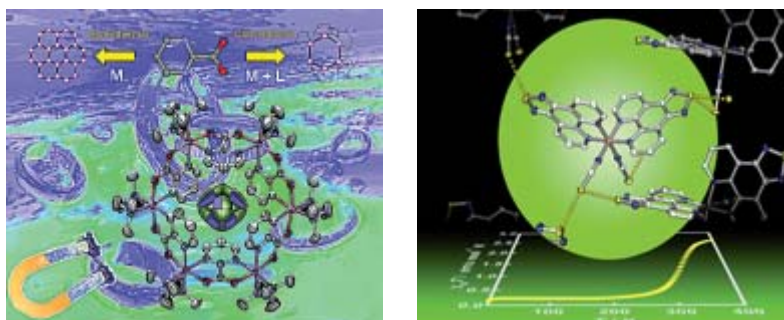


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Guest Editors Concepció Rovira and Jaume Veciana  
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# Transforming the cube: a tetranuclear cobalt(II) cubane cluster and its transformation to a dimer of dimers†

Athanassios D. Katsenis,<sup>a</sup> Ross Inglis,<sup>b</sup> Alexandra M. Z. Slawin,<sup>c</sup> Vadim G. Kessler,<sup>d</sup> Euan K. Brechin<sup>\*a</sup> and Giannis S. Papaefstathiou<sup>\*a</sup>

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An attempt to utilize a Co(II) cubane cluster as a building block to create extended frameworks results instead in the transformation of the cube into a dimer of dimers.

Polynuclear complexes based on paramagnetic metal ions offer the potential for new technological advances since many of them display fascinating physical properties.<sup>1–5</sup> The species which are most promising for technological applications include single-molecule magnets,<sup>3</sup> molecular coolants<sup>4</sup> and spin phonon traps.<sup>5</sup> The properties of such species are of molecular origin since it is the individual molecules that exhibit the physical properties rather than the bulk solids.<sup>1,2</sup> Although it has been known for some time that intermolecular interactions, often weak, between molecules in the crystal lattice may affect the observed physical properties, few investigations of the importance and controllability of such interactions exist.<sup>2</sup>

We have recently initiated a project to study in detail the weak interactions between paramagnetic metal clusters and to utilize them as building blocks for the construction of extended frameworks.<sup>6</sup> To this end, our attention turned toward the chemistry of di-2-pyridyl ketone [(py)<sub>2</sub>CO, Scheme 1] which, among others, has given rise to a number of tetranuclear clusters with a cubane topology where the metal atoms are arranged on the corners of a tetrahedron.<sup>7</sup> In some of these clusters, ferromagnetic interactions between the metal ions are observed.<sup>8</sup> Furthermore each metal centre has a potentially vacant coordination site, often occupied by a counter anion or a solvent molecule, which may be used as a connection site. We reasoned therefore that such tetranuclear clusters may serve as building blocks for the construction of extended frameworks, built on ferromagnetic clusters, if combined with linear bridging ligands such as 4,4'-bipyridine (4,4'-bpy, Scheme 1). Although many metal-organic frameworks are built on polynuclear metal

complexes,<sup>9</sup> there is only a handful of attempts where pre-isolated clusters have been utilized as building blocks for the construction of such materials.<sup>10</sup> Tailoring of extended molecular materials still remains a challenge in this field. Aiming to build such an extended framework, we first synthesized the new Co(II) cubane cluster [Co<sub>4</sub>{(py)<sub>2</sub>C(OH)O}<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)]NO<sub>3</sub> (**1**), where (py)<sub>2</sub>C(OH)O<sup>−</sup> is the monoanion of the hydrate of (py)<sub>2</sub>CO, which we then further reacted with 4,4'-bpy. However, instead of obtaining an extended framework we isolated the tetranuclear assembly [Co<sub>4</sub>{(py)<sub>2</sub>C(OMe)O}<sub>4</sub>(4,4'-bpy)<sub>2</sub>(MeOH)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>·2MeOH (**2**·2MeOH), where (py)<sub>2</sub>C(OMe)O<sup>−</sup> is the monoanion of the hemiacetal of (py)<sub>2</sub>CO. The latter can be regarded as a dimer of dimers.<sup>11</sup> Complexes **1** and **2** both show dominant ferromagnetic interactions between the Co(II) ions.

