2550 *Chem. Mater.* **2000,** *12,* 2550−2556

Synthesis and Structure of 12-Member Ring Crown-Shaped Oxovanadium Borophosphate Polyanions: $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[M(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot nH_2O$ ($M = NH_4^+, K^+$)

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Received September 21, 1999. Revised Manuscript Received June 22, 2000

Using multiethylenemultiamine to direct the crystallization of inorganic frameworks through multipoint hydrogen bonds, two new oxovanadium borophosphates, denoted VBP-J1 and VBP-J2, have been synthesized by hydrothermal methods as well as under reflux conditions. Powder X-ray diffraction patterns indicate that VBP-J1 and VBP-J2 are structural analogues. Structure determinations show that both VBP-J1, $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[NH_4(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 14H_2O$ and VBP-J2, $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[K(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 16H_2O$ crystallize in the orthorhombic space group *Pbca* with crystal data: $a = 21.454(11)$ Å, $b = 16.315(6)$ Å, $c = 29.651(12)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10378(8)$ Å^3, $Z = 4$ for VBP-J1 and $a = 21.537(2)$ Å, $b = 16.2667(13)$ Å, $c = 29.717(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10410.8(18)$ Å^3, $Z = 4$ for VBP-J2. VBP-J1 and VBP-J2 are constructed by edge-sharing $\{V_2O_{10}\}$ binuclear unit and $\{BP_2O_{10}\}$ trimer to form interesting 12-member ring crown-shaped clusters with NH_4^+ and K^+ cations encapsulated in the clusters. The ring diameters are 5.873 × 5.412 × 5.561 Å for VBP-J1 and 5.758 × 5.421 × 5.236 Å for VBP-J2. An extended network of multiple hydrogen bonds among anions, cations, and water molecules links the structure in three dimensions.

The template synthesis of novel compounds utilizing the intrinsic host−guest relationships opened up a new field for chemists to prepare new and structurally complex organic−inorganic composite materials[1] and resulted in numerous novel metal phosphates with open frameworks.[2−6] Contemporary interest in the chemistry of oxovanadium phosphates derives from their notable catalytic properties[7] and structural diversity.[8] Vanadium and oxygen in different valence states can form tetrahedral, square pyramidal, and octahedral coordination and aggregate 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 frameworks.[9−15] Notably the successful synthesis of $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7\cdot 4H_2O$ containing chiral double helices consisting of interpenetrating spirals confirms that inorganic species can also mimic biologically relevant structures.[16] The three-dimensional frameworks of $[HN(CH_2CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$ and $Cs_3[V_5O_9(PO_4)_2]\cdot xH_2O$ provide the largest cavities and the lowest framework densities known up to now.[17]

The introduction of boron into the framework has shown to generate novel motifs and unique structures. Several microporous aluminoborates have been prepared.[18,19] Recently the synthesis and structures of new oxovanadium borates clusters were reported.[20,21] These

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10.1021/cm990597l CCC: $19.00

stimulated chemists to incorporate boron into other inorganic systems. While metal phosphates have been expansively exploited, reports on the synthesis of metal borophosphates are limited in number. Borophosphates are intermediate compounds containing complex anionic structures built of BO_4, BO_3, and PO_4 groups and there is a formal relation to the large groups of aluminophosphates. Although systematic investigations of borophosphates started only six years ago, the chemistry of borophosphates extends from isolated species, oligomers, rings, and chains to layers and frameworks.[22] $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$ and $M_2[BP_2O_7(OH)]$ (M = Na, Na/Ag) have two-dimensional structures.[23,24] Up to now, $M[B_2P_2O_8(OH)]$ (M = Rb, Cs) was reported as the only three-dimensional borophosphate.[25] The synthetic $M^{II}[BPO_5]$ (M = Ca, Sr), $Ba_3[BP_3O_{12}]$, $Na_5[B_2P_3O_{13}]$, $Pb_3[BP_3O_{12}]$, $M^IM^{II}(H_2O)_2(BP_2O_8)$ (M^I = Na, K; M^{II} = Mg, Fe, Co, Ni, Zn), $Zn_3[BO_3PO_4]$, $CoBP_3O_{14}$, $Ln_7O_6(BO_3)(PO_4)_2$ (Ln = La, Nd, Gd, Dy), and two mineral phases $Mg_3B_2P_2O_8$, $Mn_3BPO_4(OH)_6$ are also examples of borophosphates.[26−34] Nonetheless the metal borophosphates are so far underexplored.

Recently three new oxovanadium borophosphates have been obtained by hydrothermal reactions, the three-dimensional oxovanadium borophosphate $[H_3NCH_2CH_2NH_3]_2[(VO)_5(H_2O)\{O_3POB(O_2)OPO_3\}_2]\cdot 1.5H_2O$ (VOBOPO-1), the first oxometalate borophosphate molecular cluster, $(H_3NCH_2CH_2NH_3)_2[Na(VO)_{10}\{HO_3POB(O)_2OPO_3H\}_5]\cdot 22.5H_2O$ (VOBOPO-2) and $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot H_2O$.[35−37] Each of these compounds contains BP_2O_{10} trimers. In this work, the syntheses and structures of organic−inorganic self-organized oxovanadium borophosphates VBP-J1 (J = Jilin University) $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[NH_4(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 14H_2O$ and VBP-J2, $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[K(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 16H_2O$ are reported. Structure determinations show that these compounds are composed of crown-shaped clusters $[V_{12}B_6P_{12}O_{72}]^{18-}$ with NH_4^+ or K^+ cations encapsulated in the rings. The organic amine serves as template, pH controller, and reductant as well.

Experimental Section

Vanadium oxide (V_2O_5, 99%), ammonium vanadate (NH_4VO_3, 99%), phosphoric acid (H_3PO_4, 85%), triethylenetetraamine (TETA, >95%), ammonium liquor ($NH_3\cdot H_2O$, 25%), boric acid (H_3BO_3, 99.5%), and potassium chloride (KCl, 99.5%) are used as the starting materials. All reagents are used without further purification. The title compounds can be prepared using hydrothermal synthesis as well as under reflux conditions.

