Synthesis and characterization of iron(III) complexes of a new ligand containing a potentially bridging carboxylate; structural characterization of a helical tetranuclear iron complex

Vladimir M. Trukhan,[a] Cortlandt G. Pierpont,[b] Kenneth B. Jensen,[c] Ebbe Nordlander[d] and Albert A. Shteinman[a]

[a] *Institute of Chemical Physics, 142432 Chernogolovka, Russia*
[b] *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, USA*
[c] *Department of Chemistry, Odense University, DK-5230 Odense M, Denmark*
[d] *Inorganic Chemistry 1, Chemical Center, Lund University, Box 124, S-221 00 Lund, Sweden.*
E-mail: Ebbe.Nordlander@inorg.lu.se

Received (in Basel) 21st December 1998, Accepted 9th April 1999

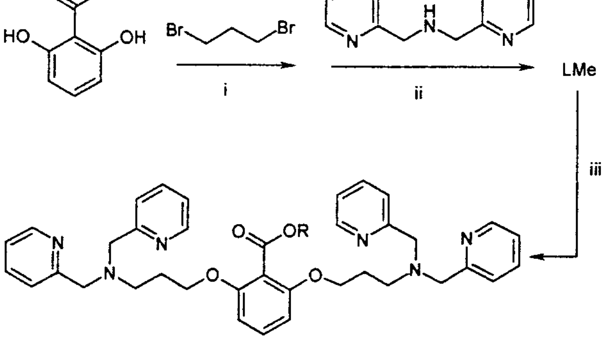
Reaction of the new polydentate ligand 2,6-bis{3-[*N*,*N*-di(2-pyridylmethyl)amino]propoxy}benzoic acid (LH) with $Fe(ClO_4)_3$ followed by addition of chloroacetic acid leads to the formation of the tetranuclear complex $[\{Fe_2OL(ClCH_2CO_2)_2\}_2](ClO_4)_4$, the crystal structure of which reveals that it consists of two $Fe^{III}_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2$ cores that are linked *via* the two L ligands in a helical structure, with the carboxylate moieties of the two ligands forming a hydrogen-bonded pair at the center of the helix.

A number of Fe_2O complexes have been synthesized to model the spectroscopic and structural properties of μ-oxo-μ-carboxylato diiron sites in proteins such as soluble methane monooxygenase (sMMO), ribonucleotide reductase (RNR) and hemerythrin.[1] In many cases, such biomimetic complexes have been found to be relatively unstable.[1,2] Efforts have therefore been made to prepare framework polydentate ligands that may stabilize complexes of this type,[3] examples include ligands in which multidentate nitrogen bases that bind to metals in a capping manner are linked to alkoxo or phenoxo groups capable of bridging two metals.[4] Binucleating polydentate ligands in which nitrogen donors are linked to a carboxylate moiety should be even more relevant for the modelling of μ-oxo-μ-carboxylate diiron sites because the carboxylate bridges in these enzymes are part of the protein.[5,6] Two successful[7,8] and two unsuccessful[9,10] attempts have been reported for the preparation of dinuclear iron complexes containing similar ligands; in these ligands, the carboxylate is one of the 'peripheral' donors at the terminus of a polydentate ligand. Here we report the synthesis of a new ligand containing a potentially bridging carboxylate moiety which is a part of the spacer that links two di(picolyl)amine groups. Reaction of this ligand with an iron(III) salt followed by addition of chloroacetic acid leads to the formation of a tetranuclear complex which consists of two linked $Fe^{III}_2(\mu\text{-}O)$ dimers.

The ligand 2,6-bis{3-[*N*,*N*-di(2-pyridylmethyl)amino]propoxy}benzoic acid (LH) has been prepared in a three-step synthesis with a general overall yield of *ca.* 60% (Scheme 1). The products LMe and LH (Scheme 1) have been identified by ^1H NMR spectroscopy, microanalysis and, in the case of LMe, FAB mass spectrometry. The ^1H NMR spectra of LMe and LH are identical except for the methyl resonance at δ 3.61 that is present in the spectrum of LMe.†

