The coordination chemistry of amine triphenolate tripod ligands with iron(III). Old organic compounds but new tripod ligands

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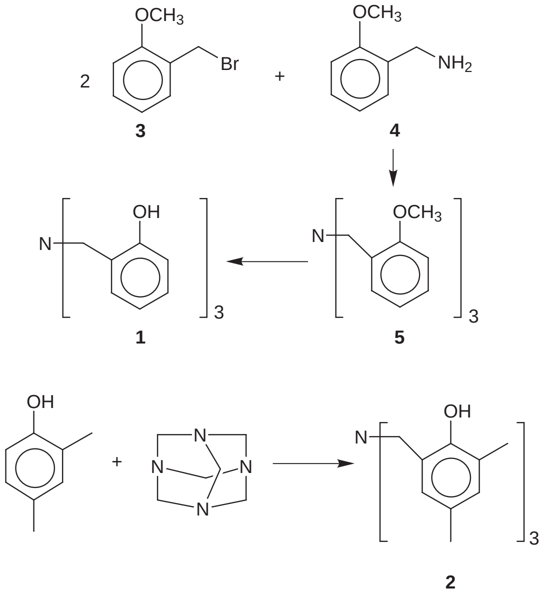
The coordination chemistry of new C_3 symmetric triphenolate amine tripod ligands has been demonstrated with Fe^{III}.

A key feature of the coordination chemistry of tripod ligands is their ability to divide the metal–ligand coordination sphere into non-labile sites and reactive sites. Saconni and the Florence school first demonstrated the rich coordination chemistry of tripod ligands in the 1960s and 1970s.[1,2] In the 1990s the chemistry of tripod ligands has undergone a renaissance.[3–5] We report the coordination chemistry of new polyphenolate amine tripod ligands: tris(2-hydroxybenzyl)amine (**1**) and tris(2-hydroxy-3,5-dimethylbenzyl)amine (**2**). Phenolate containing ligands are valuable in modeling the active sites of metal–tyrosine centers in metalloproteins[6] and homogeneous and heterogeneous catalysts.[7] Historically, the hydrochloride salt of **1** was the subject of its first and only report in 1922,[8] while the synthesis of **2** appeared in the literature in 1949.[9] The coordination chemistry of compounds **1** and **2** has never been previously reported.

Our route to **1,** which differs from the original synthesis, is outlined in Scheme 1. The reaction of 2 equiv. of 2-methoxybenzyl bromide[10] (**3**) with commercially available 2-methoxybenzylamine (**4**) in refluxing CH_3CN with added K_2CO_3 gives tris(2-methoxybenzyl)amine (**5**) in 80–85% yield. The methyl protecting groups are removed by refluxing **5** in toluene with 5 equiv. of $AlCl_3$ to give **1** in 70% yield. We were able to reproduce the synthesis of **2** by the one step Mannich reaction of 2,4-dimethylphenol with hexamethylenetetramine.[9] Since both **1** and **2**‡ were reported before the advent of modern spectroscopic techniques, the congruence of our compounds with the literature compounds was established by melting point comparisons.



Scheme 1

The reaction of the trilithium salt of **1** with $FeCl_3$ in the presence of 3 equiv. of 1-methylimidazole (1-Meim) in MeOH gave dark red crystals of $[Fe\{N(CH_2\text{-}o\text{-}C_6H_4O)_3\}(1\text{-Meim})]$ (**6**) in 65% yield. The structure of **6**, which was determined by X-ray crystallographic analysis§ (Fig. 1), consists of a trigonal bipyramidal structure with an N1–Fe–N2 angle of 173.4(1)°. The Fe atom is 0.045 Å out of the plane of the three oxygen donors toward the imidazole nitrogen. The FeO_3 plane shows small deviations from trigonal symmetry with O–Fe–O angles of 117.4(1) to 126.3(1)°. The average Fe–O bond distance [1.876(15) Å] is intermediate between the Fe–O in tetrahedral $[Fe^{III}(OC_6HMe_4\text{-}2,3,5,6)_4]^-$ [1.847(13) Å] and in octahedral Fe tris-catecholate complexes (2.02 Å).[11,12] The analogous compound, $[Fe\{N[CH_2\text{-}o\text{-}C_6H_2(OMe)_2\text{-}3,5]_3\}(1\text{-Meim})]$ (**7**), has also been characterized with ligand **2**.