Hydrothemal Synthesis. *VBP-J1,* $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[NH_4(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 14\ H_2O$. The typical synthesis of VBP-J1 using NH_4VO_3 as vanadium source was performed as followed: 1.0 g of H_3BO_3 and 1.9 g of NH_4VO_3 and 2.0 mL of H_3PO_4 were dispersed into 20 mL of water under vigorously stirring. Then the addition of 1.3−1.7 g of TETA was followed. The final mixture with molar composition of V_2O_5:B_2O_3:P_2O_5:$2NH_4^+$:2.2−2.8TETA:200H_2O was transferred into a 40-mL Teflon-lined autoclave and crystallized at 100−180 °C for 2 days. Blue polyhedral crystals were obtained after filtering and washing with water and dried at room temperature. The procedure using V_2O_5 as the vanadium source are similar to the above-mentioned, the difference is the addition of $NH_3\cdot H_2O$ followed by the addition of H_3PO_4.

VBP-J2, $[H_3NC_2H_4NH_2C_2H_4NH_2C_2H_4NH_3]_4H[K(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 16\ H_2O$. Synthesis of VBP-J2 were carried out using V_2O_5 as the vanadium source. A mixture of 0.75 g of V_2O_5, 1.0 g of H_3BO_3, 2.0 mL of H_3PO_4, 2.0 g of KCl, 1.3−1.7 g of TETA, and 20 mL of H_2O was sealed in a 40-mL Teflon-lined autoclave and crystallized at 100−180 °C for 2 days. Blue products were discovered by filtered, washed with water and dried at room temperature.

Synthesis under Reflux. The preparation of the precursor was similar to the hydrothermal synthesis with the same composition. The mixture was transferred into a 50-mL flask and refluxed at 100 °C for 4 h. Afterward, the flask was quenched into ambient temperature and laid statically at room temperature for 2 days. Blue crystals precipitated in the bottom.

Analysis. Vanadium, phosphorus, and boron contents were determined, after dissolution of the solids in concentrated hydrochloric acid, by Plasma-SPEC (1) ICP-AES analyzer with the result of 2V:2P:B.

Physical Measurements. X-ray powder diffraction patterns were performed on a Riguku D/max III with Ni-filtered Cu Kα radiation. The record speed was 8° $\min^{-1}$ over the range of 4−40° at room temperature. IR spectra were collected on a Nicolet Impact 410 in the range of 400−4000 cm^{-1} using the KBr disk method. Thermogravimetric data were recorded on Perkin-Elmer TGA-7 thermogravimetric analyzer. Samples were heated to 700° at 20°$\min^{-1}$ in air.

X-ray Crystallographic Study. The blue polyhedral crystals of VBP-J1 with approximate dimensions of 0.15 × 0.10 × 0.05 mm and VBP-J2 of 0.18 × 0.15 × 0.06 mm were selected and mounted on a Siemens SMART X-ray diffractometer with a CCD area detector. Data were collected using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. A hemisphere of data (1271 frames) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The data were integrated using the Siemens SAINT program[38] with intensities corrections for Lorentz factor, polarization, and air absorption. Additional crystallographic details are described in Table 1.

The structures were solved by direct methods and refined by full matrix least-squares techniques with the SHELXTL software package.[39] A total of 20 909 reflection intensities, of which 6902 were independent ($R_{int} = 0.0638$), were collected

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Table 1. Crystal Data and Structure Refinement for VBP-J1 and VBP-J2

identification code	VBP-J1	VBP-J2
empirical formula	$C_{24}H_{113}B_6N_{17}O_{82}P_{12}V_{12}$	$C_{24}H_{121}B_6KN_{16}O_{88}P_{12}V_{12}$
formula weight	3000.09	3129.25
temperature	293(2)K	293(2)K
wavelength	0.71073 Å	0.71073 Å
crystal system, space group	orthorhombic, *Pbca*	orthorhombic, *Pbca*
unit cell dimensions	$a = 21.454(11)$ Å, $\alpha = 90$ °	$a = 21.537(2)$ Å, $\alpha = 90$ °
	$b = 16.315(6)$ Å, $\beta = 90$ °	$b = 16.2667(13)$ Å, $\beta = 90$ °
	$c = 29.651(12)$ Å, $\gamma = 90$ °	$c = 29.717(4)$ Å, $\gamma = 90$ °
volume	10378(8) $Å^3$	10410.8(18) $Å^3$
Z, calculated density	4, 1.920 g cm^{-3}	4, 1.996 g cm^{-3}
absorption coefficient	1.338 mm^{-1}	1.381 cm^{-1}
F(000)	6072	6344
crystal size	0.15 × 0.10 × 0.05 mm	0.18 × 0.15 × 0.06 mm
θ range for data collection	1.67° to 23.23°	1.67° to 23.29°
limiting indices	$-23 \leq h \leq 23, -16 \leq k \leq 15, -32 \leq l \leq 6$	$-22 \leq h \leq 10, -15 \leq k \leq 18, -27 \leq l \leq 32$
reflections collected/unique	20909/6902 [*R*(int) = 0.0638]	20918/7345 [*R*(int) = 0.0945]
completeness to θ	92.9%	98.0%
absorption correction	empirical	empirical
max. and min. transmission	0.9333 and 0.8130	0.9205 and 0.7820
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	6902/0/718	7345/0/754
goodness-of-fit on F^2	0.973	1.053
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0660$, $wR2 = 0.1891$	$R1 = 0.0577$, $wR2 = 0.1577$
R indices (all data)	$R1 = 0.1095$, $wR2 = 0.2063$	$R1 = 0.0844$, $wR2 = 0.1765$
large diff. peak and hole	2.215 and −0.611 e A^{-3}	1.726 and −0.542 e A^{-3}

within the range $1.67° < \theta < 23.23°$ ($-23 \leq h \leq 23$, $-16 \leq k \leq 15$, $-32 \leq l \leq 6$) for VBP-J1. Of the total 20 918 reflections for VBP-J2 collected in the range of $1.67° < \theta < 23.29°$, 7345 were unique ($R_{int} = 0.0945$) ($-22 \leq h \leq 10$, $-15 \leq k \leq 18$, $-27 \leq l \leq 32$). The final cycle of refinement performed on F_0^2 afforded residuals $R = 0.0660$ and $R_w = 0.1891$ for VBP-J1 and $R = 0.0577$ and $R_w = 0.1577$ for VBP-J2. Hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Charge balancing requirement necessitated the full-pronated triethylenetetraamine and one additional proton per formula unit. The N6 of VBP-J1 and the N3, O6W, O7W, and O8W of VBP-J2 are disordered over two sites in approximately equal population. The final residual peak of VBP-J1 is 2.22 e $Å^{-3}$, which apart from V4 with the distance of 1.171 Å. The highest difference peak of VBP-J2 is 1.73 e $Å^{-3}$, which is close to V4 with the distance of 1.272 Å. Atomic positional parameters and isotropic temperature factors of VBP-J1 and VBP-J2 are listed in Tables 2 and 3, respectively. Selected bond lengths and angles of VBP-J2 are listed in Table 4.

