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Synthesis and Properties of Dinuclear μ-Oxo-μ-carboxylato Iron(III) Complexes with a Labile Coordination Site. Models of Non-haem Iron Proteins†

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The synthesis by self-assembly and the spectroscopic characterization of novel complexes containing an Fe_2O core with one or two bridge monocarboxylate (AcO^-, BzO^-, StO^-), bidentate (bpy, phen) and labile monodentate (H_2O, MeOH) terminal ligands are reported.‡

Dinuclear oxo-bridged iron(III) centres occur in a variety of non-haem iron proteins: hemerythrin (Hr), methane monooxygenase (MMO), ribonucleotide reductase (RR) and others.[1] Numerous synthetic models for such proteins have been reported,[2] establishing the accessibility and stability of this unit outside a polypeptide environment. These models usually contain tridentate terminal ligands in addition to oxo and carboxylato bridges. However, the tridentate ligands preclude coordination of potential substrates, preventing the study of the catalytic properties of these models. In order to mimic the functions of non-haem diiron proteins, new model complexes are required having vacant or labile terminal coordination sites. Earlier attempts to overcome this obstacle by using bidentate rather than tridentate ligands led to dimerisation of the Fe_2O unit to yield only Fe_4O_2-containing products. However, the $[Fe_2O(OAc)_2(bpy)_2Cl_2]$ complex was prepared by cleavage of $[Fe_4O_2(OAc)_7(bpy)_2](ClO_4)$ in the presence of an excess of bpy and chloride.[3] Recently, original but complex routes to such complexes were found, using a specially synthesized dicarboxylate ligand[4] or air oxidation of diferrous compounds.[5] Taking into account the considerable stability of the $Fe_2O(O_2CR)_2^{2+}$ unit, one might hope to obtain these complexes by self-assembly of simple compounds provided the formation of the $Fe_4O_2(O_2CR)_4^{4+}$ unit is prevented.

In the present communication a synthetic route to new dinuclear μ-oxo-μ-carboxylato iron(III) complexes $[Fe_2OC_2B_2S_2]^{2+}$ [**C**, bridge monocarboxylate (OAc, OBz, OSt); **B**, bidentate (bpy or phen); **S**, labile monodentate (H_2O, MeOH) terminal ligands] *via* self-assembly of simple molecules in solution is described.§

Synthetic procedures and spectroscopic characteristics for some of the complexes isolated are listed in Table 1 for the case of B = bpy. The spectroscopic characteristics of the corres-

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‡ *Abbreviations:* Ac, MeCO; Bz, PhCO; St, $C_{16}H_{33}CO$; bpy, 2,2′-bipyridyl; phen, 1,10-phenanthroline.

§ A related investigation has recently been brought to my attention.[6]

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Table 1 Preparation and characteristics of some μ-oxo-μ-carboxylato iron(III) complexes

Complex; **B** = bpy	Procedure[a]/ Yield (%)	λ_{max}/nm (MeOH)(ε/Fe, cm^{-1} mol^{-1} dm^3)	$\Delta\nu = \nu_{as} - \nu_s/cm^{-1}$
1, $[Fe_2O(OAc)_2\mathbf{B}_2(H_2O)_2](ClO_4)_2 \cdot 2NaClO_4$[b]	A/95	310sh, 360sh, 455(440), 488(420), 530sh, 685(60)	136
2, $[Fe_2O(OBz)_2\mathbf{B}_2(MeOH)_2](ClO_4)_2$	B/30	310sh, 360sh, 450(420), 489(360), 535sh, 690(60), 985(3)	145
3, $[Fe_2O(OBz)\mathbf{B}_4](ClO_4)_3 \cdot MeOH$[b]	B/60	307sh, 400sh, 450sh, 493, 535sh, 690	172
4, $[Fe_4O_2(OBz)_7\mathbf{B}_2](ClO_4)$	B/70	412sh, 466, 600sh[c]	150
5, $[Fe_4O_2(OAc)_7\mathbf{B}_2]Cl$	C/55	472(590)	140

