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Tetranuclear iron(III) carboxylate clusters with 1,10-phenanthroline and 2,2′-bipyridine: a new $[Fe_4(\mu_4\text{-}OHO)(\mu\text{-}OH)_2]^{7+}$ core

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Received 24th January 2001, Accepted 5th March 2001
First published as an Advance Article on the web 15th March 2001

The reactions between $Fe(ClO_4)_3{\cdot}6H_2O$, $NaO_2CMe{\cdot}3H_2O$ and L–L (L–L = 2,2′-bipyridine, 1,10-phenanthroline) in MeCN give complexes $[Fe_4(OHO)(OH)_2(O_2CMe)_4(L\text{–}L)_4](ClO_4)_3$ whose cations contain the novel $[Fe_4(\mu_4\text{-}OHO)(\mu\text{-}OH)_2]^{7+}$ core; magnetic studies indicate that both complexes have $S = 0$ ground states, consistent with the presence of strong antiferromagnetic exchange interactions.

Dinuclear and polynuclear hydroxo-, alkoxo- and oxo-bridged iron complexes are of interest from a variety of viewpoints, including magnetic materials[1] and bioinorganic chemistry.[2] An interesting sub-area of hydroxo/alkoxo/oxo iron chemistry is the small but growing family of complexes that simultaneously contain carboxylate (RCO_2^-) and neutral, bidentate chelating N-donor ligands, such as 2,2′-bipyridine (bpy)[3] and 1,10-phenanthroline (phen).[4] Up to now complexes $[Fe_2O(O_2CMe)_2Cl_2(bpy)_2]$, $[Fe_2O(O_2CCF_3)_2(Me_2bpy)_4](ClO_4)_2$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine), $[Fe_4O_2(O_2CMe)_7(bpy)_2](ClO_4)$, $[Fe_4O_2(O_2CMe)_6Cl_2(bpy)_2]$, $[Fe_6O_3(OEt)_2(O_2CMe)_9(bpy)_2](ClO_4)$, $[Fe_2O(O_2CPh)_2(phen)_4]Cl_2$, $[Fe_3O_2(O_2CMe)_2(phen)_6](ClO_4)_3$ and $Na[Fe_6O_4(OH)_2(ami)_4(phen)_8](NO_3)_9$ (ami = the zwitterionic form of β-alanine) have been structurally characterized, providing a wealth of structural types.[3,4] An inspection of the stoichiometries of the tri-, tetra- and hexa-nuclear clusters reveals that the Fe^{III} : L–L ratio (L–L = bpy, phen) is 3 : 1, 2 : 1, 1 : 2 or 3 : 4; no 1 : 1 clusters have been reported.

We have long been interested in the synthesis and magnetic study of polynuclear Co^{II}, Ni^{II} and Cu^{II} complexes using a variety of bridging and chelating ligands.[5] More recently we have extended our studies to include iron(III). We suspected that 1 : 1 clusters could exist within the $Fe^{III}/OH^-,O^{2-}/RCO_2^-$/L–L chemistry. We herein report the access to these clusters, and describe the preparation and full characterization of complex $[Fe_4(OHO)(OH)_2(O_2CMe)_4(phen)_4](ClO_4)_3$ (**1**), which contains the new $[Fe_4(\mu_4\text{-}OHO)(\mu\text{-}OH)_2]^{7+}$ core. Preliminary information is also given for the structurally similar cluster $[Fe_4(OHO)(OH)_2(O_2CMe)_4(bpy)_4](ClO_4)_3$ (**2**).

Both complexes have been obtained using the 1 : 1.75 : 1 $Fe(ClO_4)_3{\cdot}6H_2O : NaO_2CMe{\cdot}3H_2O$: L–L ratio in MeCN.‡ Their formation is summarized in eqn. (1), assuming that water is the source of the OHO^{3-} and OH^- ions.

$$4\,Fe(ClO_4)_3{\cdot}6H_2O + 4\,NaO_2CMe{\cdot}3H_2O + 4\,L\text{–}L \xrightarrow{MeCN} [Fe_4(OHO)(OH)_2(O_2CMe)_4(L\text{–}L)_4](ClO_4)_3 + 4\,NaClO_4 + 5\,HClO_4 + 32\,H_2O \quad (1)$$

