Synthesis and structures of two new 12-member ring crown-shaped oxovanadium borophosphates

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Two new oxovanadium borophosphates have been hydrothermally synthesized; they are structural analogues and are both constructed by $[(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]^{18-}$ 12-member ring clusters with NH_4^+ and K^+ cations encapsulated in the rings, respectively; an extended network of hydrogen bonds between anions, cations and crystal water molecules link the structures in three dimensions.

Template synthesis of novel compounds utilizing intrinsic host–guest relationships has opened up a new field for chemists to create microporous, host or cluster structures and has resulted in numerous novel metal phosphates with open frameworks.[1–5] The current interest in vanadium phosphates derives from their notable catalytic properties and structural diversity. Vanadium can bind to oxygen in a variety of valences to form tetrahedra, square pyramids, octahedra or large aggregates by condensation of polyhedra through shared oxygen atoms. Template controlled linking of these units has led to a large number of oxovanadium phosphates with open framework structures.[6] Notably the successful synthesis of $[NH_2Me_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)]\cdot4H_2O$ demonstrates that inorganic species can also mimic biologically relevant structures.[7] The three-dimensional frameworks $[HN(CH_2CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$ and $Cs_3[V_5O_9(PO_4)_2]\cdot xH_2O$ provide the largest cavities of open-framework structures known up to now.[8]

While metal phosphates have been expansively exploited, few reports on the synthesis of metal borophosphates have appeared. The introduction of boron into the framework has been proved to generate novel motifs and unique structures and several microporous aluminoborates have been prepared.[9] Recently the synthesis and structures of several new vanadium borate clusters were reported[10] stimulating chemists to incorporate boron into further inorganic systems. $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$ was reported as the first microporous metal phosphate.[11] The synthetic $M^IM^{II}(H_2O)_2(BP_2O_8)$ (M^I = Na, K; M^{II} = Mg, Fe, Co, Ni, Zn),[12] $M^{II}[BPO_5]$ (M^{II} = Ca, Sr), $Ba[BP_3O_{12}]$,[13] $Zn[BO_3PO_4]$,[14] $CoBP_3O_{14}$,[15] $Ln_7O_6(BO_3)(PO_4)_2$ (Ln = La, Nd, Gd, Dy)[16] and two mineral phases $Mg_3B_2P_2O_8$,[17] $MnBPO_4(OH)_6$[18] are also examples of borophosphates. Recently Zubieta *et al.* reported the synthesis and structures of VOBOPO-1, a three-dimensional oxovanadium borophosphate $[H_3NCH_2CH_2NH_3]_2(VO)_5(H_2O)\{O_3POB(O)_2OPO_3\}_2]\cdot1.5H_2O$[19] and VOBOPO-2, the first oxometalate borophosphate molecular cluster, $(H_3NCH_2CH_2NH_3)_2[Na(VO)_{10}\{HO_3POB(O)_2OPO_3H\}_5]\cdot22.5H_2O$.[20] More recently, a borophosphate anion $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot H_2O$ containing a single vanadium atom was reported.[21] Nevertheless metal borophosphates are still relatively undeveloped. Herein we report the synthesis and structures of two 12-member ring oxovanadium borophosphates, denoted VBP-J1 and VBP-J2 (J = Jilin University), templated by triethylenetetraamine.

Compounds VBP-J1 and VBP-J2 were hydrothermally synthesized using H_3BO_3 (99.5%), H_3PO_4 (85 wt%), NH_4VO_3 (99%), V_2O_5 (99%), KCl (99.5%) and triethylenetetraamine ($>95\%$) as the starting materials. Typical synthesis of VBP-J1 was performed as follows: 1.0 g H_3BO_3, 3.4 g H_3PO_4 and 1.9 g NH_4VO_3 were first dispersed into 20 ml water under vigorous stirring. Then 1.6 g of triethylenetetraamine were added. The final mixture was sealed in a 40 ml Teflon-lined stainless steel autoclave and heated at 180 °C for two days under autogenous pressure. In the synthesis of VBP-J2, NH_4VO_3 was replaced by 0.75 g V_2O_5 and 2 g KCl. The blue rhombic crystals obtained in both cases were filtered off, washed with water and dried at room temperature. The products were characterized by powder X-ray diffraction, IR, TG, chemical analysis (elemental ratio 2V : 2P : B) and single crystal determinations. Single crystals of VBP-JI (0.15 × 0.10 × 0.05 mm) and VBP-J2 (0.18 × 0.15 × 0.06 mm) were selected for structure analysis.‡

VBP-J1 and VBP-J2 are both constructed by 12-member ring $[(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]^{18-}$ clusters which are charge compensated by protonated triethylenetetraamine. An extended network of hydrogen bonds between anions, cations and crystal water molecules link the structures in three dimensions.

