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Cation-induced assembly of the first mixed molybdenum–vanadium hexadecametal host shell cluster anions

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Two novel hexadecametal–oxygen cluster compounds, $\{Ni[(NH_2)_2(C_2H_4)_2NH]_2\}_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot[(NH_2)_2(C_2H_4)_2NH]\cdot H_2O$ 1 and $\{Co[(NH_2)_2(C_2H_4)_2NH]_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$ 2 are synthesized by a hydrothermal method, and characterized by X-ray crystallography, showing that the anion of 1 has a novel tetra-capping mode, and that the first hexadecametal–oxygen host shell is observed in 2.

Transition metal oxide clusters are currently receiving considerable attention due to their diverse structural flexibility and superior electrical, magnetic, photochemical and catalytic properties.[1,2] Moreover, polyoxometalates of Keggin structures exhibit potent anti-HIV activity and some of them are under pre-clinical evaluations for the treatment of HIV.[3] It is therefore vital to design and synthesize novel metalates with different structural characteristics in order to explore their properties.

One of the strategies used in the synthesis of polyoxometalates is to employ a specific cation as inducing agent. Successful examples include the formation of the cluster anion $[M_{16}V_{14}O_{84}]^{14-}$ in the presence of Cs^+,[4] the synthesis of $[V_{10}O_{10}(H_2O)_2(PO_4)_7]^{6-}$ and $[VO_3]_n^{n-}$ using $[(CH_3)_2NH_2]^+$ and $[Cu(dpa)]^+$ (dpa = 4,4′-dipyriylamine).[5] In the last few years one of the important advances in transition metalate chemistry has been the study of capping structural polyanions and closed host cage structural metal–oxygen cluster compounds (a small guest is in the host shell).[4,6–11] Here we present the synthesis and structural investigations of novel mixed Mo/V metalates with different structures, designated as $\{Ni[(NH_2)_2(C_2H_4)_2NH]_2\}_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot[(NH_2)_2(C_2H_4)_2NH]\cdot H_2O$ **1** and $\{Co[(NH_2)_2(C_2H_4)_2NH]_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$ **2**, and we show the important role that the cation plays in the synthesis.

Compound **1** was synthesized as dark-green block-like crystals in 34% yield (based on W, 0.37 g) by the hydrothermal method. A mixture of NH_4VO_3 (0.40 g), $Ni(OAc)_2$ (0.35 g), Na_2MoO_4 (0.6 g), triethylenediamine (1.5 ml) and H_2O (10 ml) was neutralized to pH = 4.0 with 50% phosphorous acid. It was sealed in a 15 cm^3 Teflon-lined reactor, and kept at 160 °C for ten days. After being cooled to room temperature, the block-like dark-green crystals were separated (0.38 g) with filtration, then washed with water and dried in air. Analysis found: C, 12.10; N, 10.65; H, 3.20. Calc.: C, 11.89; N, 10.40; H, 3.29%. The IR spectrum exhibited a complex pattern of bands at 1079, 950 and 770 cm^{-1}, ascribed to ν(P–O), ν(M=O), ν(M–O–M) (M = V or Mo), respectively. Dark-green block crystals of **2** (0.30 g, yield 46% based on V) were obtained under the same reaction conditions using $CoCl_2$ (0.3 g) instead of $Ni(OAc)_2$. Analysis found: C, 7.50; N, 6.60; H, 2.68. Calc.: C, 7.38; N, 6.46; H, 2.61%. The IR spectrum exhibited a complex pattern of bands at 1050, 980 and 790 cm^{-1}, ascribed to ν(P–O), ν(M=O), ν(M–O–M) (M = V or Mo), respectively. The two compounds were characterized by single-crystal X-ray diffraction.†