The reaction of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with (py)<sub>2</sub>CO and Et<sub>3</sub>N in MeOH for 15 min, followed by Et<sub>2</sub>O diffusion, produced purple crystals of [Co<sub>4</sub>{(py)<sub>2</sub>C(OH)O}<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)]NO<sub>3</sub> (**1**) with ~60% yield in 5 d. Complex **1** crystallises in the monoclinic space group *P2<sub>1</sub>/c*.† A partially labeled plot of the tetranuclear cation [Co<sub>4</sub>{(py)<sub>2</sub>C(OH)O}<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sup>+</sup> is shown in Fig. 1. The cluster has a [Co<sub>4</sub>(μ<sub>3</sub>-OR)<sub>4</sub>]<sup>4+</sup> core with four Co<sup>II</sup> and four oxygen atoms from four (py)<sub>2</sub>C(OH)O<sup>−</sup> ligands occupying alternate vertices. The Co<sub>4</sub>O<sub>4</sub> cube is distorted with the Co⋯Co distances ranging from 3.154 to 3.285 Å, the Co⋯O distances ranging from 2.023 to 2.253 Å and the Co⋯O⋯Co angles ranging from 94.2 to 103.4°. Each Co<sup>II</sup> atom is coordinated to three μ<sub>3</sub>-O atoms and two N-pyridyl atoms belonging to three and two different (py)<sub>2</sub>C(OH)O<sup>−</sup> ligands, respectively, and either a terminal NO<sub>3</sub><sup>−</sup> (Co2, Co3 and Co4) or a H<sub>2</sub>O (Co1) molecule to adopt a distorted octahedral coordination environment.

The (py)<sub>2</sub>C(OH)O<sup>−</sup> ligands adopt the η<sup>1</sup>:η<sup>3</sup>:η<sup>1</sup>:μ<sub>3</sub> coordination mode being chelated to two Co atoms through the

<sup>a</sup>Laboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, 157 71 Zografou, Greece. E-mail: gspapaef@chem.uoa.gr; Fax: +30 210 – 727 – 4287; Tel: +30 210 – 727 – 4840

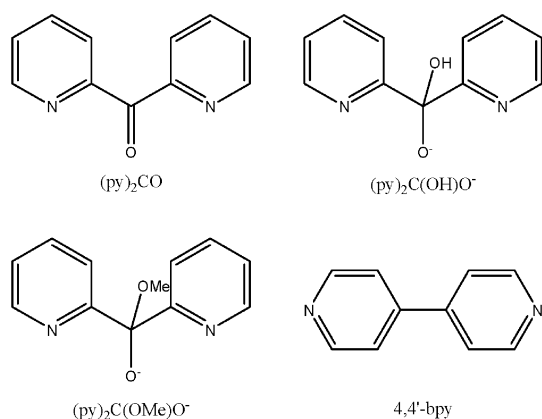
<sup>b</sup>School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: ebrechin@staffmail.ed.ac.uk; Fax: +44 11 – 275 – 4598; Tel: +44 131 650 7545

<sup>c</sup>School of Chemistry, The University of St. Andrews, Purdie Building, St. Andrews, Fife, UK KY16 9ST

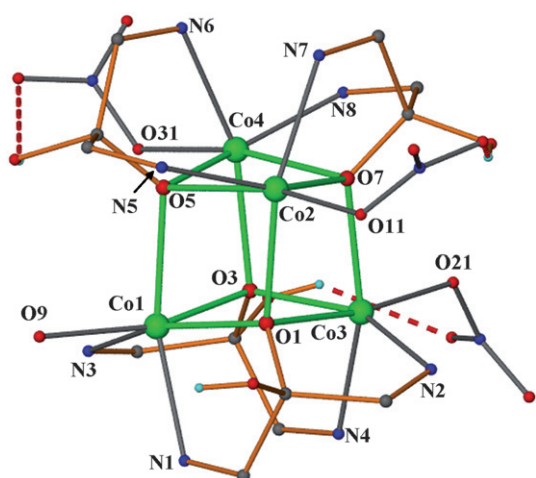
<sup>d</sup>Department of Chemistry, Swedish University of Agricultural Sciences, Box 7015, 750 07 Uppsala, Sweden

† Electronic supplementary information (ESI) available: Synthetic details for the preparation of both complexes, a figure illustrating the molecular structures and packing diagrams. CCDC reference numbers 727655 and 727656. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907546c