The asymmetric unit of VBP-J1 and VBP-J2 both contain six vanadium atoms, six phosphorus atoms and three boron atoms (Fig. 1). The vanadium atoms are all coordinated by five oxygen atoms to form square pyramids with one short vanadyl (V=O) bond [1.593(5)–1.615(5) Å]. The neighboring two vanadium atoms form an edge-sharing binuclear unit, which shows an *anti*-configuration of the vanadyl groups with respect to the $\{V_2O_2\}$ bridging group. Each binuclear unit is linked to four PO_4 groups by four oxygen atoms. Bond valence calculations give a bond valence for vanadium atoms of 4.[22]

The six phosphorus atoms are each coordinated by four oxygen atoms. The P–O distances range from 1.486(6) to 1.576(6) Å and the O–P–O angles lie between 106.4(3) and 113.0(3)°. In each PO_4 tetrahedron, two oxygen atoms are shared with the VO_5 square pyramid and one oxygen atom is shared with the BO_4 tetrahedron. The remaining oxygen atom is unshared and pendant. Each of the boron atoms is coordinated by four oxygen atoms with B–O distances in the range 1.430(9)–1.505(9) Å. The BO_4 group shares two oxygen atoms with the neighboring two PO_4 tetrahedra and forms a dense $\{O_3POB(O)_2OPO_3\}^{7-}$ borophosphate unit. Similar $\{O_3POB(O)_2OPO_3\}^{7-}$ trimers have been found in VOBOPO-1, VOBPO-2 and $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot H_2O$.[19–21] The $\{BO_4\}$ group contributes a μ_3-bridging oxygen to each of two neighboring binuclear $\{V_2O_{10}\}$ moieties. In this fashion each $\{O_3POB(O)_2OPO_3\}^{7-}$ exhibits three-point attachment to each of two binuclear $\{V_2O_5\}$ sites. The linking of six $\{V_2O_{10}\}$ moieties and six borophosphate ligands produces the 12-member ring structure with NH_4^+ or K^+ cations encapsulated in the rings (Fig. 2). In VBP-J1, the NH_4^+ cation is linked to the six *endo* oxygen atoms of the vanadyl by hydrogen bonds. In VBP-J2, the K^+ cation is six-coordinated by the six *endo* oxygen atoms of the vanadyl groups.

The ring diameters are 5.856(O8A–O8B) × 5.411(O35A–O35B) × 5.560(O22A–O22B) Å and 5.415(O24–O24A) × 5.415(O10–O10A) × 5.235(O36–O36A) Å for VBP-J1 and VBP-J2, respectively. Differences may be accounted for by the difference of the ion diameter between NH_4^+ (1.66 Å) and K^+ (1.44 Å).

In conclusion, two new oxovanadium borophosphates have been hydrothermally synthesized. They are structural analogues and have a similar motif to VOBOPO-1 and VOBOPO-2.[19,20]

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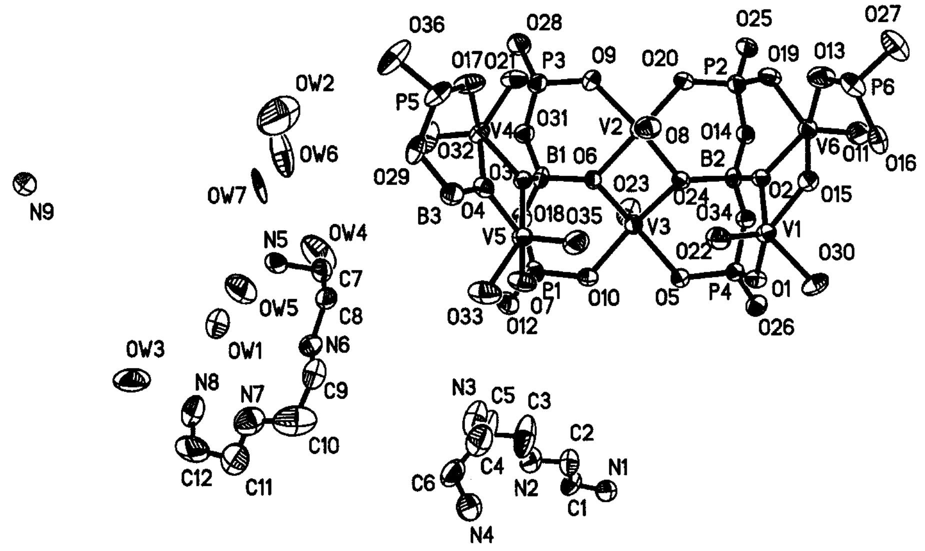

Fig. 1 The asymmetric unit of VBP-J1.

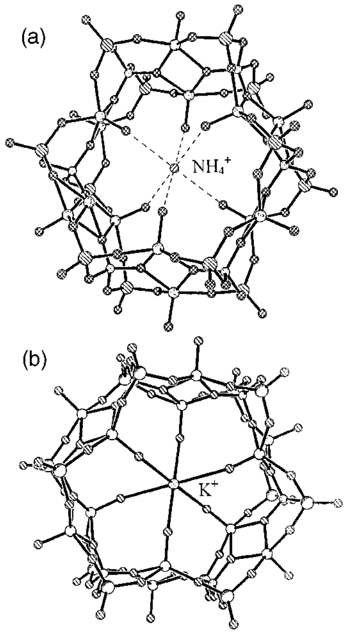

Fig. 2 The 12-member ring clusters of (a) VBP-J1 with NH_4^+ encapsulated in the center and (b) VBP-J2 with K^+ encapsulated in the center.

