

Hydrothermal synthesis and structural characterisation of a vanadium (V) borophosphate cluster containing solid: $[\text{Co}(\text{en})_3][\text{enH}_2]\{\text{V}_3\text{BP}_3\text{O}_{19}\} \cdot 4.5\text{H}_2\text{O}$

Minakshi Asnani^a, A. Ramanan^{a,*}, Jagadese J. Vittal^{b,*}

^a Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

^b Department of Chemistry, National University of Singapore, Singapore 117543

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Abstract

Hydrothermal reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{en})_3]\text{Cl}_3$ in sealed borosilicate glass tube yielded a vanadium (V) borophosphate cluster based solid, $[\text{Co}(\text{en})_3][\text{enH}_2]\{\text{V}_3\text{BP}_3\text{O}_{19}\} \cdot 4.5\text{H}_2\text{O}$ (**VBPO**). Crystal data: monoclinic space group, $P2_1-c$, $Z = 4$, $a = 12.070987 \text{ \AA}$, $b = 14.226188 \text{ \AA}$ and $c = 18.110489 \text{ \AA}$, $\beta = 95.067(1)^\circ$, $V = 3097.883 \text{ \AA}^3$. Single crystal X-ray diffraction studies revealed that discrete $[\text{V}_3\text{BP}_3\text{O}_{19}]$ clusters are linked to counter cations and water molecules through a complex hydrogen bonding network.

Keywords: Hydrothermal synthesis; Vanadium borophosphate; Single crystal X-ray diffraction

1. Introduction

In recent years, hydrothermal chemistry is extensively adopted to synthesise a number of metal vanadium phosphates and metal borophosphates [1-11] exhibiting a large variety of new structural types. The success of forming new materials in many cases is demonstrated due to the templating effects of organic amines and metal complexes: ethylenediamine and cobalt tris(ethylenediamine) are notable examples [12-18]. During our attempts to incorporate $[\text{Co}(\text{en})_3]^{3+}$ into VPO framework, we isolated single crystals of the title compound 1 in low yield. Here, we report the synthesis and the structural characterisation of the second member containing the cluster anion $[\text{V}_3\text{BP}_3\text{O}_{19}]$.

2. Experimental

2.1. Synthesis

Compound **VBPO** was obtained in minor quantities from an aqueous mixture of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (1.04 mmol)

and $[\text{Co}(\text{en})_3]\text{Cl}_3$ (1.3 mmol) treated hydrothermally at 180°C for 24 h in a borosilicate glass tube. Care must be taken as the glass tubes tend to explode at this temperature. Attempts to prepare the title compound in a teflon vessel in the presence of boric acid did not result in the same material. Also, good crystals are only obtained when $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ are used as starting material rather than V_2O_5 and H_3PO_4 . FTIR of **VBPO** showed characteristic vibrations: 3445, 3167, 1635, 1507, 1457, 1400, 1150, 1035, 981, 936, 898, 668, 544 and 465 cm^{-1} . In many reactions we invariably encountered the formation of another green solid which exhibited layered characteristics. Synthesis and characterisation of this phase with composition $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_{0.5}[\text{V}_0.2\text{P}_0.4\{\text{P}(\text{OH})_2\}_{0.44}]$ is reported elsewhere [18].

2.2. X-ray crystallography

A green block crystal with dimensions of $0.1 \times 0.1 \times 0.1 \text{ mm}$ was mounted on a Bruker APEX CCD diffractometer with a Mo K α sealed tube. The program SMART [19] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT [19] for integration of the intensity of reflections and scaling. SADABS [20] was used for

absorption correction and SHELXTL [21] for space group and structure determination and least squares refinements on F^2 . All the non-hydrogen atoms were refined anisotropically. Riding models were used to place the H atoms attached to carbon and nitrogen atoms. All the hydrogen atoms of the water molecules were located in the difference Fourier map. The least-squares refinement cy-

cles on F_2 were performed until the model converged. Experimental conditions are given in Table 1.

3. Results and discussion

Single crystal X-ray diffraction analysis of **VBPO** revealed the presence of a discrete anion $[V_3BP_3O_{19}]^{5-}$ and $[Co(en)_3]^{3+}$ and enH_2^{2+} cations linked together by means of an extensive network of hydrogen bonds. The cluster $[V_3BP_3O_{19}]^{5-}$ is built from three VO₆ octahedra, three PO₄ tetrahedra and one BO₄ tetrahedron linked through edge- and vertex-sharing (Fig. 1). A $[V_3O_{13}]$