‡ Crystal data for **1**: C<sub>44</sub>H<sub>38</sub>N<sub>12</sub>O<sub>21</sub>Co<sub>4</sub>, *M* = 1306.58, monoclinic, space group *P2<sub>1</sub>/c*, *a* = 20.4504(18) Å, *b* = 12.7826(11) Å, *c* = 20.0563(17) Å, α = 90°, β = 105.455(2)°, γ = 90°, *V* = 5053.3(8) Å<sup>3</sup>, *D<sub>c</sub>* = 1.717 g cm<sup>−3</sup>, Mo Kα radiation (λ = 0.71070 Å), 29350 reflections collected (11941 independent, *R*<sub>int</sub> = 0.0264), *R*<sub>1</sub> = 0.0554 [based on *I* > 2σ(*I*)], *wR*<sub>2</sub> = 0.1369 (all data). Crystal data for **2**·2MeOH: C<sub>74</sub>H<sub>80</sub>N<sub>16</sub>O<sub>26</sub>Co<sub>4</sub>, *M* = 1845.26, monoclinic, space group *P2<sub>1</sub>/m*, *a* = 13.463(3) Å, *b* = 14.090(3) Å, *c* = 21.268(4) Å, α = 90°, β = 93.875(9)°, γ = 90°, *V* = 4025.1(15) Å<sup>3</sup>, *D<sub>c</sub>* = 1.523 g cm<sup>−3</sup>, Cu Kα radiation (λ = 1.54178 Å), 53265 reflections collected (6967 independent *R*<sub>int</sub> = 0.0604), *R*<sub>1</sub> = 0.0459 [based on *I* > 2σ(*I*)], *wR*<sub>2</sub> = 0.1145 (all data).



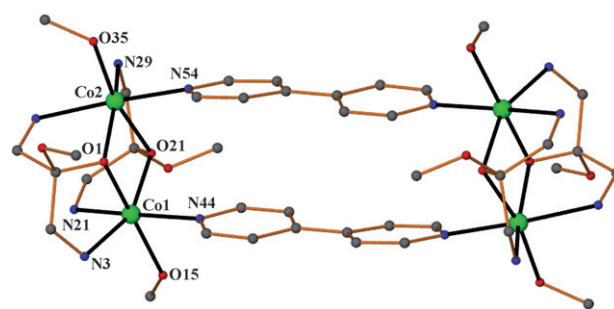
**Scheme 1** Structures of the ligands discussed in the text.



**Fig. 1** The molecular structure of the cubane core in **1**. Colour code: Co = green, O = red, N = blue, C = grey. Most H and C atoms have been omitted for clarity.

N-pyridyl and the deprotonated O alkoxo atoms while bridging a third Co atom through the alkoxo O atom. The second alkoxo O atom of the (py)<sub>2</sub>C(OH)O<sup>-</sup> ligand remains protonated and is hydrogen bonded to a neighbouring NO<sub>3</sub><sup>-</sup> anion (three coordinated and one lattice). Although the H atoms of the terminal water molecule were not located, their positions are evident from the O<sup>⋯</sup>O distances from an intramolecular H-bond with a neighbouring alkoxide (O9<sup>⋯</sup>O6 2.869 Å) and an intermolecular H-bond with the lattice NO<sub>3</sub><sup>-</sup> anion which is disordered over two positions with 53 and 47% occupancies (O9<sup>⋯</sup>O41 2.507 Å and O9<sup>⋯</sup>O43A 2.567 Å). There are no other intermolecular contacts between the ions of **1**.

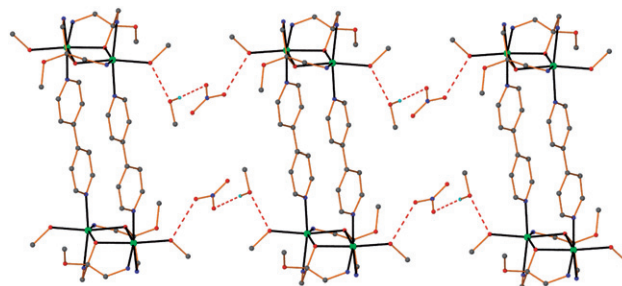
The reaction of **1** with two equivalents of 4,4'-bpy in MeOH results in an orange solution from which orange crystals of **2**·2MeOH were isolated after Et<sub>2</sub>O diffusion with ~65% yield in 2 d. At first, **1** appears to be insoluble in alcohol but after persistent stirring in MeOH for (at least) 3 h a clear pink solution results which becomes orange upon addition of solid 4,4'-bpy. The slow dissolution of **1** in MeOH is accompanied by the transformation of the hydrate anion (py)<sub>2</sub>C(OH)O<sup>-</sup> (Scheme 1) to the hemiacetal anion (py)<sub>2</sub>C(OMe)O<sup>-</sup> (Scheme 1) found in **2**·2MeOH.



