Supramolecular self-assembly of a toroidal inclusion complex, $[NH_4][Co_8(MeCO_2)_8(OMe)_{16}][PF_6]$

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Diamagnetic $[NH_4][Co_8(MeCO_2)_8(OMe)_{16}][PF_6]$, a compound with eight cobalt atoms bridged by methoxy and acetato ligands so as to form a planar ring with an ammonium ion at its centre, is isolated from the reaction between cobalt(III) acetate and methanol in the presence of NH_4PF_6.

We recently reported that slow recrystallisation of 'cobalt(III) acetate' in the presence of a halide source produced the mixed valence octanuclear compound $[Co_8O_4(MeCO_2)_6(OMe)_4Cl_4(OH_n)_4]\cdot6H_2O$ (n = 1, 2).[1] Structural characterisation of this compound showed it to contain a central $[Co_8O_8]$ core consisting of a linear array of three face-sharing $[Co_4O_4]$ cubane fragments. A similar mixed valence Co_8 core had previously been reported in the compound $[Co_8O_4(MeCO_2)_6(OH)_4L_2][ClO_4]_2$ [L = tetradentate ligand, 1,2-bis(2,2′-bipyridyl-6-yl)ethane], prepared by H_2O_2 treatment of $Co(MeCO_2)_2\cdot4H_2O$ (3 equiv.) in the presence of L (1 equiv.) and $LiClO_4$.[2] The isolation of $[Co_8O_4(MeCO_2)_6(OMe)_4Cl_4(OH_n)_4]$ suggests that supramolecular assembly of the Co_8 core (and possibly of other architectures) may occur even in the absence of polydentate ligands. Thus, another mixed valence octanuclear derivative, $[Co_8O_4(PhCO_2)_{12}L_4]$ [L_4 = $(MeCN)_3(H_2O)$], has been prepared by addition of aqueous H_2O_2 to a dmf solution of cobalt benzoate, followed by recrystallization from CH_2Cl_2–MeCN.[3,4] This material has a $[Co_8O_4]^{12+}$ framework in which trigonally bipyramidally coordinated Co^{II} atoms are bound to the oxygens of a central $[Co^{III}{}_4O_4]^{4+}$ cubane.

We report here the isolation and structural characterization of a second octanuclear material from 'cobalt(III) acetate', $[NH_4][Co_8(MeCO_2)_8(OMe)_{16}][PF_6]$ **1**. Reaction of 'cobalt(III) acetate' (0.5 g)[5] and NH_4PF_6 (0.61 mmol in 3 ml) in methanol over one week at ambient temperature gave an as yet unidentified green microcrystalline solid and large dark green, plate-like crystals of **1**. Pure **1** was obtained by decanting the remaining solution followed by rinsing and decanting diethyl ether suspensions of the microcrystalline solid. The initial yield of **1** was typically *ca.* 5% (0.03 mmol) based on NH_4PF_6. Although the yields have not been optimised, further, larger, crops of **1** and of the microcrystalline solid were obtained after leaving the filtrate for a period of several days to several weeks. Crystals suitable for single crystal X-ray diffraction analysis were obtained by leaving the reaction mixture undisturbed for several weeks. To prevent decomposition the crystals were kept under diethyl ether and subsequently used in single crystal X-ray diffraction measurements.† Single crystal X-ray diffraction‡ showed that **1** consists of a molecule of $[Co_8(MeCO_2)_8(OMe)_{16}]$ which functions as an inclusion host for an NH_4^+ cation. Charge balance is provided by a PF_6^- anion in the lattice. The $[Co_8(MeCO_2)_8(OMe)_{16}]$ molecule has a highly symmetric toroidal shape (Fig. 1), containing four $[Co_2(\mu\text{-}MeCO_2)(\mu\text{-}OMe)_2]$ units, forming eight edge-shared CoO_6 distorted octahedra. The cobalt atoms are situated at the vertices of a near regular planar octagon. Each pair of cobalt atoms is bridged by an acetate ligand and two stereochemically distinct methoxide ligands, one methoxide on either side of the Co_8 plane. The acetate ligands on adjacent pairs of cobalt atoms are alternatively above and below and at approximately 30° to the Co_8 plane. Of the eight methoxide ligands on each side of the Co_8 plane, four have O–C bonds perpendicular to the Co_8 plane, whereas the C–O bonds of the other four methoxide ligands are directed to the periphery of the molecule. This latter set of methoxide ligands eclipses the acetate ligands on the other side of the Co_8 plane. On each side of the Co_8 plane, then, the methoxide C–O bonds are alternatively perpendicular to (type A), and at approximately 30° to (type B) the Co_8 plane, similar to the orientation of the methoxide ligands in $[NBu_4]_2[V_8O_8(OMe)_{16}(C_2O_4)]$.[6] The NH_4^+ ion is situated at the centre of the $[Co_8(MeCO_2)_8(OMe)_{16}]$ molecule, with the nitrogen atom in the Co_8 plane. The NH_4^+ protons could not be located. Adjacent cobalt atoms are separated by an average of 2.863 Å, slightly longer than the hydroxy- and alkoxy-bridged Co···Co separations in the hydroxy-bridged dimers and most of the oxo-centred trimers.[7] The Co–O($MeCO_2$) distances are within the range 1.885(6)–1.916(6) Å, as observed in the dinuclear and trinuclear cobalt(III) complexes.[7] Bridging Co–O(OMe) dis-

