A series of nickel phosphonate–carboxylate cages†

Barbara A. Breeze, Muralidharan Shanmugam, Floriana Tuna and Richard E. P. Winpenny*

Received (in Cambridge, UK) 1st August 2007, Accepted 25th September 2007
First published as an Advance Article on the web 19th October 2007
DOI: 10.1039/b711650k

Three new polymetallic nickel(II) phosphonate complexes are reported; in one cage the twelve nickel centres are arranged at the vertices of a truncated tetrahedron in a similar manner to a Keggin ion.

Polyoxoanions were first discovered in the 19th century by Berzelius.[1] In 1933 Keggin[2] showed that the structure of the archetypal polyoxoanions was a truncated tetrahedron, which has become known as the Keggin ion. The Keggin ion $[XM_{12}O_{40}]^{n-}$ (X = P^{V}, Si^{IV}, B^{III}, As^{V}, Cu^{II}, Co^{III}, *etc.*, M = Mo^{VI}, W^{VI}, V^{V} or Ti^{IV}) comprises twelve metal ions linked *via* twenty-eight oxygens and can be viewed as four M_3O_4 surrounding a central tetrahedral heteroatom. Many examples of Keggin ions have been reported with metals with d^0 configuration, but there has only been one Keggin ion reported with non-d^0 metals, an $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$ ion reported by Bino and co-workers.[3] Magnetic studies of this Keggin ion show a high spin state but with very many low-lying excited states due to the topology of the spin centres.[4]

We have been synthesising cage complexes of first row transition metals with phosphonate ligands with the aim of preparing new clusters, hopefully with interesting physical properties.[5–10] We have shown that ligand displacement reactions starting from oxo-centred metal carboxylate triangles can make large clusters of trivalent metal ions,[5–8] and that use of phosphonates with pyridonate ligands can be used to make high nuclearity cages with cobalt(II).[9,10] Here we report reaction of a dinuclear nickel pivalate complex[11] with phosphonic acids, which gives three new nickel complexes. Extended lattices involving Ni phosphonates are well-known.[12]

$[Ni_2(H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ **1**‡ was mixed with phenylphosphonic acid in a 1 : 1 mole ratio in MeCN, and the reaction heated under pressure to 150 °C. On cooling crystals of $[Ni_{12}(\mu_3\text{-}OH)_4(\mu_6\text{-}O_3PC_6H_5)_4(\mu_2\text{-}O_2CCMe_3)_{12}(\mu_2\text{-}L)_6]$ **2** were found in the autoclave, where L is a disordered mixture of HO_2CMe, MeCN, H_2O and HO_2C^tBu (see below).

Structural studies§ show that **2**¶ has a core which can be thought of as an ε-Keggin with the central tetrahedral atom removed (Fig. 1). The four phenyl phosphonate ligands bind in the 6.222-mode (Harris notation[13]), thus each creates an approximately planar hexagon of Ni centres; the hexagons edge share to form the ε-Keggin structure. The triangular faces of **2** have central μ_3-OH groups. Twelve pivalate ligands surround the periphery of the complex binding in a 2.11-mode. 2.20-bridging ligands lie along the edges which are shared between two of the hexagonal faces.

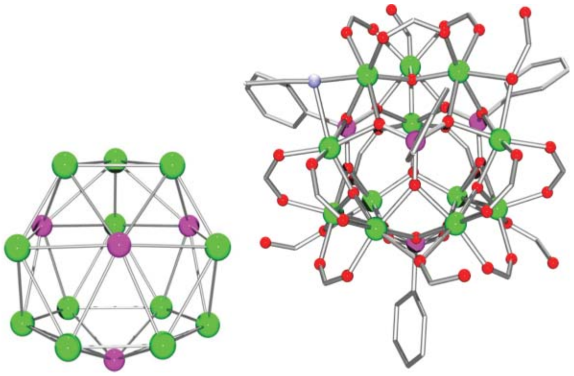

Fig. 1 The core and structure of **2** in the crystal. Ni, green; P, magenta; O, red; N, blue; C, grey lines. ^{t}Bu groups and some of the disordered L groups have been omitted for clarity.