Results and Discussions

Synthesis and Analysis. The well-crystallized products were obtained from the reaction of V_2O_5, H_3PO_4, H_3BO_3, NH_4^+/K^+, and TETA with the strictly controlled pH value in the range of 6−7. According to the literature, the V(IV) species that predominates in aqueous solution at low pH value is $VO(H_2O)_5^{2+}$. As the pH increases, hydrolysis and condensation lead to the soluble $VO(OH)(H_2O)_4^+$ and $(VO)_2(OH)_2(H_2O)_6^{2+}$. Olation is fast and the predominant species in the absence of coordinating anions is the stable dimer.[13] The amount of organoamine affects the formation of VBP-J1 and -J2 greatly. The role of organoamine appears to be adjustment of pH and maintenance of reducing reaction environment. These provide the vanadium in V(IV) state and the form of stable dimer. On the basis of powder X-ray diffraction patterns (Figures 1 and 2), compounds obtained are as a monophasic product with 75% yield (calculated with respect to the amount of vanadium in the starting solution) with pH value of ~6.4 under hydrothermal condition. Using diethylenetriamine as the template, two structural analogues of VBP-J1and VBP-J2, named VBP-J3 and VBP-J4, are obtained (Figure 2) (Note 2). No desirable products can be obtained with the changes of the organoamine such as ethylenediamine. This implies that multiamine favorites the formation of this ring-shaped structure. The title compounds can be synthesized over a wide range of 100−180 °C. XRD patterns (not shown here) show that the variation of the reaction temperature does not affect on the nature of the final solids but on the crystal size greatly. When crystallized at 100 °C, large crystals with the dimensions of 3 × 3 × 2 mm could be obtained. Since the synthesis can be performed at temperatures as low as 100 °C, the preparation was carried out under reflux conditions. The XRD results also indicate that the title compound was obtained but with small size (80 × 60 × 20 μm) and very low yield.

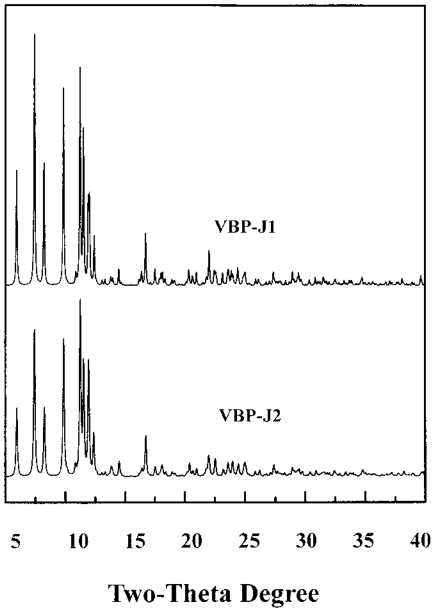

Figure 1. Simulated powder X-ray diffraction patterns of VBP-J1 and VBP-J2.

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(39) *SHELXL*, version 5.1; Siemens Industrial Automation, Inc.: Madison, WI, 1997.

Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for VBP-J1[a]

	x	y	z	U(eq)[a]		x	y	z	U(eq)[a]
V(1)	1620(1)	6404(1)	221(1)	26(1)	O(29)	−1764(3)	3257(4)	−1357(2)	39(2)
V(2)	249(1)	6936(1)	−987(1)	30(1)	O(30)	2244(3)	6098(4)	675(2)	37(2)
V(3)	1480(1)	6337(1)	−1373(1)	27(1)	O(31)	−161(3)	6206(4)	−2038(2)	32(2)
V(4)	−1032(1)	4834(1)	−1611(1)	38(1)	O(32)	−1155(4)	4532(5)	−2114(2)	57(2)
V(5)	149(1)	4021(1)	−1254(1)	31(1)	O(33)	265(3)	2829(5)	−1275(3)	58(2)
V(6)	976(1)	8058(1)	372(1)	28(1)	O(34)	2161(3)	7540(4)	−679(2)	26(2)
P(1)	1225(1)	4713(2)	−1904(1)	30(1)	O(35)	387(3)	4269(5)	−770(2)	51(2)
P(2)	604(1)	8694(2)	−594(1)	29(1)	O(36)	−2797(3)	3922(6)	−1422(3)	68(3)
P(3)	−707(1)	6663(2)	−1796(1)	30(1)	B(1)	247(5)	5654(8)	−1761(4)	30(3)
P(4)	2515(1)	6702(2)	−642(1)	26(1)	B(2)	1480(5)	7583(8)	−574(3)	25(3)
P(5)	−2181(1)	3981(2)	−1190(1)	39(1)	B(3)	−1122(6)	3147(8)	−1161(4)	33(3)
P(6)	195(1)	7889(2)	1254(1)	37(1)	N	0	5000	0	53(4)
O(1)	2366(3)	6342(4)	−181(2)	29(2)	N(1)	−1132(7)	−2361(9)	1975(4)	100(5)
O(2)	1358(3)	7391(4)	−107(2)	26(2)	N(2)	−1943(7)	−663(11)	1708(5)	128(6)
O(3)	−128(3)	5022(4)	−1550(2)	25(2)	N(3)	−354(6)	112(8)	1626(4)	80(4)
O(4)	−752(3)	3880(4)	−1259(2)	27(2)	N(4)	1145(5)	1149(7)	1880(3)	63(3)
O(5)	2255(3)	6137(4)	−1020(2)	32(2)	N(5)	1747(5)	1320(7)	4233(4)	72(3)
O(6)	584(3)	6133(4)	−1420(2)	25(2)	N(6)	1708(13)	1310(30)	5226(16)	100(16)
O(7)	916(3)	4026(4)	−1627(2)	42(2)	N(6′)	2060(20)	1510(20)	5146(8)	126(19)
O(8)	−67(3)	6478(4)	−563(2)	43(2)	N(7)	1604(4)	3034(6)	5357(3)	43(2)
O(9)	−430(3)	7179(5)	−1417(2)	39(2)	N(8)	803(4)	4059(5)	4718(3)	42(2)
O(10)	1647(3)	5215(4)	−1595(2)	39(2)	C(1)	−1748(8)	−2136(13)	1868(5)	93(5)
O(11)	1470(3)	8725(4)	545(2)	42(2)	C(2)	−1940(10)	−1310(15)	2058(7)	124(8)
O(12)	1567(3)	4367(5)	−2296(2)	44(2)	C(3)	−1401(9)	−510(20)	1501(6)	186(13)
O(13)	243(3)	8199(5)	764(2)	45(2)	C(4)	−974(8)	28(16)	1842(6)	156(10)
O(14)	1296(3)	8442(4)	−671(2)	27(2)	C(5)	88(7)	656(9)	1895(4)	75(4)
O(15)	1157(3)	7018(4)	678(2)	29(2)	C(6)	679(6)	720(9)	1634(4)	68(4)
O(16)	853(3)	7572(4)	1399(2)	37(2)	C(7)	1945(8)	637(9)	4497(6)	93(6)
O(17)	−1853(3)	4782(4)	−1309(2)	43(2)	C(8)	2200(10)	852(10)	4947(7)	111(8)
O(18)	700(3)	5290(4)	−2082(2)	29(2)	C(9)	2060(9)	1678(11)	5567(6)	91(5)
O(19)	451(3)	8610(4)	−91(2)	34(2)	C(10)	1654(6)	2388(8)	5714(4)	54(4)
O(20)	183(3)	8113(4)	−864(2)	37(2)	C(11)	1191(5)	3734(8)	5489(4)	48(3)
O(21)	−1159(3)	6029(4)	−1611(2)	40(2)	C(12)	1124(5)	4363(7)	5130(4)	49(3)
O(22)	1196(3)	5629(4)	103(2)	44(2)	O(1W)	660(4)	2225(5)	4810(3)	60(2)
O(23)	1673(3)	6935(5)	−1769(2)	46(2)	O(2W)	1475(18)	7226(13)	2356(6)	178(15)
O(24)	1154(3)	7008(4)	−882(2)	25(2)	O(3W)	2345(9)	2699(15)	1939(6)	101(8)
O(25)	520(3)	9566(4)	−759(2)	36(2)	O(4W)	2276(8)	5430(30)	2589(9)	290(30)
O(26)	3199(3)	6843(4)	−699(2)	35(2)	O(5W)	2166(9)	6212(12)	3515(7)	243(10)
O(27)	−6(4)	8539(5)	1574(2)	59(2)	O(6W)	2003(10)	9106(11)	1505(6)	255(12)
O(28)	−1034(3)	7217(4)	−2135(2)	43(2)	O(7W)	1050(9)	8851(15)	2139(6)	107(9)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The infrared spectra of VBP-J1 and -J2 are similar and complex. A large number of bands are observed in the region of 1300−400 cm^{-1}, which are expected to be the B—O, P—O, and V=O stretching vibrations and B—O and P—O bending modes. Additional strong absorption bands are in the range of 1300−3350 cm^{-1} as the result of N−H bending and stretching vibrations. The absorption peaks of VBP-J1 and -J2 in the range of 1300−1700 cm^{-1} is contributed to the characteristic absorption of triethylenetetraamine. The broad strong bands at 3500 cm^{-1} are assigned to O−H bending and stretching vibration.

