Synthesis of elliptical vanadoborates housing bimetallic centers $[Zn_4(B_2O_4H_2)(V_{10}B_{28}O_{74}H_8)]^{8-}$ and $[Mn_4(C_2O_4)(V_{10}B_{28}O_{74}H_8)]^{10-}$†

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Received (in Cambridge, UK) 23rd September 2004, Accepted 11th January 2005
First published as an Advance Article on the web 9th February 2005
DOI: 10.1039/b414697b

The hydrothermal synthesis of three new vanadoborate compounds with elliptical ($V_{10}B_{28}O_{74}H_8$) clusters is described. The clusters contain pairs of bimetallic Zn_2 or Mn_2 units.

Among metal oxide clusters the vanadoborates developed recently by Zubieta, Haushalter and others[1–4] have some of the most interesting structural and compositional diversity. They contain the anions $(V_{12}B_{18}O_{60}H_6)^{12-}$,[1] $(V_{12}B_{16}O_{58}H_8)^{12-}$,[2] and more borate-rich clusters $(V_6B_{20}O_{50}H_8)^{8-}$ and $(V_{12}B_{32}O_{84}H_8)^{16-}$ which have toroidal $(O{=}VO_2)_n$ rings, where $n = 6$ and 12, respectively. Whilst the hexavanadate 'V_6B_{20}' cluster has a closed-shell,[3] the dodecavanadate '$V_{12}B_{32}$' has a hollow 'barrel-like' structure.[4]

In attempts with Zn^{2+} or Mn^{2+} to form new metal cross-linked solids from these anionic clusters we have discovered three compounds containing a new intermediate member of this toroidal cluster family, a decavanadate $(V_{10}B_{28}O_{74}H_8)^{16-}$ with $(O{=}VO_2)_{10}$ rings. In this case, the cluster possesses an elliptical hollow which is filled by bimetallic dimer units $[M_4(\mu\text{-}L)]$ L = $B_2O_4H_2$ or C_2O_4. The two pairs of M_2 ions coordinate to four oxygens from the borate $(B_{14}O_{32}H_4)^{18-}$ ligands of the top and bottom sections of the cluster. The first of these compounds **1** $[Zn(en)_2]_2[Zn(OH_2)(en)]_4$ $[Zn_4(B_2O_4H_2)(BO_2H)_2(V_{10}B_{28}O_{74}H_8)]\cdot 10H_2O$ is formed phase pure as large blue–green blocks from the hydrothermal reaction of $Zn(OAc)_2$, V_2O_5, en, H_3BO_3 and H_2O in 2 : 1 : 4 : 6 : 100 ratio (pH 8.5, 180 °C, 10d). The yield is *ca.* 70% based on V_2O_5.‡

These typically gave pseudo-tetragonal unit cells and poor structural refinement ($R_1 > 0.10$) but an untwinned specimen allowed acceptable solution in monoclinic $P2_1/n$.

1 has several structural features of interest, the anionic cluster itself Fig. 1 comprises a new toroidal decavanadate unit sandwiched between two new B_{14}-borate ligands which are depicted in Fig. 2. The wide structural diversity found for these vanado(IV)borate clusters comes from the capacity of the separate vanadate and borate components to oligomerize in various ways and find geometric match with each other. In **1** the two are connected through formation of VB_2 rings. Given the range of VB cluster species that have been isolated from such reactions the '$V_{10}B_{28}$' clusters presumably form part of a complex equilibrium mixture of such species at high temperatures. The isolation of **1** in fair yield as the sole vanadoborate product implies its selective precipitation through a structure directing role of the zinc ions in combination with the other components from the borate 'soup'. Specifically $[Zn_4(\mu\text{-}B_2O_4H_2)]$ units are formed which are housed inside the elliptical cavity of the '$V_{10}B_{28}$' cluster and have the

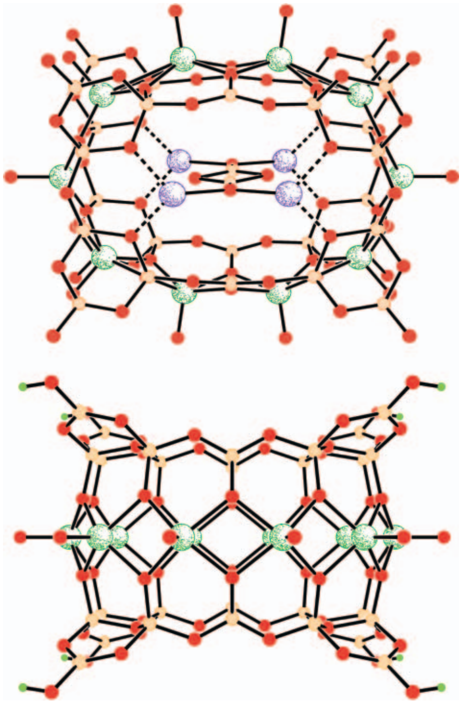

Fig. 1 Plan and side view of the $(V_{10}B_{28}O_{74}H_8)^{16-}$ cluster anion in **1** featuring bound $Zn_4(\mu\text{-}B_2O_4H_2)$ viewed from above.