There is partial occupation of these sites by pivalic acid as well as acetic acid, which probably arises from hydrolysis of MeCN under solvothermal conditions; this has been seen previously.[14]

The reaction appears to be dependent on the phosphonate used. If **1** is reacted with benzylphosphonic acid at room temperature in a 1 : 1 mole ratio crystals of $[Ni_8(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(5.221\text{-}O_3PCH_2C_6H_5)_2(O_2CCMe_3)_8(HO_2CCMe_3)_6]$ **3** form‖. The same reaction, but with a mole ratio of 1 : 1 : 1/2 of **1** with benzylphosphonic acid and Hchp gave crystals of $[Ni_9(\mu_3\text{-}OH)_3(\mu_2\text{-}OH_2)(6.222\text{-}HO_3PCH_2C_6H_5)(5.221\text{-}O_3PCH_2C_6H_5)(chp)_4(O_2CCMe_3)_8(HO_2CCMe_3)_2(H_2O)]$ **4****.

Structural studies‡ show **3** has two phosphonate ligands, both binding in a 5.221-mode, thus holding together two $\{Ni_4(\mu\text{-}OH)_2\}$ butterflies of nickel(II) ions (Fig. 2). There are eight pivalate groups binding in a 2.11-mode, two bridge body–body Ni centres within the butterflies, four bridge wing-body nickels and two bridge

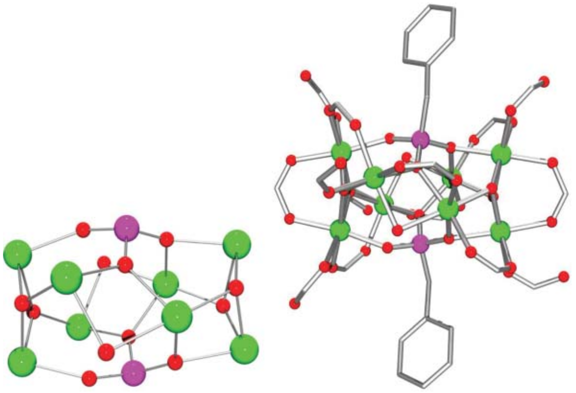

Fig. 2 The structure of **3** in the crystal. Colours as Fig. 1. ^{t}Bu groups have been omitted for clarity.

School of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL.
E-mail: Richard.Winpenny@manchester.ac.uk

† Electronic supplementary information (ESI) available: Fig. S1–S6 and X-ray data. See DOI: 10.1039/b711650k

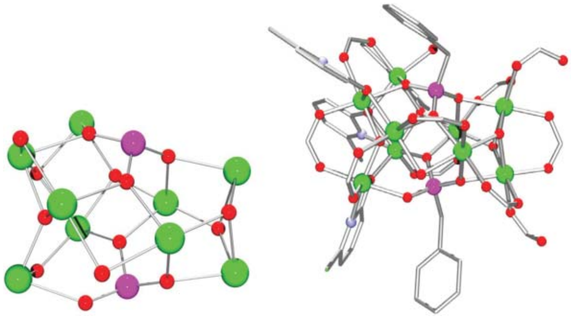

Fig. 3 The core and structure of **4** in the crystal. Ni, green; P, magenta; Cl, small green spheres; O, red; N, blue; C, grey lines. Pivalate Me_3 groups have been omitted for clarity.

between the butterflies. There are also six terminal pivalic acids. Two μ_2-OH_2 groups are found bridging between the nickel butterflies; the protonation states were assigned by bond valence sums on the O-atom.[15]