The thermal decomposition of VBP-J1 and -J2 occur in three separate steps in the range of 30−700 °C (Figure 3). The first step is at 70−210 °C corresponding to the loss of crystal water molecules. The second steps (210−540 °C) and the third step (540−700 °C) are contributed to the loss of organic amine and the collapse of the framework. The total weight loss of VBP-J1 (∼28.2%) and VBP-J2 (∼26.9%) are close to the calculated results of VBP-J1 (calcd 28.8%) and VBP-J2 (calcd 28.4%). The as-synthesized products are thermally unstable and convert to amorphous phase when calcined at 150 °C for 3 h.

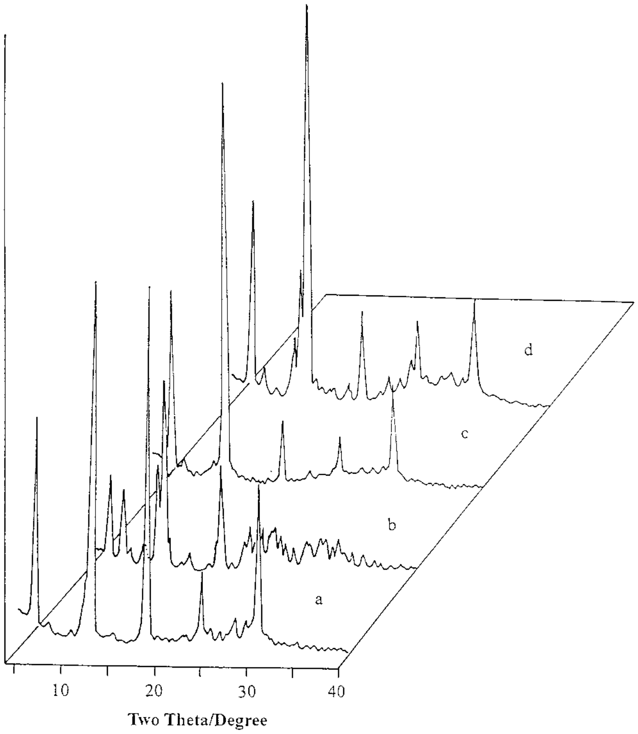

Figure 2. Powder X-ray diffraction patterns of (a) VBP-J1, (b) VBP-J2, (c) VBP-J3, and (d) VBP-J4.

Description of the Structure. The structures of VBP-J1 and VBP-J2 are both constructed by isolated 12-member ring $[(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]^{18-}$ clusters

