A new structural type in iron carboxylate cluster chemistry *via* use of bis-bipyridine ligands: $[Fe_6O_4Cl_4(O_2CPh)_4L_2][FeCl_4]_2$

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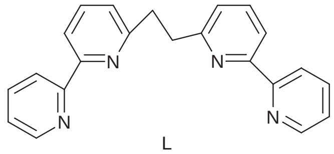
The reaction between $FeCl_3$, NaO_2CPh and L [L = 1,2-bis(2,2′-bipyridyl-6-yl)ethane] in MeCN gives the title complex 1 whose cation contains an unusual $[Fe_6(\mu_3\text{-}O)_4]^{10+}$ core, whereas in MeOH the dinuclear complex $[Fe_2(OMe)_2Cl_2(O_2CPh)L][FeCl_4]$ 2 is obtained; magnetic studies indicate that the cations of 1 and 2 both have $S = 0$ ground states, consistent with the expected antiferromagnetic exchange interactions.

In recent years, the synthesis and study of high-spin molecules (possessing large values of spin *S* in their ground state) have assumed greater importance as it has been discovered that such molecules represent the source of a new magnetic phenomenon, namely single-molecule magnetism.[1,2] As a result of a large spin and a negative magnetoanisotropy, as reflected in the zero-field splitting parameter *D*, such a single-molecule magnet (SMM) can be magnetized by an external magnetic field below some critical or blocking temperature. The first SMMs to be identified were $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = Me, Et, Ph, *etc.*) complexes (S = 9 or 10)[1–3] and their one-electron reduced versions in $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^-$ salts ($S = 19/2$).[2] More recently, the $[Mn_4O_3X(O_2CMe)_3(dbm)_3]$ (X = Cl^-, Br^-, F^-, O_2CMe^-, *etc.*; dbm^- is the anion of dibenzoylmethane) complexes with $S = 9/2$[4,5] and $[V_4O_2(O_2CR)_7(L\text{–}L)_2]^z$ salts [L–L = 2,2′-bipyridine (bpy), $z = +1$; L–L = 2-picolinate, $z = -1$] with $S = 3$[6] have also been discovered to be SMMs, as has a $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ salt (tacn = 1,4,7-triazacyclononane) with $S = 10$.[7]

Important to the future of the field of high-spin molecules, and to the possible identification of new SMMs, is the development of synthetic methodologies that can yield new metal clusters, particularly those of Mn^{III} and Fe^{III}. With this in mind, we have been investigating the ability of bis-bipyridine ligands such as L to assemble new cluster types with Mn^{III} and Fe^{III} not available with simpler ligands such as bpy itself. We herein describe access *via* this route to a new Fe_6 structural type, as well as a related Fe_2 species, confirming the potential of this ligand for cluster synthesis in Fe^{III}–Mn^{III} chemistry.



L

The reaction between $FeCl_3$, NaO_2CPh and L (4 : 4 : 1) in MeCN gave a red–brown solution and an off-white solid (NaCl). After 24 h reaction time, the solution was filtered, and the filtrate concentrated under vacuum to half its original volume and layered with Et_2O. Red–brown crystals of $[Fe_6O_4Cl_4(O_2CPh)_4L_2][FeCl_4]_2\cdot 2MeCN$ **1**·2MeCN slowly grew over 1–2 weeks in 40% yield; dried solid analysed as **1**·MeCN.† The same reaction in a 3 : 3 : 1 ratio carried out in MeOH gave an orange precipitate. This was collected by filtration and recrystallized from warm MeOH–MeCN (1 : 1) to give orange needles of $[Fe_2(OMe)_2Cl_2(O_2CPh)L][FeCl_4]$ **2** in 28% yield.† Note that the use of bpy instead of L in the MeCN reaction gives $[Fe_4O_2(O_2CPh)_7(bpy)_2][FeCl_4]$, the cation of which has been previously reported.[8]

The structures‡ of the cations of **1** and **2** are shown in Figs. 1 and 2, respectively. The centrosymmetric cation of **1** contains an unusual $[Fe_6(\mu_3\text{-}O)_4]^{10+}$ core (6 × Fe^{III}) that can be conveniently described as consisting of three edge-fused $[Fe_2O_2]$ rhombs to which are attached two additional Fe atoms Fe(1) and Fe(1′); the latter are four-coordinate with distorted tetrahedral geometry whereas the other Fe atoms are six-coordinate with distorted octahedral geometry. A side view shows the $[Fe_6O_4]$ core to be nearly planar. The L and central $PhCO_2^-$ groups bridge the Fe(2)/Fe(3) and Fe(2′)/Fe(3′) pairs. An alternative description of the structure is particularly useful: the cation consists of two $[Fe_2O_2(O_2CPh)L]^+$ fragments that are linked by inter-fragment bonds Fe(2)–O(7′) and Fe(2′)–O(7), and this incipient, supramolecular chain formation is terminated by the $[FeCl_2(O_2CPh)]$ caps at each end, whose Fe(1) and O(10) atoms bind to and prevent O(6) and Fe(3) from attaching to another $[Fe_2O_2(O_2CPh)L]^+$ fragment. Note the unusual nearly T-shaped geometry of O(7) and O(7′), with Fe(2′)–O(7)–Fe(3) angles of 159.25(21)°.

