

# Bis-bipyridine ligands in cobalt carboxylate cluster chemistry: a mixed-valence (4Co<sup>II</sup>, 4Co<sup>III</sup>) complex with a face-sharing, triple-cubane structure

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Addition of aqueous H<sub>2</sub>O<sub>2</sub> to a solution of Co(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O and L [L = 1,2-bis(2,2'-bipyridyl-6-yl)ethane] in a 3:1 molar ratio, followed by addition of LiClO<sub>4</sub>, allows isolation of [Co<sub>8</sub>O<sub>4</sub>(OH)<sub>4</sub>(O<sub>2</sub>CMe)<sub>6</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **1** which contains 4Co<sup>II</sup>, 4Co<sup>III</sup>; 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<sup>II</sup> ions.

The use of polypyridyl, oligo-2,2'-bipyridine and related ligands has been receiving much attention in recent years.<sup>1–10</sup> 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.

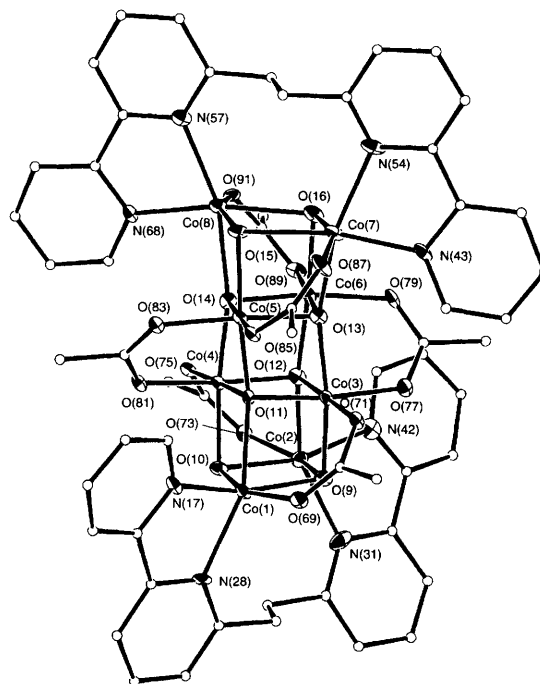
We have recently become interested in the use of the above ligands in metal carboxylate cluster chemistry, investigating (i) the self-assembly of supramolecular ensembles containing linked clusters, and (ii) the influence of the chosen ligand on the structure and/or nuclearity of the cluster formed. Progress along direction (i) has recently been communicated,<sup>11</sup> and we herein report our initial result in direction (ii), *viz.* the novel, mixed-valence cluster [Co<sub>8</sub>O<sub>4</sub>(OH)<sub>4</sub>(O<sub>2</sub>CMe)<sub>6</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **1** from the use of the bis(2,2'-bipyridyl) ligand L.<sup>12</sup>

An orange solution of Co(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O and L (1.32 g, 0.44 mmol) in EtOH (20 ml) was treated dropwise with aqueous H<sub>2</sub>O<sub>2</sub> (50%, 1 ml) to give a dark green solution. Addition of LiClO<sub>4</sub> 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<sub>8</sub>(μ<sub>4</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>]<sup>8+</sup> 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<sup>II</sup> and Co<sup>III</sup> ions, respectively, and O(9,10,15,16) are the protonated (*i.e.* OH<sup>−</sup>) atoms. This conclusion is based on: (i) ClO<sub>4</sub><sup>−</sup> and lattice solvent molecules within hydrogen-bonding distances (2.704–2.882 Å) of the OH<sup>−</sup> groups; (ii) bonds to the Co<sup>II</sup> ions [2.038(8)–2.226(11) Å] being significantly longer than bonds to Co<sup>III</sup> ions [1.852(7)–1.952(8) Å] (Fig. 2); and (iii) <sup>1</sup>H NMR and magnetic susceptibility data (*vide infra*) which show the cation to be paramagnetic. There are three types of Co...Co separations: Co<sup>II</sup>(μ-OH)<sub>2</sub>Co<sup>II</sup> (*ca.* 3.5 Å), Co<sup>II</sup>(μ-OH)(μ-O)Co<sup>III</sup> (*ca.* 2.9–3.1 Å) and Co<sup>III</sup>(μ-O)<sub>2</sub>Co<sup>III</sup> (*ca.* 2.7–2.9 Å). The peripheral ligation is provided by six MeCO<sub>2</sub><sup>−</sup> groups bridging Co<sup>II</sup>/Co<sup>III</sup> and Co<sup>III</sup>/Co<sup>III</sup> pairs, and two L ligands chelating to Co<sup>II</sup> ions

