Uncapped and polar capped prisms of cobalt and nickel

Euan K. Brechin, Simon Parsons and Richard E. P. Winpenny *

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

The structures of two new high nuclearity co-ordination complexes have been determined, a decanuclear cobalt species and an undecanuclear nickel species; the two compounds extend a series of structures based on tricapped-centred-trigonal prisms in displaying respectively no additional capping metal atoms and one capped and one 'semi-capped' face.

The beautiful structure of the dodecanuclear cobalt complex $[Co_{12}(\mu_3\text{-}OH)_6(O_2CMe)_6(mhp)_{12}]$ **1** (Hmhp = 6-methyl-2-pyridone) reported by Garner and co-workers[1] has intrigued us for some time. The compound is among the highest nuclearity cobalt compounds known with O- or N-donors, and is based on a centred tricapped-trigonal prism with two additional capping atoms attached on the three-fold axis of the compound. We recently reported two related undecanuclear nickel species which each lack one of these two additional caps.[2] This has stimulated us to look for further compounds containing this structural motif in the belief that establishing structurally related families of polymetallic compounds will lead to greater understanding of both the synthetic methods required to make such compounds, and of the physical properties they display.

Reaction of anhydrous cobalt chloride (3.9 mmol) with 2 equivalents of both Na(mhp) and $Na(O_2CPh)$ in MeOH (50 cm^3) gives a purple solution which on evaporation to dryness produces a purple residue which was dried overnight in air. The residue was then extracted with MeCN (25 cm^3) and the mixture filtered prior to being left in air for 2 d giving purple crystals in 9% yield.† X-Ray structural analysis ‡ showed that a decanuclear cobalt complex $[Co_{10}(\mu_3\text{-}OH)_6(O_2CPh)_7(mhp)_6Cl(Hmhp)_3(MeCN)]$ **2** had formed (Fig. 1). As for complex **1** the metal polyhedron is based on a centred tricapped-trigonal prism with Co(1) at the centre of the polyhedron and Co(2), Co(3), Co(4), Co(6), Co(8) and Co(9) at the edges of the trigonal prism and Co(4), Co(7) and Co(10) at the centres of the square faces. The polyhedron is held together internally by six μ_3-OH groups which each bridge between Co(1), one of the edge Co atoms and one of the Co atoms on the square faces. The exterior of the compound is coated by both mhp ligands binding to one metal through both N- and O-donors, then bridging to two further metal atoms *via* the exocyclic O atom, and by 1,3-bridging benzoate ligands.

The major difference between complexes **1** and **2** is the absence of metal atoms on the trigonal axis of the prism (Fig. 2). Steric crowding by the benzoate ligands in **2** may prevent access of further metal fragments to the upper and lower faces of the prism. The 'upper face' is occupied by three ligands: an Hmhp and a benzoate group, which are strongly hydrogen bonded to each other, and a molecule of MeCN. The 'lower face' contains two Hmhp ligands and a chloride, with these three groups disordered over the available co-ordination sites on three Co atoms within this face.

The two undecanuclear Ni complexes we reported previously, $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CMe)_6(mhp)_9(H_2O)_3]_2[CO_3]$ **3** and $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CMe)_6(mhp)_9(Hmhp)_2(O_2CMe)]$ **4**, represent intermediate structures lacking one of the caps present in **1** but not both caps as in **2**. Somewhat surprisingly we have now isolated a salt which is intermediate between **3** and **4** and the dodecanuclear parent **1**.

