An organotemplated vanadium(IV) borate polymer from boric acid 'flux' synthesis, $[H_2en]_4[Hen]_2[V_6B_{22}O_{53}H_8]\cdot 5H_2O$

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A new 1-D inorganic chain polymer $[H_2en]_4[Hen]_2[V_6B_{22}O_{53}H_8]\cdot 5H_2O$, consisting of $[V_6B_{20}O_{50}H_6]$ cluster subunits linked together through diborate bridges, has been synthesised with high yield and purity by a molten boric acid 'flux' method in which V_2O_5, en and H_3BO_3 (1 : 6 : 25) were heated together at 180 °C for 3 days; the clusters have a central band of six square-pyramidal V^{IV}=O vanadyl groups, which are capped top and bottom by two raft-like polyborate ligands of formula $[B_{10}O_{16}H_3]$.

There has been much recent interest in mixed organic–inorganic materials, especially for the formation of new microporous materials such as metal phosphates.[1,2] For these phosphoric acid is used commonly as a precursor with a variety of basic metal sources and organic templates. Since the discovery of various microporous aluminoborates by Xu and coworkers[3,4] we have been interested in the use of boric acid as a possible reagent in place of phosphoric acid to assist formation of microporous transition-metal borates. Whilst use of H_3PO_4 and H_3BO_3 in tandem can result in the formation of hybrid borate–phosphate phases,[5,6] recently Haushalter *et al.* have shown that hydrothermal reaction of vanadium oxides with boric acid can give rise to novel mixed-valence vanadium borate clusters.[7,8a] Yamase *et al.* have also reported a similar vanadoborate.[8b]

Herein we report that use of molten boric acid as flux can lead to other boron-rich cluster phases and even allow the direct connectivity of such clusters to novel inorganic polymers by additional borate bridges. Furthermore the reaction products are not only different from analogous hydrothermal syntheses, but they are typically of higher purity and yield. This becomes important for strategies in which the formed clusters are to be used as synthetic intermediates.

We find that flux reaction of V_2O_5 with 6 mol equiv. of ethylenediamine (en) and 25 H_3BO_3 at 180 °C for 3 days results in the formation of an off-white crude solid. Removal of the residual boric acid through washing with cold water allows isolation of pale-green block-shaped crystals of **1** as a phase-pure material in *ca.* 75% isolated yield based on V. X-Ray powder diffraction shows three strong peaks of approximately 1 : 2 : 1 intensity ratio with *d*-spacings of 11.2 (200), 10.6 (112) and 10.1 (112)/(004) Å respectively. We have found such peaks in the region of 10 Å *d*-spacing to be characteristic of vanadyl polyborate cluster materials and a useful diagnostic tool.[9]

A single crystal X-ray structure analysis† reveals the structure of **1** to be $[H_2en]_4[Hen]_2[V_6B_{22}O_{53}H_8]\cdot 5H_2O$ consisting of an anionic vanadium polyborate chain polymer, together with $(H_2en)^{2+}$ and $(Hen)^{+}$ counterions and five waters of solvation. The polymer has $[V_6B_{20}O_{50}H_6]$ cluster subunits linked together by linear diborate $[B_2O_3H_2]$ bridges. A portion of the polymer chain is shown in Fig. 1.

The clusters have a central band of six square-pyramidal V^{IV}=O vanadyl groups, which are capped top and bottom by two novel raft-like polyborate ligands of formula $[B_{10}O_{16}H_3]$. The charge and oxidation state of the metals and degree of protonation are often difficult to resolve in such structures, however bond valence sum calculations[10] clearly indicate a charge of V^{4+} for each vanadium centre. The six V=O distances of the asymmetric unit range between 1.607 and 1.618(4) Å and the 24 basal V–O distances from 1.945 to 1.973(4) Å. The pale-green colour is also supportive of the purely V^{IV} formulation and is in contrast with the previous findings of Haushalter and Zubieta of orange, red and dark-green mixed V^{IV}–V^{V} clusters.[7,8] All cluster hydrogens were located in difference Fourier maps and were found to be involved in short [B–OH···O] hydrogen bonds with O···O separations $\leqslant$2.8 Å. In addition, the formulation of the organic counterions was facilitated by the clear observation of four [N–H···N] hydrogen-bond contacts per asymmetric unit of less than 3.0 Å. This means that both fully protonated and partially protonated ethylenediamines must be present, although there is statistical disorder of the protons on each side of the H-bond double wells.

The toroidal arrangement of square-pyramidal vanadyl groups has each neighboring V atom in an edge-sharing arrangement. All V–V internuclear separations are essentially equivalent and between 3.029 and 3.059(2) Å, indicating there is no significant pairing of V centres to form individual V–V bonds, but rather the contacts are consistent with some weak delocalised metal–metal bonding character, through use of d(*xy*) orbitals. In the crystal structure of **1** all polymer chains run parallel to the *b*-axis; studies are being undertaken to investigate the magnetic behaviour of the polymer.