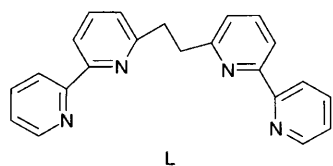
and bridging the Co<sup>II</sup>/Co<sup>II</sup> pairs. The complete cation has virtual D<sub>2</sub> symmetry.

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<sub>5</sub>Me<sub>5</sub>)<sub>4</sub>M<sub>4</sub>Mo<sub>4</sub>O<sub>16</sub>] (M = Rh, Ir)<sup>13</sup> containing a [M<sub>4</sub>Mo<sub>4</sub>(μ<sub>4</sub>-O)<sub>4</sub>(μ<sub>3</sub>-O)<sub>4</sub>] core with M and Mo in the Co<sup>II</sup> and Co<sup>III</sup> positions, respectively, for **1**. The central [Co<sub>4</sub>O<sub>4</sub>]<sup>4+</sup> cubane of **1** has been seen previously in [Co<sub>4</sub>O<sub>4</sub>(O<sub>2</sub>CR)<sub>2</sub>(bpy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>,<sup>14</sup> and in the mixed-valence 4Co<sup>II</sup>, 4Co<sup>III</sup> complex [Co<sub>8</sub>O<sub>4</sub>(O<sub>2</sub>CR)<sub>12</sub>(MeCN)<sub>3</sub>(H<sub>2</sub>O)],<sup>15</sup> where each O<sup>2−</sup> becomes μ<sub>4</sub> by attaching to a Co<sup>II</sup> ion; Co<sup>III</sup>...Co<sup>III</sup> and Co<sup>III</sup>–O<sup>2−</sup> distances in these complexes are similar to those in **1**, supporting the given oxidation state description.

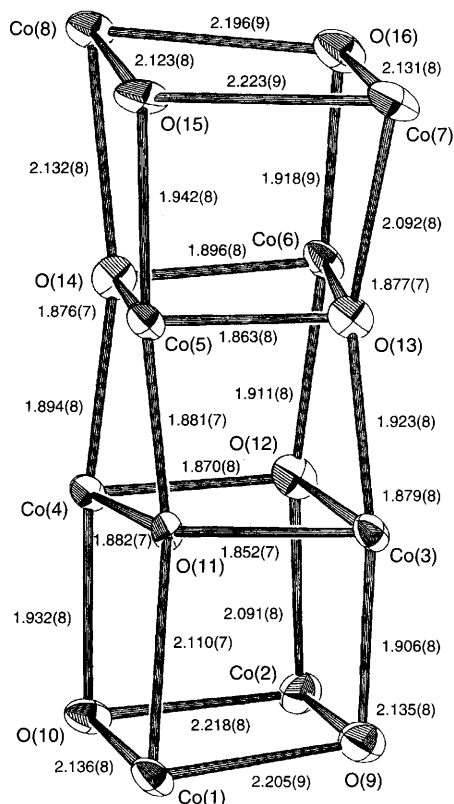
The <sup>1</sup>H NMR spectrum of **1**·0.5MeCN in CD<sub>3</sub>CN exhibits paramagnetically shifted and broadened resonances in the δ −25 to +60 range, confirming the paramagnetic nature of the cation. Solid-state magnetic susceptibility (χ<sub>m</sub>) vs. temperature measurements were performed in a 1 Tesla field: the effective magnetic moment (μ<sub>eff</sub>/Co<sub>8</sub>) slowly decreases from 8.60 μ<sub>B</sub> at 320 K to 7.27 μ<sub>B</sub> at 100 K, and then more rapidly to 1.77 μ<sub>B</sub> at 2.00 K (Fig. 3). The only unpaired electrons are on the four Co<sup>II</sup>



