Bis-bipyridine ligands in cobalt carboxylate cluster chemistry: a mixed-valence ($4Co^{II}$, $4Co^{III}$) complex with a face-sharing, triple-cubane structure

Vincent A. Grillo,[a] Ziming Sun,[b] Kirsten Folting,[a] David N. Hendrickson*[b] and George Christou*[a]

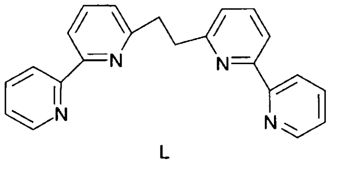
[a] *Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405-4001, USA*
[b] *Department of Chemistry-0358, University of California at San Diego, La Jolla, CA 92093-0358, USA*

Addition of aqueous H_2O_2 to a solution of $Co(O_2CMe)_2{\cdot}4H_2O$ and L [L = 1,2-bis(2,2′-bipyridyl-6-yl)ethane] in a 3 : 1 molar ratio, followed by addition of $LiClO_4$, allows isolation of $[Co_8O_4(OH)_4(O_2CMe)_6L_2](ClO_4)_2$ 1 which contains $4Co^{II}$, $4Co^{III}$; the core comprises three face-sharing cubane units, and magnetic susceptibility studies confirm the paramagnetic nature of the compound and the presence of high-spin Co^{II} ions.

The use of polypyridyl, oligo-2,2′-bipyridine and related ligands has been receiving much attention in recent years.[1–10] The formation of complexes of these ligands with mononuclear metal centres has been an important theme in supramolecular chemistry, and a variety of metal–ligand supramolecular assemblies have been obtained with fascinating structures such as double- or triple-helices, and 'capped', 'cylindrical' and 'circular' architectures.

We have recently become interested in the use of the above ligands in metal carboxylate cluster chemistry, investigating (i) the self-assembly of supramolecular ensembles containing linked clusters, and (ii) the influence of the chosen ligand on the structure and/or nuclearity of the cluster formed. Progress along direction (i) has recently been communicated,[11] and we herein report our initial result in direction (ii), *viz.* the novel, mixed-valence cluster $[Co_8O_4(OH)_4(O_2CMe)_6L_2](ClO_4)_2$ **1** from the use of the bis(2,2′-bipyridyl) ligand L.[12]

An orange solution of $Co(O_2CMe)_2{\cdot}4H_2O$ and L (1.32 g, 0.44 mmol) in EtOH (20 ml) was treated dropwise with aqueous H_2O_2 (50%, 1 ml) to give a dark green solution. Addition of $LiClO_4$ and storage of the solution at room temperature produced dark green crystals, which were collected by filtration, and recrystallised from MeCN; the yield was *ca.* 40%. The dried solid analysed as **1**·0.5MeCN.† The cation of **1**‡ consists of a $[Co_8(\mu_4\text{-}O)_4(\mu_3\text{-}OH)_4]^{8+}$ core with an unusual face-sharing, triple-cubane architecture (Figs. 1 and 2). Co(1,2,7,8) and Co(3,4,5,6) are Co^{II} and Co^{III} ions, respectively, and O(9,10,15,16) are the protonated (*i.e.* OH^-) atoms. This conclusion is based on: (i) ClO_4^- and lattice solvent molecules within hydrogen-bonding distances (2.704–2.882 Å) of the OH^- groups; (ii) bonds to the Co^{II} ions [2.038(8)–2.226(11) Å] being significantly longer than bonds to Co^{III} ions [1.852(7)–1.952(8) Å] (Fig. 2); and (iii) ^1H NMR and magnetic susceptibility data (*vide infra*) which show the cation to be paramagnetic. There are three types of Co···Co separations: $Co^{II}(\mu\text{-}OH)_2Co^{II}$ (*ca.* 3.5 Å), $Co^{II}(\mu\text{-}OH)(\mu\text{-}O)Co^{III}$ (*ca.* 2.9–3.1 Å) and $Co^{III}(\mu\text{-}O)_2Co^{III}$ (*ca.* 2.7–2.9 Å). The peripheral ligation is provided by six $MeCO_2^-$ groups bridging Co^{II}/Co^{III} and Co^{III}/Co^{III} pairs, and two L ligands chelating to Co^{II} ions and bridging the Co^{II}/Co^{II} pairs. The complete cation has virtual D_2 symmetry.



L

Complex **1** is the first example of a face-shared, triple-cubane structure for Co or any other 3d metal, but similar structures have been seen previously in $[(C_5Me_5)_4M_4Mo_4O_{16}]$ (M = Rh, Ir)[13] containing a $[M_4Mo_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4]$ core with M and Mo in the Co^{II} and Co^{III} positions, respectively, for **1**. The central $[Co_4O_4]^{4+}$ cubane of **1** has been seen previously in $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_2$,[14] and in the mixed-valence $4Co^{II}$, $4Co^{III}$ complex $[Co_8O_4(O_2CR)_{12}(MeCN)_3(H_2O)]$,[15] where each O^{2-} becomes μ_4 by attaching to a Co^{II} ion; $Co^{III}{\cdots}Co^{III}$ and Co^{III}–O^{2-} distances in these complexes are similar to those in **1**, supporting the given oxidation state description.

