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Mixed-Valence Cobalt(II/III) Carboxylate Clusters: $Co^{II}_4Co^{III}_2$ and $Co^{II}Co^{III}_2$ Complexes from the Use of 2-(Hydroxymethyl)pyridine

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Dedicated to the late F. Albert Cotton for his important contributions to Inorganic Chemistry

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Aerobic reactions of $Co(O_2CR)_2$ with 2-(hydroxymethyl)pyridine (hmpH), in the presence of ClO_4^- counterions give the hexanuclear, mixed-valence clusters $[Co^{II}_4Co^{III}_2(O_2CR)_4(hmp)_8](ClO_4)_2$ [R = Me (**1**), Ph (**2**)] which possess the unprecedented $[Co^{II}_4Co^{III}_2(\mu_3\text{-}OR')_4(\mu\text{-}OR')_4]^{6+}$ [R′ = (2-pyridyl)-CH_2-] core. Replacement of ClO_4^- by N_3^- in the reaction mixture that gives **1** leads to the linear complex $[Co^{III,II,III}_3(O_2CMe)_2(N_3)_2(hmp)_4]$ (**3**). Q-band EPR spectra and variable-temperature magnetic susceptibility studies for **1** and **2** provide strong evidence that the Co^{II} ions are antiferromagnetically coupled.

Introduction

There is currently an intense interest in the synthesis and study of polynuclear 3d-metal complexes (clusters). Among the diverse reasons for this is the discovery that 3d-metal molecular clusters can show slow relaxation of magnetisation under certain circumstances. These molecular species, named "single-molecule magnets" (SMMs),[1] have attracted great interest from both a technological viewpoint – in that such single molecules represent the smallest conceivable memory devices – and from a fundamental scientific perspective, as those clusters have allowed studies of quantum mechanichal phenomena such as tunneling.[1a,1b,1d] There thus continues to be a need for new synthetic methods[2] to such molecules.

Ligands used in synthesising 3d-metal clusters are however comparatively restricted[3] and thus discovery of new combinations ("blends") of ligands remains important in the field. With this aim, we have been exploring "ligand blend" reactions involving carboxylates (RCO_2^-) *and* anionic bridging-chelating ligands (i.e. bridging ligands that simultaneously form chelating rings), *with* or *without* additional inorganic anions (Cl^-, Br^-, NO_3^-, N_3^-, SCN^-). Our results with the anionic *gem*-diol derivatives of di-2-pyridyl ketone,[4] various 2-pyridyloximates[5] and a plethora of derivatized salicylaldoximates[6] have been very encouraging, and a series of Cr, Mn, Fe, Co, Ni and Cu carboxylate clusters with nuclearities ranging from 3 to 20 and with interesting properties (including high-spin molecules[7] and SMMs[6,8]) have been prepared.

As part of our continuing search for new preparative routes to polynuclear species, we have recently turned our attention to 2-pyridyl alcohols that present a kind of structural similarity to 2-pyridyl oximes; our goals are to investigate to what extent the use of such ligands might affect the identity of the obtained products compared with 2-pyridyl oximes and to what extent this might thus prove to be a route to new cluster types. In the present work, we report interesting clusters from the use of 2-(hydroxymethyl)pyridine (hmpH) in cobalt carboxylate chemistry. Cobalt(II), which has a large single-ion anisotropy due to the orbitally degenerate ground state, may potentially be a good candidate for making SMMs, and there are few reports in the literature of Co^{II}-based SMMs.[9] The ligand hmpH has been used extensively in the synthesis of Fe,[10] Mn[11] and Cu[12] clusters, but has been sparingly used with other 3d-metals. The deprotonated hmp^- group has been used previously in Co^{II} chemistry by Christou and Hendrickson,[9a] who reported the cubane cluster $[Co^{II}_4Cl_4(hmp)_4(MeOH)_4]$;

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this cluster proved to be the first cobalt SMM. No cobalt carboxylate clusters containing hmp⁻ have been reported. We suspected that there might be a number of Co/RCO_2^-/hmp⁻ cluster species accessible and have therefore been investigated the reactions of hmpH with Co^{II} carboxylate sources under a variety of conditions.

Results and Discussion

Synthesis and IR Characterisation

Aerobic reactions of $Co(O_2CMe)_2{\cdot}4H_2O$ and $Co(O_2CPh)_2$ with hmpH, in the presence of $NaClO_4$ (1:1:1 molar ratio), in a solvent mixture comprising MeCN and MeOH (3:1, v/v) at room temperature led to dark red solutions, from which were subsequently isolated crystals of $[Co_6(O_2CMe)_4(hmp)_8](ClO_4)_2{\cdot}MeOH$ (**1**·MeOH) and $[Co_6(O_2CPh)_4(hmp)_8](ClO_4)_2{\cdot}2(n\text{-hex})$ [**2**·2(*n*-hex)], respectively, upon conventional workup (*n*-hex = *n*-hexane). The formation of **1** and **2** can be represented by Equation (1).