A solution of hydrated nickel chloride (2.1 mmol) with 2 equivalents of both Na(chp) and $Na(O_2CPh)$ in EtOH (30 cm^3) was stirred for 24 h before being evaporated to dryness, leaving a green solid. Extraction with CH_2Cl_2 (25 cm^3) gives a green solution from which crystals of $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CPh)_6(chp)_9(EtOH)_3][Ni(chp)_3]$ **5** (Hchp = 6-chloro-2-pyridone) grow over 4 d in *ca.* 14% yield. The compound consists of two metal containing fragments (Fig. 3); an undecanuclear monocation related to **3** or **4**, and a mononuclear $[Ni(chp)_3]^-$ monoanion which is strongly hydrogen bonded to ethanol molecules attached to Ni atoms in the face of the prism which lacks a cap. Other than this feature the molecular structure of the undecanuclear unit is very similar to that of **3** and **4**,

---

† Found: C, 49.0; H, 3.9; N, 4.9. Calc. for $[Co_{10}(\mu_3\text{-}OH)_6(O_2CPh)_7(mhp)_6Cl(Hmhp)_3(MeCN)]$ **2**: C, 48.9; H, 4.0; N, 5.2. Found: C, 39.4; H, 2.9; N, 4.8. Calc. for $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CPh)_6(chp)_9(EtOH)_3][Ni(chp)_3]$ **5**: C, 40.2; H, 3.0; N, 5.0.

‡ Crystal data for $C_{105}H_{101}ClCo_{10}N_{10}O_{29}\cdot1.5CH_3CN$ **2**: $M = 2653$, triclinic, space group $P\bar{1}$, $a = 15.995(9)$, $b = 16.176(7)$, $c = 25.275(14)$ Å, $\alpha = 88.84(3)$, $\beta = 85.33(4)$, $\gamma = 61.21(3)°$, $U = 5711$ Å^3, $Z = 2$, $\rho_{calc} = 1.542$ g cm^{-3}, $T = 150.0(2)$ K, pink plate, crystal size 0.47 × 0.39 × 0.04 mm, μ(Mo-Kα) = 1.515 mm^{-1}.

Crystal data for $C_{113}H_{101}Cl_{14}N_{12}Ni_{12}O_{34}$ **5**: $M = 3372$, rhombohedral, space group $R3c$, $a = 16.279(3)$, $c = 85.61(3)$ Å, $U = 19\,647$ Å^3, $Z = 6$ (the molecule lies on a three-fold axis), $\rho_{calc} = 1.710$ g cm^{-3}, $T = 150.0(2)$ K, green block, crystal size 0.46 × 0.39 × 0.35 mm, μ(Cu-Kα) = 5.104 mm^{-1}.

Data collection and processing: Stoë STADI-4 four-circle diffractometer with Oxford Cryosystems low-temperature device,[3] graphite-monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) and Cu-Kα ($\lambda = 1.541\,84$ Å) X-radiation for **2** and **5** respectively; ω scans with learnt profile.[4] All data were corrected for Lorentz and polarisation effects, and for absorption using ψ scans. Maximum and minimum transmission factors were: for **2** 1.00, 0.549; for **5** 0.574, 0.410. Both structures were solved by direct methods using SIR92.[5] In both cases H-atoms were placed in calculated positions and included in subsequent refinements riding on parent carbon atoms. For **2** all non-H atoms were refined anisotropically with global rigid body restraints and similarity restraints applied to the mhp rings. Some disorder is evident on one face of the metal complex, involving partial occupancy of Cl and Hmhp groups. Using 1443 parameters refinement converged at $R1 = 0.0698$ for 6038 data with $F > 4\sigma(F)$, $wR2 = 0.1807$ for all 9600 independent reflections [$2\theta \leqslant 40°$] and 2508 restraints. The final ΔF synthesis maximum and minimum were +0.837 and −0.550 e Å^{-3} respectively. In **5** molecules of CH_2Cl_2 and Et_2O lie disordered about the crystallographic three-fold axis, the latter in two orientations. For **5** all non-H atoms, except in the disordered solvent, were refined anisotropically to give for 560 parameters $R1 = 0.0491$ for 3355 data with $F > 4\sigma(F)$, $wR2 = 0.1399$ for all 3542 independent reflections [$2\theta \leqslant 120°$] and 7 restraints. The final ΔF synthesis maximum and minimum were +0.756 and −0.583 e Å^{-3} respectively. All refinements used SHELXTL V.5.[6]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/208.

