COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Octanuclear cobalt and nickel cages featuring formate ligands

Cyril Cadiou,[a] Robert A. Coxall,[b] Alasdair Graham,[b] Andrew Harrison,[b] Madeleine Helliwell,[a] Simon Parsons[b] and Richard E. P. Winpenny*[a]

[a] *Department of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: richard.winpenny@man.ac.uk*

[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

Received (in Cambridge, UK) 27th February 2002, Accepted 28th March 2002
First published as an Advance Article on the web 19th April 2002

Two new octanuclear cages are reported which feature formate as a bridging carboxylate which has been formed *in situ* from decomposition of triphenylacetate used as a ligand.

Carboxylates are ubiquitous in the synthesis of polynuclear complexes.[1] They are used in supporting $\{Mn_{12}\}$ single molecule magnets,[2] in 'ferric wheels'[3] and in the highest nuclearity 3d-metal cages known.[4,5] However the smallest carboxylate, formate, is rarely found in cage complexes.[6] Most reported formate complexes are polymeric[7] with a comparatively small number of dimers known.[8] A possible explanation for this observation is that the multiple bridging modes displayed by formate – frequently μ_3- and μ_4- in addition to the common μ_2-mode shown by carboxylates – leads to insoluble polymeric species in preference to high nuclearity cages.

We have been exploring 'ligand blend' reactions, where two potentially bridging ligands, *e.g.* pyridonates and carboxylates, are present in the same reaction.[9] This has led to a large family of cages, the majority based on fragments of pentacapped trigonal prisms. In attempting to extend this family, and to create new topologies, we have begun reactions featuring sterically demanding carboxylates.[10] Triphenylacetate is one of the largest carboxylates commercially available.

Initial reactions involving $Na(O_2CCPh_3)$ and pyridonates were not promising. Unlike smaller carboxylates, cages based on pentacapped trigonal prisms did not form in good yield,[9] instead we found small quantities of crystals forming over long crystallisation periods.[10] X-Ray analyses of these crystals† showed that high nuclearity cages were forming, but the yields were dismal. Thus reaction of nickel chloride with Na(mhp) (mhp = 6-methyl-2-pyridonate) and $Na(O_2CCPh_3)$ in MeOH, followed by recrystallisation from EtOAc, produced $[Ni_{10}(OH)_6(mhp)_8(O_2CCPh_3)_6(H_2O)_2(MeOH)_2]$ **1** in *ca.* 4% yield over eleven months and crystals of $[Ni_7(OH)_2(O_2CCPh_3)_8(O_2CH)_2Cl_2(Hmhp)_6]$ **2** in *ca.* 7% yield after fifteen months. Starting with nickel nitrate and reacting with $Na(O_2CCPh_3)$ and Na(chp) (chp = 6-chloro-2-pyridonate) produces $[Ni_{10}(OH)_6(Hchp)(chp)_6(O_2CCPh_3)_6(NO_3)_2(MeCN)_3]$ **3** from MeCN, again in very poor yield. We also saw evidence for formation of cages containing $\{Ni_8Na_2\}$ cores which include formate as a bridging ligand. The structure will be discussed below, after the improved synthesis of the cage is described.

The metal array in **1** and **3** contains a central Ni site, bound to μ_3-OH, with nine surrounding Ni sites describing a tricapped-trigonal prism (**1** is shown in Fig. 1). The carboxylates are all 2.11-bridging (Harris notation[14]), and the pyridonates show the 3.21-mode. We have seen this core previously, but generally forming in yields of 30% and better.[9] The structure of **2** is new (Fig. 2), based on two hydroxide centred nickel triangles, held together by a seventh Ni centre which lies on an inversion centre. Four of the triphenylacetates show the 2.11-mode, while two chelate to Ni sites. The six Hmhp ligands bind either in the 2.20- or 1.10-modes, with the proton on the ring nitrogen involved in H-bonding interactions. Entirely unexpectedly, two formate anions are found in the structure, and they show the 3.21-binding mode.