$$6\,Co^{II}(O_2CR)_2 + 8\,\text{hmpH} + 2\,NaClO_4 + 1/2\,O_2 \xrightarrow{\text{MeCN/MeOH}} \mathbf{[Co^{II}_4Co^{III}_2(O_2CR)_4(hmp)_8](ClO_4)_2} + 6\,RCO_2H + 2\,NaO_2CR + H_2O \quad [R = Me\,(\mathbf{1}),\ Ph\,(\mathbf{2})] \tag{1}$$

The addition of the coordinating N_3^- ions to the 1:1 $Co(O_2CMe)_2{\cdot}4H_2O$/hmpH (i.e. omission of ClO_4^- ions) reaction mixture in MeCN/H_2O (3:1, v/v), in the presence of atmospheric oxygen and layering of Me_2CO onto the resulting green-brown solution gave dark red crystals of the neutral complex $[Co_3(O_2CMe)_2(N_3)_2(hmp)_4]{\cdot}H_2O$ (**3**·H_2O) in very good yield. The formation of **3** is summarised in Equation (2).

$$3\,Co^{II}(O_2CMe)_2{\cdot}4H_2O + 4\,\text{hmpH} + 2\,NaN_3 + 1/2\,O_2 \xrightarrow{MeCN/H_2O} \underset{\mathbf{3}}{\mathbf{[Co^{II}Co^{III}_2(O_2CMe)_2(N_3)_2(hmp)_4]}} + 2\,MeCO_2H + 2\,NaO_2CMe + 13\,H_2O \tag{2}$$

The IR spectra of **1** and **2** exhibit bands at 1098–1092 and 628–624 cm^{-1} assignable to the $\nu_3(F_2)[\nu_d(ClO)]$ and $\nu_4(F_2)[\delta_d(OClO)]$ modes, respectively, of the uncoordinated T_d ClO_4^- ions.[13] The spectrum of **3**·H_2O exhibits an intense band centred at 2135 cm^{-1} which is attributed to the asymmetric stretching mode of the coordinated azide.[13] Several bands appear in the 1610–1380 cm^{-1} range in the spectra of the three complexes. Contributions from the carboxylate $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes are expected in this region, but overlapping with the stretching vibrations of the 2-pyridyl and benzoate (only for **2**) rings, and $\delta(CH_2)$ renders assignments tentative. The strong bands at 1574 (**1**), 1573 (**2**), 1574 (**3**·H_2O) and 1434 (**1**), 1438 (**2**), 1434 (**3**·H_2O) have $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ characters, respectively. The difference Δ [$\Delta = \nu_{as}(CO_2) - \nu_s(CO_2)$] is 140 cm^{-1} for **1**, **3**·H_2O and 135 cm^{-1} for **2**, less than those for NaO_2CMe (164 cm^{-1}) and NaO_2CPh (184 cm^{-1}), as expected for the bridging mode of carboxylate ligation.[14]

Description of Structures

The cations of **1** (Figure 1) and **2** (Figure 2) are structurally similar in many aspects and thus only the structure of complex **1**·MeOH (the quality of this structure is superior

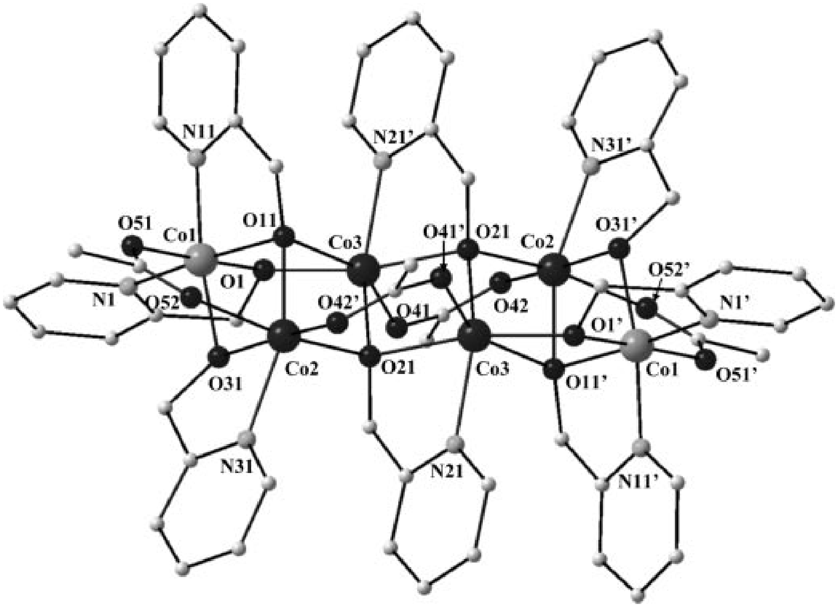


Figure 1. Partially labelled ball-and-stick presentation of the cation of **1**. H atoms are omitted for clarity. Primes are used for symmetry-related atoms.