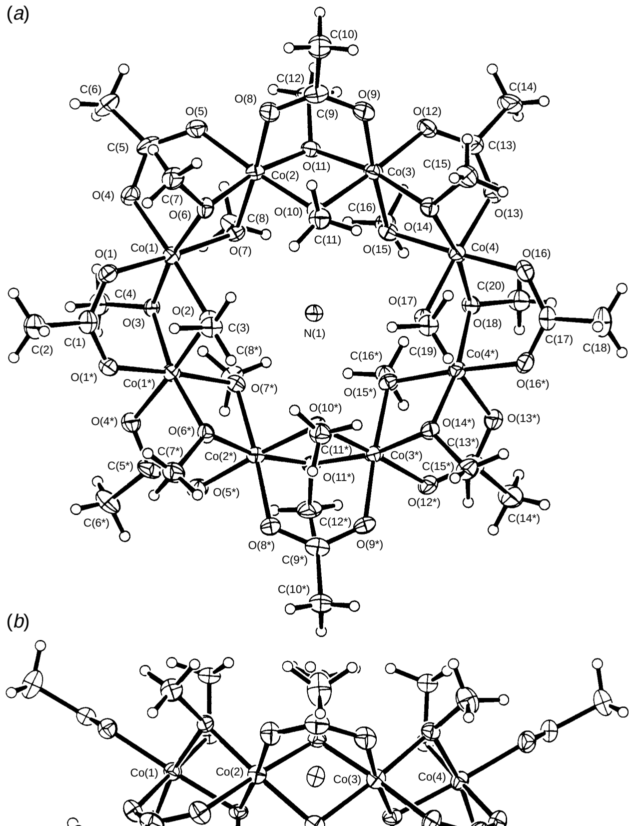

Fig. 1 ORTEP (25% probability)[17] representations of (*a*) the octanuclear $[Co_8(O_2CMe)_8(OMe)_{16}]$ host molecule and the guest NH_4^+ cation, showing the partial labelling scheme, viewed perpendicular to the Co_8 plane, and (*b*) the asymmetric unit viewed along the Co_8 plane

tances and angles are all similar and within the ranges 1.878(6)–1.918(5) Å and 97.7(4)–98.6(3)°, respectively. The Co_8 ring has a diameter of *ca*. 7.5 Å, the O_4 rings of the type A methoxides have diameters of *ca*. 5.3 Å.

The ^1H and ^{13}C NMR solution spectra are consistent with the solid state structure.[§] Both spectra indicate a single acetate environment and equal populations of two methoxide environments. The ^1H NMR spectrum in CD_3OD includes a broad peak centred at δ 7.7 attributable to the protons of the NH_4^+ ion. This peak is shifted some 0.5 ppm downfield from that of NH_4PF_6 in CD_3OD (δ 7.2). The NMR spectra and the stoichiometry indicate that $[Co_8(MeCO_2)_8(OMe)_{16}]$ is diamagnetic.