The tripod ligand coordinates to the metal to generate a chiral C_3 conformation[13] with both enantiomeric structures present in the centric crystal lattice. These tripod ligands **1** and **2** differ from the well studied $N(CH_2CH_2OH)_3$ and $N(CH_2CO_2H)_3$ ligands in the phenolate *versus* alkoxide and carboxylate donors and by having six- *versus* five-membered metal ligand chelate rings. The aminetriphenolate ligand $N(o\text{-}C_6H_4O)_3$ and its coordination chemistry with Al have been reported.[14]

The thiol analog of **1** and its $[Fe^{III}\{N(CH_2\text{-}o\text{-}C_6H_4S)_3\}(1\text{-Meim})]$ complex has recently been reported.[15] The 0.43 Å change in Fe–O *versus* Fe–S bond distance reflects the difference in the ionic radii of S and O. The larger average Fe–O–C angle [134(1)°] in **6** *versus* the Fe–S–C [110(1)°] angle is

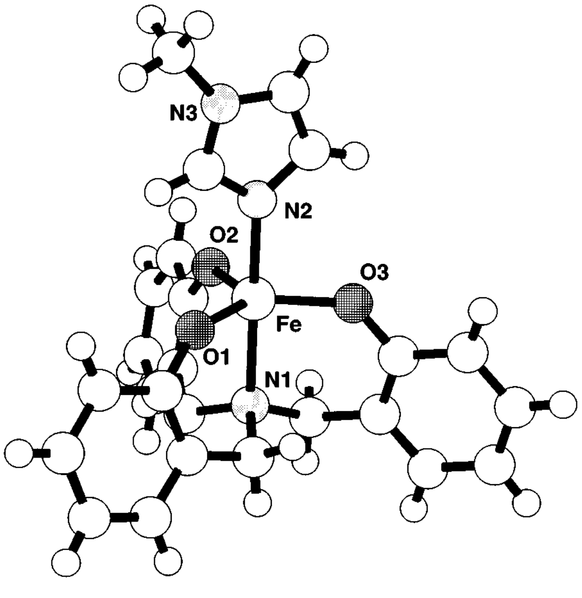


Fig. 1 Structural diagram for $[Fe\{N(CH_2\text{-}o\text{-}C_6H_4O)_3\}(1\text{-Meim})]$ (**6**). Selected distances (Å) and angles (°) Fe1–O1 1.881(3); Fe1–O2 1.888(3); Fe1–O3 1.859(3); Fe1–N1 2.191(3); Fe1–N2 2.090(4); O1–Fe1–O2–126.3(1); O1–Fe1–O3–117.4(1); O2–Fe1–O3 116.2(1); O1–Fe1–N1 87.1(1); O1–Fe1–N2 87.6(1); O2–Fe1–N1 88.9(1); O2–Fe1–N2 91.1(1); O3–Fe1–N1 89.9(1); O3–Fe1–N2 96.0(1); N1–Fe1–N2 173.4(1); Fe1–$O\text{–}C_{avg}$ 134(1).

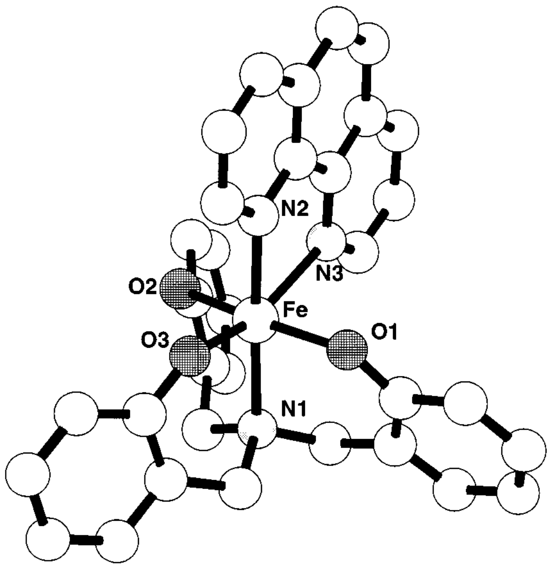


Fig. 2 Structural diagram for [Fe{N(CH_2-*o*-C_6H_4O)$_3$}(phen)] (**9**). Selected distances (Å) and angles (°): Fe1–O1 1.897(6); Fe1–O2 1.926(6); Fe1–O3 1.893(7); Fe1–N1 2.225(8); Fe1–N2 2.158(7); Fe1–N3 2.340(7); N1–Fe–O3 91.5(3); O3–Fe–N2 87.7(3); N2–Fe–N3 73.9(3); N3–Fe–N1 107.0(3); O1–Fe–O2 164.1(3); N–Fe–$O2_{avg}$ 88.4(3); N–Fe–$O1_{avg}$ 87.5(3); Fe–O–C_{avg} 128.5(7).