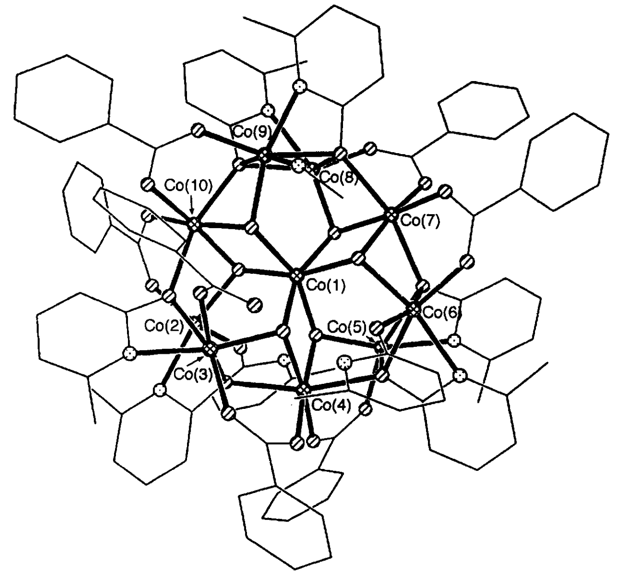

Fig. 1 The structure of the decanuclear complex **2** viewed down the non-crystallographic trigonal axis of the compound. Bond length ranges: Co–O(OH) 1.962–2.093, Co–O(mhp) 2.076–2.335, Co–O-(O_2CPh) 2.005–2.006, Co–N(mhp) 2.090–2.154, Co–N(MeCN) 2.156, Co–Cl 2.48–2.53 Å [average estimated standard deviation (e.s.d.) 0.008 Å]

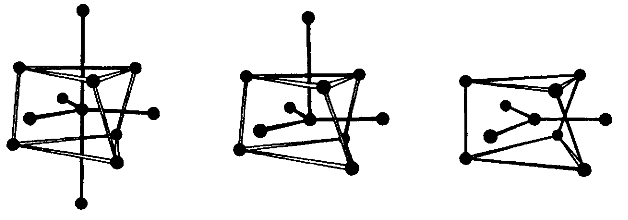
1 **3** **2**

Fig. 2 The metal polyhedra in complexes **1**–**3** showing the variation in capping of the centred-tricapped-trigonal prism on the molecular trigonal axis

differing from **2** in that one of the two capping sites on the trigonal axis is occupied by a nickel [Ni(4)] which itself has a co-ordination environment similar to that of the nickel atom [Ni(6)] within the $[Ni(chp)_3]^-$ unit. The formation of **5** was completely unexpected in that previous work with Hchp has indicated a reluctance to bond to nickel through the N atom, with the bonding mode involving bridging through the O-donor being more favoured.[2,7] The involvement of benzoate in both **2** and **5**, rather than acetate as in **1**, **3** and **4** also suggests that this family of compounds could be extended to other examples containing further carboxylates and pyridonate blends.

In **5** as in **1**, but unlike **2**–**4**, the compound lies on a crystallographically-imposed trigonal axis, however **5** is unique in that it crystallises as a twin in the polar space group *R*3*c*. Refinement of the Flack enantiopole parameter [0.35(6)] indicates that around 65% of the molecules are aligned in one direction and 35% in a second orientation. Although tri-,[8] tetra-,[9] penta-[10] and hexa-nuclear[11] co-ordination complexes have been found which crystallise in polar space groups, it is rare for higher nuclearity species so to do; a few examples are known for polyoxometallates.[12]

Acknowledgements

We thank the EPSRC for a studentship (to E. K. B.) and for funding for a diffractometer.