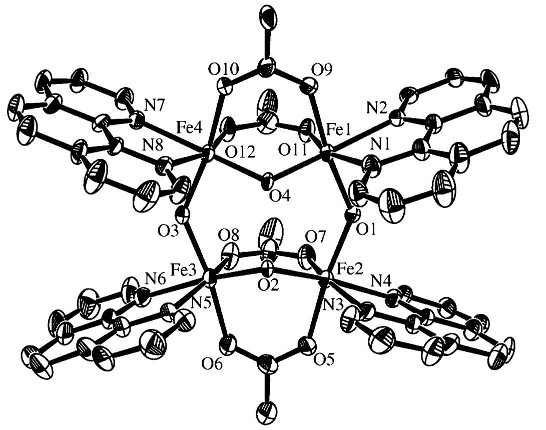

Fig. 1 An ORTEP representation of the cation of complex **1**·4.4MeCN·H_2O. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (°): Fe(1)–O(1) 1.997(7), Fe(1)–O(4) 1.883(6), Fe(1)–N(2) 2.186(9), Fe(2)–O(5) 2.035(8), Fe(3)–O(2) 1.876(7), Fe(3)–N(6) 2.186(11), Fe(4)–O(3) 2.002(7), Fe(4)–O(4) 1.869(6); O(4)–Fe(1)–N(2) 172.8(4), O(1)–Fe(2)–N(4) 89.2(3), O(8)–Fe(3)–N(5) 163.1(4), O(4)–Fe(4)–O(12) 99.5(3).

A partially labeled ORTEP plot of the cation of complex **1**·4.4MeCN·H_2O is depicted in Fig. 1.§ The four Fe^{III} atoms lie at the corners of a rectangle and deviate from their best least-square plane by only ≈0.018 Å. One O^{2-} group and two $MeCO_2^-$ ligands bridge each of the Fe(1)/Fe(4) and Fe(2)/Fe(3) pairs. Each of the Fe(1)/Fe(2) and Fe(3)/Fe(4) pairs is bridged by a single OH^- group (*vide infra*). The Fe^{III} atoms that are triply bridged are apparently "pulled" closer to one another [Fe(1) · · · Fe(4) = 3.261(2), Fe(2) · · · Fe(3) = 3.250(2) Å] than are those that are only singly bridged [Fe(1) · · · Fe(2) = 3.694(2), Fe(3) · · · Fe(4) = 3.687(2) Å]. A chelating phen molecule completes a distorted octahedral coordination at each metal ion. Atoms O(1) and O(3) are 0.21 and 0.18 Å, respectively, below the best Fe_4 plane, while atoms O(2) and O(4) are both above this plane by 0.74 and 0.73 Å, respectively.

The hydrogen atoms of the cluster were not crystallographically located. Given the crystallographically established presence of three perchlorates and the fact that the four metal centers are clearly high-spin Fe^{III} atoms, charge considerations require that three core oxygen atoms are formally protonated. Core oxygen atoms O(1) and O(3) are protonated as evidenced by (i) the close approach of two lattice MeCN molecules to hydrogen-bonding distances [O(1) · · · N(10) = 3.063(3), O(3) · · · N(9) = 3.013(3) Å], and (ii) their bond distances to Fe^{III} atoms [mean 1.995(7) Å] which are typical of $Fe^{III}\text{–}(\mu\text{-}O_{hydroxo})$ bonds.[6] The Fe–O(2,4) bond distances [mean 1.877(7) Å] are markedly shorter than the Fe–O(1,3) distances, indicating a different

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DOI: 10.1039/b100854o

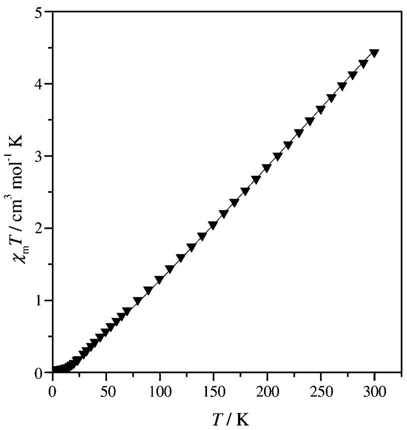

Fig. 2 Plot of the $\chi_m T$ product of a polycrystalline sample of **1**·4.4MeCN·H_2O as a function of T. The solid line is a fit of the experimental data to the $2J$ model; see the text for the fitting parameters.

nature for O(2) and O(4). However, the Fe–O(2,4) bond lengths fall outside the upper end of the range reported (1.76–1.82 Å)[6,7] for oxo-bridged diiron(III) complexes. Furthermore, we note that the bridging atoms O(4) and O(2) are not within hydrogen bonding distance of any other ligand or lattice species, but their distance [2.525(9) Å] is such that the presence of an H^+ ion between them is possible.[8,9] The presence of such an H^+ ion would confer partial hydroxo character to the O(2), O(4) oxo groups and would be expected to result in elongation of the Fe–O(oxo) distances.[8] The Fe(1) · · · Fe(4) and Fe(2) · · · Fe(3) distances [3.261(2), 3.250(2) Å] are intermediate between those found in dinuclear complexes containing the $[Fe_2(OH)(O_2CMe)_2]^{3+}$ (≈3.45 Å) and $[Fe_2O(O_2CMe)_2]^{2+}$ (3.06–3.18 Å) units.[4,6] Finally, the *trans* influence expected[6,7] for a pure bridging oxo group is also reduced, resulting in a slight elongation of the Fe–N bonds in *trans* positions with respect to the Fe–O(2,4) bonds (compared with those in *cis* positions) and suggesting that O(2) and O(4) are not μ-O^{2-} groups. Based on the above strong crystallographic evidence we are confident of our assignment of the new $[Fe_4(\mu_4\text{-OHO})(\mu\text{-OH})_2]^{7+}$ core in complex **1**·4.4MeCN·H_2O.

