

Lewis Basicity of the $[\text{Co}_4\text{O}_4]^{4+}$ Cubane Core. Preparation of a Mixed-valence (4Co^{II} , 4Co^{III}) Cluster with an Unusual $[\text{Co}_8(\mu_4\text{-O})_4]^{2+}$ Core, and New $[\text{Co}_4\text{O}_3(\text{OH})]^{5+}$ and $[\text{Co}_4\text{O}_2(\text{OH})_2]^{6+}$ Cubane Complexes

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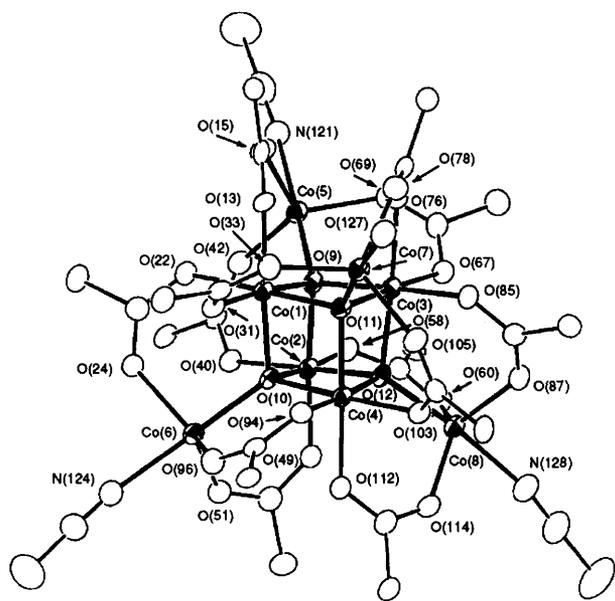
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$[\text{Co}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{MeCN})_3(\text{H}_2\text{O})]$ **1b** is formed on oxidation of cobalt(II) benzoate in MeCN or dmf with aqueous H_2O_2 , and contains a $[\text{Co}_4\text{O}_4]^{4+}$ cubane unit with each oxide attached to an additional Co atom; studies stimulated by this result show that preformed $[\text{Co}_4\text{O}_4(\text{O}_2\text{CR})_2(\text{bipy})_4]^{2+}$ ($\text{bipy} = 2,2'$ -bipyridine) can be mono- and doubly-protonated to $[\text{Co}_4\text{O}_3(\text{OH})(\text{O}_2\text{CR})_2(\text{bipy})_4]^{3+}$ and $[\text{Co}_4\text{O}_2(\text{OH})_2(\text{O}_2\text{CR})_2(\text{bipy})_4]^{4+}$, 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 $[\text{Co}_4\text{O}_4(\text{O}_2\text{CR})_2(\text{bipy})_4]^{2+}$.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 $\text{Co}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{dmf})_3(\text{H}_2\text{O})$ **1a** was $\approx 60\%$.[†] Crystals suitable for crystallography were obtained from an analogous reaction in MeCN by allowing the original reaction filtrate to stand undisturbed overnight; this afforded $[\text{Co}_8\text{O}_4(\text{O}_2\text{CPh})_{12}(\text{MeCN})_3(\text{H}_2\text{O})] \cdot 2\text{MeCN}$ (**1b**·2MeCN) in low yield (12%).[†]

The structure of **1b** (Fig. 1) is extremely unusual and



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)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/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 ¹H NMR timescale, leading to effective *D_{2d}* symmetry for the cations in solution.

Initial attempts to prepare the Co₈ cluster from addition of 4 Co^{II} ions to the [Co₄O₄]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.