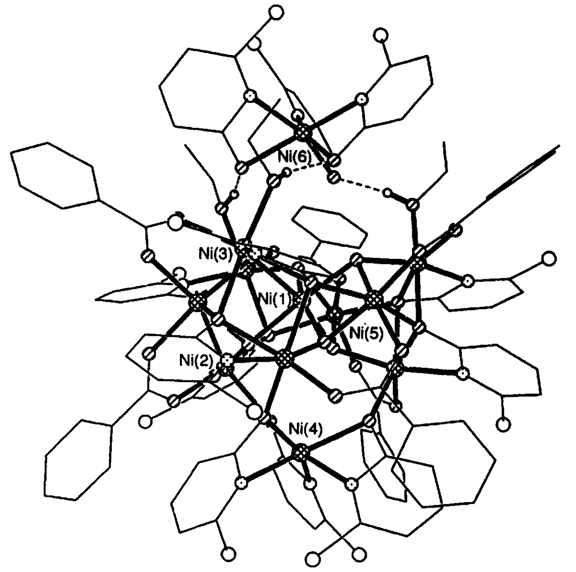

Fig. 3 The structure of complex **5** viewed perpendicular to the trigonal axis of the compound. Bond length ranges: Ni(1)–O(from OH) 2.057–2.075, other Ni–O(from OH) 1.950–2.078, Ni–O(chp) 2.106–2.254, Ni–O(O_2CPh) 1.968–2.047, Ni–O(EtOH) 2.044, Ni–N 2.071–2.137 Å (average e.s.d. 0.007 Å)

References

1 W. Clegg, C. D. Garner and M. H. Al-Samman, *Inorg. Chem.*, 1983, **22**, 1534.
2 A. J. Blake, E. K. Brechin, A. Codron, R. O. Gould, C. M. Grant, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1995, 1983.
3 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
4 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
5 A. Altomare, M. C. Burla, M. Carmelli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, SIR92, *J. Appl. Crystallogr.*, 1994, **27**, 435.
6 G. M. Sheldrick, SHELXTL V.5, University of Göttingen, 1993.
7 A. J. Blake, C. M. Grant, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1994, 2363.
8 F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1983, 539; J. B. Vincent, H.-R. Chang, K. Folting, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 5703; T. Yamagata, K. Tani, Y. Tatsuno and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1988, 466; H. Adams, N. A. Bailey, M. J. S. Dwyer, D. E. Fenton, P. C. Hellier, P. D. Hampstead and J. M. Latour, *J. Chem. Soc., Dalton Trans.*, 1993, 1207.
9 W. H. Armstrong, M. E. Roth and S. J. Lippard, *J. Am. Chem. Soc.*, 1987, **109**, 6318; H. M. Haendler, *Acta Crystallogr., Sect. C*, 1990, **46**, 2054; H. Yang, M. A. Khan and K. M. Nicholas, *J. Chem. Soc., Chem. Commun.*, 1992, 210; S. Teipel, K. Griesar, W. Haase and B. Krebs, *Inorg. Chem.*, 1994, **33**, 456; N. W. Eilerts, J. A. Heppert, M. L. Kennedy and F. Takusagawa, *Inorg. Chem.*, 1994, **33**, 4813.
10 J. K. Stallick and C. O. Quicksall, *Inorg. Chem.*, 1976, **15**, 1577; R. C. Bott, G. Smith, D. S. Sagatys, T. C. W. Mak, D. E. Lynch and C. H. L. Kennard, *Aust. J. Chem.*, 1993, **46**, 1055.
11 K. Y. Matsumato, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 492; K. Nishikawam, A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 889.
12 D. Hou, K. S. Hagen and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1993, 426; V. W. Day, T. A. Eberspacher, W. G. Klemperer and C. W. Park, *J. Am. Chem. Soc.*, 1993, **115**, 8469.

Received 2nd *July* 1996; *Communication* 6/04627D