**Fig. 2** The molecular structure of the tetranuclear assembly in **2**. Colour code: Co = green, O = red, N = blue, C = grey. All H and most C atoms have been omitted for clarity.

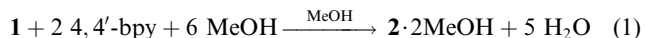
**2**·2MeOH crystallises in the monoclinic space group  $P2_1/n$ .<sup>††</sup> A view of the crystal structure of **2** reveals that two dinuclear units [Co<sub>2</sub>{(py)<sub>2</sub>C(OMe)O<sub>2</sub>(MeOH)<sub>2</sub>}]<sup>2+</sup> have assembled with two molecules of 4,4'-bpy to form the cationic tetranuclear rectangular assembly [Co<sub>4</sub>{(py)<sub>2</sub>C(OMe)O<sub>4</sub>(4,4'bpy)<sub>2</sub>(MeOH)<sub>4</sub>}]<sup>4+</sup> (Fig. 2) that lies on a centre of inversion. Each Co<sup>II</sup> atom adopts a distorted octahedral environment being coordinated to three N-atoms in a *mer* orientation, two of which originate from the 2-pyridyl groups of two (py)<sub>2</sub>C(OMe)O<sup>-</sup> anions and the third from a 4,4'-bpy molecule, and three O-atoms in a *mer* orientation that originate from two (py)<sub>2</sub>C(OMe)O<sup>-</sup> anions and a terminal MeOH molecule. The Co<sup>⋯</sup>Co distance within the dinuclear unit is 3.085 Å while it is 11.336 Å along the 4,4'-bpy bridge. The Co<sup>⋯</sup>O and Co<sup>⋯</sup>N distances range from 2.003 to 2.162 Å and 2.095 to 2.172 Å respectively, while the Co<sup>⋯</sup>O<sup>⋯</sup>Co angles are 96.6 and 95.2°. The (py)<sub>2</sub>C(OMe)O<sup>-</sup> ligands adopt a η<sup>1</sup>:η<sup>2</sup>:η<sup>1</sup>:μ<sub>2</sub> coordination mode and chelate two Co atoms through the N-pyridyl and the deprotonated O-alkoxo atoms. The lattice MeOH molecules and two of the four NO<sub>3</sub><sup>-</sup> ions assemble with the terminal MeOH molecules to form a one-dimensional ladder-like hydrogen-bonded array that runs parallel to the *a* axis (Fig. 3). The ladders pack in a herringbone fashion with the non hydrogen-bonded NO<sub>3</sub><sup>-</sup> anions sitting between them (Fig. S1).<sup>†</sup>

A careful inspection of the molecular structures of **1** and **2** reveals that both are built up from the same dinuclear unit, namely [Co<sub>2</sub>{(py)<sub>2</sub>C(OR)O<sub>2</sub>L<sub>2</sub>}]<sup>n+</sup> where R = H, L = NO<sub>3</sub><sup>-</sup> or H<sub>2</sub>O and *n* = 0 or 1 for **1** and R = Me, L = MeOH, *n* = 2 for **2**, respectively. These dimers either self-assemble (in the case of **1**) by means of Co–O bonds through the deprotonated alkoxo O



**Fig. 3** The hydrogen-bonded ladder in **2**. Color code as in Fig. 2. Most H and C atoms have been omitted for clarity.

atoms of one dimer and the Co atoms of the other dimer to create the cubane, or (in the case of **2**) through the two 4,4'-bpy molecules to create the rectangular dimer of dimers. Most importantly, the latter results from the former; Eqn (1) summarises the transformation of **1** to **2**.