These initial reactions suggested to us that the use of the very bulky carboxylate, $O_2CCPh_3^-$, had reduced the preference for formation of trigonal prisms without introducing a new preferred target. It is as if we have blocked the global minima for this reaction sequence and opened up a host of local minima as possible alternatives. Structurally this allows us to map the secondary products for these reactions, but for synthetic purposes these reactions are disappointing – giving mixtures of products in very low yields with excessive crystallisation times.

The formation of formate was intriguing. It has long been known that triphenylacetate can decompose to give formate,[15]

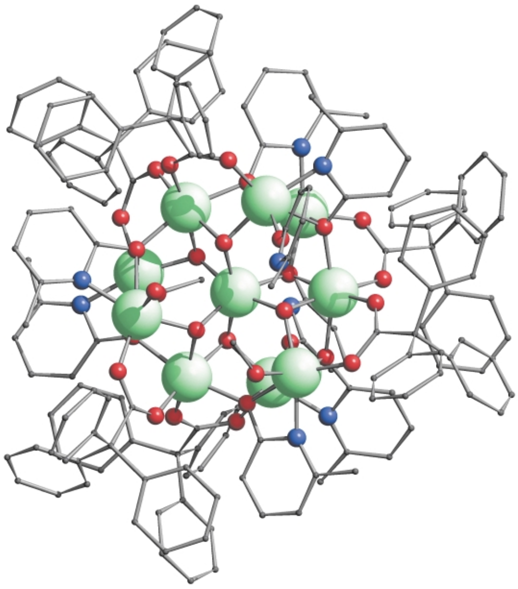

Fig. 1 Structure of **1** in the crystal. Colour scheme: Ni, light green; N, blue; O, red; C, grey.

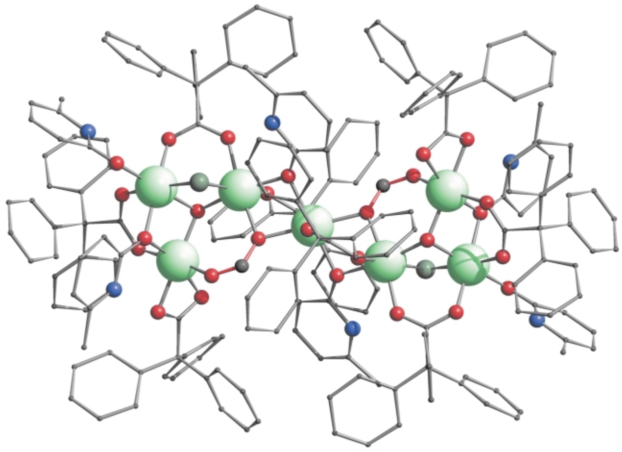

Fig. 2 Structure of **2** in the crystal. Colour scheme as Fig. 1, plus Cl, dark green. Formate ions are shown with red bonds and larger C atoms.

DOI: 10.1039/b202062a

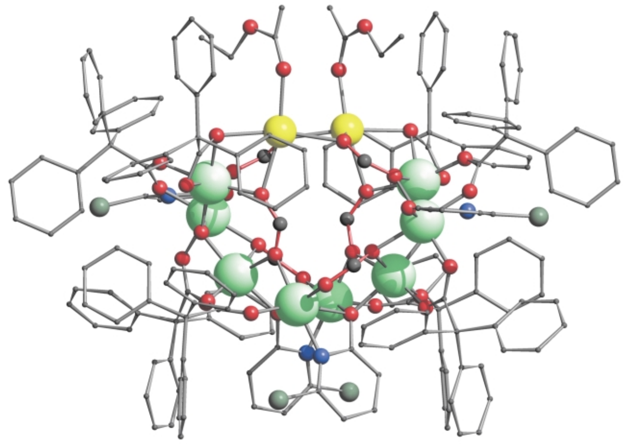

Fig. 3 Structure of **4** in the crystal. Colour scheme as Fig. 2, plus Na, yellow. Formate ions are shown with red bonds and larger C atoms.

but this normally happens at high temperatures. Therefore we repeated these reactions, but refluxed the MeOH solutions prior to evaporation to dryness and crystallisation. Crystalline products could then be obtained in moderate yield.