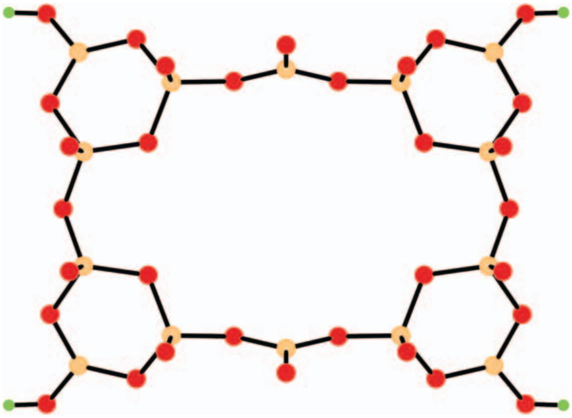

Fig. 2 Tetradecaborate $(B_{14}O_{32}H_4)^{18-}$ ligand of '$V_{10}B_{28}$' elliptical clusters in **1–3**. Ten O atoms are directed out to bind to the V_{10} ring.

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† Electronic Supplementary Information (ESI) available: Preparation and characterization details for **1–3**, supplementary figures. See http://www.rsc.org/suppdata/cc/b4/b414697b/
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correct size and functionality to bind *via* eight Zn–O bonds shown by the dashed lines in Fig. 1. The Zn_2 dimers in **1** are then capped by monohydroborate $(BO_3H)^{2-}$ groups that are reminiscent of carbonate or carboxylate bridges.

The identity of the (μ_4-$B_2O_4H_2$) unit at the core of the cluster is difficult to establish, since the H-atoms are hard to locate by X-ray diffraction. The formation of diborate B_2O_2 rings is rare but precedented.[5–7] Marder and co-workers[7] showed that the ring is stabilized by Lewis acid coordination of the bridging oxygens, which supports protonation of the diborate cores.

If based solely upon a vanadium(IV) oxidation state the $[Zn_4(\mu\text{-}B_2O_4H_2)(V_{10}B_{28}O_{74}H_8)]$ cluster in **1** has a high anionic 8-charge, which is increased to 12- including the $(BO_3H)^{2-}$ caps. Overall charge balance is then brought to the crystal structure by the presence of six other Zn^{2+} ions per cluster. Four of these are bound directly to the cluster surface as $[Zn(en)(H_2O)]$ groups and the other two are derived from a half-share of four $[Zn(en)_2]$ which linearly bridge clusters *via* V=O–Zn–O=V linkages to form a 2D network, as shown in Fig. 3. The cross-linking of the structure in this manner and the close packing of the 2D sheet with adjacent layers rotated by 90° gives rise to the pseudo-tetragonal arrangement of **1**.

The novel '$V_{10}B_{28}$' cluster type found in **1** was found not to be entirely unique, since parallel reactions in the manganese system have also led to preparation of two related compounds **2** and **3**. Compound **2** is formed in *ca.* 50% isolated yield as pale-green bars as the major (70%) product from hydrothermal reaction of $KMnO_4$, V_2O_5, en and H_3BO_3 in 2 : 1 : 12 : 15 ratio for 4 d at 140 °C. The crystal structure determination reveals **2** to be $K_6(H_3O)_8$ $[Mn_4(C_2O_4)(V_{10}B_{28}O_{74}H_8)(B_4O_9H_2)].24H_2O$. In **2** the deca-vanadate clusters are connected together by linear tetraborate $(B_4O_9H_2)$ bridges to form linear 1D anionic chains. The cluster cores are now assembled from Mn_2 dimers that are connected *via* $(\mu_4\text{-}C_2O_4)^{2-}$ ligands. The presence of the oxalate is unexpected, but apparently arises from the permanganate oxidation of the ethylenediamine starting reagent.