Table 1
Crystallographic data for **VBPO**

Chemical formula	C ₈ H ₄₃ B Co N ₈ O _{23.5} P ₃ V ₃
Formula weight	942.47
Crystal system	Monoclinic
Space group	P2(1)/c
<i>a</i> (Å)	12.0709(7)
<i>b</i> (Å)	14.2261(8)
<i>c</i> (Å)	18.1104(9)
$67(1)_3$	95.067(1)
I^2 (Å)	3097.8(3)
Temperature (K)	298(2)
Z	4
ρ_{calc} (g cm ⁻³)	2.021
<i>A</i> (Å)	0.71073
θ range (°)	1.82–25.00
$R_i[I > 2s(I)]$	0.0466
wR_2	0.0977
No. of reflections collected	17 879
F ₀₀₀ P	1922
GOF	0.998
Total parameters	460
Absorption coefficient (mm ⁻¹)	1.664

$R_i = (|F_o| - |F_c|) / |F_o|$; $wR_2 = [w(F_o^2 - F_c^2) / (wF_o^4)]^{1/2}$; GOF = $[W(\sum(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$ where "n" is the number of reflections and "p" is the number of parameters refined.

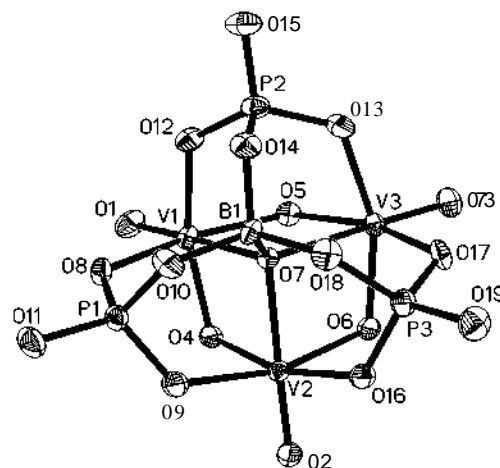


Fig. 1. $[V_3P_3BO_{19}]^{5-}$ cluster anion; 50% thermal ellipsoids.

Table 2
Selected non-bonding interactions [distances (Å) and angles (°)] in **VBPO**

X-H...O	(X-H...O) (Å)	(X-O) (Å)	(X-H...O) (°)
N(1)-H(1C)···O(18) ^a	2.447	3.2869	155.34
N(1)-H(1D)···O(2) ^a	2.041	2.8931	157.47
N(2)-H(2C)···O(11) ^a	2.09	2.8911	147.69
N(2)-H(2D)···O(8) ^a	2.333	2.9741	171.59
N(3)-H(3D)···O(6) ^a	2.006	2.8738	161.51
N(4)-H(4C)···O(14) ^a	2.324	3.2064	166.7
N(4)-H(4D)···O _o (i) ^a	2.102	2.9188	150.56
N(5)-H(5D)···O(12) ^a	2.337	2.9686	127.18
N(5)-H(5D)···O(8) ^a	2.369	3.2038	154.49
N(6)-H(6C)···O(11) ^a	1.911	2.799	169.08
N(6)-H(6D)···O(16) ^a	2.296	3.1229	152.8
N(6)-H(6D)···O(2) ^a	2.332	2.996	130.53
N(8)-H(8D)···O(3) ^a	2.3987	3.1199	138.25
N(7)-H(7C)···O(16) ^a	1.924	2.799	167.36
N(7)-H(7D)···O _o 2 ^b	2.022	2.83	150.42
N(8)-H(8C)···O(17) ^a	2.022	2.8596	156.4
O(1S)-H(1SB)···O(8) ^b	2.25	3.0444	158.96
O(2S)-H(2SB)···O(13) ^b	1.972	2.788	164.23
O(4S)-H(4SA)···O(1) ^b	2.024	2.8053	157.48
O(4S)-H(4SB)···O(15) ^b	1.845	2.6677	178.24
O(5S)-H(5SB)···O(5) ^b	2.2924	2.1568	154.3

^a Hydrogen bonds with ethylenediammonium cations.

^b Hydrogen bonds with water molecules.

^o Hydrogen bonds with cluster anions.

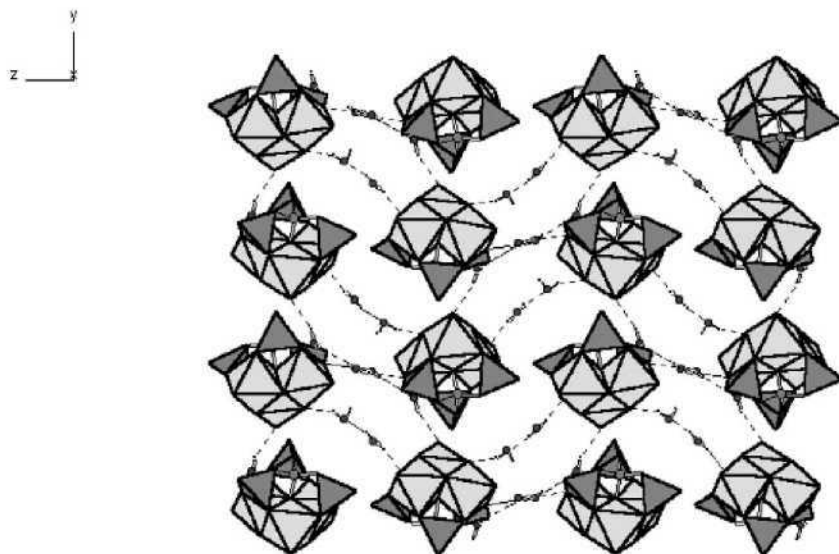


Fig. 2. Hydrogen bonding of the anionic cluster with water molecules.