In addition to the discovery of novel magnetic properties, our original goal was to make new classes of microporous materials. The use of cluster subunits is very attractive in this regard since their large size means that even their close packing must allow for significantly large cavity formation. A number of open-framework molybdenum phosphates with cluster subunits have been reported[11,12] and recently an organically templated Fe-PO was recently synthesised by Lii in which large channels are found since Fe_4 cluster subunits are involved.[13]

Formation of the 1-D polymer **1** is also suggestive that useful materials either for magnetic or porous properties might be formed by connecting metal polyborate clusters together *via* suitable cross linking agents. For this purpose however, a synthetic preparation of the structural building block is necessary. Through modification of the flux conditions, we have now isolated a second compound **2**, which contains the cluster building block from **1.** Thus reaction of V_2O_5 : en : H_3BO_3 in the ratio 1 : 2 : 8 at 180 °C for 3 days affords **2** as pale-green bar-shaped crystals in virtually quantitative yield based on V. From these conditions it is essentially phase-pure based on optical examination and powder X-ray diffraction, for which

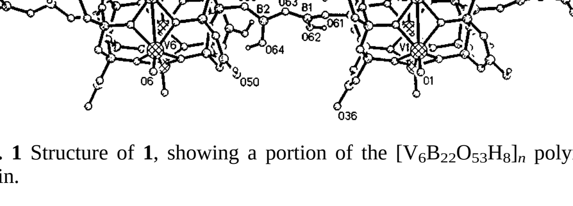

Fig. 1 Structure of **1**, showing a portion of the $[V_6B_{22}O_{53}H_8]_n$ polymer chain.

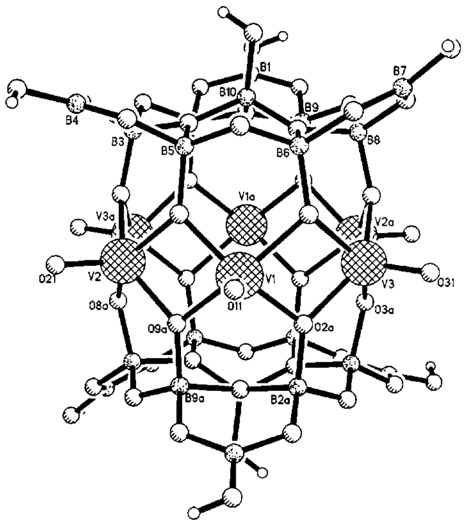

Fig. 2 Side view of the $[V_6B_{20}O_{50}H_8]$ cluster anion of **2**.

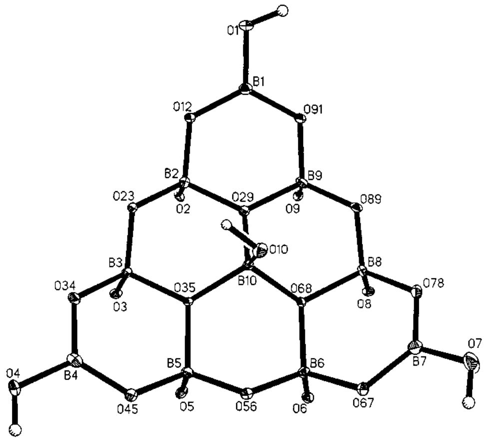

Fig. 3 Raft-like $[B_{10}O_{16}H_4]$ ligand from **2**.

there are 3 different characteristic *d*-spacings of 11.6 (010), 10.6 (001) and 9.8 Å (100)/(101) with an approximate 2 : 1 : 1 intensity ratio.

Single crystal X-ray structure determination† shows **2** to be $[H_2en]_4[V_6B_{20}O_{50}H_8]\cdot 5H_2O$. The structure of the $[V_6B_{20}O_{50}H_8]$ cluster anion of **2** is illustrated in Fig. 2 and its condensed raft-like B_{10} polyborate ligand is shown in Fig. 3. In this case the central boron is terminated by a hydroxy group, rather than being connected to a diborate bridge as in **1**. Boric acid was also used to synthesise the interesting copper polyborate cluster $[Cu_4O\{B_{20}O_{32}(OH)_8\}]^{6-}$ from solution.[14] Although this also has a B_{20} formulation, in this compound the polyborate moiety has an open ring-like structure about a central Cu_4O core.