[a] A: $Fe(ClO_4)_3 \cdot 9H_2O$ (0.4 mmol), **B** (bpy, phen) (0.4 mmol), $NaClO_4$ (2 mmol) and NaOAc (1 mmol) were dissolved in H_2O (2 ml) containing AcOH (1 mmol); the green solid formed was filtered, dried *in vacuo* and stored in a refrigerator. B: $Fe(ClO_4)_3 \cdot 9H_2O$ (0.5 mmol), CNa (BzO, StO) (1 mmol), **B** (bpy, phen) (1 mmol) were dissolved in MeOH (30 ml) and filtered; after concentration of the solution, the solid was isolated and dried. CNa: **B** = **1**(**2**), 0.4(**3**) and 3(**4**). C: $FeCl_3 \cdot 6H_2O$ (1 mmol), AcONa (3 mmol), **B** (bpy, phen) (0.5 mmol) were dissolved in H_2O (3 ml). The solid formed was recrystallized from CH_2Cl_2–hexane. [b] ^1H NMR spectrum shown in Fig. 1. [c] UV-VIS and IR spectra (in CH_2Cl_2) agree well with those reported.[7]

ponding phen complexes are very similar to those of the bpy ones. Satisfactory microanalyses for Fe, C, H, N (± 0.5%) were obtained for all synthesized complexes.

The Mössbauer spectra of these complexes show that they contain iron in a high-spin state. The observation of a characteristic absorption in the visible region, which is very similar to that of Hr or RR, suggests that there is antiferromagnetic interaction between the iron atoms in the complexes, supporting μ-oxo bridging. The IR spectra contain bands due to symmetric and asymmetric CO_2^- stretching in addition to those of bpy, which are shifted because of coordination. The value of $\Delta\nu = \nu_{as} - \nu_s = 140$–$170$ cm^{-1} provides evidence for bridge bidentate coordination of the CO_2^- group to iron atoms. In connection with the well-known Gif systems,[8] it is worth noting here that using py instead of bipy leads to the appearance of an analogous spectrum, indicating the formation of the $Fe_2O(O_2CR)_2$ centre with py terminal ligands.

The proton NMR spectrum of **1** in CD_3OD (Fig. 1) is typical for dinuclear iron complexes with antiferromagnetic exchange between the iron atoms. The spectrum shows peaks at about δ_H 20, 16, 14 and 8 that have been assigned to the bpy C—H resonances, the peak at δ 10.5 has been assigned to the Me group of the acetate ligand. A correlation was found[9] between the extent of antiferromagnetic coupling and the chemical shift of the bridging acetate methyl group resonance in these complexes. Probably, the same trend should be apparent for the bpy C—H resonances. The observed chemical shifts in the ^1H NMR spectrum of **1** correspond to the value of the antiferromagnetic coupling constant $J \simeq 120$–130 cm^{-1}. The effective room-temperature magnetic moment per iron atom, derived from chemical shifts relative to Me_4Si or solvent protons is about 1.6–1.7 μ_B for bis-carboxylates in CD_3OD and about 2.0 μ_B for monocarboxylate. Both μ and J agree with values reported for other μ-oxo-μ-carboxylato dinuclear iron complexes.[2]

The observation of the dominant peak of the Fe—O—Fe symmetric stretch at 540 cm^{-1} in the Raman spectrum of **2** and its isotopic shift to 520 cm^{-1} on substitution of ^{16}O for ^{18}O in the bridge is a strong confirmation[2] of the proposed structure of **2**.

Thus, the above dinuclear μ-oxo-μ-carboxylato iron complexes are formed in solution, owing to spontaneous association of the reactants [eqn. (1)].

$$2Fe(ClO_4)_3 + 2\mathbf{B} + CH + H_2O \xrightarrow{S} [Fe_2OC\mathbf{B}_2S_2](ClO_4)_2 + 4HClO_4 \quad (1)$$

These complexes are inclined to dimerise to give tetranuclear species, owing to the lability of the coordination site. This may be prevented by an increase in the monodentate ligand concentration. The favourable influence of a hydroxylic solvent and acidity is probably due to H-bonding of the β-oxo bridges.