to that of the benzoate cluster) will be described in detail. Selected interatomic distances and angles for the two hexanuclear complexes are listed in Tables 1 and 2. The cation of **1** lies on a crystallographic inversion centre, and consists of six distorted octahedral metal ions held together by four 3.31 (Harris notation[15]) or η^1:η^3:μ_3 hmp$^-$ ligands, four 2.21 or η^1:η^2:μ hmp$^-$ ligands (Scheme 1), two *syn*,*syn* 2.11 or η^1:η^1:μ $MeCO_2^-$ groups (those containing atoms O51/O52 and their symmetry equivalents) and two *syn*,*anti* 2.11 or η^1:η^1:μ $MeCO_2^-$ (those containing atoms O41/O42 and their symmetry equivalents). Harris notation[15] describes the binding mode as $X.Y_1Y_2Y_3{\cdots}Y_n$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal ions attached to the different donor atoms. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here O before N. The chromophores are $Co(1)O_4N_2$, $Co(2)O_5N$ and $Co(3)O_5N$. Charge considerations require a $4Co^{II}$, $2Co^{III}$ oxidation-state description (mixed-valent complex). Cobalt–ligand distances fall into two well-separated groups with all distances from Co(1) being less than 1.93 Å, and those from Co(2) and Co(3) being at least 2.01 Å; thus,[16] Co(1) and its symmetry-related Co(1′) are assigned as the Co^{III} ions. The core of the cluster (Figure 3) appears to be $[Co^{II}_4Co^{III}_2(\mu_3\text{-OR}')_4(\mu\text{-OR}')_4]^{6+}$, where R′ is the (2-pyridyl)CH_2- group. It can be conveniently described as consisting of two $[Co^{II}_2Co^{III}O_4]$ partial cubanes (cubanes missing a vertex). The linking of the partial cubane subunits is achieved via the alkoxide-type oxygen atoms O(21) and O(21′) which become μ_3. The four Co^{II} ions define a rhombus. The Co^{II}_3 triangular faces are each bridged by a μ_3-oxygen [O(21), O(21′)]. An alternative description of the core is as containing a $[Co_6O_8]^{6+}$ rod- or ladder-like unit which consists of four edge-sharing triangles, with Co(1) and Co(1′), respectively, below and above (0.223 Å) the plane of the central four Co^{II} ions. The Co(1)–(O,N) and Co(2,3)–(O,N) bond lengths agree well with values expected for low-spin Co^{III} and high-spin Co^{II}, respectively, in octahedral environments.[16–18]

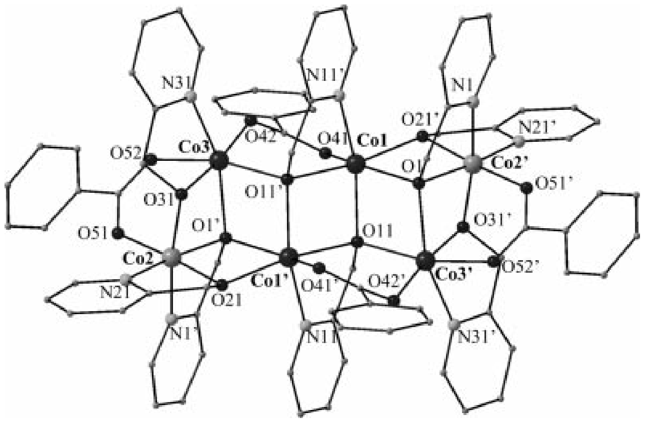


Figure 2. Partially labelled ball-and-stick presentation of the cation of **2**. H atoms are omitted for clarity. Primes are used for symmetry-related atoms.

Table 1. Selected interatomic distances [Å] and angles [°] for complex $[Co_6(O_2CMe)_4(hmp)_8](ClO_4)_2{\cdot}MeOH$ (**1**·MeOH).[a]