Reaction of LH with 2 equiv. of $Fe(ClO_4)_3$ in methanol leads to the formation of a green–yellow product, which has tentatively been assigned the formula $[Fe_2OL(H_2O)_2](ClO_4)_3$ **1** on the basis of UV–VIS, IR, ^1H NMR spectroscopy and microanalysis.‡ Addition of 10 equiv. of chloroacetic acid to a solution of **1** in ethanol results in the formation of a brown complex **2**. The UV–VIS and ^1H NMR spectra§ of complex **2** indicate that it contains a μ-oxo-bis-μ-carboxylate diiron core. The assignments of the ^1H NMR spectra of **1** and **2** are based on their similarities to the spectra of oxo-bridged diiron complexes of related ligands, *viz.* $\{PyCH_2\}_2N(CH_2)_nCO_2^-$ (n = 1,2).[11] All features in the NMR spectra of **1** and **2** appear in the range δ 0–28, indicative of relatively strong antiferromagnetic coupling between the iron atoms. There are broad features above δ 20 (PyCH_2 and *o*-Py protons), sharper peaks at δ 15–18 (*m*-Py protons), and a very sharp peak at δ *ca.* 6 (*p*-Py protons). In addition, there are sharp peaks of the spacer polymethylene chain at δ 3–9. However, the mass spectrum of **2** (*vide infra*) and the analytical data suggest that it is a tetranuclear complex (a 'dimer of dimers') rather than a simple diiron complex.

It was possible to grow crystals of **2** from a MeOH–MeCN solution. In order to confirm the proposed tetranuclear structure and to assess whether the carboxylate moiety of **2** acts as a bridge between the metals, the crystal structure of **2** was determined.¶ The molecular structure of **2** is shown in Fig. 1. The Fe–O–Fe moieties are bridged by two chloroacetates while the non-bridging facial positions are filled by two di(picolyl)amine moieties from two molecules of L so that the two L ligands link the two diiron–μ-oxo units. The average Fe–μ–oxo distance is 1.79 Å and the average Fe–O–Fe angle is 121.8°; the intra-dimer Fe-Fe distances are 3.102(4) Å [Fe(1)–Fe(2)] and 3.138(4) Å [Fe(3)–Fe(4)] while the interdimer Fe–Fe distances vary from *ca.* 10.5 Å to 10.8 Å . Complex **2** is structurally and, to some extent, chemically related to previously structurally characterized tetranuclear *bis*-Fe_2O species[12] but there are several features of the molecular structure of **2** that render it unique. The conformation of the linking ligands is such that the whole molecule acquires a helical shape; the dihedral angle between the Fe–O–Fe planes in **2** is 42.5°. The center of the helix is held together through the central carboxylates of the two



Scheme 1 Synthetic route to LMe and LH. *Reagents and conditions*: i, Me_2CO, K_2CO_3, 72 h, 94% yield; ii, Et_3N, 96 h, 77% yield; iii, KOH–EtOH–H_2O, 12 h, 84% yield.