The spectroscopic behaviour of **1** and **2** depends on the type of solvent used: it is normal in hydroxylic solvents (H_2O, MeOH) and abnormal in non-hydroxylic ones (MeCN, CH_2Cl_2), in which there is no characteristic absorption in the visible spectrum. Since the dinuclear structure of the complexes is retained in the latter solutions, it may be assumed that there is some disturbance of the antiferromagnetic interactions in this case. Confirmation of this assumption and further details were obtained by Raman spectroscopy and magnetic measurements. The ν_S (Fe—O—Fe) shift of complex **2** to 497 cm^{-1} in MeCN solution may be explained by the formation of a strong intramolecular H-bond between the bridging O and a *cis*-H_2O. On the other hand, intermolecular H-bonding of μ-O and S in H_2O or MeOH prevents their intramolecular bonding. H-Bonding as well as protonation of the μ-oxo bridge disturbs the antiferromagnetic interaction and hence may result in a decrease in intensity of the visible spectrum. Further confirmation of this assumption is seen in the different values of the effective magnetic moment for **2** in these solvents, as measured by the Evans method from the paramagnetic shifts of the solvent signals in ^1H NMR spectra. A decrease in antiferromagnetic exchange as a result of intramolecular H-bonding has been observed for oxy- and hydroxy-Hr, although this was not accompanied by effects in the visible spectra.[1] It is possible that the non-characteristic visible spectrum of MMO is caused by the formation of a strong intramolecular H-bond between μ-O and *cis*-H_2O in a dry cavity of the enzyme. The presence of H_2O in a *cis*-position relative to the μ-oxo group in MMO seems logical, taking into account the necessity of a labile site to bind substrates, and has been confirmed indirectly by X-ray studies of RR.[1]

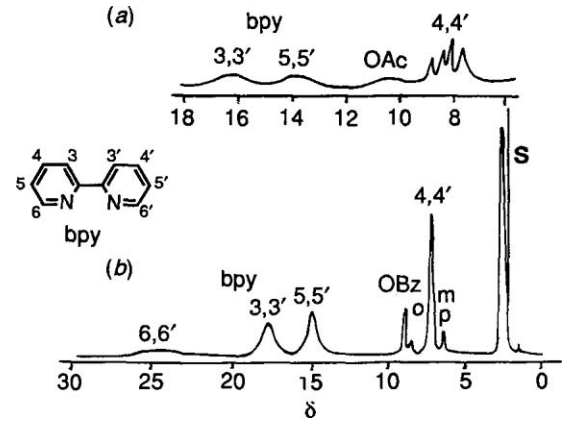

Fig. 1 ^1H NMR spectra of (*a*) $[Fe_2O(OAc)_2(bpy)_2(H_2O)_2](ClO_4)_2$ **1** (in CD_3OD) and (*b*) $[Fe_2O(OBz)(bpy)_4](ClO_4)_3$ **3** (in CD_3CN)

A monodentate ligand in the coordination site of these complexes can be substituted by other neutral or charged ligands. The red $[Fe_2O(bpy)_2(CNS)_2]$ complex produced shows a characteristic unresolved doublet 2050–2020 cm^{-1} due to valent C—N vibration of CNS^-, in addition to ν_s and ν_{as} stretches of the CO_2^- group. In MeOH solution this complex has a broad absorption band at 450 nm comparable with that at 452 nm for metHr (CNS).[1] Complexes of type **1** or **2** with a

labile coordination site are more active in catalysing alkane oxidation by H_2O_2 than those of type **3–5**, without this site.[10] The mechanism of these reactions appears to involve H_2O substitution by H_2O_2.
vely.

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