consistent with the known Fe^{III} coordination chemistry of thiolate and phenolate ligands.[11,16,17] In an attempt to prepare a four coordinate complex, the reaction of $Li_3N(CH_2$-*o*-$C_6H_4O)_3]$ with $FeCl_3$ was repeated in the absence of 1-Meim. However the X-ray structure§ of the product, [Fe{N(CH_2-*o*-C_6H_4O)$_3$}(DMF)] (**8**), revealed that a molecule of solvent was coordinated to the iron. The crystal of **8** is isomorphous and is essentially isostructural with **6**. The atomic positions of the non-hydrogen atoms of the DMF molecule are structurally equivalent to five of the atoms of the 1-Meim in **6**. The reaction of **8** with 1,10-phenanthroline in DMF followed by the addition of MeOH gave dark red crystals of [Fe{N(CH_2-*o*-C_6H_4O)$_3$}(phen)] (**9**) in 50% yield. The structure of **9**§ (Fig. 2) demonstrates that the tripod ligands can support an octahedral coordination center. The phen ligand has a distinctly asymmetric coordination with Fe–N2 2.158(7) Å and Fe–N3 2.340(7) Å distances. The distortion results from a short contact between a benzyl proton and the hydrogen atom *ortho* to N3.

Compounds **6–9** have magnetic moments indicative of high spin Fe^{3+} and have an intense phenolate to Fe charge transfer transition at 399 nm (ε = 7960 dm^3 mol^{-1} cm^{-1}), 422 (8320), 405 (9700), and 399 (7751) respectively.[18] A quasireversible Fe^{III}–Fe^{II} redox couple was observed in the cyclic voltammogram of **7** occurring at $E_{1/2} = -0.78$ V (ΔE = 107 mV) *versus* Ag/AgCl in DMF solution. Only irreversible oxidation processes were observed for all the compounds.[19]

The chemistry of these tripod ligands with other metal ions is under investigation. We thank the National Institutes of Health for support.

Notes and References

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‡ Compound **1**: ^1H NMR ([$^2H_6$]DMSO): δ 4.25 (s; 6 H; CH_2), 6.82 (t; 3 H; 3-H), 6.93 (d; 3 H; 1-H), 7.24 (m; 6 H; 3,4-H), 8.40 [s(br); 1 H; NH^+], 10.5 (s; 3 H; OH). FAB-MS: 335 [M^+]. Compound **2**: ^1H NMR ($CDCl_3$): δ 2.23 (s; 18 H; CH_3), 3.61 (s; 6 H; CH_2), 6.52 [s(br); 3 H; OH], 6.72 (s; 3 H; 6-H), 6.84 (s; 3 H; 4-H). FAB-MS: 419 [M^+].

§ *Crystal data* for **6** (crystallized from DMF–isopropanol): $FeC_{25}H_{24}N_3O_3$, M = 469.85, monoclinic, space group $P2_1/c$, a = 14.837(3), b = 9.410(8), c = 17.162(3) Å, β = 110.836(9)°, U = 2239(1) Å^3, Z = 4, Mo-Kα radiation (λ = 0.71073 Å), μ = 7.016 cm^{-1}. The structure was solved and refined using standard crystallographic techniques with $R(R_w)$ = 0.040(0.039) for 1993 observed reflections $I > 3\sigma(I)$. For **7**: $FeC_{31}H_{36}O_3N_3$, M = 554.49, monoclinic, space group $P2_1/n$, a = 16.409(4), b = 10.841(1), c = 17.082(4) Å, β = 110.37(1)°, U= 2849(1) Å^3, Z = 4, μ(Mo-Kα) = 7.127 cm^{-1}; $R(R_w)$ = 0.053(0.025) for 1733 reflections $I > 3\sigma(I)$. For **8**: $FeC_{24}H_{25}N_2O_4$, M = 449.3, monoclinic, space group $P2_1/c$, a = 14.670(3), b = 9.413(9), c = 16.807(3) Å, β = 108.054(8)°, U = 2206(1) Å^3, Z = 4, μ(Mo-Kα) = 5.65 cm^{-1}, $R(R_w)$ = 0.039(0.047) for 2888 observed reflections $I > 3\sigma(I)$. For **9** (crystallized from DMF–MeOH): $FeC_{33}H_{26}N_3O_3$, M = 568.44, monoclinic, space group $P2_1/c$, a = 12.042(3), b = 18.356(3), c = 12.713(4) Å, β = 110.02(1)°, U = 2640(2) Å^3, Z = 4, μ(Mo-Kα) = 6.087 cm^{-1}, $R(R_w)$ = 0.050(0.044) for 2888 observed reflections $I > 3\sigma(I)$. CCDC 182/921.

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