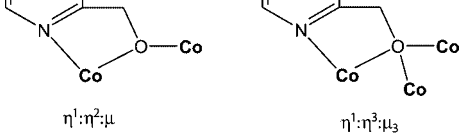
Co(1)···Co(2)	2.953(2)	Co(2)···Co(3)	3.311(3)
Co(1)···Co(3)	3.099(2)	Co(3)···Co(3′)	3.189(2)
Co(1)–O(1)	1.877(2)	Co(2)–O(42′)	2.017(2)
Co(1)–O(11)	1.913(2)	Co(2)–O(52)	2.134(3)
Co(1)–O(31)	1.900(2)	Co(2)–N(31)	2.107(3)
Co(1)–O(51)	1.914(2)	Co(3)–O(1)	2.038(2)
Co(1)–N(1)	1.914(3)	Co(3)–O(11)	2.296(2)
Co(1)–N(11)	1.926(3)	Co(3)–O(21)	2.078(2)
Co(2)–O(11)	2.131(2)	Co(3)–O(21′)	2.144(2)
Co(2)–O(21)	2.152(2)	Co(3)–O(41)	2.068(2)
Co(2)–O(31)	2.060(2)	Co(3)–N(21′)	2.128(3)
O(1)–Co(1)–O(51)	175.8(9)	Co(1)–O(1)–Co(3)	104.6(1)
O(11)–Co(1)–N(1)	170.6(1)	Co(1)–O(11)–Co(2)	93.7(1)
O(31)–Co(1)–N(11)	170.6(1)	Co(1)–O(11)–Co(3)	94.4(1)
O(11)–Co(2)–N(31)	155.3(1)	Co(1)–O(31)–Co(2)	96.3(1)
O(21)–Co(2)–O(52)	166.3(9)	Co(2)–O(11)–Co(3)	96.7(1)
O(31)–Co(2)–O(42′)	172.0(9)	Co(2)–O(21)–Co(3)	103.0(1)
O(1)–Co(3)–O(21′)	169.21(8)	Co(2)–O(21)–Co(3′)	114.6(1)
O(11)–Co(3)–O(41)	155.26(9)	Co(3)–O(21)–Co(3′)	98.2(1)
O(21)–Co(3)–N(21′)	151.07(9)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x*, –*y* + 1, –*z*.

Table 2. Selected interatomic distances [Å] and angles [°] for complex $[Co_6(O_2CPh)_4(hmp)_8](ClO_4)_2{\cdot}2(n\text{-hex})$ [**2**·2(*n*-hex)].[a]

Co(1)···Co(2)	3.117(2)	Co(2)···Co(3)	2.932(3)
Co(1)···Co(3)	3.309(2)	Co(1)···Co(1′)	3.237(3)
Co(1)–O(1)	2.305(7)	Co(2)–O(51)	1.931(7)
Co(1)–O(11)	2.067(7)	Co(2)–N(1′)	1.941(9)
Co(1)–O(11′)	2.181(7)	Co(2)–N(21)	1.910(9)
Co(1)–O(21′)	2.061(7)	Co(3)–O(1′)	2.127(7)
Co(1)–O(41)	2.057(7)	Co(3)–O(11′)	2.129(7)
Co(1)–N(11′)	2.108(8)	Co(3)–O(31)	2.032(7)
Co(2)–O(1′)	1.926(6)	Co(3)–O(42)	1.996(7)
Co(2)–O(21)	1.867(7)	Co(3)–O(52)	2.130(7)
Co(2)–O(31)	1.912(7)	Co(3)–N(31)	2.111(9)
O(1)–Co(1)–O(41)	155.2(3)	Co(1)–O(11)–Co(1′)	99.3(3)
O(11)–Co(1)–N(11′)	150.4(3)	Co(1)–O(11)–Co(3)	114.1(3)
O(11′)–Co(1)–O(21′)	167.1(3)	Co(1′)–O(1)–Co(2)	94.5(3)
O(1′)–Co(2)–N(21)	171.3(4)	Co(1′)–O(1)–Co(3)	96.5(3)
O(21)–Co(2)–O(51)	176.4(3)	Co(1′)–O(11)–Co(3)	104.1(3)
O(31)–Co(2)–N(1′)	170.6(4)	Co(1′)–O(21)–Co(2)	105.0(3)
O(1′)–Co(3)–N(31)	157.2(3)	Co(2)–O(1)–Co(3)	92.5(3)
O(11′)–Co(3)–O(52)	166.6(3)	Co(2)–O(31)–Co(3)	96.0(3)
O(31)–Co(3)–O(42)	173.3(3)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x*, –*y* + 2, –*z* + 1.



Scheme 1. The crystallographically established coordination modes of hmp$^-$ in complexes **1**, **2** and **3**.

The core $[Co^{II}_4Co^{III}_2(\mu_3\text{-OR}')_4(\mu\text{-OR}')_4]^{6+}$ is unprecedented in cobalt chemistry. Complexes **1** and **2** join a very small family of $Co^{II}_4Co^{III}_2$ clusters.[17]

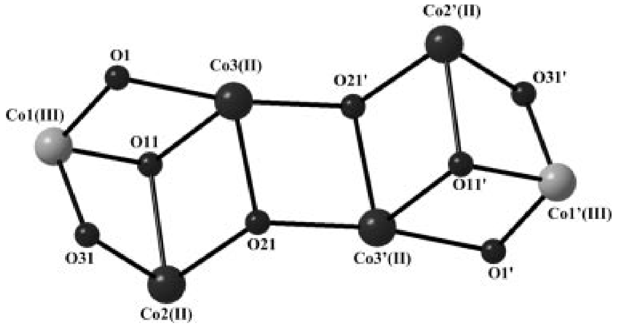


Figure 3. The $[Co^{II}_4Co^{III}_2(OR')_8]^{6+}$ core of complexes **1** and **2**.