The structure of **4** contains eight metal centres arranged in a similar, but not identical core to that of **3**, but with an additional metal centre being bound to the cage, leading to one phosphonate binding in a 6.222-mode and the other in a 5.221-mode (Fig. 3). An additional change is that while one of the butterflies retains two μ_3-OH groups on the body–body edge, in the second butterly one of these OH groups is replaced by an O from a 3.31-chp, and binds to the ninth nickel rather than bridging the body–body vector. The four chp ligands in **4** show three modes: two are 3.31-bound, one is 2.21-bound and one shows the 2.20-mode. There are eight 2.20-pivalates and two terminal pivalic acids. Protonation states of the μ_3-OH, μ_2-OH_2 and the $HPO_3CH_2C_6H_5$ group were assigned by oxygen bond valence sums.[15]

The magnetic behaviour†† of powder samples of **2**, **3** and **4** has been studied under a constant magnetic field of 0.1 T and 0.5 T in the temperature range 2 to 300 K (Fig. 4). All show room temperature $\chi_m T$ values close to that calculated for the appropriate number of non-interacting Ni(II) centres, and a decline in $\chi_m T$ as T falls. For **2** the variable temperature behaviour can be fitted to a Hamiltonian (see ESI eqn 1†) which contains an exchange parameter (J_1) for exchange within the oxo-centred triangle, which occurs twelve times, and a second parameter (J_2) for the exchange between triangles, *i.e.* along edges of the hexagon. This occurs six times in the model. The best fit of the data was achieved with $J_1 = -6.5\ cm^{-1}$, $J_2 = 13.3\ cm^{-1}$ and $g = 2.25$, for a Hamiltonian of the form $H = -J.\hat{S}_a.\hat{S}_b$. The observation of a ferromagnetic exchange between the triangles can be explained by acute bridging angle at the μ_3-OH atom within the Ni triangles. Although the strongest exchange interaction is ferromagnetic, the resulting ground state is $S = 0$.

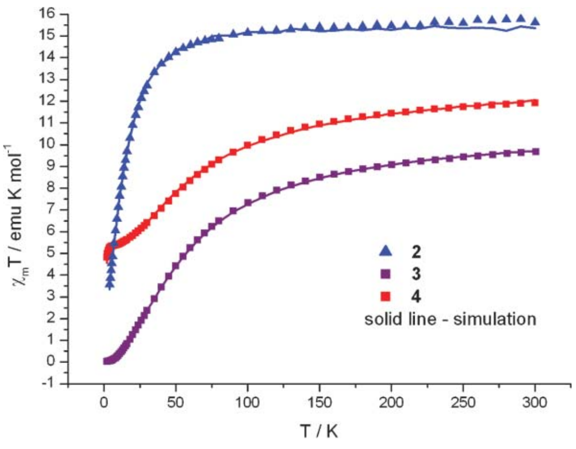

Fig. 4 Variable temperature DC measurement on polycrystalline samples of **2**, **3** and **4** at 0.5 T.

For **3** the magnetic behaviour can also be modelled with a Hamiltonian (see ESI eqn 2†) containing two exchange parameters. The first (J_1) is assigned to the four Ni···Ni vectors that are bridged by two μ_2-O atoms; these vectors are the two body–body contacts within the butterflies, where the O-atoms are derived from two μ_3-hydroxides, and the nearest contacts between butterflies, where the oxygens come from a phosphonate and a bridging water. The second (J_2) is assigned to the eight body–wing contacts within butterflies. All Ni···Ni contacts not bridged by a monoatomic bridge were neglected, and an excellent fit of the data was achieved with $J_1 = 7.6\ cm^{-1}$, $J_2 = -22.4\ cm^{-1}$, $g = 2.42$. Again the spin ground state is zero.