The cation of **2** contains a $[Fe_2(\mu\text{-}OMe)_2]^{4+}$ core with bridging L and $PhCO_2^-$ groups, and octahedral geometry at each Fe^{III} completed by terminal Cl^- ions. The dinuclear unit is thus similar to the repeating $[Fe_2O_2(O_2CPh)L]^+$ fragment of **1**, with aggregation blocked by the MeO^--for-O^{2-} substitution at

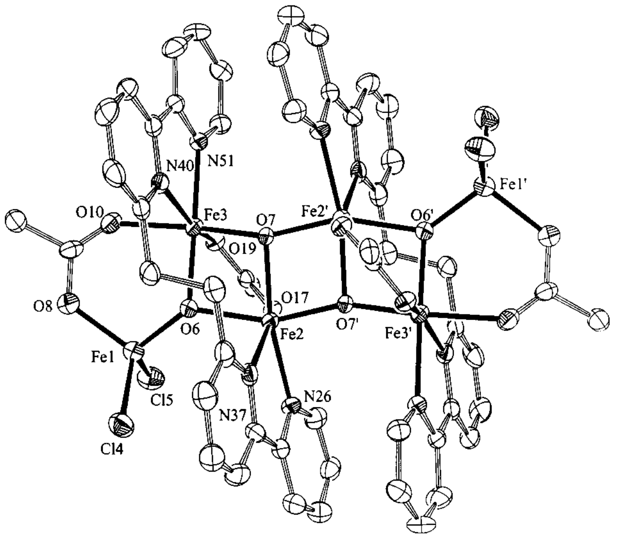


Fig. 1 The structure of the cation of **1**; only the *ipso* C atoms of the Ph rings are shown. Selected interatomic distances (Å) are: Fe(1)···Fe(2) 3.483(2), Fe(1)···Fe(3) 3.357(2), Fe(2)···Fe(3) 2.932(2), Fe(2)···Fe(2′) 3.054(2), Fe(2)···Fe(3′) 3.692(2), Fe(1)–O(6) 1.806(4), Fe(2)–O(6) 1.994(4), Fe(2)–O(7) 2.045(4), Fe(2)–O(7′) 1.889(4), Fe(3)–O(6) 1.965(4), Fe(3)–O(7) 1.864(4). Primed and unprimed atoms are related by the inversion centre.

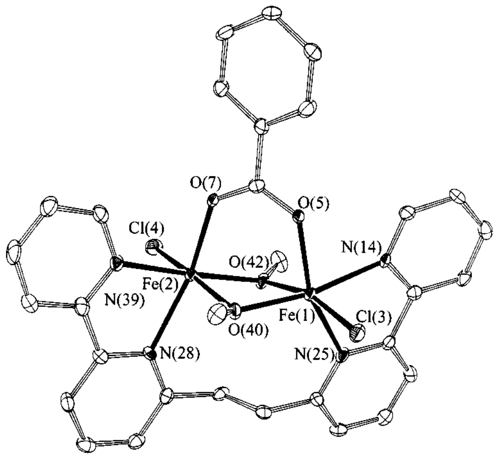


Fig. 2 The structure of the cation of **2**. Selected interatomic distances (Å) and angles (°) are: Fe(1)···Fe(2) 3.088(2), Fe(1)–O(40) 1.981(4), Fe(1)–O(42) 1.993(4), Fe(1)–Cl(3) 2.290(2), Fe(2)–O(40) 2.013(4), Fe(2)–O(42) 1.973(4), Fe(2)–Cl(4) 2.271(2); Fe(1)–O(40)–Fe(2) 101.31(19), Fe(1)–O(42)–Fe(2) 102.29(18).

the bridging position and terminal Cl^- ions on the Fe atoms. The Fe(1)···Fe(2) distance in **2** [3.088(2) Å] is only slightly longer than the Fe(2)···Fe(3) distance in **1** [2.932(2) Å].

Comparison of **1** and **2** shows that L is a binucleating ligand and it adopts the same bridging mode in both complexes with the ethylene bridge forcing the two bpy halves to be essentially parallel. There appears to be no reason why longer chains of $[Fe_2O_2(O_2CPh)L]^+$ repeating units with $[FeCl_2(O_2CPh)]$ caps should not be possible, yielding the supramolecular $[Fe_{2n+2}O_{2n}Cl_4(O_2CPh)_{n+2}L_n]^{n+}$ family of which **1** is the $n = 2$ member. This possibility is currently being investigated by changes in the reagent ratios.