Further support of our assignment comes from FT-IR spectroscopy. Two medium broad bands observed in the spectrum of the fully desolvated form **1** at ≈3580 and 3070 cm^{-1} are assigned to the O–H stretching modes of the bridging OH^- and OHO^{3-} groups, respectively.[2,10] Upon deuteration of **1**, two broad peaks are observed: one centred at ≈2630 and a second at ≈2250 cm^{-1}. With use of the fact that deuteration results in an isotopic red shift of ≈$2^{1/2}$, these peaks are assigned to the O–D stretching modes of the OD^- and ODO^{3-} groups, respectively. Of particular significance in the low-frequency region is the medium peak at 870 cm^{-1} in **1**, which disappears upon deuteration, and a new peak at 640 cm^{-1}, which is observed in the spectrum of the deuterated complex. Therefore, the 870 cm^{-1} band is assigned to the bridging OH^- deformation mode.[6,10]

Examples of iron(III) clusters containing the μ_4-OHO^{3-} group are known.[8,11] The O · · · O distances in these complexes are in the range 2.394(1)–2.426(4) Å, slightly shorter than the O · · · O distance in **1**·4.4MeCN·H_2O [2.525(9) Å]. However, in all the reported cases the OHO^{3-} moiety was coplanar with the four Fe^{III} atoms. This makes our cation the first example of an out-of-plane μ_4-OHO^{3-} group found in iron cluster chemistry and only the second in general.[12] The μ_4-OHO^{3-} ligand is currently of great bioinorganic interest, because it has been proposed to exist, either in an in-plane , or in an out-of-plane fashion, in the oxygen-evolving Mn_4 complex of photosystem II during the S_1, S_2 states.[13]

An alternative description of the structure is also useful: the cation consists of two $[Fe_2O(O_2CMe)_2(phen)_2]^{2+}$ fragments triply bridged by two μ-OH^- groups and one proton.

Solid-state magnetic susceptibility (χ_m) data (Fig. 2) were collected on a powdered sample of the phen cluster in the temperature range 3.0 to 300 K. The $\chi_m T$ value decreases rapidly from 4.46 cm^3 mol^{-1} K at room temperature to 0.035 cm^3 mol^{-1} K at ≈16 K where a plateau is reached. The room temperature value is considerably less than expected for four non-interacting Fe^{III} atoms (17.52 cm^3 mol^{-1} K) indicating strong antiferromagnetic exchange interactions. Inspection of the molecular structure of **1** reveals that there are two main exchange pathways. The first one, J_1, refers to the $Fe^{III}O(O_2CMe)_2Fe^{III}$ interactions and the second one, J_2, refers to the $Fe^{III}(OH)Fe^{III}$ interactions. Thus, the Hamiltonian formalism $H = -J_1(S_1S_2 + S_3S_4) - J_2(S_1S_3 + S_2S_4)$ was used to fit the data, taking into account an amount of an $S = 5/2$ impurity (ρ); the obtained fitting parameters were $J_1 = -74(3)$ cm^{-1}, $J_2 = -22(3)$ cm^{-1}, $g = 2.0(1)$ and $\rho = 0.0108$. The energy spectrum according to the fitting values shows that the first excited $S = 1$ state is well separated from the diamagnetic $S = 0$ ground state ($\Delta E = 51$ cm^{-1}). A further verification for the amount of the impurity comes from magnetization measurements at 2 and 4 K. The non-zero magnetization, although the ground state is $S = 0$, is in accordance with the small percentage of the impurity found in the susceptibility data. So, the magnetization data were simulated quite well using the percentage ($p = 0.00182$) of the Brillouin function for an $S = 5/2$ system.

The $S = 0$ ground state of the Fe_4 cation of **1** is not surprising; this is a very common ground state for Fe_x^{III} clusters where x is an even number. Some important exceptions, however, include Gatteschi's complexes $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ ($S = 10$, tacn is triazacyclononane)[1c,d] and $[Fe_4(OMe)_6(dpm)_6]$ ($S = 5$, dpm$^-$ is the anion of dipivaloylmethane),[1c,d] and Hendrickson's complex $[Fe_6O_2(OH)_2(O_2CMe)_{10}L_2]$ ($S = 5$, L^- is the anion of 2-(*N*-methylimidazol-2-yl)-2-hydroxypropane),[1b] where the non-zero ground state is caused by the spin frustration phenomena induced by the Fe_x topologies present in these complexes.