Table 3. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for VBP-J2

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
V(1)	956(1)	6923(1)	4622(1)	25(1)	O(30)	910(2)	10937(3)	6617(2)	37(1)
V(2)	147(1)	10948(1)	6242(1)	27(1)	O(31)	−1175(2)	8969(3)	6623(2)	38(1)
V(3)	229(1)	8072(1)	5980(1)	25(1)	O(32)	−1155(3)	10495(4)	7119(2)	47(2)
V(4)	−1033(1)	10169(1)	6617(1)	31(1)	O(33)	−1840(2)	10217(4)	6304(2)	47(2)
V(5)	1461(1)	8623(1)	6381(1)	26(1)	O(34)	−750(2)	11114(3)	6257(2)	27(1)
V(6)	1583(1)	8590(1)	4782(1)	23(1)	O(35)	274(3)	12142(3)	6247(2)	46(2)
K	0	10000	5000	39(1)	O(36)	368(3)	10690(4)	5750(2)	43(2)
P(1)	2166(1)	8974(2)	3818(1)	39(1)	B(1)	233(4)	9334(5)	6763(3)	24(2)
P(2)	177(1)	7123(1)	3741(1)	34(1)	B(2)	1455(4)	7405(5)	5576(3)	22(2)
P(3)	−724(1)	8325(1)	6796(1)	28(1)	B(3)	−1110(4)	11848(6)	6166(3)	29(2)
P(4)	2485(1)	8273(1)	5643(1)	24(1)	N(1)	816(3)	949(4)	295(2)	37(2)
P(5)	570(1)	6298(1)	5586(1)	24(1)	N(2)	1630(3)	1956(4)	−357(2)	39(2)
P(6)	1213(1)	10262(1)	6906(1)	26(1)	N(3′)	1803(7)	3755(11)	−157(4)	37(3)
O(1)	2787(3)	8902(5)	3597(2)	68(2)	N(3)	2215(10)	3378(11)	−156(5)	57(5)
O(2)	1750(2)	8245(3)	3643(2)	37(1)	N(4)	1743(4)	3696(5)	771(3)	58(2)
O(3)	−42(3)	6498(4)	3402(2)	54(2)	N(5)	1128(4)	2584(5)	6977(3)	64(2)
O(4)	837(2)	7433(3)	3589(2)	34(1)	N(6)	1973(4)	4321(7)	6707(3)	78(3)
O(5)	229(2)	6768(4)	4217(2)	40(1)	N(7)	336(3)	5082(5)	6619(2)	45(2)
O(6)	2216(2)	8904(3)	4335(2)	36(1)	N(8)	−1165(3)	6139(5)	6872(2)	43(2)
O(7)	1136(2)	7960(3)	4316(2)	29(1)	C(1)	1144(4)	645(5)	−118(3)	48(2)
O(8)	1457(3)	6258(3)	4462(2)	37(1)	C(2)	1214(4)	1254(6)	−476(3)	42(2)
O(9)	2321(2)	8666(3)	5188(2)	29(1)	C(3)	1659(4)	2611(6)	−707(3)	50(2)
O(10)	1152(2)	9356(3)	4899(2)	39(1)	C(4)	2088(7)	3278(8)	−583(4)	92(4)
O(11)	1330(2)	7598(3)	5106(2)	24(1)	C(5)	2222(7)	4204(7)	79(5)	99(5)
O(12)	432(2)	6369(3)	5079(2)	34(1)	C(6)	1961(6)	4399(6)	508(4)	77(4)
O(13)	477(2)	5433(3)	5753(2)	34(1)	C(7)	1768(5)	2818(7)	6865(4)	63(3)
O(14)	3167(2)	8124(3)	5686(2)	32(1)	C(8)	1948(5)	3635(8)	7048(4)	72(3)
O(15)	2127(2)	7431(3)	5676(2)	23(1)	C(9)	1379(5)	4539(9)	6495(3)	75(4)
O(16)	1262(2)	6545(3)	5669(2)	24(1)	C(10)	950(5)	5005(9)	6830(4)	77(4)
O(17)	154(2)	6889(3)	5849(2)	32(1)	C(11)	−99(4)	5607(6)	6892(3)	49(2)
O(18)	1125(2)	7978(3)	5880(2)	24(1)	C(12)	−678(4)	5706(6)	6617(3)	50(2)
O(19)	2238(2)	8815(3)	6035(2)	31(1)	O(1W)	3470(3)	2214(3)	7696(2)	44(2)
O(20)	1643(3)	8007(3)	6781(2)	41(1)	O(2W)	−658(3)	7770(4)	4806(2)	51(2)
O(21)	569(2)	8843(3)	6424(2)	25(1)	O(3W)	2156(6)	6235(7)	6448(4)	133(4)
O(22)	−455(2)	7828(3)	6404(2)	36(1)	O(4W)	2367(6)	2818(13)	8068(4)	218(9)
O(23)	1637(2)	9742(3)	6611(2)	37(1)	O(5W)	4700(9)	2297(15)	7567(5)	274(11)
O(24)	−74(2)	8560(3)	5561(2)	38(1)	O(6W)	3059(11)	4160(12)	8552(5)	111(8)
O(25)	−1038(3)	7761(3)	7128(2)	39(1)	O(6W′)	2603(7)	4172(8)	8290(6)	74(5)
O(26)	−176(2)	8783(3)	7045(2)	29(1)	O(7W)	3805(9)	3867(13)	7886(5)	93(6)
O(27)	682(2)	9688(3)	7089(2)	27(1)	O(7W′)	4107(8)	3255(10)	7675(4)	72(5)
O(28)	1548(2)	10634(3)	7300(2)	38(1)	O(8W)	2771(10)	836(15)	7359(7)	96(8)
O(29)	−140(2)	9959(3)	6556(2)	25(1)	O(8W′)	2646(11)	130(20)	7523(10)	194(18)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

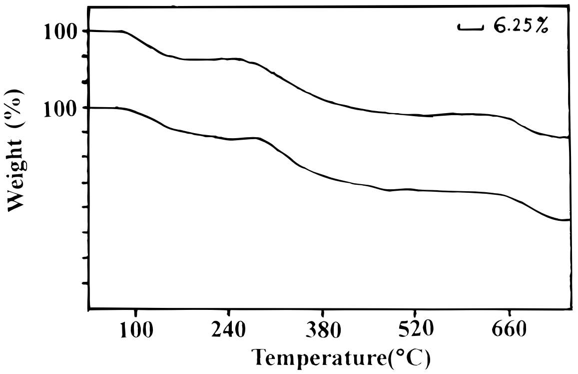

Figure 3. The TGA curves of VBP-J1 (a) and VBP-J2 (b).

which are charge compensated by pronated triethylenetetraamine. An extended network of hydrogen bonds among anions, cations, and crystal water molecules links the structure in three dimensions.