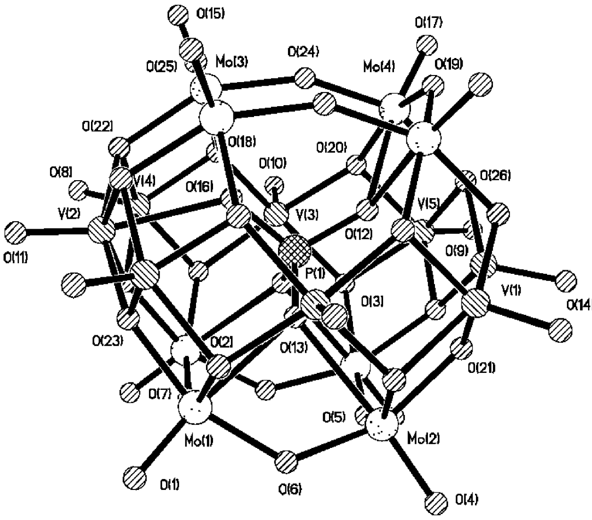

Fig. 1 The tetra-capping Keggin structure for the anion of compound **1**.

The structure of **1** contains a novel tetra-capping Keggin structural anion (Fig. 1), which is based on the well-known α-Keggin structure with four additional five-coordinated terminal VO^{2+} units and contains a central P^{5+} in a tetrahedral environment. The PO_4 tetrahedron has P–O distances of 1.547(13)–1.557(11) Å, and bond angles in the range 107.7(7)–110.4(5)°. The structure of **1** is formed by capping the classic α-Keggin anion of idealised T_d point symmetry at four of the six faces defined by C_2 symmetry axes. The unusual feature of **1** is that the V=O groups cap four of the $[PMo^{V}_3Mo^{VI}_5V^{IV}_4O_{40}]^{6-}$ Keggin anions to give a structure in which the eight V atoms form a central belt, and each trimetallic group of $[Mo^{V}_3Mo^{VI}_5V^{IV}_4(PO_4)]^{14-}$ (Keggin part) contains one V and two Mo atoms. The two Mo_4 rings are bonded above and below this V_8 belt. The V–O and Mo–O bond lengths in MoO_6 octahedra are Mo–O_t, 1.664(6)–1.706(5) Å; Mo–O_b, 1.853(10)–2.037(10); and Mo–O_c, 2.425(10)–2.487(10), V–O_t, 1.562(14)–1.713(10); and V–O_b, 1.890(11)–2.105(9) Å, respectively. The assignment of the oxidation states of molybdenum atoms is based on bond valence sum calculations,[11] which gives values of 5.768 for Mo_1, 5.307 for Mo_2, 5.552 for Mo_3 and 5.845 for Mo_4, the average value calculated for the oxidation of Mo is 5.634 (expected value for $Mo^{V}_3Mo^{VI}_5$ is 5.625), and the calculated result is consistent with the formula of heteropoly compound **1**. The cluster anion charge is balanced by the cation, $\{Ni[(NH_2)_2(CH_2)_2NH]_2\}^{2+}$ and the remaining lattice volume is occupied by water and triethylenediamine molecules. The cluster anions and cation are linked by hydrogen bonds.

By replacing Ni^{2+} by Co^{2+} in a similar hydrothermal reaction to that for **1**, compound **2** was obtained, in which the first hexadecametal host shell, $[Mo^{V}_2Mo^{VI}_6V^{IV}_8O_{40}]^{5-}$, containing a disordered guest PO_4^{3-} is discovered, as shown in Fig. 2. This shell structure is similar to that of the host cage $[V_{18}O_{42}(VO_4)]^{6-}$.[9a] The host cage of **2** is composed of eight VO_5 square pyramids which are linked together through shared edges to form a central belt. In each shared corner four square pyramidal MoO_5