For **4** the symmetry of the cage is much lower and therefore, in principle, we should require at least three exchange parameters to model the magnetic behaviour§; J_1 is assigned to six Ni···Ni vectors bridged by two μ_2-O atoms, J_2 is assigned to five Ni···Ni vectors bridged by only μ_3-O atoms and J_3 is assigned to four Ni···Ni vectors bridged by μ_3-O atoms as well as μ_2-pivalates. However, in order to avoid over-parameterization, we initially required J_2 and J_3 to be equal. This allows a very good fit of the magnetic behaviour, even reproducing a maximum at 10 K. The best fit parameters are: $J_1 = 19.4\ cm^{-1}$, $J_2 = J_3 = -22.1\ cm^{-1}$, $g = 2.37$. These parameters lead to an $S = 2$ ground state, with an $S = 3$ low lying spin excited state at 1.9 cm^{-1} above the ground state. The magnetisation (M) against field (H) behaviour at 1.8 K was also fitted using the twelve lowest energy states (Fig. 5), which confirms we have a good picture of the energy states of this molecule even by using a Hamiltonian which is much simpler than might seem required by the structure of the cage. Interestingly the saturation value of 6.7 μ_B is due to population of the $S = 3$ first excited state rather than the $S = 2$ ground state. No zero-field splitting of any state was required to achieve the fit shown.

According to a reported magneto-structural correlation derived from studies on clusters with a $[Ni^{II}_4(\mu_3\text{-}O)_4]$ core,[16] Ni–O–Ni

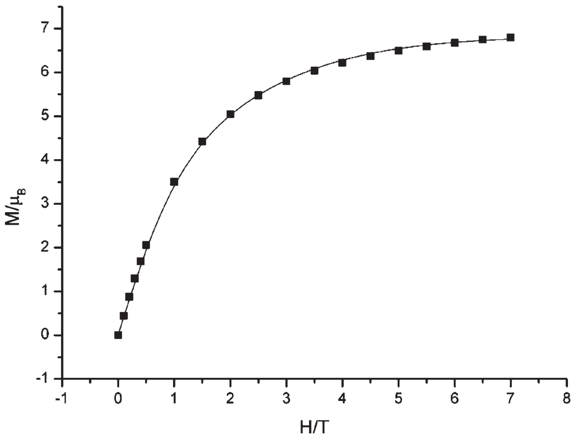

Fig. 5 Magnetisation against field plot for **4** at 1.8 K.

angles smaller than 99° favour ferromagnetic interactions, whereas wider angles tend to give anti-ferromagnetic couplings. Here the exchange coupling constant (J_1) is ferromagnetic, with values of +13.3, +7.6 and +19.4 $\mathrm{cm^{-1}}$ for **2**, **3** and **4** respectively. The relevant Ni–O–Ni bond angles observed are: for **2**, 78.1–89.5°; for **3**, 90.8–99.9°; **4**, 91.3–96.6°, therefore all fall within the range for ferromagnetic exchange.[16,17] The exchange coupling constant (J_2) is anti-ferromagnetic, with values of −6.5, −22.4 and −22.1 $\mathrm{cm^{-1}}$ for **2**, **3** and **4** respectively. The relevant Ni–O–Ni bond angles are in the range: for **2**, 115.9–119.5°; for **3**, 113.9–137.5°; for **4**, 122.8–133.9°, consistent with the observed anti-ferromagnetic exchange coupling constants. AF interactions are also observed for Ni···Ni contacts that are bridged by μ_3-oxo and μ_2-carboxylate/oximate with Ni–O–Ni bond angles $\geqslant$ 110° [$J = -8\ \mathrm{cm^{-1}}$ to $-55.6\ \mathrm{cm^{-1}}$].[18] The trend in anti-ferromagnetic exchange interactions is **3** $|J_2| \approx$ **4** $|J_2| >$ **2** $|J_2|$, which agrees with the trend in their Ni–O–Ni bond angles for **2**, **3** and **4**. The observed exchange coupling constants are very similar to previously reported values for high nuclearity nickel clusters.[16–18]

Previously we have shown that oxo-centred carboxylate triangles can be reacted with phosphonates to produce larger clusters;[5–8] the results here show that the approach can be extended to other metal carboxylate complexes. The structure of **2** is the second example of a Keggin structure being found with an open-shell ion,[3] and this is strongly connected with the 6.222 binding mode observed for the phosphonate.

This work was supported by the EC Research and Training Network QuEMolNa″ (MRTN-CT-2003-504880), by the EC Network of Excellence MAGMANet and by the EPSRC(UK). One of us (MS) thanks Prof. R. Sessoli and Dr L. Sorace for training in fitting magnetic data, and we thank Dr Madeleine Helliwell for help with the crystallography.

