A hexanuclear iron(III) complex of a hexadentate fully conjugated diimine ligand derived from 1,4-diformyl-2,3-dihydroxybenzene†

Humphrey L. C. Feltham, David S. Larsen and Sally Brooker*

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A fully conjugated acyclic diimine ligand, H_4L^3, formed from 1,4-diformyl-2,3-dihydroxybenzene and 2-aminophenol, was reacted with iron(II) acetate to give the hexanuclear complex $[Fe^{III}_6(L^3)_4(\mu\text{-OMe})(\mu\text{-OH})(MeOH)_4]$ (2). Crystals of 2·ADPOX·7.5MeOH·H_2O, where ADPOX is 2-amino-10,10*a*-dihydro-3H-phenoxazin-3-one, were obtained by slow evaporation and the X-ray structure determination revealed that the six octahedral iron(III) ions are bridged by four fully-deprotonated $(L^3)^{4-}$ ligands that are arranged in a [2 × 2] grid-like arrangement relative to one another.

The synthesis of the dialdehyde 1,4-diformyl-2,3-dihydroxybenzene (**1**) was first reported in 2001[1] and, since then, the research groups of Nabeshima and MacLachlan have used **1** to prepare ligands for use in ion-discrimination,[2] self-assembly,[3] molecular devices[4] and macrocycle synthesis.[1,5] Prior to our work, all complexes of acyclic ligands derived from **1** contained at most four metal ions. Complexes of macrocyclic ligands derived from **1** were typically of diamagnetic metal ions, except in a few instances, in which case no structures were reported.[6] Large, polynuclear complexes of paramagnetic metal ions may have useful properties, including single molecule magnetism (SMM),[7] yet until our work only one, trimetallic, complex of a ligand derived from **1** had been magnetically scrutinized.[8]

In order to access large nuclearity polymetallic complexes[9] we have recently reported the use of **1** to prepare some new acyclic diimine ligands, including H_4L^1, H_4L^2 and H_4L^3 (Fig. 1), and the subsequent formation of hexa-, hepta- and dodecanuclear nickel(II) complexes of these ligands.[10] Here we report the results of the analogous complexations with iron(II) acetate in air.

Despite numerous attempts, the products obtained from reactions of H_4L^1 or H_4L^2 with $Fe(OAc)_2$ could not be crystallized. On the basis of data obtained from 'sporting methods'—ESI-MS, IR spectroscopy and elemental analysis—there was insufficient evidence to satisfactorily establish a structure for these products.

The ligand H_4L^3 (Fig. 1) was formed *in situ* in refluxing methanol as per the previously reported procedure.[10] Two equivalents of $Fe(OAc)_2$ in methanol were added dropwise to the ligand solution, resulting in a rapid colour change to black and the formation of a black precipitate. The precipitate was filtered off and the filtrate slowly evaporated, resulting in single crystals of $[Fe^{III}_6(L^3)_4(\mu\text{-OMe})(\mu\text{-OH})(MeOH)_4]$·ADPOX·7.5MeOH·$H_2O$ (**2**·ADPOX·7.5MeOH·H_2O), where ADPOX is 2-amino-10,10*a*-dihydro-3*H*-phenoxazin-3-one (Fig. 2). The formation of ADPOX by oxidation of 2-aminophenol has been reported before (Fig. 2, where ROH is EtOH and the oxidant is *p*-benzoquinone).[11] In the present case, the methanol reaction solution was refluxed in air, so presumably iron and/or oxygen from the air oxidized some of the 2-aminophenol, generating some ADPOX *in situ* (Fig. 2).

The reaction was repeated with the correct 3 : 2 M : L ratio for **2**, rather than the 2 : 1 ratio employed initially. Complex **2** precipitated from the reaction solution as an analytically pure black powder in 26% yield. The filtrate was concentrated *in vacuo* resulting in a second crop of black powder but microanalysis data indicated that this second crop was not **2** or **2**·ADPOX so it was discarded.

