A Doubly bridged Binuclear Iron(III) Complex containing Inequivalent Metal Environments. Synthesis, Structure and Magnetism

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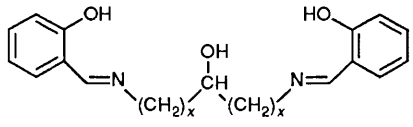
New doubly bridged iron(III) complexes $[Fe_2(L^A)(OMe)(Cl)_2MeOH]$ **1** and $[Fe_2(L^B)(OH)Cl_2]$ **2**, have been synthesized using the binucleating ligands H_3L^A = *N,N'*-bissalicylidene-1,3-diaminopropan-2-ol) and H_3L^B = *N,N'*-bissalicylideneimine-1,5-diaminopentan-3-ol; the crystal structure of **1** shows inequivalent coordination environments, a feature which is relevant to Fe geometries in iron–oxo proteins, and **1** shows an intramolecular antiferromagnetic *J* value of $-10.6\ cm^{-1}$.

Binuclear iron complexes continue to attract attention largely because of their use as models for iron–oxo proteins[1,2] and catalysts for the oxidation of hydrocarbons[3] but also because of attempts to correlate the geometries of the bridging moieties in crystalline species with the size and sign of the magnetic exchange *J parameter*.[2,4,5] The current state of Fe · · · Fe magnetostructural correlations has recently been summarized by Holm *et al.*[4] in order to make comparisons with the unexpected ferromagnetic coupling found in some di-μ-alkoxo bridged Fe–hydrosalicylamide complexes, a group of old compounds which we had also studied some years ago.[6] Some excellent synthetic models of types $LFe(O)(OAc)_2FeL$ and $L'Fe(O)(OAc)FeL'$ have recently been developed to mimic the μ-oxo-μ-carboxylato-bridged centres in the oxidized forms of the proteins haemerythrin (Hr), ribonucleotide reductase (RRB2) and methane monooxygenase (MMO).[1,2] The 'terminal' chelate ligands in such models have generally been tridentate (L = triazacyclo-



$x = 1$; H_3L^A

$x = 2$; H_3L^B

$[Fe_2(L^A)(OMe)(Cl)_2(MeOH)]$

1

$[Fe_2(L^B)(OH)(Cl)_2]$

2

$[Fe_2(L^A)_2]$

3

nonane,[7] tris-pyrazolylborate[8] or tripodal bis-pyridylamines[9]) or tetradentate (L′ = tripyridylmethylamine[10]) in nature in order to obtain triply or doubly bridged structures appropriate to Hr[11] and RRB2,[12] respectively. Only in very few instances have monodentate/bidentate combinations of terminal ligands been employed[3,13] (*e.g.* L = 2,2′-bipyridine, Cl^-) in order to model more accurately the labile 'met' sites in proteins such as chlorohemerythrin.[1] Even in these cases the models are essentially symmetrical in structure and in coordination number around each Fe,[14] a situation which does not apply to the proteins in either the deoxy ($Fe^{II} \cdots Fe^{II}$) or oxy ($Fe^{III} \cdots Fe^{III}$) forms.[1,11,12] In this paper we report results of our studies employing binucleating Schiff's base ligands of the types shown (H_3L^A and H_3L^B)[15] in which the μ-alkoxo endogenous bridging group holds the two Fe^{III} atoms in close proximity, while the salicylideneamine fragments provide O,N-donor sets. In complexes such as $[Fe_2(L^A)(OMe)(Cl)_2$-MeOH] **1** and $[Fe_2(L^B)(OH)(Cl)_2]$ **2**, obtained by heating $FeCl_3$, ligand and NaOMe together in (almost) dry methanol, the exogenous OMe^- or OH^- groups provide a second bridge and the Cl^- groups provide a 'labile' terminal site.