The variable temperature magnetic behaviour of **1** and **2**, measured using an applied field of 0.1 T, is plotted as the  $\chi_m T$  product versus  $T$  (where  $\chi_m$  is the molar magnetic susceptibility) in Fig. 4. The explanation of magnetic behaviour of cobalt(II) complexes is complicated by the orbitally degenerate ground state of the ion when six-coordinate<sup>12</sup> and so derivation of the magnitude of the exchange interactions between cobalt centres is effectively impossible, and indeed assigning a “spin ground state” to such clusters is essentially meaningless. Therefore only a qualitative report of the magnetic susceptibility data follows. The room temperature  $\chi_m T$  values of  $\sim 10.9$  and  $\sim 10.3 \text{ cm}^3 \text{ K mol}^{-1}$  for **1** and **2**, respectively, are consistent with the presence of four  $s = 3/2$  ions with anisotropic  $g$ -values. As the temperature is decreased the value of  $\chi_m T$  increases for both complexes, **1** reaching a maximum value of  $\sim 14.8 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K. **2** displays a broad maximum of  $\sim 10.3 \text{ cm}^3 \text{ K mol}^{-1}$  at 100 K before decreasing sharply below this temperature to a value of  $\sim 9.3 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K. Such broad maxima are typical of cobalt(II) compounds and in this case can be attributed to a combination of single ion spin-orbit coupling, and/or intra-(dimer  $\leftrightarrow$  dimer) and intermolecular (tetramer  $\leftrightarrow$  tetramer) anti-ferromagnetic exchange coupling. For **1** the data is suggestive of dominant ferromagnetic exchange and for **2** it is suggestive of ferromagnetic intra-dimer exchange with either no, or very weak inter-dimer and inter-tetramer anti-ferromagnetic exchange. The magnetisation curves for the two complexes are essentially analogous; Fig. 4 shows those for complex **1** obtained in fields of up to 7 T. There is a rapid increase in  $M$  with applied field with

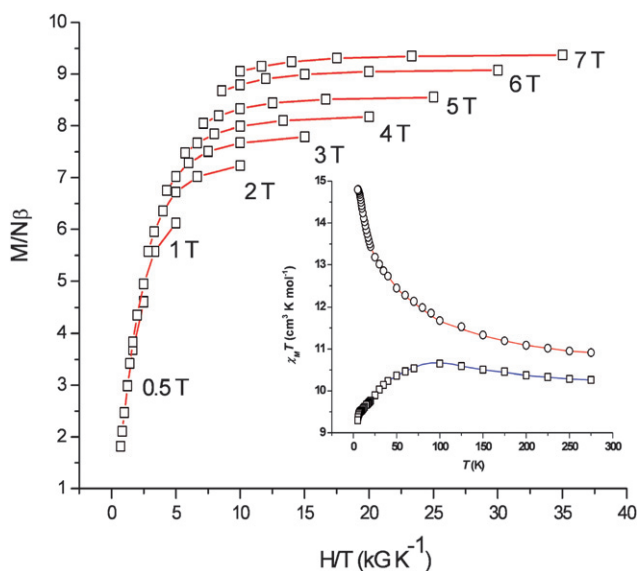
the magnetisation saturating at approximately  $M/N\beta \approx 9.5$  in both cases clearly indicating a magnetic ground state for both. Ac susceptibility data measured between 100 and 1500 Hz on **1** showed no evidence of any frequency-dependent peaks ruling out the possibility of slow relaxation of the magnetisation and SMM behaviour.

In summary, we have synthesised and characterised a new tetranuclear Co(II) cluster with a cubane topology which is based on the hydrate of di-2-pyridyl ketone and dominated by ferromagnetic interactions. In an attempt to utilize this magnetic cluster as a building block for the construction of an extended framework, we serendipitously transformed the cube into a rectangular tetranuclear assembly which can be regarded as a dimer of dimers. Both the cubane and the dimer of dimers are composed of the dinuclear units  $[\text{Co}_2\{\text{(py)}_2\text{C(OR)O}\}_2\text{L}_2]^{n+}$  which either self-assemble with themselves to give the cubane, or assemble with two molecules of 4,4'-bpy to give the rectangular assembly. We are presently investigating this reaction system further by incorporating other bi- or polydentate ligands.

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**Fig. 4** Plot of reduced magnetisation ( $M/N\beta$ ) versus for complex **1**. Inset: plot of  $\chi_m T$  versus  $T$  for **1** (red line) and **2** (blue line).

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