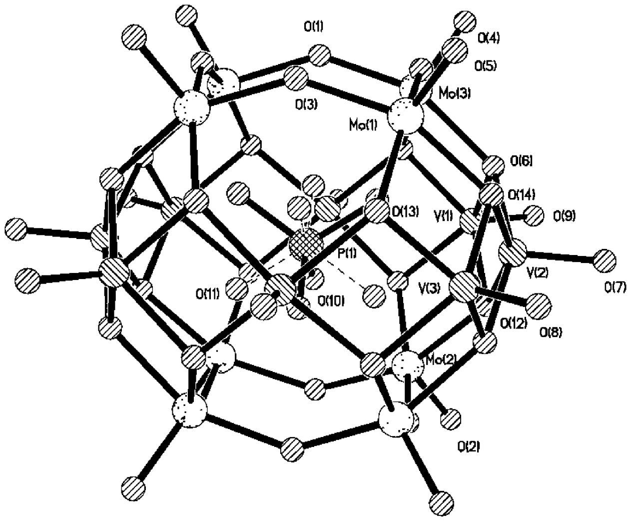

Fig. 2 The hexadecametal–oxygen host shell for the anion of compound **2**.

are bonded above and between the central V_8 belt. The Mo–O and V–O distances are Mo–O_t, 1.652(10)–1.678(7), Mo–O_b, 1.834(11)–1.991(9), and V–O_t, 1.600(8)–1.643(13) and V–O_b, 1.918(7)–1.983(9) Å, respectively. As found in $[V_{18}O_{42}(VO_4)]^{6-}$,[9a] the disordered PO_4 tetrahedron is in the center, and the P–O bond distances are 1.501(8)–1.503(8) Å, which are 0.05 Å shorter than the P–O bond lengths in **1**. The O(10) atom of the disordered PO_4 tetrahedron forms a weak contact with the Mo(2) atom with a distance of 2.516(11) Å, which is longer than the Mo–O_c bond length in **1** and other Keggin structural compounds.[1] The host shell lies on a four-fold axis, centred on the P(1) atom. Although a similar symmetry has been observed previously in an inorganic supramolecule,[5,6] this appears to be the first example of a hexadecametal–oxygen host shell structure. The Co^{2+} cations are coordinated by two triethylenediamine ligands, and Co–N distances are between 2.019(16) and 2.145(15) Å. Bond valence calculations give values of 5.7335, 5.970 and 5.596, respectively, for Mo atoms (average value of 5.767, expected value of 5.75 for $Mo^V{}_2Mo^{VI}{}_6$).

In conclusion, we have demonstrated that cations play a crucial role in the synthesis of mixed Mo/V hexadecametal–oxygen cluster anions, by defining their structural features and maintaining charge balance. Synthesis of larger metal–oxygen cluster anions by careful selection of initiator cation and an exploration of the properties of these metalates is currently under way.

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Notes and references

† Crystal data for **1**: $C_{28}H_{93}Mo_8N_{21}Ni_3O_{45}PV_8$, orthorhombic, *Cmc*2(1), $a = 14.293(3)$, $b = 22.480(5)$, $c = 26.103(5)$ Å; $V = 8387(3)$ Å^3, $Z = 4$. Data were collected on a CAD 4 diffractometer at 20 °C in the range $1.69 < 2\theta < 29.98$ using the ψ scan technique. Based on 3889 reflections with $I > 2\sigma(I_o)$ and 577 parameters gave R (Rw) = 0.0685 (0.1819).

Crystal data for **2**: $C_{16}H_{68}Co_2Mo_8N_{12}NaO_{50}V_8P$, tetragonal, *P*4(2)/*ncm*, $a = b = 22.057(3)$, $c = 14.125(3)$ Å, $V = 6872.3(19)$ Å^3, $Z = 4$. Data were collected on a CAD 4 diffractometer at 20 °C in the range $1.85 < 2\theta < 29.97$ using the ψ scan technique. Based on 3059 reflections with $I > 2\sigma(I_o)$ and 247 parameters gave R (Rw) = 0.0784 (0.1817). An empirical absorption correction was applied. These structures were solved by direct methods and refined using SHELX-97 programs.[12] All non-hydrogen atoms (except disordered water molecules) were refined anisotropically, and the remaining disordered O atoms (water molecules) were refined anisotropically. CCDC reference numbers 150889 and 150890. See http://www.rsc.org/suppdata/dt/b0/b010227j/ for crystallographic data in CIF or other electronic format.