The ^1H NMR spectrum of **1**·0.5MeCN in CD_3CN exhibits paramagnetically shifted and broadened resonances in the δ −25 to +60 range, confirming the paramagnetic nature of the cation. Solid-state magnetic susceptibility (χ_m) *vs.* temperature measurements were performed in a 1 Tesla field: the effective magnetic moment (μ_{eff}/Co_8) slowly decreases from 8.60 μ_B at 320 K to 7.27 μ_B at 100 K, and then more rapidly to 1.77 μ_B at 2.00 K (Fig. 3). The only unpaired electrons are on the four Co^{II}

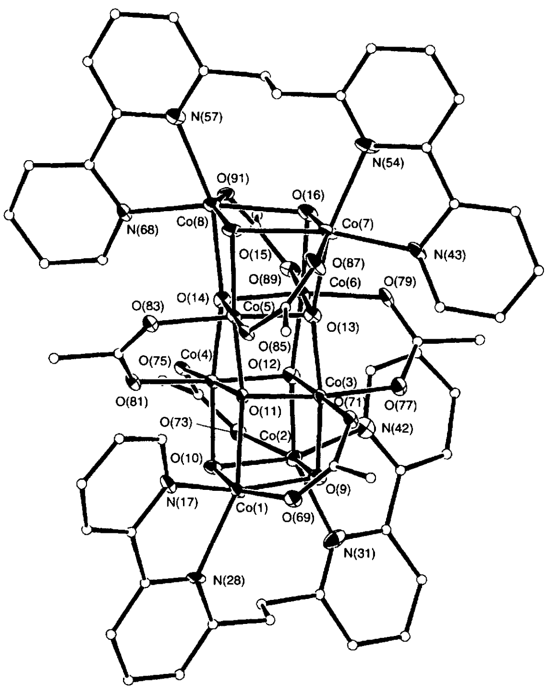


Fig. 1 The structure of the $[Co_8O_4(OH)_4(O_2CMe)_6L_2]^{2+}$ cation of **1**. Selected interatomic distances (Å) are: Co(1)···Co(2) 3.518(3), Co(1)···Co(3) 2.896(2), Co(1)···Co(4) 3.066(2), Co(2)···Co(3), 3.054(2), Co(2)···Co(4) 2.904(2), Co(3)···Co(4) 2.796(2), Co(3)···Co(5) 2.860(2), Co(3)···Co(6) 2.699(2), Co(4)···Co(5) 2.693(2), Co(4)···Co(6) 2.864(2), Co(5)···Co(6) 2.799(2), Co(5)···Co(7) 2.906(2), Co(5)···Co(8) 3.066(2), Co(6)···Co(7) 3.082(2), Co(6)···Co(8) 2.906(2), Co(7)···Co(8) 3.476(2).

centres, and the above values correspond to 4.30, 3.63 and 0.88 μ_B per Co^{II} at 320, 100 and 2.00 K, respectively. The 300 K value may be compared with the spin-only (g = 2) value of 3.87 μ_B for high-spin Co^{II} (S = 3/2); the data are thus consistent with four high-spin Co^{II} ions in **1** and $g > 2$, as expected for Co. The decrease in μ_{eff} with temperature is consistent with (i) extensive first-order spin–orbit coupling and resultant splittings between the Kramers doublets of the orbitally degenerate ground state of high-spin Co^{II} in near-octahedral coordination;[16] (ii) antiferromagnetic exchange interactions within each Co^{II}/Co^{II} pair mediated by the μ_3-OH^- ions; or (iii) both of these effects. Possibility (iii) is the most likely. The μ_{eff} *vs.* T behaviour in Fig. 3 is similar to that observed for dinuclear Co^{II} species.[17]

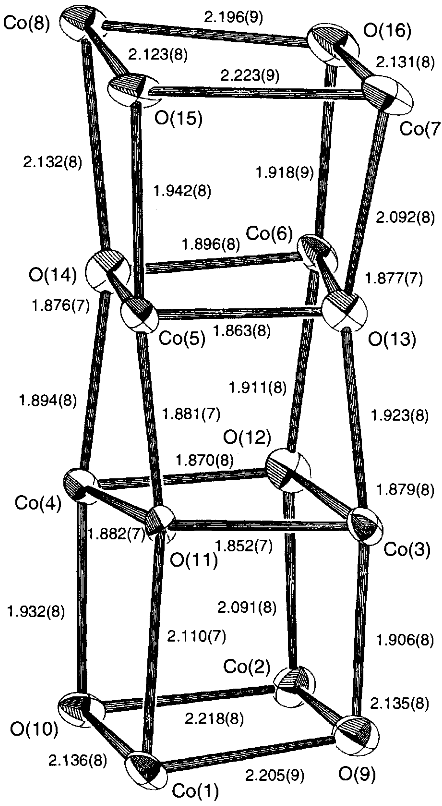


Fig. 2 The $[Co_8O_4(OH)_4]^{8+}$ core of **1**, showing Co–O bond lengths; the OH^- oxygen atoms are O(9), O(10), O(15) and O(16)