To establish the identity of the oxalate in the core, reactions using manganese(II) acetate in conjunction with both oxalic acid and ethylenediamine were made. These tended to afford the microporous non-borate solid $(enH_2)[Mn_2(\mu_2\text{-}C_2O_4)(V_4O_{12})]$.[8] However, for $Mn(OAc)_2$,V_2O_5, en, H_3BO_3, $C_2O_4H_2$, H_2O in 2 : 1 : 15 : 15 : 5 : 100 ratio at 110 °C 7 d a related compound **3** was found as a 5% minor component. This is best formulated as $(H_3O)_{14}[Mn_4(C_2O_4)_3(V_{10}B_{28}O_{74}H_8)].32H_2O$. The crystal structure of **3** is disordered with respect to the $[Mn_4(C_2O_4)_3]$ cores which have two 50 : 50 orientations imposed by crystallographic symmetry. It is noteworthy that the overall structure of **3** in tetragonal *P*4$_2$/*mnm* has a pseudo-isostructural nature with the polymorphs of **1**. Critically despite its disorder the structure of **3** supports the identification of the core group in **2** as μ_4-oxalate. In both compounds, the oxalate has two side-bound η^1,η^2-coordination modes with inversion symmetry, which is an established mode for metals such as manganese.

In both **2** and **3** the K^+ and $(H_3O)^+$ counter-cations are found coordinated or hydrogen bonded to the cluster surface. The presence of hydroxonium ions is necessitated by charge balance for the two structures and their assignment and differentiation from aqua groups, which are also found in both structures, is supported by their strong H-bonding to the O=V groups and the requirement that they do not contact each other or the K ions.

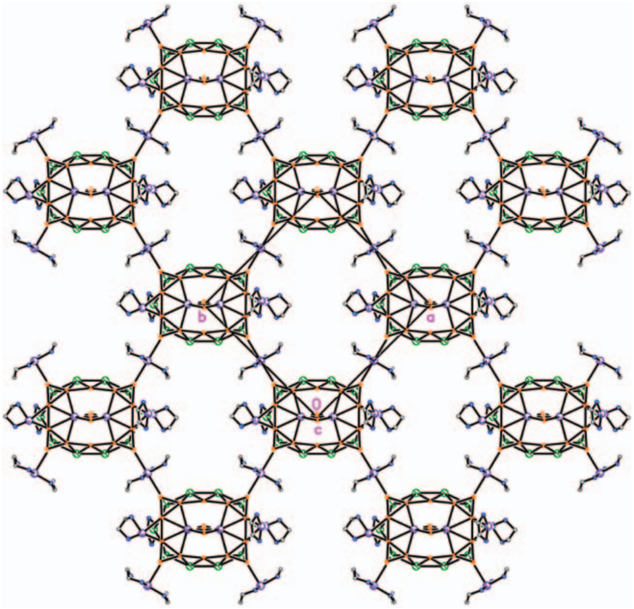


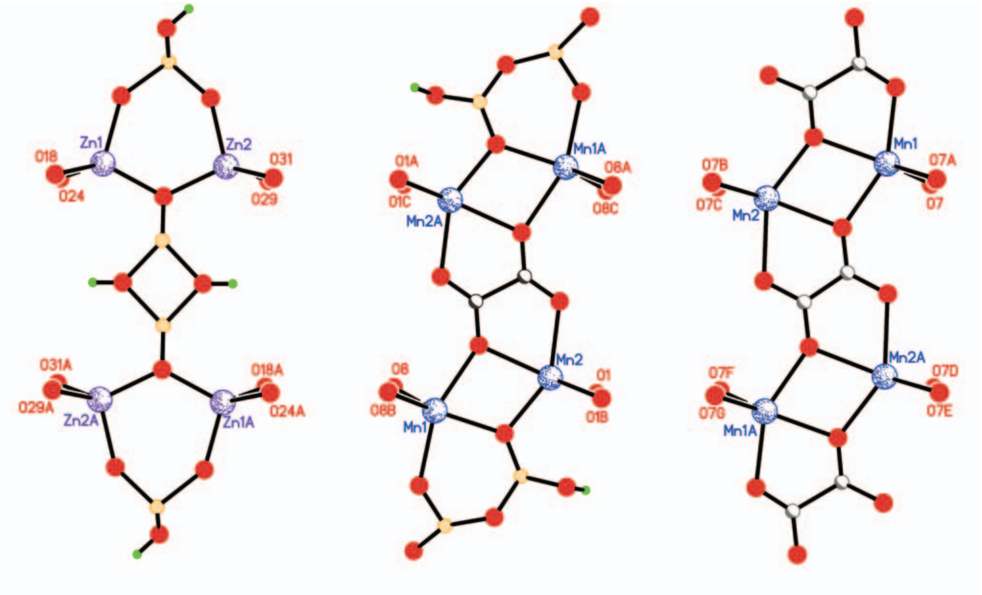
Fig. 3 2D Network of **1** showing $[Zn(en)(H_2O)]$ and bridging $[Zn(en)_2]$.