1 (*a*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983; (*b*) V. W. Day and W. G. Klemperer, *Science*, 1985, **228**, 533; (*c*) M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; (*d*) M. T. Pope and A. Müller, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Dordrecht, 1994.

2 (*a*) C. L. Hill, *Chem. Rev.*, 1998, **98**, 1; (*b*) L. C. W. Baker and D. C. Glick, *Chem. Rev.*, 1998, **98**, 3; (*c*) Y. P. Jeannin, *Chem. Rev.*, 1998, **98**, 51; (*d*) P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77; (*e*) N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199; (*f*) A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239; (*g*) E. Coronado and C. J. Gomez-Garcia, *Chem. Rev.*, 1998, **98**, 273.

3 (*a*) E. De Clercq, *Metal-Based Drugs*, 1997, **4**, 173; (*b*) Z. Guo and P. J. Sadler, *Adv. Inorg. Chem.*, 2000, **49**, 183.

4 (*a*) Y. Zhang, R. C. Haushalter and A. Clearfield, *J. Chem. Soc., Chem. Commun.*, 1995, 1149; (*b*) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, 1586.

5 R. L. Laduca, R. Finn and J. Zubieta, *Chem. Commun.*, 1999, 1669.

6 (*a*) D. Hou, S. K. Hagen and C. L. Hill, *J. Chem. Soc., Chem. Commun.*, 1993, 426; (*b*) A. Müller, M. Koop, P. Schiffels and H. Bogge, *Chem. Commun.*, 1997, 1715; (*c*) Q. Chen and C. L. Hill, *Inorg. Chem.*, 1996, **35**, 2403; (*d*) Y. Xu, J. Q. Xu, G. Y. Yang, T. G. Wang, Y. Xing, Y. H. Ling and H. Q. Jia, *Polyhedron*, 1998, **17**, 2441.

7 (*a*) I. Khan, J. Zubieta and P. Toscano, *Inorg. Chim. Acta*, 1992, **193**, 17; (*b*) I. Khan, Q. Chen and J. Zubieta, *Inorg. Chim. Acta*, 1993, **212**, 199; (*c*) I. Khan, Q. Chen and J. Zubieta, *Inorg. Chem.*, 1993, **32**, 2924; (*d*) L. Pettersson, C. M. Schramm, S. L. Downey and J. H. Grate, *Inorg. Chem.*, 1994, **33**, 3141.

8 Y. Xu, H. G. Zhu, H. Cai and X. Z. You, *Chem. Commun.*, 1999, 787.

9 (*a*) M. I. Khan, E. Yohannes and R. J. Doedens, *Angew. Chem., Int. Ed.*, 1999, **38**, 1292; (*b*) J. R. D. Debord, R. C. Haushalter, L. M. Meyer, D. J. Rose, P. J. Zapf and J. Zubieta, *Inorg. Chim. Acta*, 1997, **256**, 165.

10 (*a*) A. Müller, E. Krichemeyer, M. Penk, H. J. Walberg and H. Bogge, *Angew. Chem., Int. Ed.*, 1987, **26**, 1045; (*b*) A. Müller, E. Krichemeyer, M. Penk, R. Rohlfing, A. Armatage and H. Bogge, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1674; (*c*) A. Müller, R. Rohlfing, E. Krichemeyer and H. Bogge, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 909; (*d*) M. I. Khan, A. Müller, S. Dillinger, H. Bogge, Q. Chen and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1780; (*e*) A. Müller, R. Rohlfing, J. Doring and M. Penk, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 588; (*f*) A. Müller, H. Reuter and S. Dillinger, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2328; (*g*) T. Yamase, M. Suzuki and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1997, 2463.

11 M. O'Keeffe and A. Navrotsky, *Structure and Bonding in Crystals*, eds. M. O'Keffe and A. Navrotsky, Academic Press, New York, 1981, vol. II, p. 1.

12 G. M. Sheldrick, SHELX-97, Program for crystal structure determination, University of Göttingen, 1997.