate.[39–41] The occurrence of such a geometry in our case was unexpected, and means that, to the best of our knowledge, compound **3** is the only example of a seven-coordinate iron(III) derivative in the chemistry of TPAs.

In conclusion, the new BCATTPA ligand stabilizes coordination of iron(III) and iron(II) chloride at the nitrogen-containing site. One hydroxy group from the catechol substituents is involved in the coordination, which leaves one substituted pyridyl arm uncoordinated. Coordination of an anionic phenol residue enhances the kinetics of reaction with O_2, and the presence of free phenol protons is certainly not innocent as it induces a different reactivity to that observed with neutral derivatives. A radical-based mechanism is very likely, but this point still needs to be confirmed. Finally, and to the best of our knowledge, the dinuclear compound whose structure is reported here is the first example of a seven-coordinate iron(III) derivative within the chemistry of tris(2-pyridylmethyl)amine ligands.

Experimental Section

General: ^{1}H NMR spectra were recorded in CD_3CN for the complexes and $CDCl_3$ for the ligands at ambient temperature on a Bruker AC 300 spectrometer at 300.1300 MHz using the residual signal of CD_2HCN ($CHCl_3$) as a reference for calibration.

The UV/Vis spectra were recorded with a Varian Cary 05 E UV/Vis NIR spectrophotometer equipped with an Oxford instrument DN1704 cryostat, using optically transparent Schlenk cells.

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

Cyclic voltammetry measurements were performed with a PAR 173 A potentiostat in a 0.1 M acetonitrile solution of $(TBA)PF_6$ (supporting electrolyte), using platinum electrodes and the saturated calomel electrode as reference.

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

Bis[2-(2,3-Dimethoxyphenyl)-6-pyridylmethyl](2-pyridylmethyl)amine (BDMPTPA): Br_2TPA[5] (800 mg, 1.78 mmol) and $[Pd(PPh_3)_4]$ (140 mg, 0.12 mmol) were suspended in degassed toluene (100 mL) under argon. Sodium carbonate (7.2 mL of a 2 M aqueous solution) and commercially available 2,3-dimethoxyphenylboronic acid (1 g, 5.5 mmol) dissolved in ethanol (5 mL) were added under argon. The reaction mixture was refluxed under argon for 24 h. The orange-colored solution was then evaporated to dryness and the remaining oil was dissolved in dichloromethane. This organic phase was washed with aqueous sodium carbonate and distilled water, and dried over magnesium sulfate. After filtration and concentration by rotary evaporation, the medium was deposited at the top of a column filled with aluminum oxide and mounted with dichloromethane. The column was washed with diethyl ether, and the compound eluted with a 75/25 diethyl ether/acetone mixture. A pale-yellow oil (837 mg, 84 %) was obtained. Elemental analysis calcd (%) for $C_{34}H_{34}N_4O_4$: C 72.60, H 6.05; found: C 72.85, H 6.21; ^{1}H NMR ($CDCl_3$): $\delta = 8.5$ (d, $^3J = 4.9$ Hz, 1 H_{arom}), 7.7–7.5 (m, 6 H_{arom}), 7.4–6.8 (m, 9 H_{arom}), 4.0 (s, 4 H), 3.9 (s, 2 H), 3.8 (s, 6 H), 3.6 ppm (s, 6 H).

Bis[2-(2,3-dihydroxyphenyl)-6-pyridylmethyl)(2-pyridylmethyl)amine (BCATTPA): BBr_3 (10 mL of a 0.8 M CH_2Cl_2 solution) was added, under argon, to BDMPTPA (680 mg, 1.21 mmol) dissolved in CH_2Cl_2 (100 mL) in a Schlenk tube. The medium was refluxed for 4 h under argon. The reaction mixture was then poured into methanol (200 mL), evaporated to dryness on a rotary evaporator, and five such cycles of addition of methanol and evaporation of solvent were performed in order to eliminate any volatile compounds. Finally, the brownish oil was suspended in dichloromethane. This suspension was extracted with dilute hydrochloric acid at pH 1. The acidic phase was washed several times with dichloromethane, and the organic layer discarded. The pH of the aqueous phase was then raised to 9, at which a pale yellow compound could be extracted with dichloromethane. Addition of hexane, followed by evaporation, yielded a light brownish solid (350 mg, 57.7 %). The ^{1}H NMR spectrum indicated that this compound was clean. Recrystallization from dichloromethane/diethyl ether gave the analytically pure ligand as a yellow, microcrystalline powder. Elemental analysis calcd (%) for $C_{30}H_{26}N_4O_4$: C 71.14, H 5.14; found: C 71.45, H 5.51; ^{1}H NMR ($CDCl_3$): $\delta = 12.8$ (br s, 2 OH), 5.9 (s, 2 OH), 8.5 (d, $^3J = 4.7$ Hz, 1 H_{arom}), 7.9–7.6 (m, 6 H_{arom}), 7.5–6.7 (m, 9 H_{arom}), 4.0 ppm (s, 6 H).