The crystal structure† of **1** shows that we had, somewhat fortuitously, obtained asymmetry in the coordination environments around each Fe, *i.e.* five-coordinate Fe(1) and six-coordinate Fe(2). It can be seen in Fig. 1 that a methanol molecule is bonded to Fe(2), and this is strongly bonded as judged by the similarity in bond lengths Fe(2)–O(4) and Fe(2)–O(5). The strain in the L^A ligand framework is apparent, for instance, in the unequal length and non-parallel disposition of the Fe–N bonds and of the non-trigonal O(2) bridging atom (solid angle = 333°). This, in turn, leads to the irregular disposition of the two Fe–Cl bonds and the grossly distorted coordination geometry around Fe(1). Relief of ligand strain can be achieved during formation of the bright red chloride-free complex, $[Fe_2(L^A)_2]$ **3**, prepared by the reaction of $FeCl_3$ and the ligand in 1 : 1 ratio in methanol in the presence of triethylamine. By analogy with the structurally characterized $[Mn_2L^A{}_2$·tetrahydrofuran] analogue,[16,17] each L^A ligand in **3** straddles across both metal ions but only one provides a μ-alkoxo group as the single bridge in the structure, the alkoxo group on the other being in a terminal position.

Variable temperature magnetic data for **1** in the range 4.2 to 300 K show that weak antiferromagnetic coupling exists (Fig. 2). The J value of -10.6 cm^{-1}, obtained by fitting the data to an $S_1 = S_2 = 5/2$ model, is compared in Table 1 to values found in some related di-bridged complexes. Even though **1** is not a symmetrical $Fe^{III}{}_2(OR)_2$ example, by virtue of endogenous alkoxo and exogenous OMe^- groups, its J value and bridge geometry correlate closely in the manner recently pointed out by Holm *et al.*[4] The weak ferromagnetism observed by Holm's group in the case of $Fe_2(salmp)_2$ was ascribed to a combination of the smaller r(Fe · · · Fe) and Fe–O–Fe angles and to distortions in the Fe coordination spheres. The distortions, which are also manifest in **1**, do not lead to net ferromagnetism in the present case. In relation to the iron–oxo proteins, it should be noted that the exogenous bridging ligand in the doubly bridged RRB2 protein is an O^{2-} atom[12] and the J value is correspondingly much more negative[1] than in the complexes listed in Table 1. The present magneto-structural parameters are much more akin to those found in the iron sites of purple acid phosphatase and methane monooxygenase enzymes for which definitive evidence of a μ-oxo bridge is lacking.[1]‡

Cyclic voltammetric studies on acetonitrile solutions of **1** show a near-reversible wave at $E_{1/2} = +0.02$ V [rel. to standard calomel electrode (SCE); glassy carbon electrode; $(Bu_4N)(ClO_4)$ supporting electrolyte, $i_{pc}/i_{pa} = 0.90$, $\Delta E_p = 70$ mV, scan rate = 100 mV s^{-1}, $T = 20$ °C]. A less well defined reduction wave is observed at *ca.* −0.8 V together with a

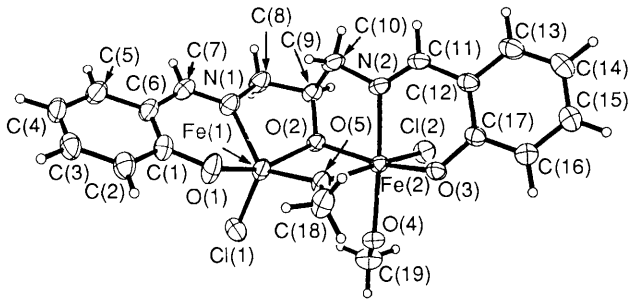


Fig. 1 ORTEP diagram of **1**. Selected distances (Å) and angles (°): Fe(1)–O(1), 1.893(3); Fe(1)–N(1), 2.072(3); Fe(1)–Cl(1), 2.239(2); Fe(1)–O(2), 2.005(2); Fe(1)–O(5), 1.939(2); Fe(2)–O(3), 1.944(2); Fe(2)–N(2), 2.109(3); Fe(2)–Cl(2), 2.316(1); Fe(2)–O(4), 2.085(2); Fe(2)–O(2), 2.017(2); Fe(2)–O(5), 2.076(2); Fe(1) · · · Fe(2), 3.140; Fe(1)–O(2)–Fe(2), 102.7(1); Fe(1)–O(5)–Fe(2), 102.9(1); Fe(1) displaced 0.598 Å towards Cl(1) from O(1),N(1),O(2),O(5) best-plane; Fe(2) displaced 0.056 Å towards O(4) from Cl(2),O(2),O(3),O(5) best-plane, angle between these planes is 24.1°.