Both of the asymmetric units of VBP-J1 and VBP-J2 contain six vanadium atoms, six phosphorus atoms, and three boron atoms (Figure 4). The vanadium atoms are all coordinated by five oxygen atoms to form square pyramids with one short vanadyl (V═O) bond (V−O distance in the range of 1.583(7)−1.614(5) Å). Every two neighboring vanadium atoms form edge-sharing binuclear unit, which adopt an anti configuration of the vanadyl groups with respect to the $\{V_2O_2\}$-bridging group. Each binuclear unit is linked to the four PO_4 groups by four oxygen atoms. Bond valence calculations give a bond valence sum for vanadium atoms of 4.[40]

The six phosphorus atoms are each coordinated by four oxygen atoms. The P−O distance range from 1.485(7) Å to 1.575(6) Å and the O−P−O angles lie between 106.2(3)° and 112.8(4)°. In each PO_4 tetrahedron, two oxygen atoms are shared with the VO_5 square pyramid and one oxygen atom shared with the BO_4 tetrahedron. The remaining oxygen atom is unshared and pendant. The boron atoms are coordinated by four oxygen atoms with the B−O distances in the range of 1.434(9)−1.511(9) Å. The BO_4 group shares two oxygen atoms with the neighboring two PO_4 tetrahedral and forms $\{BP_2O_{10}\}^{7-}$ dense boronphosphate. Similar $\{BP_2O_{10}\}^{7-}$ trimers have been found in VOBOPO-1, VOBPO-2, and $[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)H_2O$.[35−37] Of the known borophosphates, the anionic $[B_xP_yO_z]^{n-}$ building units exist in various forms of isolated BO_4, PO_4, chains of corner-sharing BO_4 and PO_4 and tetrahedra together with BO_3 units, $[BPO_7]^{6-}$ isolated dimers, $[BP_2O_8]^{3-}$ trimers linked together to form infinite helices. In the

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(40) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of VBP-J2[a]

V(1)−O(8)	1.599(5)	P(2)−O(35)#1	1.541(6)	V(1)−O(7)	1.955(5)	P(2)−O(5)	1.532(5)
V(1)−O(12)	1.984(5)	P(3)−O(25)	1.508(5)	V(1)−O(11)	1.983(5)	P(2)−O(4)	1.575(6)
V(1)−O(5)	1.990(5)	P(3)−O(22)	1.531(5)	V(2)−O(36)	1.594(5)	P(3)−O(31)	1.518(6)
V(2)−O(34)	1.952(5)	P(4)−O(14)	1.495(5)	V(2)−O(29)	1.958(5)	P(3)−O(26)	1.580(5)
V(2)−O(35)	1.962(6)	P(4)−O(19)	1.556(5)	V(2)−O(30)	1.985(5)	P(4)−O(9)	1.538(5)
V(3)−O(24)	1.614(5)	P(5)−O(13)	1.505(5)	V(3)−O(18)	1.959(5)	P(4)−O(15)	1.574(5)
V(3)−O(21)	1.963(5)	P(5)−O(12)	1.539(5)	V(3)−O(17)	1.971(5)	P(5)−O(17)	1.528(5)
V(3)−O(22)	1.979(5)	P(6)−O(28)	1.503(5)	V(4)−O(32)	1.604(6)	P(5)−O(16)	1.565(5)
V(4)−O(29)	1.963(5)	P(6)−O(30)	1.540(5)	V(4)−O(34)	1.969(5)	P(6)−O(23)	1.521(5)
V(4)−O(31)	1.976(6)	K(1)−O(36)	2.618(5)	V(4)−O(33)	1.973(5)	P(6)−O(27)	1.574(5)
V(5)−O(20)	1.603(5)	K(1)−O(24)	2.879(5)	V(5)−O(21)	1.958(5)	K(1)−O(10)	2.711(5)
V(5)−O(18)	1.958(5)	B(1)−O(26)	1.511(9)	V(5)−O(23)	1.982(5)	B(1)−O(21)	1.474(9)
V(5)−O(19)	1.988(5)	B(1)−O(27)	1.485(9)	V(6)−O(10)	1.591(5)	B(1)−O(29)	1.434(9)
V(6)−O(11)	1.956(5)	B(2)−O(15)	1.478(9)	V(6)−O(6)	1.973(5)	B(2)−O(11)	1.457(9)
V(6)−O(7)	1.973(5)	B(2)−O(18)	1.480(9)	V(6)−O(9)	1.998(5)	B(2)−O(16)	1.485(9)
P(1)−O(1)	1.493(6)	B(3)−O(7)#1	1.469(9)	P(1)−O(33)#1	1.534(6)	B(3)−O(34)	1.449(10)
P(1)−O(6)	1.544(5)	B(3)−O(2)#1	1.498(10)	P(1)−O(2)	1.575(6)	B(3)−O(4)#1	1.497(10)
P(2)−O(3)	1.506(6)						