Metalation of BCATTPA with $FeCl_3$: Preparation of 1: A solution of BCATTPA (100 mg, 0.2 mmol) in THF (50 mL) was added to a THF solution (100 mL) of anhydrous $FeCl_3$ (32.5 mg, 0.2 mmol). THF or acetonitrile can be equally used as reaction solvent. The medium was stirred for 16 h. It was then concentrated under vacuum, and precipitation was induced by addition of diethyl ether. Subsequent solubilization and precipitation with diethyl ether yielded a dark violet solid (120 mg, yield 90 %). Elemental analysis calcd (%) for $C_{30}H_{25}Cl_2FeN_4O_4$: C 56.96, H 3.95; found: C 56.58, H 3.52; UV/Vis (room temperature): λ (ε) = 263.2 (13.67), 297.5 (13.01), 354.0 (shoulder, close to 4), 617.0 nm (0.82 [$\times 10^3$ mmol^{-1} cm^2]). MS FAB$^+$: m/z 560 (BCATTPAFe$^+$). The ^{1}H NMR spectrum is supplied in the Supporting Information section. No well-defined signals can be observed in the paramagnetic region. Molecular conductivity (0.39 mM, 295 K): $\Lambda = 38$ S cm^2 mol^{-1}. Cyclic voltammetry (CH_3CN, 0.1 M $(TBA)PF_6$, 200 mV s^{-1}, room temp.): $E_{1/2} = 10$ mV (vs. SCE), along with other waves at $E_{1/2} = 460$, $E_a = 1050$, and $E_a = 1300$. IR (Nujol): $\nu_{OH} = 3412$ cm^{-1}.

Metalation of BCATTPA by $FeCl_2$: preparation of 2: This reaction was carried out according to an already published procedure.[20] THF or acetonitrile can be equally used as reaction solvent. The bright orange compound obtained with a yield of 85 to 90 % is extremely air sensitive, even in the solid state. We believe that this is the reason why a satisfactory elemental analysis could not be obtained. Elemental analysis calcd (%) for $C_{30}H_{26}Cl_2FeN_4O_4$: C 56.87, H 4.11, Cl 11.21, Fe 8.85; found: C 51.97, H 3.75, Cl 8.56, Fe 6.52; C/Cl, Cl/Fe, C/Fe, H/Cl ratios [molar]: calcd: 5.07 [15.0], 1.26 [2.0], 6.42 [30.0], 0.36 [13.0]; found: 5.98 [17.7], 1.31 [2.0], 7.85 [36], 0.44 [15.6]; UV/Vis (room temperature): λ (ε) = 260.0 (11.72), 290.0 (13.05), 355.0 (2.98), 446.0 nm (0.72 [$\times 10^3$ mmol^{-1} cm^2]); ^{1}H NMR (CD_3CN, room temp.): δ (FWHH) = 127 (br), 50.2 (305 Hz), 47.7 (150), 46.7 (129), 35.6 (452), 20.4 (312), 17.7 (128), −6.9 (342), 9.0–3.0 ppm (sharp signals, uncooordinated catecholatopyridyl protons). The spectrum is supplied in the Supporting Information. Molecular conductivity (0.09 mM, 295 K): $\Lambda = 107$ S cm^2 mol^{-1}. Cyclic voltammetry (CH_3CN, 0.1 M $(TBA)PF_6$, 200 mV s^{-1}, room temperature): $E_{1/2} = 10$ mV (vs. SCE). We also observed the presence of other waves at potentials similar to those reported for **1** ($E_{1/2} = 460$, $E_a = 929$, $E_a = 1300$).

Reduction of 1 with Zn/Hg: A solution of **1** in dry and degassed CH_3CN (100 mg in 100 mL) was transferred into a Schlenk tube containing a few drops of 10% Zn/Hg. The medium was stirred and the color turned bright orange within 10 min. It was then filtered, concentrated, and a bright orange solid was obtained upon addition of diethyl ether. The solid was washed several times with dry and degassed diethyl ether and dried under vacuum. All spectroscopic features (UV/Vis, cyclic voltammetry, ^{1}H NMR) are identical to those obtained from a clean sample of **2**.