Complex **2** has a very similar structure,§ and almost identical magnetic and IR (including deuteration experiments) properties, to those of **1**.

The ^1H NMR spectrum of **1** (0–70 ppm) in $CDCl_3/CD_3CN$ (6 : 1 v/v) is simple displaying broadened and shifted resonances, features typical of paramagnetic NMR. Two acetate signals appear in the 20–24 ppm region.[3] In addition to the acetate peaks, there are eight additional peaks in the 6–63 ppm region, assignable to the phen protons. The broadest resonance at 57.8 ppm and the shoulder at 62.4 ppm must be due to the 2,9 protons, since they are the closest to the metal center.

In summary, the use of phen and bpy in iron(III) carboxylate chemistry has provided access to two new planar Fe_4^{III} complexes with an unprecedented $[Fe_4(\mu_4\text{-OHO})(\mu\text{-OH})_2]^{7+}$ core. The identification of **1** and **2** emphasizes the belief that the Fe^{III}/O^{2-}, OR'^-/RCO_2^-/L–L chemistry (R′ = H, Me, . . .) is rich and exciting.

Acknowledgements

We are grateful to Prof. D. Gatteschi (Department of Chemistry, University of Florence) for permitting us to collect variable-temperature magnetic susceptibility data at his laboratory and for helpful discussions. The authors wish to thank the Greek General Secretariat of Research and Technology (Grant 99ED139) for support of this work.

Notes and references

‡ Synthetic procedure for compound **1**. To a stirred deep red solution of $Fe(ClO_4)_3$·$6H_2O$ (6.93 g, 15.0 mmol) and NaO_2CMe·$3H_2O$ (3.57 g, 26.2 mmol) in MeCN (35 mL) was added a solution of phen·H_2O (2.97 g, 15.0 mmol) in the same solvent (19 mL). A noticeable colour change to dark green occurred and the solution soon began to deposit a dark green microcrystalline precipitate. The solid was collected by filtration, repeatedly washed with cold MeCN and dried *in vacuo*. The yield was 4.12 g (≈70%). X-Ray quality single crystals of **1**·4.4MeCN·H_2O were grown from a similar reaction mixture, within 4–5 days, with the reactants concentrations scaled down to *ca.* 1 : 10. The dried sample analysed as **1**·H_2O. Calc. (Found) for $C_{56}H_{49}Cl_3Fe_4N_8O_{25}$: C, 43.0 (42.4); H, 3.2 (3.2); N, 7.2 (7.1)%. An analogous procedure was employed for the preparation and crystallization of **2**. Calc. (Found) for $C_{48}H_{47}Cl_3Fe_4N_8O_{24}$: C, 39.8 (39.6); H, 3.3 (3.3); N, 7.7 (7.5)%. The

deuterated complexes $[Fe_4(ODO)(OD)_2(O_2CMe)_4(L–L)_2](ClO_4)_3$ were prepared exactly as described for the normal complexes using $Fe(ClO_4)\cdot 6D_2O$, $NaO_2CMe\cdot 3D_2O$, phen·D_2O/bpy and CD_3CN.

§ *Crystal data*. For **1**·4.4MeCN·H_2O: $C_{64.8}H_{62.2}Cl_3Fe_4N_{12.4}O_{25}$, $M = 1744.42$, monoclinic, space group $P2_1/n$, $a = 18.162(9)$, $b = 39.016(19)$, $c = 13.054(7)$ Å, $\beta = 104.29(2)°$, $U = 8963.7$ Å^3, $T = 298$ K, $Z = 4$, μ(Mo-Kα) 0.796 mm^{-1}, 10810 reflections measured, 10253 unique ($R_{int} = 0.0694$), $R1$ and $wR2$ are 0.0993 and 0.2676, respectively, for 6721 reflections with $I > 2\sigma(I)$. For **2**·3.88MeCN: $C_{55.76}H_{58.64}Cl_3Fe_4N_{11.88}O_{24}$, $M = 1608.98$, monoclinic, space group $P2_1/n$, $a = 18.800(10)$, $b = 19.221(10)$, $c = 24.390(12)$ Å, $\beta = 109.13(2)°$, $U = 8326.7$ Å^3, $T = 298$ K, $Z = 4$, μ(Mo-Kα) 0.850 mm^{-1}, 5953 reflections measured, 5728 unique ($R_{int} = 0.0425$), $R1$ and $wR2$ are 0.1088 and 0.3200, respectively, for 4595 reflections with $I > 2\sigma(I)$. CCDC reference numbers 157029 and 157030. See http://www.rsc.org/suppdata/dt/b1/b100854o/ for crystallographic data in CIF or other electronic format.

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