The crystal structure of $\mathbf{3}\cdot H_2O$ reveals the formation of a linear trinuclear molecule (Figure 4). Selected interatomic distances and angles for this complex are listed in Table 3. The central metal ion, Co(1), which is located on a crystallographic inversion centre, is octahedrally coordinated by six-oxygen atoms belonging to four hmp⁻ and two $MeCO_2^-$ ligands. The six sites on each of the distorted octahedral, terminal Co ions are occupied by the N,O-atoms [N(1), O(1), N(11), O(11)] that belong to the "chelating" part of two hmp⁻ ligands, one N-atom [N(21)] of a terminal azido ligand and one O-atom [O(22′)] of a *syn,syn*-η^1:η^1:μ (2.11) $MeCO_2^-$ group. The three nitrogen atoms are in the facial configuration. The core appears to be $[Co^{II}Co^{III}_2(\mu\text{-}OR')_4]^{4+}$. Charge considerations require a formal $2Co^{III}$, Co^{II} description of **3**, and the terminal metal ions are clearly low-spin Co^{III} ions based[16] on their Co–N,O bond lengths (all <1.95 Å) compared with those of the central Co(1) ion which has Co–O distances in the range 2.062(2)–2.097(2) Å, indicating that this is a Co^{II} ion. The hmp⁻ ions function as η^1:η^2:μ (2.21) ligands; each ligand chelates one Co^{III} ion through the 2-pyridyl and the alkoxide oxygen forming a five-membered chelating ring and bridges this metal centre with the central Co^{II} ion through the μ deprotonated oxygen atom (Scheme 1).

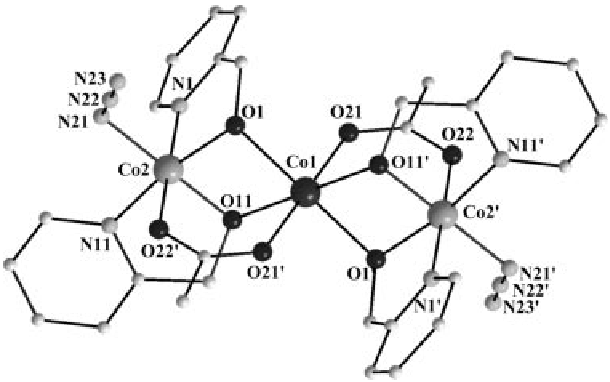


Figure 4. Molecular structure of the mixed-valence (III/II/III) complex **3** with selecting atom labelling. Primes are used for symmetry-related atoms.

Complex **3** joins a handful of structurally characterised linear, valence-trapped $Co^{III}Co^{II}Co^{III}$ complexes[18] and an even smaller group of $Co^{II/III}$ clusters comprising both azido and carboxylate ligands.[19]

Magnetic and EPR Studies

Magnetic susceptibility measurements were carried out on a polycrystalline sample of cluster **1** over 3–300 K and a magnetic field of 1 T (Figure 5). The $\chi_M T$ product at 300 K is 10.83 $cm^3 mol^{-1} K$, significantly higher than the spin-only value of 7.48 $cm^3 mol^{-1} K$ for four non-interacting $S = 3/2$ ions (with $g = 2$), and is due to the significant orbital contribution of Co^{II} ions in octahedral environments. Assuming a g_{av} value of 2.2, the theoretical $\chi_M T$ value is 9.08 $cm^3 mol^{-1} K$. $\chi_M T$ drops upon cooling, down to 2.12 $cm^3 mol^{-1} K$ at 3 K. The $(\chi_M)^{-1}$ vs. T plot gives a Weiss constant of $\Theta = -11.5$ K with $C = 11.2$ $cm^3 mol^{-1} K$ (over the 20–300 K range). The room temperature $\chi_M T$ values of **2** at both 1 and 0.1 T are almost the same (≈ 11.0 $cm^3 mol^{-1} K$). There is a continuous decrease in $\chi_M T$ with decreasing temperature, which is more pronounced below ca. 50 K (as in **1**). The $\chi_M T$ product (1 T field) reaches the value of 2.20 $cm^3 mol^{-1} K$ at 2 K. In a 0.1 T field, however, this decrease is steeper (1.65 $cm^3 mol^{-1} K$ at 2 K). Because the data for **1** are available only at 1 T, the magnetic field effects are unknown for this compound.