The crystal structure of **2** is well-ordered and all H-atoms were located in difference Fourier maps. Once more the bond valence sums give V^{4+} for all centres [V=O = 1.605–1.627(2) Å, V–O = 1.932–1.980(2) Å]. The temperature dependent magnetization was measured in a constant applied field of 1 T (MPMS-5S Quantum Design SQUID magnetometer) and indicates that the compound is paramagnetic down to 1.8 K. The calculated moment is 4.03 μ_B per formula unit. This is in contrast to the layer compound $[H_2en][V_2O_5]$ which shows anti-ferromagnetic coupling between adjacent edge-sharing square pyramidal V^{IV} centres at low temperature.[15] Modelling of the magnetic behaviour is being undertaken, but implies only partial pairing of the six electrons from the d^1 metal centres. We postulate that two electrons are paired in the all-bonding (in-phase) combination of vanadium d(*xy*) orbitals and that the others singly occupy the partially bonding and anti-bonding combinations to give rise to four unpaired electrons and $S = 2$ ground state for the cluster, which may explain the observed magnetic moment. EPR studies will be undertaken to confirm this hypothesis.

Whereas the polymer **1** is practically insoluble in all solvents, (except 1.0 M NaOH which destroys it), the salt **2** is sparingly soluble in hot dmf–water and affords a stable pale-green solution. In this sense it is similar to the large open polyanionic Mo_{154} molybdates and related aggregates.[16] We are now exploring the use of a facile dissolution–precipitation method for synthesis of further hybrid materials from **2**. For example, addition of Ca^{2+} ions to a saturated solution of **2** results in ready precipitation of the calcium salt of the vanadyl cluster as a fine powder.

The advantage of this two-stage synthetic approach is that the complex polyborate cluster can be formed under quite different conditions than are used for its subsequent cross-linking, affording a reasonable degree of design flexibilty. In summary, use of a boric acid flux method can give high yields of phase-pure vanadium borate materials, including both inorganic polymers and discrete cluster compounds. Synthesis of other boron-rich transition-metal phases from the boric acid melt and their potential as synthetic intermediates for formation of microporous materials is under investigation.

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Notes and references

† *Crystal data* for **1**: $C_{12}H_{74}B_{22}N_{12}O_{58}V_6$, monoclinic, *C*2/*c*, $T = 218$ K, $a = 22.602(3)$, $b = 14.181(2)$, $c = 40.225(5)$ Å, $\beta = 96.22(2)°$, $V = 12{,}816(3)$ Å^3, $Z = 8$, $D_c = 1.93$ Mg m^{-3}, μ(Mo-Kα) = 0.98 mm^{-1}, $R = 6.20\%$, $wR = 6.95\%$ for 9199 unique observed data to $2\Theta_{max} = 53.5°$. For **2**: $C_8H_{65}B_{20}N_8O_{58.5}V_6$, triclinic, *P*1, $T = 218$ K, $a = 11.426(2)$, $b = 11.919(2)$, $c = 12.030(2)$ Å, $\alpha = 86.00(2)$, $\beta = 62.39(2)$, $\gamma = 77.09(2)°$, $V = 1413.2(4)$ Å^3, $Z = 1$, $D_c = 2.03$ Mg m^{-3}, μ(Mo-Kα) = 1.10 mm^{-1}, $R = 3.96\%$, $wR = 4.29\%$ for 5095 unique observed data to $2\Theta_{max} = 55.0°$. CCDC 182/990.

1 P. Feng, X. Bu and G. D. Stucky, *Nature*, 1997, **388**, 735.
2 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 46.
3 J. Wang, S. Feng and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1989, 265.
4 J. Yu, R. Xu, Q. Kan, Y. Xu and B. Xu, *J. Mater. Chem.*, 1993, **3**, 77.
5 S. Sevov, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2630.
6 C. J. Warren, R. C. Haushalter, D. J. Rose and J. Zubieta, *Chem. Mater.*, 1997, **9**, 2694.
7 J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1008.
8 (*a*) C. J. Warren, D. J. Rose, R. C. Haushalter and J. Zubieta, *Inorg. Chem.*, 1998, **37**, 1140; (*b*) T. Yamase, M. Suzuki and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1997, 2463.
9 M. Wu, H. H-Y. Sung, X. Zhang and I. D. Williams, *J. Solid State Chem.*, submitted.
10 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
11 R. C. Haushalter, K. G. Strohmaier and F. W. Lai, *Science*, 1989, **246**, 1289.
12 R. C. Haushalter and L. A. Mundi, *Chem. Mater.*, 1992, **4**, 31.
13 K-H. Lii and Y-F. Huang, *Chem. Commun.*, 1997, 839.
14 G. Heller and J. Pickardt, *Z. Naturforsch., Teil B*, 1985, **40**, 462.
15 Y. Zhang, C. J. O'Connor, A. Clearfield and R. C. Haushalter, *Chem. Mater.*, 1996, **8**, 595.
16 A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath and C. Menke, *Angew Chem., Int. Ed. Engl.*, 1995, **34**, 2122.

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