The complex crystallizes in the *P*-1 space group. The entirety of the complex and an ADPOX molecule are contained in the asymmetric unit (Fig. 3). All six Fe^{III} ions have octahedral geometries; four lie at the intersections of approximately perpendicular ligands (Fe1, Fe2, Fe5, Fe6). The complex has a grid-like [2 × 2] structure; two of the four ligands lie parallel to one another and the pair of remaining ligands lie roughly perpendicular to them (Fig. 3). Whilst two of the ligands are reasonably closely aligned with each other, and are only 3.5 Å apart (the distance between the centroids of the catecholate rings), in the other pair of planes the ligands are offset from each other and are 7.5 Å apart.

Both the catechol moiety and the phenol 'arms' of all four ligands are deprotonated, so the ligands are tetraanions, $(L^3)^{4-}$. A methoxide anion (O150) bridges Fe4 and Fe5, and a hydroxide anion (O100) bridges Fe2 and Fe3. No OAc anions

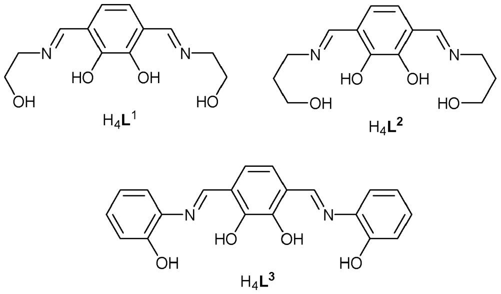

Fig. 1 The diimine ligands investigated by this research group.

Department of Chemistry and the MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: sbrooker@chemistry.otago.ac.nz; Fax: +64 3 479 7906; Tel: +64 3 479 7919

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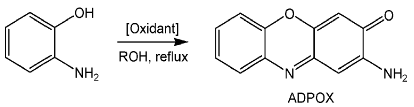

Fig. 2 Oxidation of 2-aminophenol in refluxing alcohol gives ADPOX.

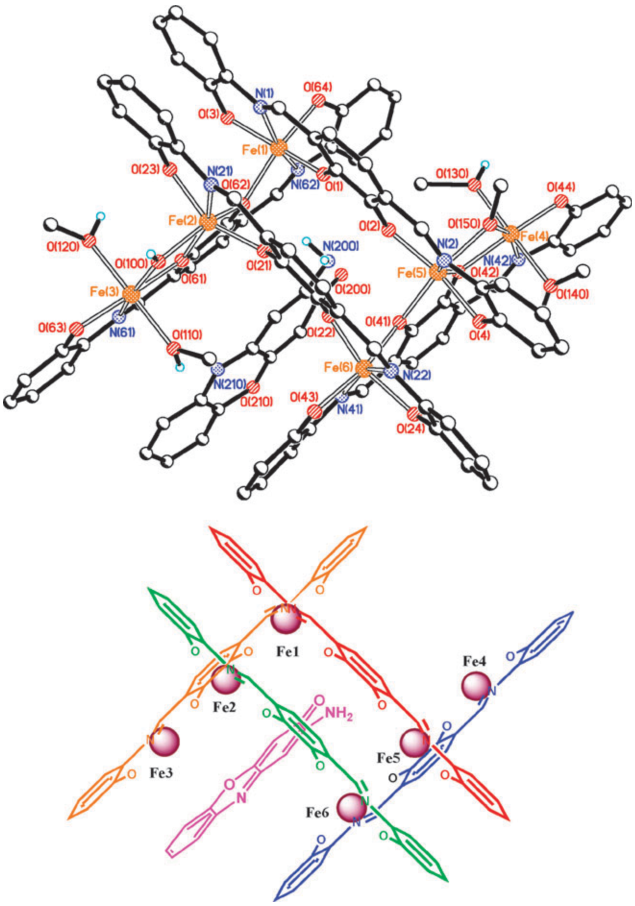

Fig. 3 (*Top*) The structure of **2**·ADPOX·7.5MeOH·H_2O. For clarity, solvent molecules and non-acidic hydrogen atoms have been omitted. (*Bottom*) Simplified schematic of the structure of **2**·ADPOX·7.5MeOH·H_2O showing the general arrangement of ligands and octahedral iron(III) centres, with solvent molecules omitted.

