Lewis Basicity of the $[Co_4O_4]^{4+}$ Cubane Core. Preparation of a Mixed-valence $(4Co^{II}, 4Co^{III})$ Cluster with an Unusual $[Co_8(\mu_4\text{-}O)_4]^{2+}$ Core, and New $[Co_4O_3(OH)]^{5+}$ and $[Co_4O_2(OH)_2]^{6+}$ Cubane Complexes

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$[Co_8O_4(O_2CPh)_{12}(MeCN)_3(H_2O)]$ **1b** is formed on oxidation of cobalt(II) benzoate in MeCN or dmf with aqueous H_2O_2, and contains a $[Co_4O_4]^{4+}$ cubane unit with each oxide attached to an additional Co atom; studies stimulated by this result show that preformed $[Co_4O_4(O_2CR)_2(bipy)_4]^{2+}$ (bipy = 2,2′-bipyridine) can be mono- and doubly-protonated to $[Co_4O_3(OH)(O_2CR)_2(bipy)_4]^{3+}$ and $[Co_4O_2(OH)_2(O_2CR)_2(bipy)_4]^{4+}$, 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.[1] 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.[2] More recently, we have developed an interest in cobalt carboxylates,[3] an area that has been relatively unexplored for this otherwise well-studied metal.[4] We herein report the preparation of the octanuclear, mixed-valence title compound possessing a most unusual Co/O^{2-} core, and describe the result of protonation experiments on the discrete ion $[Co_4O_4(O_2CR)_2(bipy)_4]^{2+}$.[3]

Cobalt(II) benzoate in dmf was treated with 8 equiv. of aqueous H_2O_2 (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 $Co_8O_4(O_2CPh)_{12}(dmf)_3(H_2O)$ **1a** 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 $[Co_8O_4(O_2CPh)_{12}(MeCN)_3(H_2O)]\cdot 2MeCN$ (**1b**·2MeCN) in low yield (12%).†

The structure of **1b**‡ (Fig. 1) is extremely unusual and consists of a central $[Co_4O_4]$ 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 μ_4 and possess distorted tetrahedral (actually trigonal-pyramidal) geometry. The cubane and peripheral Co atoms are additionally bridged by a total of twelve $PhCO_2^-$ groups. A terminal MeCN group on Co(5), Co(6) and Co(8), and a terminal H_2O group [O(127)] 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.[5] Ignoring the difference in terminal $MeCN/H_2O$ ligation and the slight non-planarity in bridging RCO_2^- planes, the overall molecule and the $[Co_4O_4]^{4+}$ core have approximately T_d symmetry. This is to be contrasted with the cation of $[Co_4O_4(O_2CC_6H_4Me\text{-}p)_2(bipy)_4](ClO_4)_2$ **2** where the overall ion *and* the $[Co_4O_4]^{4+}$ core both have distinct D_{2d} symmetry.[3] Charge considerations require a formal $4Co^{II}$, $4Co^{III}$ description of **1b**, and the cubane Co atoms are clearly low-spin Co^{III} ions based on their six-coordination and shorter Co–O bonds (all <2.0 Å) compared with Co–O/N bond lengths at the peripheral (high-spin) Co^{II} atoms (1.972–2.174 Å).