Notes and references

‡ **1** was synthesised as reported.[11]

§ Crystal data: **2**: $C_{104.35}H_{171.9}N_{3.2}Ni_{12}O_{47.8}P_4$, monoclinic, $P2_1/c$, a = 28.765 (6), b = 19.213 (4), c = 28.414 (6) Å, β = 90.00(3)°, V = 15703(6) $\mathrm{Å^3}$, M = 3064.55, D_c = 1.296 g $\mathrm{cm^{-1}}$, Z = 4, $R1$ = 0.0696 for 28535 reflections; **3**: $C_{90}H_{165}NNi_8O_{41.6}P_2$, monoclinic, $P2_1/c$ a = 21.512(5), b = 16.983(3), c = 34.416(6) Å, β = 91.234(17)°, V = 12571(4)$\mathrm{Å^3}$, M = 2484.09, D_c = 1.309 g $\mathrm{cm^{-1}}$, Z = 4, $R1$ = 0.0682 for 28524 reflections; **4**: $C_{87.7}H_{133}Cl_{3.6}N_{6.2}Ni_9O_{36}P_2$, monoclinic, $P2_1/c$, a = 15.1594(5), b = 22.9262(5), c = 34.2611(9) Å, β = 97.160(3), V = 11814.5(6) Å, M = 2562.15, D_c = 1.440 g $\mathrm{cm^{-1}}$, Z = 4, $R1$ = 0.0699 for 14380 reflections.CCDC 656183–656185]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711650k Data collection, structure solution and refinement used SHELXL.[19]

¶ **2**. Compound **1** (0.10 g, 0.1 mmol) and $H_2O_3PC_6H_5$ (0.016 g, 0.1 mol) were dissolved in MeCN (8 ml) and added to a small autoclave and heated to 150 °C for 12 h, then cooled to rt at a rate of 0.05 °C $\mathrm{min^{-1}}$. Green plates of **2** suitable for X-ray diffraction studies using synchrotron radiation were formed directly. Yield 55%, Anal. calcd (found)) C 41.43 (41.27); H 5.80 (5.92); P 3.96 (4.19); Ni 22.22 (21.82). The calculated value assumes replacement of MeCN by H_2O during analysis.

‖ **3**. **1** (0.10 g, 0.1 mmol) and $H_2O_3PCH_2C_6H_5$ (0.017 g, 0.1 mmol) were dissolved in MeCN (20 ml) and stirred for 6 h at rt. The solution was filtered and left to stand at rt for 4 weeks, after which time small green crystals of **3** were isolated, yield 35%. The green precipitate was recrystallised from toluene/MeCN layering to give green crystals of **3**.piv. ½ C_7H_8, yield 20% (based on total Ni). Anal. calcd (found); C 44.70 (44.76); H 6.82 (6.66); P 2.51 (2.53); Ni 18.77 (18.54).

** **4**. **1** (0.10 g, 0.1 mmol), $H_2O_3PCH_2C_6H_5$ (0.017 g, 0.1 mmol) and Hchp (0.006 g, 0.05 mmol) were dissolved in MeCN (20 ml) and left to stir for 18 h at rt. The solution was filtered and left to stand at rt for 2 weeks, after which time green crystals of **4** were isolated. Yield 65%. Anal. calcd (found) C 40.63 (40.64); H 5.36 (5.28); Cl 5.32 (5.27); P 2.36 (2.42); Ni 19.84 (19.62).

†† Magnetic measurements were in the temperature range 1.8–300 K, using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Data were fitted with CLUMIN.[20] Supplementary information† includes more detail of the fitting procedure.