The geometries for the $[M_4(\mu\text{-}L)]$ cores shown in Fig. 4 are different for Zn and Mn. In **1** the Zn ions both lie outside the cluster perimeter (indicated by the labelled oxygens in the figure) and the environments are symmetric, whereas for Mn in **2** and **3** they are asymmetric, and one Mn center is within the cluster perimeter and the other projects outside. It is interesting that both these metals readily tend to bimetallic center formation where suitable ligand bridges may be found. Zn_2 and Mn_2 units lie at a number of enzymatic centers[9] which have been modelled by coordination complexes.[10]

In **1–3** the Zn and Mn ions have low 4- and 5-coordination numbers, respectively, and have Zn–Zn and Mn–Mn separations of between 3.42 and 3.51 Å. The coordination spheres are distorted from tetrahedral and trigonal bipyramidal geometries by the constraints of binding to 3 or 4 oxygens of the cluster and core, as shown in Fig. 4. Whilst these structural features are intriguing, investigation of potential bimetallic reactivity in such cluster compounds will require synthesis of soluble modified species with labile capping ligands. Of **1–3** only **3** is water soluble but is formed in low quantity and has tightly bound capping oxalate groups.

In summary, the preparation of **1–3** shows novel incorporation of heterometallic ions into elliptical vanadoborate cluster species. The high level of organization in these indicates the powerful role of supramolecular effects in organo-directed multi-component metal oxide syntheses. Finally, it is noteworthy that none of the individual borate fragments herein have been reported previously, though several recent syntheses indicate a similar complexity of borate speciation.[11]

We are grateful to the Research Grants Council, Hong Kong for financial support (HKUST 6128/01P).



1 **2** **3**

Fig. 4 Core geometries for **1–3** with symmetric [$Zn_4(\mu\text{-}B_2O_4H_2)$], [$Mn_4(\mu\text{-}C_2O_4)(B_4O_9H_2)$] and [$Mn_4(C_2O_4)_3$]. Attachment to the cluster perimeters are indicated by the labelled oxygen atoms.

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Notes and references

‡ Crystal data for **1**: $C_{16}H_{90}B_{32}N_{16}O_{98}V_{10}Zn_{10}$, M_r 3584.06, T = 100(2) K, λ = 0.71073 Å, monoclinic, $P2_1/n$, a = 17.0801(8), b = 17.0717(8), c = 20.1404(10) Å, β = 90.011(1)°, V = 5872.7(5) Å^3, Z = 2, D_c = 2.027 Mg m^{-3}, μ = 2.88 mm^{-1}, 2θmax = 50.0°, data/restraints/parameters 10078/0/738, S = 1.008, R_1 = 0.0657, wR_2 (all) = 0.1547, Δe +1.26 and −1.59 e Å^{-3}; for **2**: $C_2H_{82}B_{32}K_6Mn_4O_{119}V_{10}$, M_r 3320.4, T = 100(2) K, λ = 0.71073 Å, orthorhombic, $Pnnm$, a = 15.516(3), b = 15.892(3), c = 21.353(4) Å, V = 5142.9(17) Å^3, Z = 2, D_c = 2.14 Mg m^{-3}, μ =1.73 mm^{-1}, 2θmax = 50.0°, data/restraints/parameters 4378/0/359, S =1.020, R_1 = 0.0586, wR_2 (all) = 0.1532, Δe + 1.275 and −0.84 e Å^{-3}; for **3**: $C_6H_{114}B_{28}Mn_4O_{132}V_{10}$, M_r 3330.8, T = 298(2) K, λ = 0.71073 Å, tetragonal, $P4_2/mnm$, a = 17.1826(6) Å, c = 19.5059(11) Å, V = 5759.0(4) Å^3, Z = 2, D_c = 1.92 Mg m^{-3}, μ =1.34 mm^{-1}, 2θmax = 50.0°, data/restraints/parameters 2538/1/188, S = 1.055, R_1 = 0.0473, wR_2 (all) = 0.1373, Δe + 0.65 and −0.54 e Å^{-3}. CCDC reference numbers 252643–252645. See http://www.rsc.org/suppdata/cc/b4/b414697b for crystallographic data in CIF or other electronic format.

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