Lewis Basicity of the [Co₄O₄]⁴⁺ Cubane Core. Preparation of a Mixed-valence 4Co⁰/², 4Co³⁺ Cluster with an Unusual [Co₆(H₄-O)₄]²⁺ Core, and New [Co₄O₃(OH)]⁵⁺ and [Co₄O₂(OH)]²⁺ Cubane Complexes

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[Co₄O₄(O₂CPh)₁₂(µ₂-MeCN)₃(H₂O)]¹⁺ (1b) is formed on oxidation of cobalt(i) benzoate in MeCN or dmf with aqueous H₂O₂, and contains a [Co₄O₄]⁺ cubane unit with each oxide attached to an additional Co atom; studies stimulated by this result show that preformed [Co₄O₄(O₂CR)₂(bipy)]²⁺ (bipy = 2,2'-(bipyridine) can be mono- and doubly-protonated to [Co₄O₃(OH)(O₂CR)₂(bipy)]³⁺ and [Co₄O₃(OH)₂(O₂CR)₂(bipy)]⁴⁺, respectively.

Our interest in high-nuclearity 3d metal carboxylate aggregates has steadily grown over the last few years as it has become apparent that they encompass a range of interesting structural types and, quite frequently, possess unusual magnetic properties. The latter has been particularly true for Mn, where a propensity for ferromagnetic exchange interactions and/or topology-derived spin frustration effects have led to a number of complexes possessing large spin (S) values in their ground states. More recently, we have developed an interest in cobalt carboxylates, an area that has been relatively unexplored for this otherwise well-studied metal. We herein report the preparation of the octanuclear, mixed-valence title compound possessing a most unusual Co/O₂⁻ core, and describe the result of protonation experiments on the discrete ion [Co₄O₄(O₂CR)₂(bipy)]²⁺. Cobalt(ii) benzoate in dmf was treated with 8 equiv. of aqueous H₂O₂ (50%), causing a colour change from purple to dark emerald green. After 4 h, the solution was filtered and the filtrate evaporated to dryness in vacuo with gentle warming. The resultant crystalline solid was slurried in cold MeCN, and the crystals collected by filtration and washed with MeCN; the yield of [Co₄O₄(O₂CPh)₁₂(µ₂-MeCN)₃(H₂O)]¹⁺ (1b) was ≈60%.

Crystals suitable for crystallography were obtained from an analogous reaction in MeCN by allowing the original reaction filtrate to stand undisturbed overnight; this afforded [Co₄O₄(O₂CPh)₁₂(µ₂-MeCN)₃(H₂O)]¹⁺ in low yield (12%).

The structure of 1b (Fig. 1) is extremely unusual and consists of a central [Co₄O₄] cubane unit [Co(1)-Co(4)] with each of the bridging oxide atoms [O(9)-O(12)] also attached to a fourth Co atom [Co(5)-Co(8)]. Thus, the oxygen atoms are µ₄ and possess distorted tetrahedral (actually trigonal-pyramidal) geometry. The cubane and peripheral Co atoms are additionally bridged by a total of twelve PhCO₂⁻ groups. A terminal MeCN group on Co(5), Co(6) and Co(8), and a terminal H₂O group on Co(12) on Co(7) complete five-coordination at the peripheral Co atoms, which possess distorted trigonal-bipyramidal geometry; this is an extremely rare coordination number for Co with predominately O ligands. Ignoring the difference in terminal MeCN/H₂O ligation and the slight non-planarity in bridging RCO₂⁻ planes, the overall molecular and the [Co₄O₄]⁺ core have approximately D₅h symmetry. This is to be contrasted with the cation of [Co₄O₄(O₂CC₆H₄Me-p)₂(bipy)]³⁺, where the overall ion and the [Co₄O₄]⁺ core both have distinct D₂d symmetry. Charge considerations require a formal 4Co¹⁺, 4Co¹⁺ description of 1b, and the cubane Co atoms are clearly low-spin Co⁰. Cocrystallization of 1b with LiClO₄ led to a colour change from brown to greenish-brown and the slow crystallisation of the diprotonated complex, as hoped; a white crystalline solid was deposited in 75% yield.

The oxygen atoms bridging three tripositive Co ions should retain sufficient basicity to bind to a fourth Co centre and thus become µ₄; this suggested to us that it might be possible to protonate the µ₄-O₂⁻ ions of complex 2, a belief that was subsequently confirmed. Treatment of 2 in MeCN with aqueous HClO₄ (70%) ([MeCN] = H₂O = 12:1 v/v; final pH <0) led to a colour change from brown to greenish-brown and the slow crystallisation of the diprotonated complex [Co₄O₄(OH)(O₂CC₆H₄Me-p)(bipy)]⁴⁺, a white crystalline solid was deposited in 75% yield. The monoprotonated version was obtained by adding an aqueous solution of [Ce(NO₃)₄]³⁺ to 2 in MeCN ([MeCN] = H₂O = 4:1 v/v; pH = 1). The presence of the trianionic counter-ion favoured precipitation of the trications (monoprotonated) complex, as hoped; a black crystalline solid was deposited in 75% yield and identified as [Co₄O₄(OH)(O₂CC₆H₄Me-p)(bipy)]⁴⁺ of complex 4, the initial appearance of a structurally-characterised, mixed O²⁻/OH⁻ cubane for any metal.