1 J. Berzelius, *Poggendorff Ann. Phys Chem*, 1826, **6**, 369.

2 J. F. Keggin, *Nature*, 1933, **131**, 908.

3 A. Bino, M. Ardon, D. Lee, B. Spingler and S. J. Lippard, *J. Am. Chem. Soc.*, 2002, **124**, 4578.

4 J. van Slageren, P. Rosa, A. Caneschi, R. Sessoli, H. Casellas, Y. V. Rakitin, L. Cianchi, F. Del Giallo, G. Spina, A. Bino, A.-L. Barra, T. Guidi, S. Carretta and R. Caciuffo, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 014422/1.

5 E. I. Tolis, M. Helliwell, S. Langley, J. Raftery and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2003, **42**, 3804.

6 S. Maheswaran, G. Chastanet, S. J. Teat, T. Mallah, R. Sessoli, W. Wernsdorfer and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2005, **44**, 5044.

7 S. Khanra, M. Kloth, H. Mansaray, C. A. Muryn, F. Tuna, E. C. Sañudo, M. Helliwell, E. J. L. McInnes and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2007, **46**, 5568.

8 E. I. Tolis, L. P. Engelhardt, P. V. Mason, G. Rajaraman, K. Kindo, M. Luban, A. Matsuo, H. Nojiri, J. Raftery, C. Schröder, G. A. Timco, F. Tuna, W. Wernsdorfer and R. E. P. Winpenny, *Chem.–Eur. J.*, 2006, **12**, 8961.

9 S. Langley, M. Helliwell, R. Sessoli, P. Rosa, W. Wernsdorfer and R. E. P. Winpenny, *Chem. Commun.*, 2005, **40**, 5029.

10 S. Langley, M. Helliwell, J. Raftery, E. I. Tolis and R. E. P. Winpenny, *Chem. Commun.*, 2004, 142.

11 G. Chaboussant, R. Basler, H.-U. Gudel, S. T. Ochsenbein, A. Parkin, S. Parsons, G. Rajaraman, A. Sieber, A. A. Smith, G. A. Timco and R. E. P. Winpenny, *Dalton Trans.*, 2004, **17**, 2758.

12 For example: R. Modi, G. B. Hix, M. Tremayne and E. MacLean, *New J. Chem.*, 2005, **29**, 427–429; Z. Chen, L. Weng and D. Zhao, *Inorg. Chem. Commun.*, 2007, **10**, 447–450.

13 Harris notation describes the binding mode as [X.Y1Y2Y3···Yn], 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. 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.

14 A. J. Belsky and T. B. Brill, *J. Phys. Chem. A*, 1999, **103**, 3006.

15 I. D. Brown and K. W. Wu, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, **B32**, 1957.

16 (*a*) M. A. Halcrow, J.-S. Sun, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1995, **34**, 4167–4177; (*b*) J. M. Clemente-Juan, B. Chansou, B. Donnadieu and J.-P. Tuchagues, *Inorg. Chem.*, 2000, **39**, 5515–5519.

17 (*a*) A. Sieber, C. Boskovic, R. Bircher, O. Waldmann, S. T. Ochsenbein, G. Chaboussant, H. U. Gudel, N. Kirchner, J. v. Slageren, W. Wernsdorfer, A. Neels, H. Stoeckli-Evans, S. Janssen, F. Juranyi and H. Mutka, *Inorg. Chem.*, 2005, **44**, 4315–4325; (*b*) M. Murrie, D. Biner, H. Stoeckli-Evans and H. U. Güdel, *Chem. Commun.*, 2003, 230–231.

18 (*a*) T. C. Stamatatos, E. Diamantopoulou, C. P. Raptopoulou, V. Psycharis, A. Escuer and S. P. Perlepes, *Inorg. Chem.*, 2007, **46**, 2350–2352; (*b*) T. C. Stamatatos, E. Diamantopoulou, A. Tasiopoulos, V. Psycharis, R. Vicente, C. P. Raptopoulou, V. Nastopoulos, A. Escuer and S. P. Perlepes, *Inorg. Chim. Acta*, 2006, **359**, 4149–4157.

19 *SHELX-PC Package*. Bruker Analytical X-ray Systems: Madison, WI, 1998.

20 D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.*, 1993, **123**, 231–240.