Although single-ion spin-orbit coupling effects (giving a doublet ground state) could give rise to this qualitative behaviour,[17c] the low temperature $\chi_M T$ data for two hexanuclear clusters extrapolate to zero at 0 K suggesting a diamagnetic ground state and hence significant antiferromagnetic interactions. This is supported by Q-band EPR spectra for **1** at low temperature which show two features, at ca. 0 and 2 kG, which must arise from different low-lying spin

Table 3. Selected interatomic distances [Å] and angles [°] for complex $[Co_3(O_2CMe)_2(N_3)_2(hmp)_4]\cdot H_2O$ ($\mathbf{3}\cdot H_2O$).[a]

Co(1)···Co(2)	2.933(9)	Co(2)···Co(2′)	5.867(9)
Co(1)–O(1,1′)	2.062(2)	Co(2)–O(22′)	1.927(2)
Co(1)–O(11,11′)	2.097(2)	Co(2)–N(1)	1.934(2)
Co(1)–O(21,21′)	2.081(2)	Co(2)–N(11)	1.935(2)
Co(2)–O(1)	1.890(2)	Co(2)–N(21)	1.946(2)
Co(2)–O(11)	1.892(2)		
O(1)–Co(1)–O(1′)	180.0(5)	O(11)–Co(2)–N(21)	177.0(9)
O(11)–Co(1)–O(11′)	180.0(5)	O(22′)–Co(2)–N(1)	176.6(8)
O(21)–Co(1)–O(21′)	180.0(5)	*cis* O–Co(2)–N	83.7(8)–93.4(9)
cis O–Co(1)–O	87.6(7)–92.8(6)	Co(1)–O(1)–Co(2)	95.7(8)
O(1)–Co(2)–N(11)	171.0(8)	Co(1)–O(11)–Co(2)	94.5(7)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $1/2 - x$, $½ - y$, $1 - z$.

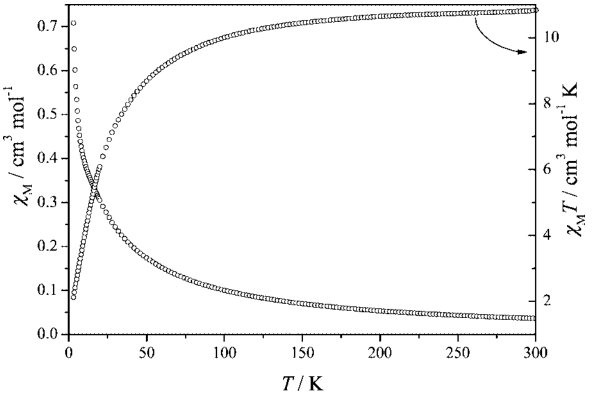


Figure 5. $\chi_M T$ vs. T and χ_M vs. T plots for complex **1**.

states as shown by their different temperature dependences (Figure 6). However, due to the complexity of systems comprising coupled Co^{II} ions, a quantitative analysis of the susceptibility behaviour is not possible.

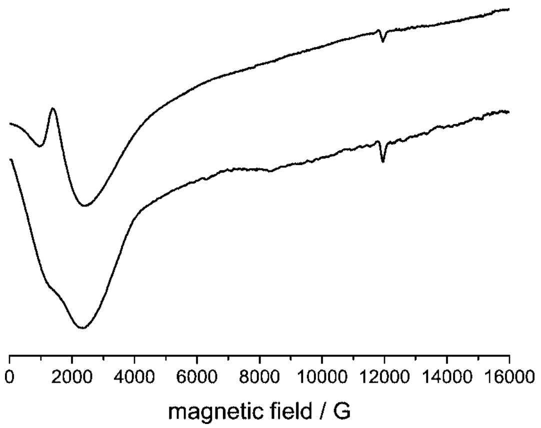


Figure 6. Q-Band (33.9 GHz) EPR spectra of a powder of **1** at 20 (top) and 5 K (bottom). The weak signal at 12000 G is most probably due to an impurity.

The room-temperature value of $\chi_M T$ for $\mathbf{3}\cdot H_2O$ at 0.1 T is 2.88 cm^{3}mol^{-1}K (μ_{eff} per Co^{II} = 4.80 BM), to be compared with the spin-only (g = 2) $\chi_M T$ value of 1.87 cm^{3}mol^{-1} K (μ_{eff} per Co^{II} = 3.87 BM). This value is within the range observed for six-coordinate, high-spin cobalt(II) complexes.[18h,20] Because of the intrinsic orbital angular momentum in the octahedral ground state $^4T_{1g}$ (F), there is consistently a considerable orbital contribution, and effective magnetic moments for such compounds around room temperature are between 4.7 and 5.2 BM.[20] The $\chi_M T$ product decreases slowly to 2.13 cm^{3}mol^{-1}K (μ_{eff} per Co^{II} = 4.13 BM) at around 25 K and then drops to 1.80 cm^{3}mol^{-1} K (μ_{eff} per Co^{II} = 3.80 BM) at 3 K. This behaviour may be understood as arising from the combined effects of orbital degeneracy and zero-field splitting.[18h] The magnetic data confirm that complex $\mathbf{3}\cdot H_2O$ is in the mixed-valence state Co^{III}(S = 0) – Co^{II}(S = 3/2) – Co^{III}(S = 0) as suggested by the X-ray structural analysis.