O(8)−V(1)−O(7)	108.1(2)	O(1)−P(1)−O(33)#1	112.0(4)	O(8)−V(1)−O(12)	106.3(3)	O(7)−V(6)−O(9)	147.4(2)
O(7)−V(1)−O(12)	145.4(2)	O(33)#1−P(1)−O(6)	109.2(3)	O(8)−V(1)−O(11)	108.3(2)	O(1)−P(1)−O(6)	111.6(3)
O(7)−V(1)−O(11)	77.1(2)	O(33)#1−P(1)−O(2)	108.0(3)	O(12)−V(1)−O(11)	89.2(2)	O(1)−P(1)−O(2)	107.8(4)
O(8)−V(1)−O(5)	105.4(3)	O(3)−P(2)−O(5)	112.7(3)	O(7)−V(1)−O(5)	89.2(2)	O(6)−P(1)−O(2)	108.2(3)
O(12)−V(1)−O(5)	84.9(2)	O(5)−P(2)−O(35)#1	108.4(3)	O(11)−V(1)−O(5)	146.1(2)	O(3)−P(2)−O(35)#1	110.1(4)
O(36)−V(2)−O(34)	110.6(3)	O(5)−P(2)−O(4)	108.6(3)	O(36)−V(2)−O(29)	108.4(3)	O(3)−P(2)−O(4)	107.9(3)
O(34)−V(2)−O(29)	77.9(2)	O(25)−P(3)−O(31)	110.7(3)	O(36)−V(2)−O(35)	103.0(3)	O(35)#1−P(2)−O(4)	109.1(3)
O(34)−V(2)−O(35)	90.1(2)	O(31)−P(3)−O(22)	110.5(3)	O(29)−V(2)−O(35)	148.6(2)	O(25)−P(3)−O(22)	110.2(3)
O(36)−V(2)−O(30)	105.4(3)	O(31)−P(3)−O(26)	108.2(3)	O(34)−V(2)−O(30)	143.9(2)	O(25)−P(3)−O(26)	108.4(3)
O(29)−V(2)−O(30)	89.2(2)	O(14)−P(4)−O(9)	111.6(3)	O(35)−V(2)−O(30)	83.7(2)	O(22)−P(3)−O(26)	108.8(3)
O(24)−V(3)−O(18)	108.7(2)	O(9)−P(4)−O(19)	110.2(3)	O(24)−V(3)−O(21)	110.8(2)	O(14)−P(4)−O(19)	111.3(3)
O(18)−V(3)−O(21)	77.51(19)	O(9)−P(4)−O(15)	107.8(3)	O(24)−V(3)−O(17)	107.2(3)	O(14)−P(4)−O(15)	109.6(3)
O(18)−V(3)−O(17)	88.5(2)	O(13)−P(5)−O(17)	110.0(3)	O(21)−V(3)−O(17)	141.9(2)	O(19)−P(4)−O(15)	106.2(3)
O(24)−V(3)−O(22)	106.8(3)	O(17)−P(5)−O(12)	109.9(3)	O(18)−V(3)−O(22)	144.5(2)	O(13)−P(5)−O(12)	111.6(3)
O(21)−V(3)−O(22)	88.7(2)	O(17)−P(5)−O(16)	108.4(3)	O(17)−V(3)−O(22)	82.5(2)	O(13)−P(5)−O(16)	108.4(3)
O(32)−V(4)−O(29)	107.7(3)	O(28)−P(6)−O(23)	112.6(3)	O(32)−V(4)−O(34)	107.3(3)	O(12)−P(5)−O(16)	108.5(3)
O(29)−V(4)−O(34)	77.4(2)	O(23)−P(6)−O(30)	109.3(3)	O(32)−V(4)−O(31)	107.0(3)	O(28)−P(6)−O(30)	110.5(3)
O(29)−V(4)−O(31)	88.9(2)	O(23)−P(6)−O(27)	107.8(3)	O(34)−V(4)−O(31)	145.5(2)	O(28)−P(6)−O(27)	108.6(3)
O(32)−V(4)−O(33)	106.3(3)	O(36)−K(1)−O(36)#1	180.000(1)	O(29)−V(4)−O(33)	145.8(2)	O(30)−P(6)−O(27)	107.9(3)
O(34)−V(4)−O(33)	89.2(2)	O(24)−K(1)−O(24)#1	180.00(17)	O(31)−V(4)−O(33)	84.7(2)	O(10)−K(1)−O(10)#1	180.000(1)
O(20)−V(5)−O(21)	107.7(3)	O(29)−B(1)−O(27)	111.7(6)	O(20)−V(5)−O(18)	108.6(3)	O(29)−B(1)−O(21)	111.5(6)
O(21)−V(5)−O(18)	77.66(19)	O(29)−B(1)−O(26)	109.4(6)	O(20)−V(5)−O(23)	105.7(3)	O(21)−B(1)−O(27)	109.6(6)
O(21)−V(5)−O(23)	89.8(2)	O(27)−B(1)−O(26)	104.3(5)	O(18)−V(5)−O(23)	145.6(2)	O(21)−B(1)−O(26)	110.1(6)
O(20)−V(5)−O(19)	106.0(3)	O(11)−B(2)−O(15)	111.6(6)	O(21)−V(5)−O(19)	146.2(2)	O(11)−B(2)−O(18)	111.2(6)
O(18)−V(5)−O(19)	90.19(19)	O(11)−B(2)−O(16)	109.2(6)	O(23)−V(5)−O(19)	82.7(2)	O(18)−B(2)−O(15)	109.2(6)
O(10)−V(6)−O(11)	112.1(3)	O(15)−B(2)−O(16)	105.3(6)	O(10)−V(6)−O(6)	110.4(3)	O(18)−B(2)−O(16)	110.2(6)
O(11)−V(6)−O(6)	137.5(2)	O(7)#1−B(3)−O(2)#1	110.7(6)	O(10)−V(6)−O(7)	106.0(3)	O(34)−B(3)−O(7)#1	112.2(6)
O(11)−V(6)−O(7)	77.34(19)	O(4)#1−B(3)−O(2)#1	104.9(6)	O(6)−V(6)−O(7)	89.9(2)	O(34)−B(3)−O(2)#1	109.8(6)
O(10)−V(6)−O(9)	106.5(3)	O(34)−B(3)−O(4)#1	110.1(6)	O(11)−V(6)−O(9)	88.6(2)	O(7)#1−B(3)−O(4)#1	108.9(6)
O(6)−V(6)−O(9)	80.8(2)						

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y + 2, -z + 1$.

recent synthesized oxovanadium borophosphates, only the $[BP_2O_{10}]^{7-}$ trimers were found. This suggests that the $[BP_2O_{10}]^{7-}$ trimer represents a common structural unit in the chemistry of borophosphates. The $\{BO_4\}$ group contributes a tribridging oxygen to each of the two neighboring binuclear $\{V_2O_{10}\}$ moieties. In this fashion, each $\{O_3POB(O)_2OPO_3\}^{7-}$ exhibits three-point attachment of each of two binuclear $\{V_2O_5\}$ sites. The linking of six $\{V_2O_{10}\}$ moieties and six borophosphate ligands forms the 12-member ring structures of VBP-J1 and -J2 with NH_4^+ or K^+ cations encapsulated in the rings. In VBP-J1, the NH_4^+ cation is linked to the six endo-oxygen atoms of the vanadyl by hydrogen bonds (the distance of N−O8, 2.937 Å; N−O22, 2.781 Å; N−O35, 2.706 Å). In VBP-J2, the six endocyclic vanadyl groups, one from each of the $\{V_2O_{10}\}$ binuclear units, are coordinated to the K^+ cation at distances in the range of 2.618(5)−2.879(5) Å.

The diameters of the rings are 5.873(O8−O8A) × 5.412(O35−O35A) × 5.561(O22−O22A) Å for VBP-J1 and 5.758(O24−O24A) × 5.425(O10−O10A) × 5.236(O36−O36A) Å for VBP-J2, respectively. This exiguous difference may be due to the difference of the ion diameter between NH_4^+ (1.66 Å) and K^+ (1.44 Å) cations. Comparison with VOBOPO-2 [Na^+ (0.97 Å) cation encapsulated in the 10-member ring cluster] suggests that the cation size affect the ring size.

The inequivalent water molecules and protonated multiamine cations intercalated between the rings are hydrogen bonded to the oxygen atoms of the clusters or to each other in complex arrangement. Thus, an extended network through multipoint hydrogen bonds forms. The three-dimensional structures along (100) direction and (110) direction are showed in Figure 5.