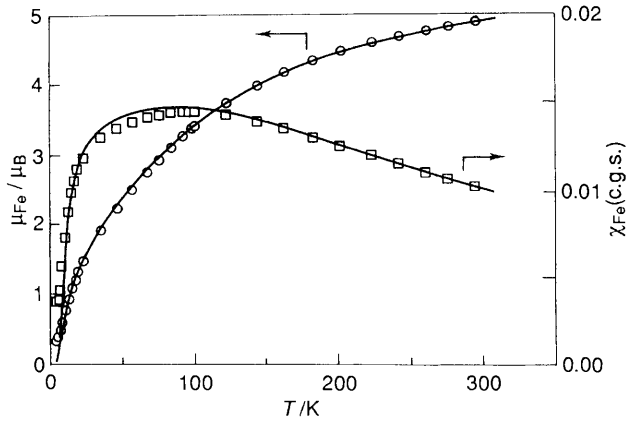


Fig. 2 Temperature dependent susceptibility (□) and moment (○) data for **1**. Solid lines are those calculated for an $S = 5/2$ dimer model using $g = 1.98$, $J = -10.6$ cm^{-1}. *N.B.* The levelling off of χ_{Fe} at very low temperatures is due to a small percentage of monomer impurity.

† *Crystal data* for **1**, $C_{19}H_{21}Cl_2Fe_2N_2O_5$, $M_r = 540.0$; monoclinic, at 293 K, $a = 7.887(3)$, $b = 24.823(9)$, $c = 11.680(4)$ Å, $\beta = 106.18(3)°$, $U = 2196(1)$ Å^3, space group $P2_1/n$, $Z = 4$; Mo-Kα radiation ($\lambda = 0.71073$ Å); data/parameters = 14.1, $R = 0.038$, $R_w = 0.048$; goodness of fit = 1.31. The structure was solved by direct methods using SHELXTL PLUS (G.M. Sheldrick, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1988). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ We have just become aware of a report by Krebs *et al.*[25] who have structurally characterized some purple acid phosphatase models using pyridyl[18,19] or imidazolyl[18] analogues of **1** which contain phosphate groups in place of our bridging or terminal OMe^- groups.

Table 1 Magnetic and $Fe_2(OR)_2$ structural features of some di-bridged $Fe^{III} \cdots Fe^{III}$ complexes

Complex	μ_{Fe}/μ_B (295 K)	J/cm^{-1}	$r(Fe \cdots Fe)$/Å	Fe–O–Fe/° (av.)	r(Fe–O)/Å (av.)	Ref. [a]
1	4.94	−10.6	3.140	102.9(1)	1.94–2.08	t.w.
2	4.48	n.d.[a]	n.d.	n.d.	n.d.	t.w.
3	5.11	−6.9	n.d.	n.d.	n.d.	t.w., 23
$[Fe_2L(OMe)_2Cl_2]$[b]	4.73	−16.3	3.106	103(1)	1.99	24
$[Fe_2(saltrien)(OMe)Cl_2]$[c]	5.20	−8.0	3.139	100(1) 105(1)	1.98–2.05	5
$[Fe_2(salmp)_2]\cdot 2dmf$[d]	5.89	+1.21	3.063	97.06(9)	2.04	4

[a] t.w. = this work; n.d. = not determined; [b] H_2L = 1,4-piperazine-bis(*N*-ethylenesalicylideneimine); *c* H_3saltrien = trissalicylidenetriethylenetetramine. [d] H_3salmp = 2-(bissalicylideneaminomethyl)phenol ('hydrosalicylamide'); dmf = dimethylformamide.

strong irreversible oxidation wave at +1.6 V. The +0.02 V wave is most likely due to the $Fe_2^{III}/Fe^{II}Fe^{III}$ couple. It lies at a more negative potential than in related μ-phenoxo-μ-carboxylato binuclear systems in which the Fe atoms are bonded to pyridyl[18,19] or imidazolyl[18] terminal groups, but it is at a more positive potential than in a di-μ-phenoxo iron salicylideneamine complex.[4] The $Fe^{II}Fe^{III}$ derivative of **1** should be chemically or electrochemically readily accessible while the Fe^{II}_2 form will be more difficult to obtain. Reaction of the latter with O_2, or of **1** or **2** with O_2^{2-}, should prove interesting for comparison with recent related studies.[20,21] Reactions of the Fe–Cl moieties in **1** or **2** with OH^- may also provide some interesting new μ-oxo or μ-hydroxo frameworks which may be relevant to reactivity features of OH^--bound hemerythrins.[22]

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