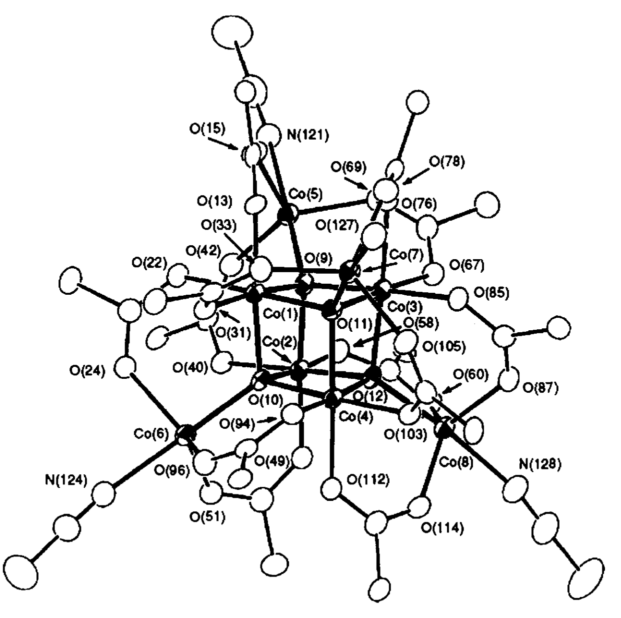

Fig. 1 ORTEP representation of complex **1b**. Selected distances (Å): Co(1)···Co(2) 2.809(1), Co(1)···Co(3) 2.823(1), Co(1)···Co(4) 2.838(1), Co(2)···Co(3) 2.824(1), Co(2)···Co(4) 2.842(1), Co(3)···Co(4) 2.820(1), Co(1)–O(10) 1.888(3), Co(2)–O(10) 1.884(3), Co(4)–O(6) 1.889(3), Co(1)–O(9) 1.881(3), Co(2)–O(9) 1.880(3), Co(3)–O(9) 1.885(3), Co(5)–O(9) 2.007(3), Co(6)–O(10) 2.012(3), Co(7)–O(11) 2.006(3), Co(8)–O(12) 2.012(3).

Although the $[Co_4O_4]^{4+}$ core has been seen once before in $[Co_4O_4(O_2CC_6H_4Me\text{-}p)_2(bipy)_4](ClO_4)_2$ **2**, the $[Co_8(\mu_4\text{-}O)_4]^{12+}$ unit is unprecedented. Indeed, the $[M_8(\mu_4\text{-}O)_4]$ core is previously unknown in a molecular complex for *any* metal; the only previous example is in the 3D polymeric lattice of $Pb_9O_4Br_{10}$, and related $TlPb_8O_4Br_9$, where recognizable $[Pb_8(\mu_4\text{-}O)_4]^{8+}$ sub-fragments are to be found, bridged by Br^- and either Tl^+ or additional Pb^{2+} ions.[6]

It is interesting that oxide ions bridging three tripositive Co^{III} ions should retain sufficient basicity to bind to a fourth Co centre and thus become μ_4; this suggested to us that it might be possible to protonate the $\mu_3\text{-}O^{2-}$ ions of complex **2**, a belief that was subsequently confirmed. Treatment of **2** in MeCN with aqueous $HClO_4$ (70%) ($MeCN : H_2O \approx 12 : 1$ v/v; final pH <0) led to a colour change from brown to greenish-brown and the slow crystallisation of the diprotonated complex $[Co_4O_2(OH)_2(O_2CC_6H_4Me\text{-}p)_2(bipy)_4](ClO_4)_4\cdot 3H_2O$ **3** in 75% yield.† The monoprotonated version was obtained by adding an aqueous solution of $[Ce(NO_3)_6]^{3-}$ to **2** in MeCN ($MeCN : H_2O \approx 4 : 1$ v/v; pH ≈ 1).§,[7] The presence of the trianionic counter-ion favoured precipitation of the tricationic (monoprotonated) complex, as hoped; a black crystalline solid was deposited in 75% yield and identified as $[Co_4O_3(OH)(O_2CC_6H_4Me\text{-}p)_2(bipy)_4][Ce(NO_3)_6]\cdot 2H_2O$ (**4**·2H₂O).† Complex **4** represents the initial example of a structurally-characterised, mixed O^{2-}/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 $[Co_4O_4(O_2CC_6H_4Me\text{-}p)_2(bipy)_4]^{2+}$ 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 $(CD_3)_2Co$ 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 T_d symmetry and supports retention of the solid-state structure on dissolution in this solvent (the terminal MeCN/H_2O groups being displaced by acetone groups). The ^1H NMR spectrum of **4** in $(CD_3)_2SO$ 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^-/H_2O resonance (δ 4.89). The spectrum of **3** in $(CD_3)_2SO$ 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 H_2O groups, is fast on the ^1H NMR timescale, leading to effective D_{2d} symmetry for the cations in solution.