Topological analogues of the $[Co_8(MeCO_2)_8(OMe)_{16}]$ structure have been reported in vanadium $\{[V_8O_8(OMe)_{16}(C_2O_4)]^{2+}$, $[MeCN(V_{12}O_{32})]^{4-}\}$,[6,8] chromium $\{[Cr_8F_8(Me_3CCO_2)_{16}]\}$,[9] molybdenum $\{[Mo_8O_{16}(OR)_8(C_2O_4)]^{2+}$; R = Me, Et$\}$,[6,10] iron $\{[Fe_8F_8(Me_3CCO_2)_{16}]\}$[11] and copper $\{[Cu_8L_8(OH)_8]$; L = 3,5-dimethylpyrazole$\}$[12] chemistries. The M_8 (M = V, Cr, Mo, Fe, Cu) rings of these compounds have diameters of some 7–9 Å.[6,9–12] The internal cavities of the similarly planar, cyclic, octameric $[Cu_8L_8(OH)_8]$ (L = 3,5-dimethylpyrazole) and $[M_8F_8(Me_3CCO_2)_{16}]$ (M = Cr, Fe) have diameters of *ca*. 6–7 Å.[9,11,12] The related $[Mo_8O_{16}(OMe)_8(PMe_3)_4]$ has a puckered Mo_8 ring with alternating five- and six-coordinated molybdenum atoms.[13] In some cases, solvent molecules are occluded in the structure, in others, oxalato ligands bridge four alternating metal atoms about the ring. The nitrogen atom of occluded Et_2NH is coplanar with the Fe_8 ring of $[Fe_8F_8(Me_3CCO_2)_{16}]$,[11] whereas occluded acetones are situated on either side of the Cr ring of $[Cr_8F_8(Me_3CCO_2)_{16}]$.[9] However, little precedent exists for this structural motif in cobalt chemistry (although compounds containing Co_6 rings are known[14–16]) and its association with the chemistry of 'cobalt(III) acetate' is completely unanticipated. It is not yet clear whether $[Co_8(MeCO_2)_8(OMe)_{16}]$ self assembles (possibly about a cationic template) as a result of a reaction between one or more constituents of 'cobalt(III) acetate' and methanol, or whether a species such as $[Co_8(MeCO_2)_8(OH)_{16}]$ self assembles in 'cobalt(III) acetate' and reacts with alcohols analogously to other species derived from 'cobalt(III) acetate'. What is clear is that the deceptively simple 'cobalt(III) acetate' can form a wide variety of ionic and neutral species and that the driving force for self assembly in these systems must be considerable, even in the presence of only the ubiquitous acetate ligand. A detailed study of related inclusion complexes will be published later.

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Footnotes and References

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[†] Elemental analysis: calc. for $C_{32}H_{76}Co_8F_6NO_{32}P\cdot 0.5C_4H_{10}O$: C, 24.9; H, 5.0; N, 0.9. Found: C, 25.0; H, 4.9; N, 0.9%.

[‡] *Crystal data* for $Co_8(MeCO_2)_8(OMe)_{16}\cdot NH_4\cdot PF_6\cdot 1.4C_4H_{10}O$, $C_{37.60}Co_8H_{86}F_6NO_{33.40}P$: M = 1703.11, monoclinic, space group $P2_1/m$ (no. 11), a = 8.621(1), b = 25.345(6), c = 16.368(3) Å, β = 104.81(1)°, U = 3457(1) $Å^3$, $F(000)$ = 1733.60, Z = 2, D_c = 1.632 g cm^{-3}, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 19.90 cm^{-1}; R value 0.048 (R_w 0.042) for 3022 absorption-corrected reflections with $I > 3\sigma(I)$. CCDC 182/664.

[§] ^1H NMR (200 MHz, CD_3OD, TMS reference) δ 7.74 (1 H, br s, NH_4), 2.45 (6 H, s, μ-O_2CMe), 2.23 (6 H, s, μ-OMe), 2.16 (6 H, s, μ-OMe); ^{13}C NMR (200 MHz, CD_3OD, TMS reference) δ 192.31 (μ-O_2CMe), 52.89 (μ-OMe), 51.67 (μ-OMe), 24.02 (μ-O_2CCH_3); ESIMS (90 V) *m/z* 1458.1 ($[M - PF_6]^+$).

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