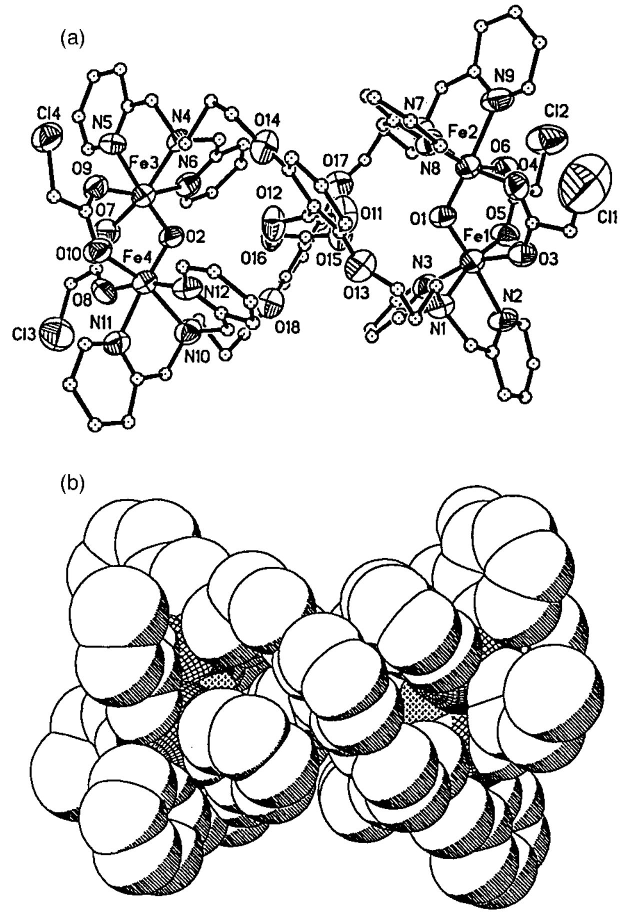


Fig. 1 (a) XP[13] and (b) space-filling drawings of the molecular structure of **2**, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 20% level. Selected distances (Å) and angles (°): Fe(1)–O(1) 1.776(6), Fe(2)–O(1) 1.787(6), Fe(3)–O(2) 1.794(6), Fe(4)–O(2) 1.786(6), Fe(1)–N(1) 2.196(8), Fe(1)–N(2) 2.215(9), Fe(1)–N(3) 2.100(10), Fe(1)–O(3) 2.028(8), Fe(1)–O(5) 2.013(7), Fe(1)–O(1)-Fe(2) 121.1(4), Fe(3)–O(2)–Fe(4)122.5(4).

L ligands which form a hydrogen-bonded pair, the O(11)–O(15) and O(12)–O(16) distances are 2.61 and 2.60 Å, respectively. It is usually observed that the tertiary nitrogen atoms of di(picolyl)amines coordinate *trans* to the μ-oxo ligand in this type of diiron–oxo species but in **2**, the tertiary amines are coordinated *cis* to the oxo ligand and *trans* to one of the bridging carboxylates so that the apices by the bridging oxygens of the Fe_2O units point towards each other. It is likely that the 'girdle' that is formed by the hydrogen-bonded pair of central carboxylates prevents the two ligands from binding to the Fe_2O unit in the favoured coordination mode, instead they bind in the observed 'inverted' coordination mode.

Repeated attempts to detect the molecular ion of **2** by electrospray mass spectrometry (ESMS) have thus far proven unsuccessful. However, we do detect prominent peaks at *m/z* 952, 601 and 426; these peaks are consistent with the molecular formulation(s) $\{[Fe_4L_2(ClCH_2CO_2)_2](ClO_4)_{4-x}\}^{x+}$ (x = 2–4, respectively). Furthermore, we have prepared a number of other carboxylate derivatives of **1**. It appears that in solution, these iron–oxo carboxylate species are in equilibrium with other complexes of similar composition, the nature of which is currently under investigation. We are currently preparing a number of derivatives of LH containing other nitrogen donors and are attempting to use these ligands to synthesize structural and functional model complexes for the active sites of sMMO and RNR R2.

This research was supported by grants from the Russian Foundation for Basic Research (no. 97-03-32253), INTAS (no. 97-1289), the Swedish Natural Science Research Council (NFR) and the Royal Swedish Academy of Sciences. C. G. P. thanks the STINT foundation for financial support. We thank Professor Fred Menger and Prof. Jean-Pierre Tuchagues for useful synthetic information and Maria Johansson for assistance with the crystallographic data collection.

Notes and references

† LMe: ^1H NMR ($CDCl_3$, 25 °C): δ 8.50 (d, 4H, py-H$^\alpha$), 7.58 (t, 4H, py-H$^\beta$), 7.46 (d, 4H, py-H$^\delta$), 7.19 (t, 1H, Ar-H,*p*), 7.11 (t, 4H, py-H$^\eta$), 6.46 (d, 2H, Ar-H,*m*), 3.98 (t, 4H, OCH_2), 3.82 (s, 8H, pyCH_2N), 3.61 (s, 3H, OCH_3), 2.70 (t, 4H, NCH_2), 1.96 (t, 4H, CH_2). FAB-MS, *m/z* (rel. intensity, %): 647 (M, 100), 554 (M–CH_2py, 40), 448 (M − 2CH_2py, 45). Anal. $C_{38}H_{42}N_6O_4$. Calc.: C, 70.56; H, 6.55; N, 13.00. Found: C, 69.9; H, 6.85; N, 13.6%.