The best conditions we have obtained so far involve reaction of nickel nitrate (3.44 mmol) with $Na(O_2CCPh_3)$ (3.44 mmol) and Na(chp) (6.88 mmol) in MeOH (100 ml), followed by refluxing for 24 h.‡ The solution is then filtered, evaporated to dryness and extracted with sequential aliquots of EtOAc. Green crystals form in *ca.* 30% yield in 3 days. The equivalent reaction using cobalt nitrate produces purple crystals in *ca.* 25% yield.

X-Ray analyses† show formation of complexes of formula $[M_8Na_2(OH)_2(chp)_2(O_2CCPh_3)_8(HCO_2)_6(Hchp)_2(EtOAc)_2]$ [M = Ni, **4** (Fig. 3); Co, **5**]. The structures are highly unusual, with the eight Ni or Co sites describing a C-shaped topology, with the open segment of the C containing two Na sites. All the metal sites are six-coordinate, with distorted octahedral geometries. Within the C-shape are found six formate ligands. Two adopt the 3.21-mode, binding to three Ni/Co sites; two adopt the 4.22-mode, binding three Ni/Co sites and a Na; while the final two adopt the 4.22-mode, binding to two Ni/Co sites and two Na atoms. Two μ_3-OH ligands are found, bridging Ni/Co sites within the sides of the C-shape. The chp ligands show the 4.31-bridging mode at the top of the C-curve, and the Hchp ligands the 2.20-mode. The triphenylacetate ligands all bind in a 2.11 fashion.

The structure is therefore new, and seemingly unrelated to any previous Ni or Co cage reported in the literature.[1] The involvement of formate within the core of the cage suggests this is a vital component in the formation of this unusual structure. Inclusion of formate in a cage structure appears to be new, and is achieved because the formate is formed *in situ* by decomposition of triphenylacetate. This offers the possibility of including formate in other structures, and also suggests a means of including other new ligands in cages by use of ligand precursors that might decompose on heating. Addition of formate itself to reaction solutions generates insoluble materials, not **4** nor **5**.

Preliminary magnetic studies§ of both **4** and **5** show a fall in $\chi_m T$ against T at low temperature (χ_m is the molar magnetic susceptibility). For **4** the room temperature value is 9.8 emu K mol^{-1} (calc. value = 9.7 emu K mol^{-1} for g = 2.2). For **5** the room temperature value is 24.2 emu K mol^{-1}, which is not impossible for high spin cobalt(II) as it would require a g-value of 2.54. The fall in $\chi_m T$ leads to values at 1.8 K of 5.8 and 13.0 emu K mol^{-1} for **4** and **5** respectively.

This work was supported by the EPSRC and a TMR network on 'Molecules as Nanomagnets' (HPRN-CT-1999-0012).

Notes and references

† *Crystal data* for $C_{170}H_{156}N_8Ni_{10}O_{30}\cdot 3.75C_4H_8O_2$, **1**·3.75EtOAc: M = 3708.5, monoclinic, space group $P2_1/c$, a = 29.828(13), b = 18.635(8), c = 31.480(13) Å, β = 93.60(5)°, V = 17463(13) Å^3, Z = 4, T = 220.0(2) K, $R1$ = 0.0815. For $C_{198}H_{166}Cl_2N_6Ni_7O_{28}\cdot 5CH_2Cl_2$, **2**·5CH$_2Cl_2$: M = 3983.9, triclinic (twinned *via* 2[001]*), space group $P\bar{1}$, a = 14.799(9), b = 16.541(9), c = 22.688(12) Å, α = 76.986(15), β = 81.437(18), γ = 78.429(12)°, V = 5270(5) Å^3, Z = 1 (the molecule lies on an inversion centre), T = 150.0(2) K, $R1$ = 0.1079. For $C_{166}H_{174}Cl_7N_{12}Ni_{10}O_{31}\cdot 8C_2H_3N\cdot 2H_2O$, **3**·8MeCN·2H$_2$O: M = 4032.89, triclinic, space group $P\bar{1}$, a = 18.3048(14), b = 18.7041(15), c = 27.2303(12) Å, α = 88.149(2), β = 76.9650(10), γ = 71.0330(10)°, V = 8581.1(10) Å^3, Z = 2, T = 150.0(2) K, $R1$ = 0.0565. For $C_{194}H_{158}Cl_4N_4Na_2Ni_8O_{38}\cdot 3C_4H_8O_2\cdot H_2O$, **4**·3EtOAc·H$_2$O: monoclinic, space group $P2/c$, a = 28.295(6), b = 17.718(4), c = 39.725(6) Å, β = 101.317(18)°, V = 19528(7) Å^3, Z = 4, T = 220.0(2) K, $R1$ = 0.0982. For $C_{194}H_{158}Cl_4Co_8N_4Na_2O_{38}\cdot 2.25C_4H_8O_2\cdot 0.75H_2O$, **5**·2.25EtOAc·0.75H$_2$O: monoclinic, space group $P2/c$, a = 28.29(5), b = 17.630(10), c = 39.81(5) Å, β = 101.31(9)°, V = 19470(44) Å^3, Z = 4, T = 150.0(2) K, $R1$ = 0.0666. Data collection, structure solution and refinement used programs SIR92[11] and SHELXL-97.[12] In **1** and **2** only Ni and Cl atoms were refined anisotropically. Figures were produced using SCHAKAL.[13] Full details have been deposited and will be published later. CCDC 180242–180246. See http://www.rsc.org/suppdata/cc/b2/b202062a/ for crystallographic data in CIF or other electronic format.