Initial attempts to prepare the Co_8 cluster from addition of 4 Co^{II} ions to the $[Co_4O_4]^{4+}$ core of **2** have been unsuccessful, probably because of the kinetically-inert nature of Co^{III}. 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.

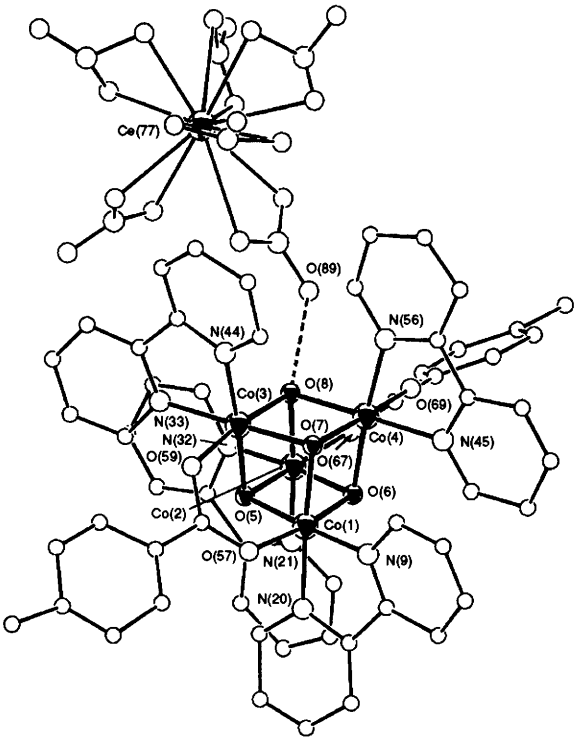

Fig. 2 ORTEP representation of complex **4**. Selected distances (Å): Co(1)···Co(2) 2.870(4), Co(1)···Co(3) 2.675(4), Co(1)···Co(4) 2.844(4), Co(2)···Co(3) 2.888(4), Co(2)···Co(4) 2.710(4), Co(3)···Co(4) 2.933(4), Co(1)–O(6) 1.893(13), Co(2)–O(6) 1.862(14), Co(4)–O(6) 1.868(13), Co(1)–O(7) 1.871(13), Co(3)–O(7) 1.877(14), Co(4)–O(7) 1.881(13), Co(2)–O(8) 1.939(12), Co(3)–O(8) 1.932(12), Co(4)–O(8) 1.929(13).

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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 $Co_8O_4(O_2CPh)_{12}(MeCN)(H_2O)_3$.

‡ *Crystal data* for **1b**·2MeCN: $C_{94}H_{77}Co_8N_5O_{29}$, M = 2212.12, triclinic, $P\bar{1}$, a = 15.056(4), b = 23.548(6), c = 14.697(4) Å, α = 90.74(1), β = 114.75(1), γ = 75.12(1)°, V = 4546 Å^3, Z = 2, D_c = 1.616 g cm^{-3}, λ = 0.710 69 Å, T = −153 °C, $6 < 2\theta < 45°$, $R(R_w)$ = 0.0401 (0.0424) for 10207 unique reflections with $F > 3\sigma(F)$. 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**: $C_{63}H_{53}CeCo_4N_{15}O_{27}$, M = 1828.05, orthorhombic, *Pbca*, a = 22.603(4), b = 34.759(6), c = 18.167(3) Å, V = 14273 Å^3, Z = 8, D_c = 1.701 g cm^{-3}, λ = 0.71069 Å, T = −154 °C, $6 < 2\theta < 45°$, $R(R_w)$ = 0.0863 (0.0878) for 4249 unique reflections with $I > 3\sigma(I)$. 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 NO_3^- groups; the eighteen O atoms were modelled as twelve full-weight atoms and twelve half-weight atoms. Hydrogen atoms were included in the final refinement cycles in fixed, calculated positions. One toluate group of the cation has rather large thermal parameters suggesting some disorder, and the solvate PhCN and H_2O molecules refined with occupancies of ≈0.5 and 0.67, respectively.

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 $(NH_4)_2Ce(NO_3)_6$ and NH_4NO_3 with H_2O_2 followed by boiling to decompose excess H_2O_2.

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