The reaction between FeCl₃, NaO₂CPh and L (L = 1,2-bis(2,2’-bipyridyl-6-yl)ethane) in MeCN gives the title complex 1 whose cation contains an unusual [Fe₆(μ₃-O)₄]¹⁰⁺ core, whereas in MeOH the dinuclear complex [Fe₂(OMe)₂Cl₂(O₂CPh)L][FeCl₄] 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 [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄]⁺ salts (R = Me, Et, Ph, etc.) complexes (S = 9 or 10)¹,³ and their one-electron reduced versions in [Mn₁₂O₁₁(O₂CR)₁₆(H₂O)₄]⁺ salts (S = 19/2).² More recently, the [Mn₃O₇X(O₂CMe)₃(dbm)]⁻ (dbm = dibenzoylmethane) complexes with S = 9/2,⁵ and [V₆O₂(O₂CR)₇(L–L)]²⁺ salts [L–L = 2,2’-bipyridine (bpy), z = + 1; L–L = 2-picolinate, z = −1] with S = 36 have also been discovered to be SMMs, as has a [Fe₆O₄(OH)₁₂(tacn)₆]²⁺ salt (tacn = 1,4,7-triazacyclonane) with S = 10.⁶

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 Mn³⁺ and Fe³⁺. With this in mind, we have been investigating the ability of bis-bipyridine ligands such as L to assemble new cluster types with Mn³⁺ and Fe³⁺ not available with simpler ligands such as bpy itself. We herein describe access via this route to a new Fe₆ structural type, as well as a related Fe₂ species, confirming the potential of this ligand for cluster synthesis in Fe³⁺–Mn³⁺ chemistry.

The reaction between FeCl₃, NaO₂CPh 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 Et₂O. Red-brown crystals of [Fe₂O₂Cl₄(O₂CPh)₂L₂][FeCl₄]·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 [Fe₂(OMe)₂Cl₂(O₂CPh)L][FeCl₄] 2 in 28% yield.†

Note that the use of bpy instead of L in the MeCN reaction gives [Fe₂O₂(O₂CPh)₂(bpy)]²⁺[FeCl₄]⁻, the cation of which has been previously reported.³

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 [Fe₆(μ₃-O)₄]¹⁰⁺ core (6 × Fe³⁺) that can be conveniently described as consisting of three edge-fused [Fe₂O₂] 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 [Fe₆O₄] core to be nearly planar. The L and central PhCO₂⁻ 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 [Fe₂O₂(O₂CPh)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 [FeCl₄(O₂CPh)]⁻ caps at each end, whose Fe(1) and O(10) atoms bind to and prevent O(6) and Fe(3) from attaching to another [Fe₂O₂(O₂CPh)L]⁺ fragment. Note the unusual nearly T-shaped geometry of O(7) and O(7'), with Fe(2')–O(7)–Fe(7) angles of 159.25(21)°.

The cation of 2 contains a [Fe₂(μ-OMe)₂]⁺⁺ core with bridging L and PhCO₂⁻ groups, and octahedral geometry at each Fe³⁺ completed by terminal Cl⁻ ions. The dinuclear unit is thus similar to the repeating [Fe₂O₂(O₂CPh)L]⁺ fragment of 1, with aggregation blocked by the MeO⁻–for-O²⁻ substitution at 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.

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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(42) 1.981(4), Fe(1)–O(42) 1.993(4), Fe(1)–Cl(1) 2.290(2), Fe(2)–O(40) 2.013(4), Fe(2)–O(42) 2.013(4), Fe(2)–Cl(1) 2.271(2); Fe(1)–O(40)–Fe(2) 101.31(19), Fe(1)–O(42)–Fe(2) 102.29(18).

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–O–Fe 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, 5.89. C₁₂H₁₉Cl₁₀Fe₂N₈O₈ requires C, 41.56; H, 2.78; N, 5.89; Complex 2: Found: C, 41.36; H, 2.38; N, 6.24. C₁₂H₁₉Cl₁₀Fe₂N₈O₈ requires C, 41.29; H, 2.34; N, 6.21%).
‡ Crystal data for 1:2MeCN: C₂₀H₂₀Cl₂Fe₂N₈O₈, Mᵣ = 2179.60, monoclinic, P2₁/a, a = 15.317(2), b = 18.303(3), c = 16.168(3) Å, β = 108.91(1)°, U = 4288.1 Å³, Z = 2, T = 104 K. Residuals were R(F) = 0.0551 and Rₑ(F) = 0.0576 using 5610 unique reflections; reflections with F < 3σ(F) were given zero weight. Crystal data for 2: C₁₂H₂₀Cl₂Fe₂N₈O₈, triclinic, P₁, a = 14.099(6), b = 18.510(7), c = 7.108(3) Å, α = 96.77(2), β = 99.45(2), γ = 81.16(2), U = 18.00 Å³, Z = 2, T = 101 K. Residuals were R(F) = 0.0558 and Rₑ(F) = 0.0431 using 4691 unique reflections; reflections with F < 2.33σ(F) were given zero weight. CCDC 182940.


Received in Cambridge, UK, 19th May 1998; 8/03760D