Conclusions

Two new oxovanadium borophosphates have been synthesized. They are structural analogues and have the similar motif of VOBOPO-1 and VOBOPO-2. Their successful synthesis gives us possibilities to synthesize larger ring clusters using larger cation instead of the NH_4^+ and K^+. Furthermore, the various vanadium oxygen polyhedron with the numerous linkage forms of

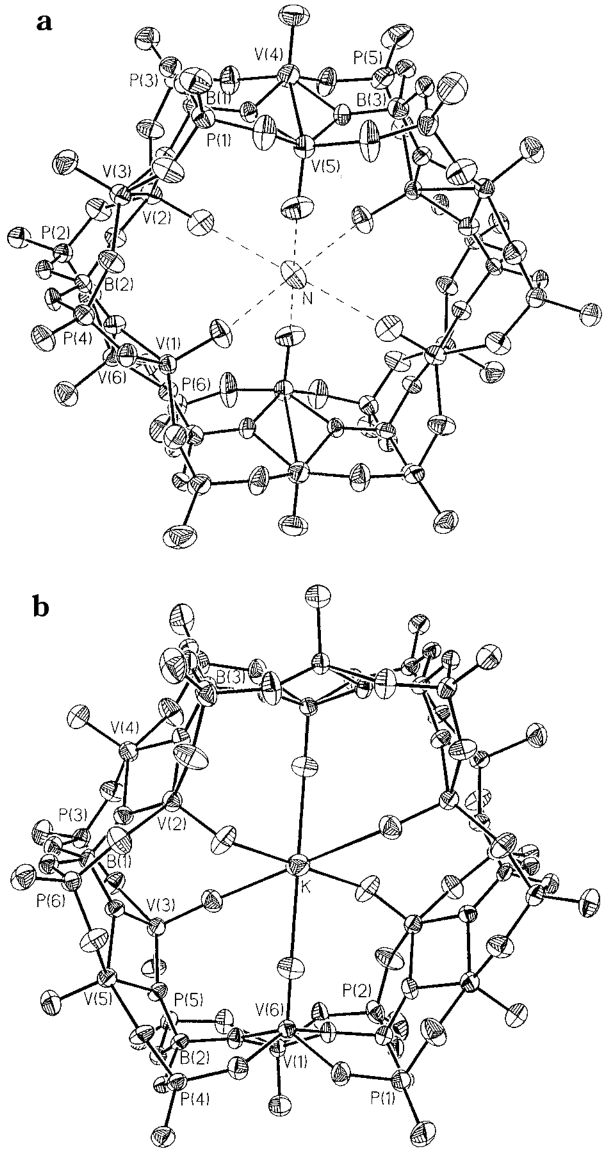

Figure 4. The structures of 12-member ring-shaped cluster anions, 50% thermal ellipsoids: VBP-J1, $[NH_4(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]^{17-}$ and (b) VBP-J2, $[K(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]$.$^{17-}$

the vanadium oxygen polyhedron, boron oxygen polyhedron and the PO_4 tetrahedron are expected to synthesize more oxovanadium borophosphates.

Acknowledgment. The authors are grateful to the financial support by the National Science Foundation of China and the Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University.

Notes Added in Revision

1. In the process of revision of this paper, Allan J. Jacbson and co-workers reported three oxovanadium borophosphate cluster anions, in which compound **3** is also constructed by 12-member ring clusters $[A \supset \{(VO)_2BP_2O_{10}\}_6] \cdot nH_2O$ ($A = NH_4^+$, K^+, Rb^+, Cs^+). Crystal data of $A = NH_4^+$: rhombohedral, space group $R\bar{3}m$, $a = 14.116(2)$ Å, $\alpha = 71.96(2)°$, $V = 8081.8(8)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.651$ g cm^{-1}. The structure of the ring-shaped cluster was the same as VBP-J1 and VBP-J2. This compound did not contain organic species. The intercluster space is occupied by the alkali cations and water molecules. In three-dimensional structure, clusters are oriented with the rings parallel to each other. [Bontchev R. P.; Do, J.; Jacobson, A. J. *Angew. Chem. Int. Ed.* **1999**, 38, 1937.]

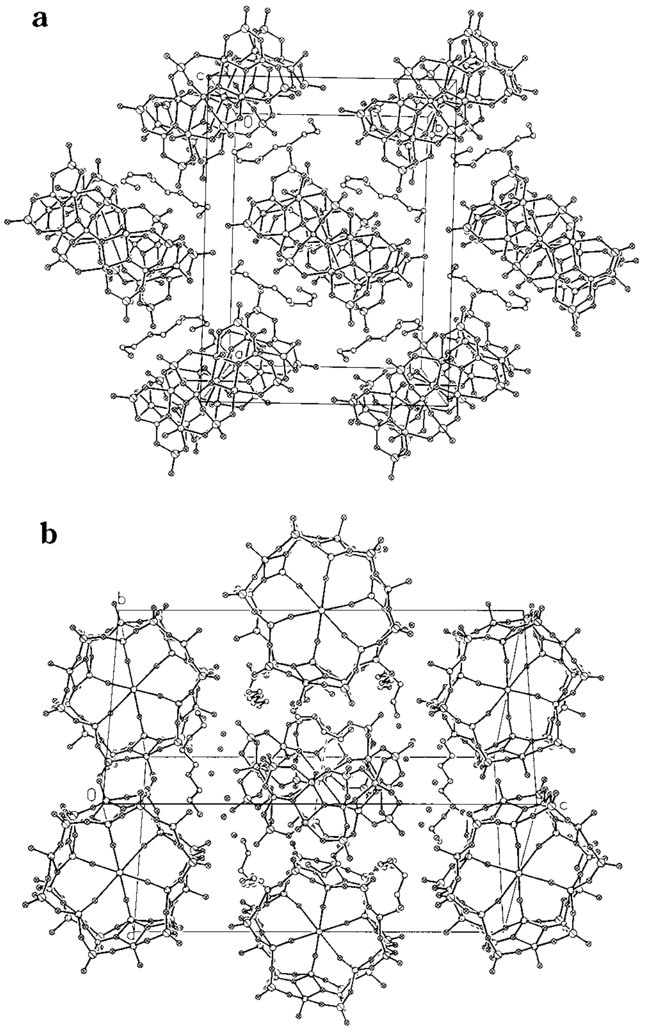

Figure 5. View of the crystal structure of compound VBP-J2 along (100) direction (a) and (110) direction (b).

2. By using diethylenetriamine as the template, two structural analogues of VBP-J1 and VBP-J2 are obtained. Refinement of VBP-J3 shows that its crystal data are $a = 16.8919$ Å, $b = 29.7532$ Å, $c = 20.4661$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10285.97$ Å^3.

Supporting Information Available: Complete tables of crystallographic conditions, atomic positional parameters, bond lengths and angles, anisotropic temperature factors and structure factors for VBP-J1 and VBP-J2. This material is available free of charge via the Internet at http://pubs.acs.org.

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