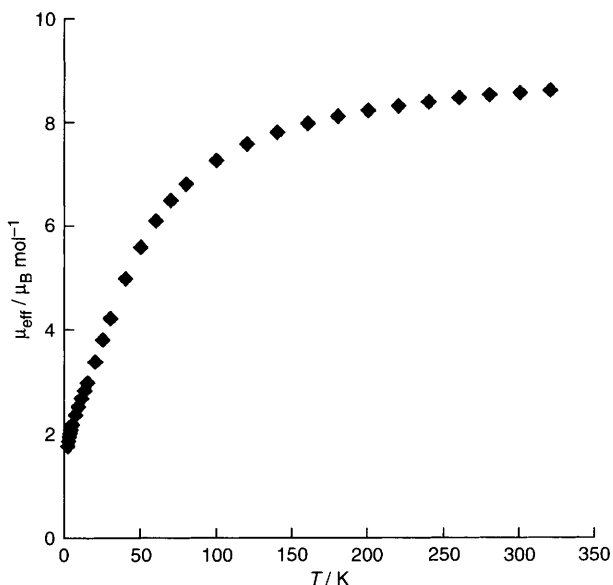
**Fig. 1** The structure of the [Co<sub>8</sub>O<sub>4</sub>(OH)<sub>4</sub>(O<sub>2</sub>CMe)<sub>6</sub>L<sub>2</sub>]<sup>2+</sup> cation of **1**. Selected interatomic distances (Å) are: Co(1)···Co(3) 3.518(3), Co(1)···Co(4) 3.066(2), Co(2)···Co(3) 3.054(2), Co(2)···Co(4) 2.904(2), Co(3)···Co(4) 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  $0.88 \mu_B$  per  $\text{Co}^{\text{II}}$  at 320, 100 and 2.00 K, respectively. The 300 K value may be compared with the spin-only ( $g = 2$ ) value of  $3.87 \mu_B$  for high-spin  $\text{Co}^{\text{II}}$  ( $S = 3/2$ ); the data are thus consistent with four high-spin  $\text{Co}^{\text{II}}$  ions in **1** and  $g > 2$ , as expected for Co. The decrease in  $\mu_{\text{eff}}$  with temperature is consistent with (i) extensive first-order spin-orbit coupling and resultant splittings between the Kramers doublets of the orbitally degenerate



**Fig. 2** The  $[\text{Co}_8\text{O}_4(\text{OH})_4]^{8+}$  core of **1**, showing Co–O bond lengths; the  $\text{OH}^-$  oxygen atoms are O(9), O(10), O(15) and O(16)



**Fig. 3** Plot of the effective magnetic moment ( $\mu_{\text{eff}}$ ) per  $\text{Co}_8$  vs. temperature for **1**·0.5MeCN

ground state of high-spin  $\text{Co}^{\text{II}}$  in near-octahedral coordination;<sup>16</sup> (ii) antiferromagnetic exchange interactions within each  $\text{Co}^{\text{II}}/\text{Co}^{\text{II}}$  pair mediated by the  $\mu_3\text{-OH}^-$  ions; or (iii) both of these effects. Possibility (iii) is the most likely. The  $\mu_{\text{eff}}$  vs.  $T$  behaviour in Fig. 3 is similar to that observed for dinuclear  $\text{Co}^{\text{II}}$  species.<sup>17</sup>

The use of bis-bpy ligand **L** has allowed access to a novel  $\text{Co}_8$  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.

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## 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:*  $\text{C}_{56}\text{H}_{58}\text{Cl}_2\text{Co}_8\text{N}_8\text{O}_{28}$  (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,  $\beta = 90.31(1)^\circ$ ,  $U = 7609.3$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 180$  K. 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.

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