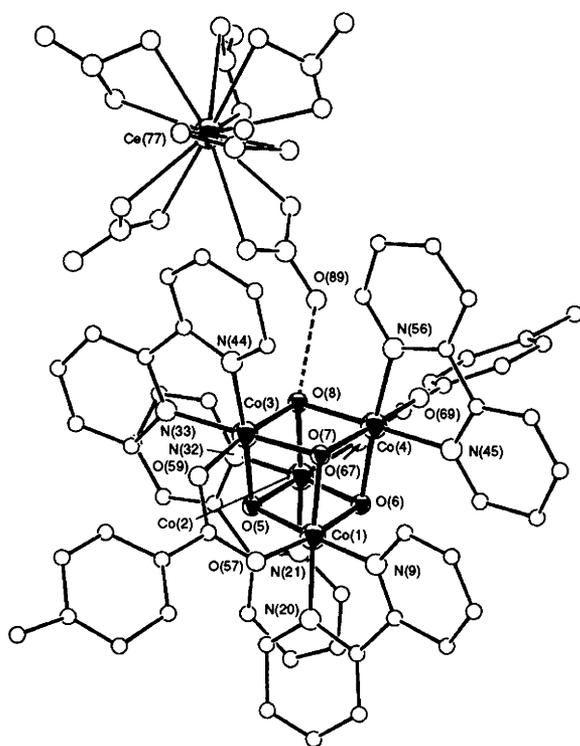


Fig. 2 ORTEP representation of complex **4**. Selected distances (Å): Co(1)⋯Co(2) 2.870(4), Co(1)⋯Co(3) 2.675(4), Co(1)⋯Co(4) 2.844(4), Co(2)⋯Co(3) 2.888(4), Co(2)⋯Co(4) 2.710(4), Co(3)⋯Co(4) 2.933(4), Co(1)–O(6) 1.893(13), Co(2)–O(6) 1.862(14), Co(4)–O(6) 1.868(13), Co(1)–O(7) 1.871(13), Co(3)–O(7) 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 Co₈O₄(O₂CPh)₁₂(MeCN)(H₂O)₃.

‡ *Crystal data* for **1b**·2MeCN: C₉₄H₇₇Co₈N₅O₂₉, *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 Å³, *Z* = 2, *D_c* = 1.616 g cm⁻³, λ = 0.710 69 Å, *T* = –153 °C, 6 < 2 θ < 45°, *R*(*R_w*) = 0.0401 (0.0424) for 10207 unique reflections with *F* > 3 σ (*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**: C₆₃H₅₃CeCo₄N₁₅O₂₇, *M* = 1828.05, orthorhombic, *Pbca*, *a* = 22.603(4), *b* = 34.759(6), *c* = 18.167(3) Å, *V* = 14273 Å³, *Z* = 8, *D_c* = 1.701 g cm⁻³, λ = 0.71069 Å, *T* = –154 °C, 6 < 2 θ < 45°, *R*(*R_w*) = 0.0863 (0.0878) for 4249 unique reflections with *I* > 3 σ (*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 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 H₂O 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 (NH₄)₂Ce(NO₃)₆ and NH₄NO₃ with H₂O₂ followed by boiling to decompose excess H₂O₂.

References

- D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Bashkin, S. Wang, H.-L. Tsai, J. B. Vincent, P. D. W. Boyd, J. C. Huffman, K. Folling, Q. Li and W. E. Streib, *J. Am. Chem. Soc.*, 1992, **114**, 2455; J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1991, **113**, 3012; G. Christou, S. P. Perlepes, K. Folling, J. C. Huffman, R. J. Webb and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1990, 746.
- R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folling, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804; S. Wang, H.-L. Tsai, W. E. Streib, G. Christou and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1992, 677; D. P. Goldberg, A. Caneschi, S. J. Lippard, *J. Am. Chem. Soc.*, 1993, **115**, 9299; M. W. Wemple, H.-L. Tsai, W. E. Streib, D. N. Hendrickson and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1994, 1031.
- K. Dimitrou, K. Folling, W. E. Streib and G. Christou, *J. Am. Chem. Soc.*, 1993, **115**, 6432.
- D. A. Buckingham and C. R. Clark, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 635; B. O. West, *Polyhedron*, 1989, **8**, 3, 219.
- I. Bertini, P. Dapporto, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1975, **14**, 7, 1639.
- H.-L. Keller, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 4, 324.
- A. W. Maverick and Q. Yao, *Inorg. Chem.*, 1993, **32**, 5626.