trimer, made of three edge-shared VO₆ octahedra and a [BP₃O₁₃] unit, made from three phosphorus and one boron tetrahedra, are linked via common oxygen atoms to form the cluster anion [V₃BP₃O₁₉]. The cluster anion is almost identical to the one reported by Bontchev et al. [15] with comparable bond distances and bond angles. The octahedral coordination symmetry of the complex [Co(en)₃]³⁺ is very close to ideal with three pairs of identical Co-N distances of 1.960 Å, and angles within the range 85.24(15)-92.7(16)°. The distances agree well

with those reported in the literature [17]. Bond distances and bond angles of ethylenediammonium cations are comparable to those found in the literature [8].

There is extensive hydrogen bonding present in the structure (Table 2 and Figs. 2 and 3). The structure shows interesting O-H...O and N-H...O hydrogen bond interactions. The four water molecules, one ethylenediammonium and one tris(ethylenediammonium) cobalt(III) cation are hydrogen bonded to either oxygen atoms of the cluster anion or to each other in a complex arrangement. Four water molecules link the cluster anions through four inequivalent oxygen atoms, O(1), O(13), O(5), O(8) leading to the formation of a 16-membered ring and consequently to infinite H₂O...cluster...H₂O chains through the gross structure. These hydrogen bonds are fairly flexible as noticed by the amount of twisting observed in the structure. This twisting can be quantified by the angle made by superimposing the O...O vector of the two cluster anions linked via intervening water molecules, the O(1)...O(8)...O(5)...O(13) torsional angle is 10.79°. Oδ15...Hδ4SBP is the shortest non-bonding interaction occurring in the structure (1.845 Å) and the most directional (178.24°).

The ethylenediammonium cations are linked to four oxygen atoms of the cluster anion, O(10), O(3), O(17), O(2). A strong C-H...O also exists, Cδ7P-Hδ7B...Oδ3P, 2.340 Å; O(3)...Hδ7B...Cδ7P, 135.26°. All ethylenediammonium cations are almost in a *trans* configuration, Nδ8...Cδ8...Cδ7...Nδ7P torsional angle is 73.99°. Additional hydrogen bonds exist between the cluster and tris(ethylenediamine) cobalt(III) cation. Each O(8) cluster oxygen atom acts as a hydrogen bond acceptor to three protons, (H2D), (H5D), (H1SB).

In conclusion, it should be noted that VBPO is only the second example of a solid containing the vanadium boro-

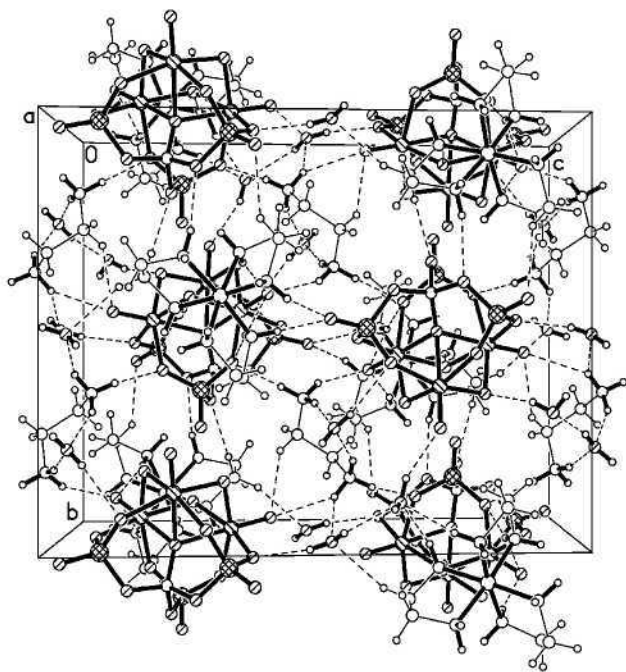


Fig. 3. Hydrogen bonding of the cluster with water molecules and counter cations.

phosphate cluster. The solid is also an unusual example in which the clusters are linked to each other through water molecules mediated by strong hydrogen bonds.

Supplementary material

Complete tables of crystallographic conditions, atomic positional parameters, listing of bond distances and angles, anisotropic temperature factors for compound VBPO (CCDC reference number 197940).

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