Complex 3 has yet to be obtained in a form suitable for crystallography, but suitable single crystals of 4-PhCN·H₂O were obtained on recrystallisation of 4·2H₂O from PhCN·EtOH. The structure of 4 (Fig. 2) shows an intimately interacting anion/cation pair; the cation looks at first glance to be the same as in the parent cation [Co₄O₄(O₂CC₆H₄Me-p)(bipy)]²⁺ of 2, but closer inspection clearly indicates that it is monoprotonated. Specifically, (i) Co-O(8) distances (av. 1.933 Å) are noticeably longer than the other Co-O distances.
in the core (av. 1.878 Å), and (ii) the O(8)···O(89) distance (2.723 Å) is strongly suggestive of an O-H···O hydrogen-bonding interaction. These data are consistent with O(8) being an OH` ion.

The 1H NMR spectrum of complex 2 in (CD3)2SO displays only three, paramagnetically-shifted resonances assignable to the o-, m- and p-protons of the benzoate groups at δ 32.34, 17.60 and 10.99, respectively, in a 2:2:1 relative integration ratio. This is consistent with idealised T₄ symmetry and supports retention of the solid-state structure on dissolution in this solvent (the terminal MeCN/H₂O groups being displaced by acetone groups). The 1H NMR spectrum of 4 in (CD3)2SO shows only one set of four bipy resonances (δ 8.97, 8.51, 8.32 and 7.17) and one set of three p-toluate resonances (δ 6.58, 6.28 and 2.06), together with an OH`/H₂O resonance (δ 4.89). The spectrum of 3 in (CD3)2SO is extremely similar to that of 4, with only slight changes in the chemical shifts of the bipy and p-toluate resonances. These data indicate that exchange of H` between the four oxide oxygen atoms, and between the latter and free H₂O groups, is fast on the *H NMR timescale, leading to effective D₄sd symmetry for the cations in solution.

Initial attempts to prepare the Co₈ cluster from addition of 4 CoII ions to the [CoO₄]₄⁺ core of 2 have been unsuccessful, probably because of the kinetically-inert nature of CoII. We currently have no evidence of a tri- or tetra-protonated cubane core, these probably being disfavoured by charge build-up. The doubly-protonated cubane can, however, be deprotonated back to 2 with KOH in MeOH.

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Footnotes
† Analytical data (C, H, N) for 1a, 3 (C, H, N, Cl) and 4 (C, H, N) were satisfactory. Complex 1b·2MeCN loses solvent on drying in vacuo and appears to be hygroscopic, analysing satisfactorily (C, H, N) for Co₄O₄(O₂CPh)₄(MeCN)(H₂O).‡ Crystal data for 1b·2MeCN: C₈H₄Co₄N₆O₁₈, M = 2212.12, triclinic, P1, a = 15.056(4), b = 23.548(6), c = 14.697(4) Å, α = 90.72(4), β = 114.75(1), γ = 75.12(1)°, V = 4546 Å³, Z = 2, D₀ = 1.616 g cm⁻³, T = -153 °C, 6 < 2θ < 45°, R(Ref) = 0.0401 (0.0424) for 10 207 unique reflections with F > 3σ(F). The structure was solved by MULTAN and Fourier techniques, and refined by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in fixed, calculated positions in the final refinement cycles except for those on the water molecule which were omitted.

Crystal data for 4: C₈H₆Co₄N₄O₄·H₂O, M = 1828.05, orthorhombic, Pnma, a = 22.603(4), b = 34.759(6), c = 15.056(4) Å, V = 14273 Å³, Z = 8, D₀ = 1.701 g cm⁻³, λ = 0.71069 Å, T = -154 °C, 6 < 2θ < 45°, R(Ref) = 0.0863 (0.0878) for 4249 unique reflections with I > 3σ(I). The structure was solved by MULTAN and Fourier techniques, and refined by full-matrix least squares. The non-hydrogen atoms of the cation and the Ce atom were refined with anisotropic thermal parameters; all other non-hydrogen atoms were refined isotropically. There is disorder in the anion NO₃⁻ groups; the eighteen O atoms in the core (av. 1.878 Å), and refined with anisotropic thermal parameters; hydrogen atoms were included in fixed, calculated positions in the final refinement cycles except for those on the water molecule which were omitted.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors. Issue No. 1.

§ Prepared in situ by treatment of an aqueous solution of (NH₄)₂Ce(NO₃)₆ and NH₄NO₃ with H₂O₂ followed by boiling to decompose excess H₂O₂.

References