This successful synthesis leads to the possibility to synthesize larger rings using larger cations than NH_4^+ and K^+. Furthermore the various vanadium oxygen polyhedra with numerous linkage forms of the vanadium oxygen polyhedra, boron oxygen polyhedra and PO_4 tetrahedra are expected to lead to a variety of oxovanadium borophosphates.

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Notes and references

‡ *Crystal data*: VBP-J1: $C_{24}H_{120}B_6N_{17}O_{86}P_{12}V_{12}$, M = 3071.15, orthorhombic, *Pbca*, a = 21.454(11), b = 16.315(6), c = 29.651(12) Å, V = 10378(8) Å^3, Z = 4, D_c = 1.966 g cm^{-3}, T = 293(2) K, λ = 0.7103 Å, μ = 1.343 mm^{-1}; final R_1 = 0.0586, R_w = 0.1708.

VBP-J2: $C_{28}H_{128}B_6KN_{20}O_{84}P_{12}V_{12}$, M = 3076.38, orthorhombic, *Pbca*, a = 21.537(2), b = 16.2667(13), c = 29.717(4) Å, V = 10410.8(18) Å^3, Z = 4, D_c = 2.027 g cm^{-3}, T = 293(2) K, λ = 0.7103 Å, μ = 1.381 mm^{-1}; final R_1 = 0.0576, R_w = 0.1540.

CCDC 182/1429. See http://www.rsc.org/suppdata/cc/1999/2219/ for crystallographic files in .cif format.

1 J. Yu, K. Sugiyama, K. Hiraga, N. Togaashi, O. Terasaki, Y. Tanaka, S. Nakata, S. Qiu and R. Xu, *Chem. Mater.*, 1998, **10**, 3636 and references therein.
2 J. Yu, K. Sugiyama, S. Zheng, S. Qiu, J. Chen, R. Xu, Y. Sakamoto, O. Terasaki, K. Hiraga, M. Light, M. B. Hursthouse and J. M. Thomas, *Chem. Mater.*, 1998, **10**, 1208 and references therein.
3 M. Cchindller, W. Joswig and W. H. Baur, *J. Solid State Chem.*, 1997, **134**, 286 and references therein.
4 K. H. Lii, Y. F. Huang, V. Zima, C. Y. Huang, H. M. Lin, Y. C. Jiang, F. L. Liao and S. L. Wang, *Chem. Mater.*, 1998, **10**, 2609 and references therein.
5 H. H. Y. Sung, J. Yu and I. D. Williams, *J. Solid State Chem.*, 1998, **140**, 46 and references therein.
6 Y. Lu, R. C. Haushalter and J. Zubieta, *Inorg. Chim. Acta*, 1998, **268**, 257 and references therein.
7 V. Soghmonian, Q. Chen, R. C. Haushalter, J. Zubieta and C. J. O'Connor, *Science*, 1993, **259**, 1569.
8 M. Isaque Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta and J. L. Dye, *Chem. Mater.*, 1996, **8**, 43.
9 J. Yu, R. Xu, Q. Kan, Y. Xu and B. Xu, *J. Mater. Chem.*, 1993, **3**, 77 and references therein.
10 C. J. Warren, R. C. Haushalter, D. J. Rose and J. Zubieta, *Inorg. Chim. Acta*, 1998, **282**, 123 and references therein, J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1008; T. Yamase, M. Suzuki and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1997, 2463; C. J. Warren, D. J. Rose, R. C. Haushalter and J. Zubieta, *Inorg. Chem.*, 1998, **37**, 1140.
11 S. C. Sevov, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2630.
12 R. Kniep, H. G. Will, I. Boy and C. Rohr, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1013.
13 R. Kniep, G. Gozel, B. Eisenman, C. Rohr, M. Asbrand and M. Kizilyalli, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 749.
14 K. Bluhm and C. H. Park, *Z. Naturforsch, Teil B*, 1997, **52**, 102.
15 R. P. Bontchev and S. C. Sovov, *Inorg. Chem.*, 1996, **35**, 6910.
16 Y. Shi, J. Liang, H. Zhang, W. Zhuang and G. Rao, *J. Solid State Chem.*, 1997, **129**, 45.
17 P. F. S. Grysta, G. H. Swihart, R. Dimitrievich and M. B. Hossain, *Am. Mineral*, 1991, **76**, 1400.
18 P. B. Moore and S. Ghose, *Am. Mineral*, 1971, **56**, 1527.
19 C. J. Warren, R. C. Haushalter, D. J. Rose and J. Zubieta, *Chem. Mater.*, 1997, **9**, 2649.
20 C. J. Warren, R. C. Haushalter, D. J. Rose and J. Zubieta, *Inorg. Chem. Commun.*, 1998, **1**, 4.
21 R. P. Bontchev, J. Do and A. J. Jacobson, *Inorg. Chem.*, 1999, **38**, 2231.
22 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

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