Oxygenation of 2: preparation of 3: Complex **2** (50 mg) was dissolved in dry and degassed CH_3CN (50 mL). Upon exposure to dry dioxygen, the medium turned dark violet within a fraction of a second. The solution was concentrated and a black solid was obtained upon addition of diethyl ether. The solid was washed with three portions (50 mL each) of diethyl ether, dried under vacuum, and recrystallized from CH_3CN/diethyl ether to give 20 mg of product The three portions of diethyl ether used for washing were collected, the solvent evaporated. The corresponding ^{1}H NMR spectrum showed no evidence for the presence of any free ligand amongst the numerous and unassignable signals in the range $\delta =$ 3–8 ppm. Elemental analysis calcd (%) for $C_{30}H_{22}Cl_2Fe_2N_4O_4$: C 52.55, H 3.21; found: C 52.90, H 3.62; UV/Vis (room temperature): λ (ε) = 266.0 (12.67), 300.0 (14.64), 350.0 (shoulder), 590.0 nm (1.10[$\times 10^3$ mmol^{-1}cm^2]). The ^{1}H NMR spectrum is supplied in the Supporting Information. No well defined signals can be observed in the paramagnetic region.

X-ray analysis

Single crystals of $[(BCATTPA)Fe^{III}Cl_2]\cdot Et_2O$ and $[(BCATTPA)Fe^{III}_2Cl_2]\cdot CH_3CN$ were mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo_{K\alpha}$ radiation; $\lambda = 0.71073$ Å). Quantitative data were obtained at 173 K for both complexes. The complete conditions of data collection (Denzo software) and structure refinements are given as Supporting Information. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods (SIR97) and refined against *F*2 using the SHELXL97 software suite (*Kappa CCD Operation Manual*, Nonius B.V., Delft, The Netherlands, **1997**; G. M. Sheldrick, *SHELXL97*, Program for the refinement of crystal structures, University of Göttingen, Germany, **1997**). The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Crystal data for $[(BCATTPA)Fe^{III}Cl_2]\cdot Et_2O$ (1·Et_2O): Violet crystals, $0.10 \times 0.10 \times 0.10$ mm^3; $C_{34}H_{35}Cl_2FeN_4O_5$, $M = 706.41$ g mol^{-1}. Monoclinic, space group $P2_1/c$, $a = 14.360(5)$, $b = 13.589(5)$, $c = 16.874(5)$ Å, $\beta = 94.654(5)°$, $V = 3281.9(19)$ Å^3, $\rho_{calcd} = 1.430$ g cm^{-3}, $Z = 4$, $1.42° < \theta < 29.17°$. Of 8835 total reflections, 4546 were considered to be observed [$I > 2\sigma(I)$], with 405 parameters. Final results: $R = 0.0623$ and $R_w = 0.1553$; GOF = 0.879; maximum residual electronic density: 1.068; minimum residual electronic density: −0.913.

Crystal data for $[(BCATTPA)Fe^{III}_2Cl_2]\cdot CH_3CN$ (3·CH_3CN): Dark red crystals, $0.10 \times 0.07 \times 0.03$ mm^3; $C_{32}H_{25}Cl_2Fe_2N_4O_5$, $M = 726.17$ g mol^{-1}. Orthorhombic, space group $P2_12_12_1$, $a = 12.6320(10)$, $b = 14.631(2)$, $c = 16.550(2)$ Å, $V = 3058.8(6)$ Å^3, $\rho_{calcd} = 1.577$ g cm^{-3}, $Z = 4$, $1.86° < \theta < 30.04°$. Of 8900 total reflections, 5877 were considered to be observed [$I > 2\sigma(I)$], with 406 parameters. Final results: $R = 0.0567$ and $R_w = 0.1218$; GOF = 0.936; Flack x: 0.00(2); maximum residual electronic density: 0.544; minimum residual electronic density: −0.717.

CCDC-298849 and CCDC-298850 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported as a collaborative action between CNRS (Project no. 17703-France) and CNRST (Project no. chimie 08/05-Morocco). Both organisations are gratefully acknowledged for their support. The authors thank Professor Richard Welter and Laboratoire DECOMET for the X-ray diffraction studies. We wish to give special thanks to Dr. Remy Louis, for his constant encouragement and support. The Institut de Chimie, CNRS and ULP are gratefully acknowledged for financial support.

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Received: February 28, 2006