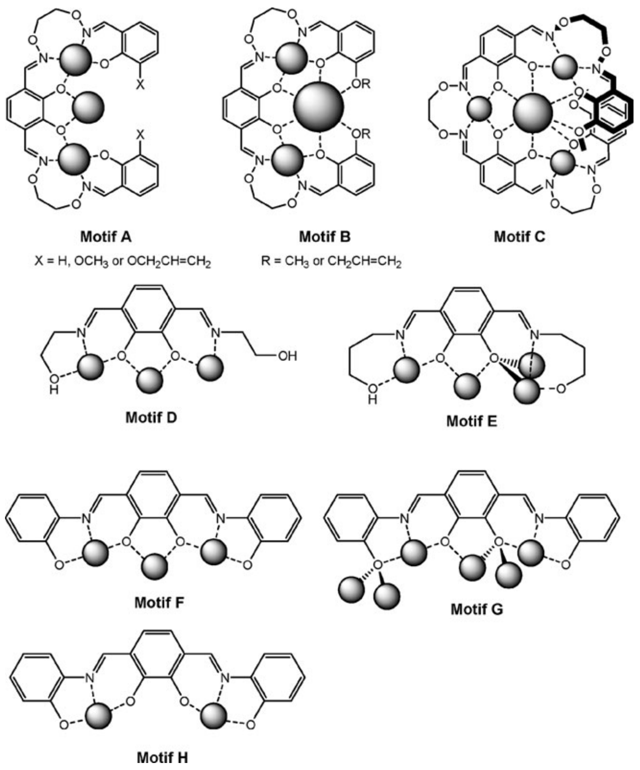

Fig. 4 The existing binding motifs A–G, and new binding motif H (seen here in **2**·ADPOX·7.5MeOH·H_2O), for a ligand derived from **1**.

are present either as coordinated ligands or as counterions. This overall anionic charge of −18 is consistent with all six Fe^{III} ions being in the +3 oxidation state. Two of the Fe^{III} ions (Fe1, Fe6) are in N_2O_4 donor sets and the remaining four are in NO_5 donor sets. Coordinated methanol molecules (O110, O120, O130 and O140) occupy the remaining sites on the Fe^{III} ions.

Interestingly, four catecholate oxygen atoms (O1, O2, O21 and O22) do not bridge metal ions but instead are each coordinated to one Fe^{III} ion only. This is a new binding mode for a catecholate oxygen atom of any ligand derived from **1** (Fig. 4, motif H), bringing the total number of binding modes crystallographically observed to date to eight.[9]

As was the case with the nickel(II) complexes of this new family of ligands (Fig. 1),[10] a high nuclearity cluster has formed with iron(III) and $H_4\mathbf{L}^3$. The structure of $[Ni^{II}_{12}(\mathbf{L}^3)_6(MeOH)_6(H_2O)_4]$—the complex resulting from reaction of $H_4\mathbf{L}^3$ with nickel(II) acetate, also in refluxing methanol[10]—bears some similarities to that of **2**·ADPOX·7.5MeOH·H_2O. Specifically, both structures feature pseudo grid-like arrangements of fully deprotonated ligands and metal ions (the Ni^{II}_{12} complex has six offset $(\mathbf{L}^4)^{3-}$ ligands in a pseudo [4 × 2] grid arrangement, with 8 of 12 nickel ions at the intersection of the ligands), and lack acetate ions. However, the present Fe^{III}_6 structure features binding motifs F and H (Fig. 4) whereas motifs F and G are present in the Ni^{II}_{12} complex. Binding motifs D and E, respectively, are observed in $[Ni^{II}_7(H_2\mathbf{L}^1)_4(OAc)_6(MeOH)_2]\cdot 7MeOH\cdot 4H_2O$ and $[Ni^{II}_6(H_2\mathbf{L}^2)_2(OAc)_6(\mu\text{-}OMe)_2(MeOH)_2]\cdot 0.5MeOH\cdot 0.5H_2O\cdot Et_2O$. In contrast to the complexes of $H_4\mathbf{L}^3$, both of these structures feature acetate ions, and neither has a grid-like arrangement of ligands.