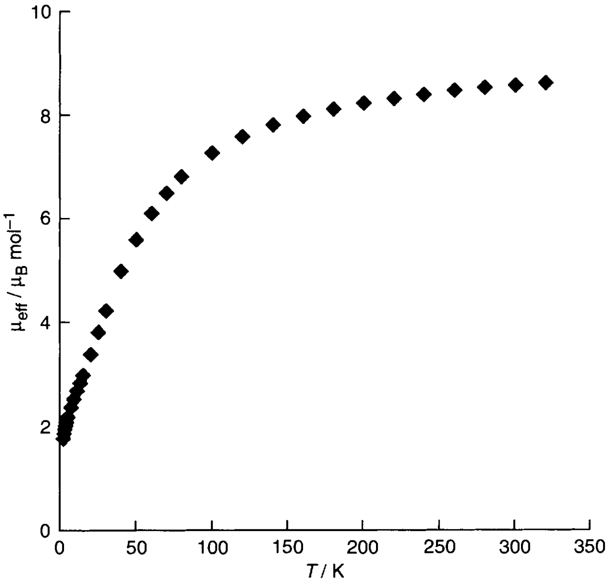


Fig. 3 Plot of the effective magnetic moment (μ_{eff}) per Co_8 *vs.* temperature for **1**·0.5MeCN

The use of bis-bpy ligand L has allowed access to a novel Co_8 cluster and represents a 'proof of feasibility' for the belief that such ligands may provide a rich source of new transition-metal clusters. Further studies are in progress.

This work was supported by the National Science Foundation.

Footnotes

† The complex analysed satisfactorily (C, H, N) for **1**·0.5MeCN.

‡ Suitable single crystals of **1**·x solv. were grown by slowly evaporating a MeCN–EtOH solution. *Crystal data*: $C_{56}H_{58}Cl_2Co_8N_8O_{28}$ (excl. solv.), M_r = 1833.47, monoclinic, space group $P2_1/n$, a = 23.159(4), b = 24.568(4), c = 13.374(3) Å, β = 90.31(1)°, U = 7609.3 Å^3, Z = 4, T = 180K. Residuals were $R(F)$ = 0.0844 and $R_w(F)$ = 0.0790 using 9967 unique reflections; reflections with $F < 3\sigma(F)$ were given zero weight.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/198.

References

1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
2 R. Krämer, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703; E. Leize, A. Van Dorsselaer, R. Krämer and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 990.
3 C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani and A. F. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 7440.
4 W. Zarges, J. Hall, J.-M. Lehn and C. Bolm, *Helv. Chim. Acta*, 1991, **74**, 1843.
5 T.-M. Garrett, U. Koert, J.-M. Lehn, A. Rigault, D. Meyer and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 557.
6 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565.
7 P. Baxter, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 69; P. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284.
8 M.-T. Youinou, R. Ziessel and J.-M. Lehn, *Inorg. Chem.*, 1991, **30**, 2144; M.-T. Youinou, N. Rahmouni, J. Fischer and J. A. Osborn, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 733.
9 K. T. Potts, K. A. Gheysen Raiford and M. Keshavarz-K, *J. Am. Chem. Soc.*, 1993, **115**, 2793.
10 E. C. Constable, R. Chotalia and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, 771; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; (*c*) E. C. Constable, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 1256.
11 V. A. Grillo, M. J. Knapp, J. C. Bollinger, D. N. Hendrickson and G. Christou, *Angew. Chem., Int. Ed. Engl.*, in the press.
12 T. Garber, S. Van Wallendael, D. P. Rillema, M. Kirk, W. E. Hatfield, J. H. Welch and P. Singh, *Inorg. Chem.*, 1990, **29**, 2863.
13 Y. Hayashi, K. Toriumi and K. Isobe, *J. Am. Chem. Soc.*, 1988, **110**, 3666.
14 K. Dimitrou, K. Folting, W. E. Streib and G. Christou, *J. Am. Chem. Soc.*, 1993, **115**, 6432.
15 K. Dimitrou, J.-S. Sun, K. Folting and G. Christou, *Inorg. Chem.*, 1995, **34**, 4160.
16 M. W. Makinen, L. C. Kuo, M. B. Yim, G. B. Wells, J. M. Fukuyama and J. E. Kim, *J. Am. Chem. Soc.*, 1985, **107**, 5245; L. Banci, A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Struct. Bonding (Berlin)*, 1982, **52**, 37.
17 M. A. Laffey and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 313; J. M. Kuszaj, B. Tomlonovic, D. P. Murtha, R. L. Lintvedt and M. D. Glick, *Inorg. Chem.*, 1973, **12**, 1297.

Received, 1st July 1996; Com. 6/04555C