Conclusions and Perspectives

In summary, the initial use of the hmp$^-$/RCO_2^- "blend" in Co chemistry has provided two $Co^{II}_4Co^{III}_2$ clusters with an unprecedented core and one linear $Co^{III}Co^{II}Co^{III}$ complex. The nuclearity of the mixed-valent cluster, [Co_6] or [Co_3], is controlled partly by the nature of the extra inorganic anion. Magnetic and Q-band EPR studies of the hexanuclear cobalt acetate cluster have provided preliminary useful insights into the complex interplay between single-ion properties and exchange interactions in polynuclear Co complexes. We stated in the Introduction that it was our suspicion that Co/RCO_2^-/hmp$^-$ chemistry might prove a rich new area for what is otherwise a well-studied metal. This work and a variety of unpublished results seem to suggest that our suspicions were correct.

Experimental Section

General: All manipulations were performed under aerobic conditions using materials (Merck, Aldrich) as received. Elemental analyses (C,H,N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory with an EA 108 Carlo–Erba analyzer. IR spectra (4400–450 cm^{-1}) were recorded from KBr pellets with a Perkin–Elmer PC 16 FTIR spectrometer. Variable-temperature magnetic susceptibility measurements were carried out at the Institute of Materials Science of the NCSR "Demokritos" on polycrystalline samples of complexes **1**–**3** in the 2.0–300 K temperature range using a Quantum Design MPMS SQUID susceptometer under magnetic fields of 1.0 and 0.1 T. Q-band (34 GHz) EPR spectra of **1** were obtained with a Bruker ESP300E spectrometer.

Safety Note: Perchlorate and azide salts are potentially explosive; such compounds should be synthesised and used in small quantities, and treated with utmost care at all times.

Preparations

Synthesis of $[Co_6(O_2CMe)_4(hmp)_8](ClO_4)_2\cdot MeOH$ (1·MeOH): A colourless solution of hmpH (0.10 mL, 1.00 mmol) in MeCN (5 mL) was added to a stirred pink suspension of $Co(O_2CMe)_2\cdot 4H_2O$ (0.26 g, 1.04 mmol) in MeCN (25 mL). The resulting purple suspension was stirred for 20 min, during which time a colourless solution of $NaClO_4\cdot H_2O$ (0.14 g, 1.00 mmol) in MeOH (10 mL) was added in small portions to finally give a deep red slurry. The latter was stirred for a further 24 h, during which time all the solids were completely dissolved. The resulting deep red solution was filtered and layered with Et_2O (90 mL). After 3 d dark orange-red crystals were obtained and collected by filtration, washed with cold MeOH (2 × 5 mL) and Et_2O (2 × 5 mL), and dried in vacuo; the yield was 0.140 g (65% based on hmpH). The dried solid analysed as solvent-free. $C_{56}H_{60}Cl_2Co_6N_8O_{24}$ (1653.65): calcd. C 40.68, H 3.66, N 6.78; found C 40.43, H 3.81, N 6.81. Main IR data: IR (KBr): ṽ = 3428 (mb), 2920 (w), 2830 (w), 1574 (s), 1478 (m), 1434 (s), 1346 (w), 1286 (m), 1228 (w), 1092 (vs), 1044 (s), 760 (m), 728 (w), 674 (s), 628 (m), 546 (w), 494 (w) cm^{-1}.

Synthesis of $[Co_6(O_2CPh)_4(hmp)_8](ClO_4)_2\cdot 2(n\text{-hex})$ [2·2(*n*-hex)]: This complex was prepared in the same manner as complex **1**, except that $Co(O_2CPh)_2$ (0.31 g, 1.00 mmol) was used in place of $Co(O_2CMe)_2\cdot 4H_2O$, and the solution was layered with Et_2O/*n*-hexanes (1:1, v/v) instead of Et_2O. Dark orange crystals of the product were collected by filtration, washed with cold MeOH (2 × 5 mL) and

Et_2O (2 × 5 mL), and dried in vacuo; the yield was 0.112 g (47% based on hmpH). The dried solid analysed as solvent-free. $C_{76}H_{68}Cl_2Co_6N_8O_{24}$ (1901.93): calcd. C 48.00, H 3.60, N 5.89; found C 48.17, H 3.81, N 5.94. Main IR data. IR (KBr): ṽ = 3430 (mb), 2923 (w), 2835 (w), 1573 (s), 1479 (m), 1438 (s), 1345 (w), 1284 (m), 1229 (w), 1098 (vs), 1041 (m), 763 (m), 729 (w), 674 (s), 624 (m), 543 (w), 492 (w) cm^{-1}.