‡ Satisfactory elemental analyses were obtained for **4** and **5**. Insufficient material was obtained for **1**–**3** to obtain elemental analysis.

§ Variable temperature magnetic measurements on **4** and **5** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 100 G field. The data have been adjusted for the diamagnetism of the sample.

1 R. E. P. Winpenny, *Adv. Inorg. Chem.*, 2001, **52**, 1 and refs. cited therein.

2 R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.

3 K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823.

4 S. P. Watton, P. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati and S. J. Lippard, *Angew. Chem., Int. Ed.*, 1998, **37**, 2774.

5 A. L. Dearden, S. Parsons and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2001, **40**, 151.

6 J. L. Sessler, J. D. Hugdahl, V. Lynch and B. Davis, *Inorg. Chem.*, 1991, **30**, 334; S. Brooker, V. McKee and T. Metcalfe, *Inorg. Chim. Acta*, 1996, **246**, 171; T. J. Boyle, T. M. Alam, C. J. Tafoya and B. L. Scott, *Inorg. Chem.*, 1998, **37**, 5588.

7 For example, see: A. Kaufman, C. Afshar, M. Rossi, D. E. Zacharias and J. P. Glusker, *Struct. Chem.*, 1993, **4**, 191; M. J. Bird and T. R. Lomer, *Acta Crystallogr., Sect. B*, 1971, **27**, 859; M. Bukowska-Strzyzewska, *Acta Crystallogr.*, 1965, **19**, 357; A. Cornia, A. Caneschi, P. Dapporto, A. C. Fabretti, D. Gatteschi, W. Malavasi, C. Sangregorio and R. Sessoli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1780.

8 For example, see: F. A. Cotton and G. W. Rice, *Inorg. Chem.*, 1978, **17**, 688; W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 3653; S. Youngme, W. Somjitsripunya, K. Chinnakali, S. Chantrapromma and H.-K. Fun, *Polyhedron*, 1999, **18**, 857.

9 R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2002, 1; E. K. Brechin, A. Graham, A. Parkin, S. Parsons, A. M. Seddon and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2000, 3242; C. Benelli, E. K. Brechin, S. J. Coles, A. Graham, S. G. Harris, S. Meier, A. Parkin, S. Parsons, A. M. Seddon and R. E. P. Winpenny, *Chem. Eur. J.*, 2000, **6**, 883.

10 A. Graham, S. Meier, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 2000, 811.

11 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

12 G. M. Sheldrick, SHELXL-93, program for crystal structure refinement, University of Göttingen, Germany, 1993.

13 E. Keller, SCHAKAL 99, program for representation of crystallographic models, University of Freiburg, Germany, 1999.

14 Harris notation describes the binding mode as $[X.Y_1Y_2Y_3\ldots Y_n]$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. Therefore for mhp, there will be two values for Y. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence O before N. See: R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2000, 2349.

15 E. Fischer and O. Fischer, *Justus Liebigs Ann. Chem.*, 1878, **194**, 262.