Solid-state magnetic susceptibility data were collected in a 1 Tesla field. The effective magnetic moment $\mu_{\rm eff}$ ($\chi_{\rm m}T$) value for **1** slowly decreases from 10.30 μ_B (13.26 cm^3 K mol^{-1}) at 13.0 K and then decreases rapidly to 6.76 μ_B (5.71 cm^3 K mol^{-1}) at 2.0 K. Subtracting out the expected values for the $[FeCl_4]^-$ anions ($S = 5/2$) shows that $\mu_{\rm eff}$ and $\chi_{\rm m}T$ for the cation decrease to essentially zero at low temperatures, indicating a $S = 0$ ground state. Similarly, $\mu_{\rm eff}$ ($\chi_{\rm m}T$) values for **2** are 9.33 (10.88), 5.90 (4.35) and 5.19 μ_B (3.37 cm^3 K mol^{-1}) at 300, 9.00 and 2.00 K (Fig. 3), respectively. Subtracting out the contribution from the $[FeCl_4]^-$ anion again indicates a $S = 0$ ground state, and fitting of the 13.0–300 K data (lower T data were affected by zero-field splitting in the anion and were omitted) to a Heisenberg exchange model ($\hat{H} = -2JS_1S_2$) gives $J = -10.48$ cm^{-1} with g held at 2.00 (solid line in Fig. 3). This value is as expected from the empirical J *vs.* $2P$ relationship, where $2P$ is the shortest Fe–O–Fe bond distances, which suggests J for **2** should be 10.89 cm^{-1} for $2P = 3.966$ Å.[9] Plots of $\mu_{\rm eff}$ *vs.* T and magnetization *vs.* magnetic field for compounds **1** and **2** are available as supplementary information. See http://www.rsc.org/suppdata/cc/1998/1753.

In summary, the use of the bis-bipyridine ligand L has allowed access to a new Fe_6 structural type, as well as an Fe_2 species. The ability of L to provide new high nuclearity Fe and Mn species is under continuing investigation, as is the use of this ligand to access Fe_2 species of biological relevance to the many Fe biomolecules containing a dinuclear oxo-bridged unit.

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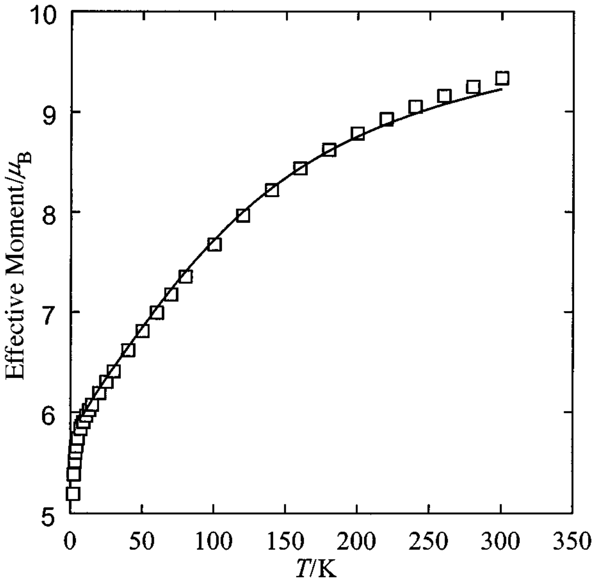

Fig. 3 Plot of effective magnetic moment *vs.* T for complex **2**. The solid line is a fit of the 13.0–300 K data to the appropriate theoretical equation for an exchange-coupled Fe^{III}_2 cation and non-interacting $S = 5/2$ anion. See the text for the fitting parameters.

Notes and References

† The complexes analysed satisfactorily (Complex **1**·MeCN. Found: C, 41.34; H, 2.71; N, 5.68. $C_{74}H_{59}Cl_{12}Fe_8N_9O_{12}$ requires C, 41.56; H, 2.78; N, 5.89%. Complex **2**. Found: C, 41.36; H, 3.28; N, 6.24. $C_{31}H_{29}Cl_6Fe_3N_4O_4$ requires C, 41.29; H, 3.24; N, 6.21%).

‡ *Crystal data* for **1**·2MeCN: $C_{76}H_{62}Cl_{12}Fe_8N_{10}O_{12}$, $M_r = 2179.60$, monoclinic, $P2_1/a$, $a = 15.317(2)$, $b = 18.303(3)$, $c = 16.168(3)$ Å, $\beta = 108.91(1)°$, $U = 4288.1$ Å^3, $Z = 2$, $T = 104$ K. Residuals were $R(F) = 0.0551$ and $R_w(F) = 0.0576$ using 5610 unique reflections; reflections with $F < 3\sigma(F)$ were given zero weight. *Crystal data* for **2**: $C_{31}H_{29}Cl_6Fe_3N_4O_4$, triclinic, $P\bar{1}$, $a = 14.099(6)$, $b = 18.510(7)$, $c = 7.108(3)$ Å, $\alpha = 96.77(2)$, $\beta = 99.45(2)$, $\gamma = 81.16(2)°$, $U = 18.00.0$ Å^3, $Z = 2$, $T = 101$ K. Residuals were $R(F) = 0.0558$ and $R_w(F) = 0.0431$ using 4691 unique reflections; reflections with $F < 2.33\sigma(F)$ were given zero weight. CCDC 182/940.

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