Synthesis of $[Co_3(O_2CMe)_2(N_3)_2(hmp)_4]\cdot H_2O$ (3·H_2O): A colourless solution of hmpH (0.10 mL, 1.00 mmol) in MeCN (5 mL) was added to a stirred pink suspension of $Co(O_2CMe)_2\cdot 4H_2O$ (0.26 g, 1.04 mmol) in MeCN (25 mL). The resulting purple suspension was stirred for 20 min, during which time a colourless aqueous solution (10 mL) of NaN_3 (0.07 g, 1.00 mmol) was added in small portions to finally give a dark green slurry. The latter was stirred for a further 12 h and all the unreacted solids were completely dissolved. The resulting dark brown-green solution was filtered and layered with Me_2CO (90 mL). After 6 d dark red crystals of the product were isolated and collected by filtration, washed with cold Me_2CO (2 × 5 mL) and dried in vacuo over silica gel; the yield was 0.151 g (70% based on hmpH). The dried solid analysed as **3**·H_2O. $C_{28}H_{32}Co_3N_{10}O_9$ (829.42): calcd. C 40.55, H 3.89, N 16.89; found C 40.33, H 4.00, N 17.24. Main IR data. IR (KBr): ṽ = 3428 (m), 2135 (vs), 1574 (s), 1478 (m), 1434 (s), 1346 (m), 1286 (m), 1044 (m), 760 (m), 728 (w), 686 (m), 628 (w), 546 (m), 494 (w) cm^{-1}.

X-ray Crystallographic Studies: Crystals of **1**·MeOH, **2**·2(*n*-hex), and **3**·H_2O were mounted in air and covered with epoxy glue. Diffraction measurements for **1**·MeOH and **3**·H_2O were made with a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo-K_α radiation. The X-ray data set for **2**·2(*n*-hex) was collected on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu-K_α radiation. Complete crystal data and parameters for data collection and refinement are listed in Table 4. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the ranges $11 < 2\theta < 23°$ (for **1**·MeOH and **3**·H_2O) and $22 < 2\theta < 54°$ [for **2**·2(*n*-hex)]. Intensity data were recorded using the θ–2θ scan method. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarisation and Ψ-scan absorption corrections were applied using the Crystal Logic software package. For all the three structures, all hydrogen atoms were located by difference maps and were refined isotropically, except those of the methyl groups which were introduced at calculated positions as riding on bonded atoms. No H-atoms for the solvate methanol (for **1**·MeOH), *n*-hexane [for **2**·2(*n*-hex)] and water (for **3**·H_2O) were included in the refinement. All non-hydrogen atoms were refined anisotropically, except of the carbon atoms of the benzoates and the solvate *n*-hexane molecules which were refined isotropically. The oxygen atoms of the perchlorate anion in **1**·MeOH were found disordered and were refined over two positions with occupation factors of total sum one. All structures were solved by direct methods using SHELXS-86[21] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97.[22]

CCDC-642412 (for **1**·MeOH), -642411 [for **2**·2(*n*-hex)] and -642410 (for **3**·H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for complexes $[Co_6(O_2CMe)_4(hmp)_8](ClO_4)_2\cdot MeOH$ (**1**·MeOH), $[Co_6(O_2CPh)_4(hmp)_8](ClO_4)_2\cdot 2(n\text{-hex})$ [**2**·2(*n*-hex)], and $[Co_3(O_2CMe)_2(N_3)_2(hmp)_4]\cdot H_2O$ (**3**·H_2O).

	1·MeOH	**2**·2(*n*-hex)	**3**·H_2O
Empirical formula	$C_{57}H_{64}Cl_2Co_6N_8O_{25}$	$C_{88}H_{96}Cl_2Co_6N_8O_{24}$	$C_{28}H_{32}Co_3N_{10}O_9$
Mol. weight	1685.64	2074.21	829.42
Colour and habit	red prisms	red prisms	red prisms
Crystal size [mm]	0.32 × 0.33 × 0.60	0.10 × 0.10 × 0.20	0.10 × 0.25 × 0.55
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$C1_2/c$
a [Å]	10.679(6)	12.286(5)	24.584(8)
b [Å]	15.578(8)	31.000(16)	8.309(3)
c [Å]	20.572(11)	12.336(6)	17.228(6)
α [°]	90	82.533(19)	90
β [°]	99.06(2)	89.972(14)	102.05(1)
γ [°]	90	83.876(17)	90
V [Å^3]	3380(3)	4632(4)	3442(2)
Z	2	2	8
$\rho_{calcd.}$ [g cm^{-3}]	1.656	1.487	1.601
T [°C]	25	25	25
λ (Mo-K_α) [Å]	0.71073		0.71073
λ (Cu-K_α) [Å]		1.54180	
μ [mm^{-1}]	1.602	9.393	1.495
$F(000)$	1716	2136	1692
$2\theta_{max}$ [°]	50	90	50
No. of reflections collected	6126	8104	6046
No. of indep. reflections/R_{int}	5954/0.0476	7458/0.0619	3025/0.0116
Data with $I > 2\sigma(I)$	5425	5784	2750
Parameters refined	585	1003	285
GOF (on F^2)	1.111	1.018	1.060
$R1$ [a]	0.0396	0.0782	0.0295
$wR2$ [b]	0.1055	0.2070	0.0917
Residuals [e Å^{-3}]	0.457/–0.451	1.184/–0.558	0.700/–0.373

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = \{\Sigma\{w[(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

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