LH: ^1H NMR ($CDCl_3$, 25 °C): 8.50 (d, 4H, py-H$^\alpha$), 7.58 (t, 4H, py-H$^\beta$), 7.46 (d, 4H, py-H$^\delta$), 7.19 (t, 1H, Ar-H,*p*), 7.11 (t, 4H, py-H$^\eta$), 6.46 (d, 2H, Ar-H,*m*), 3.98 (t, 4H, OCH_2), 3.82 (s, 8H, pyCH_2N), 2.70 (t, 4H, NCH_2), 1.96 (t, 4H, CH_2). Anal. $C_{37}H_{40}N_6O_4$. Calc.: C, 70.23; H, 6.37; N, 13.28; Found: C, 70.57; H, 6.54; N, 12.99%.

‡ $[Fe_2OL(H_2O)_2](ClO_4)_3$ **1**: UV–VIS [MeCN; λ_{max}/nm (ε_M(Fe)dm^3 mol^{-1} cm^{-1})]: 220 (35000), 259 (20000), 330 (4000), 474 (659), 520sh (535), 724 (97). IR (KBr), ν/cm^{-1}:1608, 1541 (CO_2, as), 1463, 1419 (CO_2, s), 537 (Fe–O–Fe, s), 473. ^1H NMR (CD_3CN, 25 °C): δ 26 (*o*-py), 15.4, 14.0 (pyCH_2N), 11.6, 11.3 (*m*-py), 8.9, 8.6 (*m*-Ph), 8.0 (*p*-Ph), 7.3 (*p*-py), 6.7, 4.4, 3.9, 3.6 (CH_2). Anal. $C_{37}H_{43}Cl_3Fe_2N_6O_{19}$. Calc.: C, 40.63; H, 3.96; N, 7.68; Cl, 9.72; Found: C, 40.47, H, 4.10, N, 7.69; Cl, 10.20%.

§ $[\{Fe_2OL(ClCH_2CO_2)_2\}_2](ClO_4)_4$ **2**: UV–VIS [MeCN; λ_{max}/ nm (ε_M(Fe)/ dm^3 mol^{-1} cm^{-1}): 211 (23000), 245sh (15000), 344 (4200), 380sh (3100), 472 (840), 510 (730), 555sh (220), 721 (155). IR (KBr), ν/cm^{-1}: 1687 (CO_2H), 1607 (py), 1570 (CO_2, as), 1463, 1418 (CO_2, s), 536 (Fe–O–Fe). ^1H NMR (CD_3CN, 25 °C): δ 28 (*o*-py), 15.6 (pyCH_2N), 12.0 (*m*-py), 11.5 (O_2CC*H*Cl), 8.5 (*m*-Ph), 7.8 (*p*-Ph), 7.4 (*p*-py), 6.7, 5.4, 4.1 (CH_2).

¶ *Crystal data*: $C_{84}H_{80}Cl_8Fe_4N_{12}O_{36.75}$, brown, crystal dimensions 0.23 × 0.21 × 0.18 mm, M = 2352.60, triclinic, space group $P\bar{1}$ (no. 2), a = 16.4575(3), b = 17.8346(2), c = 19.3790(3) Å, α = 77.521(1), β = 89.245(1), γ = 86.432(1)°, U = 5542.9(2) Å^3, Z = 2, D_c = 1.410 Mg m^{-3}, μ = 0.788 mm^{-1}, $F(000)$ = 2404, 45710 reflections collected ($1.1 < \theta < 31.8°$) at 293(2) K, 31848 independent reflections used in the structure refinement [$F_o > 2\sigma(F_o)$], R_1 (F) = 0.0973, wR_2 (F^2) = 0.2047, goodness-of-fit (F^2) = 0.854. Data were collected with a Siemens SMART CCD area detector, using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å) from a Rigaku rotating anode X-ray generator. The intensity measurements were corrected for Lorentz, polarization and absorption effects. The positions of the metal atoms were found by direct methods,[13] and all the non-hydrogen atoms were located from difference Fourier syntheses. The hydrogen atoms were placed in calculated positions. A disorder in the orientations of the CH_2Cl groups of the chloroacetates containing Cl3A and Cl1A was detected and was successfully modelled; the conformations shown in Fig. 1 are favoured. The final refinement was carried out by full-matrix least-squares calculations[13] on F^2 and with anisotropic thermal parameters for all non-hydrogen atoms. CCDC 182/1215. See http://www.rsc.org/suppdata/cc/1999/1193/ for crystallographic files in .cif format.

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Communication 8/09888C