In **2**·ADPOX·7.5MeOH·H_2O, as expected, the extensive conjugation within $(\mathbf{L}^3)^{4-}$ leads to a fairly planar conformation for the four ligands. However, the phenol arms of the two ligands that sandwich ADPOX are twisted out of the plane of the catecholate moieties by up to 26°. The other two ligands are also twisted slightly, but to a lesser extent (<13°).

Five complete and five half-occupancy methanol molecules of solvation, as well as two half-occupancy water molecules of solvation are present in the structure. Numerous hydrogen bonds are present in the lattice, and there are weak π–π stacking interactions between the aromatic ring of ADPOX and the closest phenolate rings of the ligands that sandwich it.

In summary the first structurally characterised iron complex of any ligand derived from 1,4-diformyl-2,3-dihydroxybenzene has been prepared and revealed to be hexanuclear. The catecholate oxygen atoms of two of the four ligands (those perpendicular to ADPOX) in the complex each bind to only one metal ion, a new binding motif for ligands derived from 1,4-diformyl-2,3-dihydroxybenzene (Fig. 4, motif H).

Experimental

$[Fe^{III}_6(L^3)_4(\mu\text{-OMe})(\mu\text{-OH})(MeOH)_4]$ (2)

To a refluxing MeOH (350 mL) solution of 2-aminophenol (0.130 g, 1.19 mmol), **1** (0.098 g, 0.590 mmol) in methanol (5 mL) was added. After five minutes, $Fe(OAc)_2$ (0.154 g, 0.885 mmol) in methanol (30 mL) was added dropwise to the orange solution, resulting in the formation of a black precipitate. After 30 minutes at reflux the suspension was allowed to cool. The black powder, $[Fe^{III}_6(\mathbf{L^3})_4(\mu\text{-OMe})(\mu\text{-OH})(MeOH)_4]$ (**2**), was collected, washed with cold methanol and air dried (0.071 g, 26% yield). Found: C, 54.15; H, 4.06; N, 5.93. Calc. for $Fe_6C_{85}H_{68}O_{22}N_8$: C, 54.06; H, 3.63; N, 5.93%. IR (KBr disk) ν/cm^{-1} = 3383 (b); 1601 (s); 1577 (s); 1472 (s); 1458 (s); 1387 (w); 1330 (s); 1296 (s); 1260 (w); 1225 (w); 1149 (w); 856 (w); 831 (w); 745 (s); 584 (b). Slow evaporation of the filtrate of a M : L 2 : 1 reaction yielded a few small crystals of **2**·ADPOX·7.5MeOH·H_2O suitable for X-ray crystallography.

X-Ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker Kappa Apex II area detector diffractometer at 92 K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were corrected for absorption using SCALE.[12] The structure was solved using SHELXS-97,[13] and refined against F^2 using all data by full matrix least squares techniques with SHELXL-97.[13] All non-hydrogen atoms were modelled anisotropically, except for the half-occupancy solvent molecules. Hydrogen atoms on carbon atoms were inserted at calculated positions and rode on the atoms to which they were attached. Hydrogen atoms on oxygen and nitrogen atoms were either found from the difference map or manually inserted at positions which optimized hydrogen bonding interactions. The regions comprising partial occupancy solvents of crystallization were modeled as well as possible with this dataset: nevertheless the highest residual peaks occurred in this region and this is reflected in the R_1 value. Further details are available in the CIF file.†

$[Fe^{III}_6(L^3)_4(\mu\text{-OMe})(\mu\text{-OH})(MeOH)_4]$·ADPOX·7.5MeOH·$H_2O$ M_r = 2359.11 g mol^{-1}, triclinic, P-1, a = 16.940(4) Å, b = 17.775(5) Å, c = 19.317(5) Å, α = 74.707(4)°, β = 80.588(7)°, γ = 75.863(7)°, V = 5410(2) Å^3, Z = 2, T = 92 K, 48 640 reflections collected, 17 749 independent reflections $R(\text{int})$ = 0.15, R_1 = 0.157 [$I > 2\sigma(I)$], w$R2$ = 0.356 (all data). CCDC 732073 contains the supplementary crystallographic data for this paper.

Acknowledgements

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