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Hydrothermal Synthesis and Single-Crystal Structural Characterization of $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$

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The layered compound $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$ has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction. The structure is orthorhombic, space group *Pbca* with a = 12.805(4) Å, b = 10.592(3) Å, c = 15.037(5) Å, Z = 8, D_x = 2.462 g/cm^3, R = 0.0372, and R_w = 0.0500 for 2038 independent reflections. The structure is formed from layers of vanadium and oxygen atoms and methylenediphosphonate groups, with coordinated water molecules directed into the interlayer space, resulting in a layer repeat distance (d_{001}) of 15.037(5) Å. The layers contain two types of $V^{4+}O_6$ octahedra connected through corners by $[O_3PCH_2PO_3]^{4-}$ groups. V(1) is coordinated by one terminal oxygen atom and three oxygen atoms from water molecules, and chelated by one $[O_3PCH_2PO_3]^{4-}$ group. V(2) is coordinated by one terminal oxygen atom, one water molecule, and two oxygen atoms from separate $[O_3PCH_2PO_3]^{4-}$ groups, and chelated by one $[O_3PCH_2PO_3]^{4-}$ group. The connectivity can be represented as $VO_{1/1}(H_2O)_{3/1}O_{2/2}VO_{1/1}(H_2O)_{1/1}O_{4/2}(O_{3/2}PCH_2PO_{3/2})$. The structure illustrates the versatility of the $[O_3PCH_2PO_3]^{4-}$ group as a connecting unit.

Introduction

Vanadyl organophosphonates $VORPO_3 \cdot xH_2O$ form a group of layered compounds with alternating organic and inorganic interlayers. They are interesting not only because of their ability to intercalate alcohols (*1*), but also because their composition and structural features are controlled by the size of the organic group as well as by the method of preparation. For example, when $R = CH_3$ and C_2H_5, x is 1.5 and the inorganic layers consist of face-sharing V_2O_9 dimers connected by RPO_3 groups through corners (*2*), in an arrangement analogous to that found in $VO(HPO_4) \cdot 0.5\ H_2O$ (*3*). In contrast, the compounds $VOC_6H_5PO_3 \cdot 2H_2O$ and $VOC_6H_5PO_3 \cdot H_2O$ (*4*) which are prepared by reflux and hydrothermal methods, respectively, are structurally different. The dihydrate contains isolated VO_6 octahedra and RPO_3 tetrahedra in a corner-sharing array, and the phenyl groups from adjacent layers interpenetrate. The monohydate contains one-dimensional —V=O—V=O— chains connected by the RPO_3 groups through corners to form a two-dimensional layer with phenyl groups extending into the interlayer space. The phenyl groups in the monohydrate do not interpenetrate, but form a bilayer. As part of our research effort in the synthesis of new organic/inorganic

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structures, the reaction between V_2O_3 and the chelating diphosphonic acid $H_2O_3PCH_2PO_3H_2$ has been investigated under hydrothermal conditions. The present paper reports the synthesis and structure of the new vanadium (IV) compound, $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$.

Experimental

Synthesis

The synthesis of vanadyl methylenediphosphonate was investigated by reaction of $CH_2(PO_3H_2)_2$ (Alfa) and V_2O_3 (Alfa) under hydrothermal conditions in 23 ml Teflon-lined autoclaves (Parr Instruments). Distilled water was added to fill ~60% of the total volume. The mixture was heated in an oven at 200°C for ~24 hr. Reaction mixtures with V/P ratios of 0.90, 1.00, and 1.50 were all heated under the same conditions. The product of the reaction did not depend on the ratio of reactants, as shown by powder X-ray diffraction patterns. The color of the products varied from light to dark blue, due to crystal size effects. The optimum synthesis conditions for both yield and crystal quality (0.706 g $CH_2(PO_3H_2)_2$ and 0.600 g V_2O_3) resulted in deep blue, platy crystals (1.2 g, 80% yield based on vanadium). They were filtered, washed several times with distilled water, and air-dried. Chemical analysis: observed, C 3.33%, H 2.67%, V 26.88%, P 16.60%; Calculated for $CH_{10}V_2P_2O_{12}$, C 3.18%, H 2.67%, V 26.96%, P 16.39%. Major IR bands (solid/KBr pellet, cm^{-1}): 3430 (s), 3230 (s), 2930 (m), 1640 (m), 1620 (m), 1385 (w), 1150 (s), 1110 (s), 1070 (vs), 1030 (vs), 975 (s), 950(s), 810 (m), 575 (m), 530 (m), 480 (w).

Thermogravimetric analysis (10°C/min. in He) showed a weight loss which begins at 130°C and has a maximum rate at ~225°C. The weight loss curve changes slope at about 250°C suggesting the existence of an intermediate hydrate. However, the two steps are not sufficiently well resolved to unambiguously determine the intermediate composition. The weight loss corresponding to removal of all of the coordinated water molecules is complete by 400°C.

X-ray Crystallography

Crystal data: orthorhombic, *Pbca* (#61) a = 12.805(4) Å, b = 10.592(3) Å, c = 15.037(5) Å, Z = 8, D(calcd) = 2.462 g/cm^3. A Nicolet R3m/V diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å) and a graphite monochrometer was used to collect 2791 diffraction maxima ($2\theta < 55°$) from a light blue irregular plate of dimensions 0.09 × 0.24 × 0.40 mm at 298 K. Of these, 2298 were unique, R_{int} = 0.018, and 2038 observed ($F > 3\sigma(F)$). No absorption correction was applied to the data (μ = 2.143 mm^{-1}). The structure was solved by direct methods and refined by full-matrix least-squares methods; vandadium, phosphorus, and oxygen atoms were refined anisotropically to R = 0.0372, R_w = 0.0500, GOF = 1.40. Hydrogen atoms were located in a difference map and included in the refinement as riding on the oxygen or carbon atoms to which they were attached. The highest peak on the final difference Fourier map was 0.93 $e^-/Å^3$. All computations were performed using SHELXTL PLUS (Nicolet) on a Micro VAX II.

Results

The atomic coordinates and important bond distances and angles are listed in Tables I and II. The structure consists of layers of corner-sharing VO_6 octahedra and $[O_3PCH_2PO_3]^{4-}$ polyhedra stacked along the c axis to give a layer repeat distance of 15.037(5) Å, as shown in Fig. 1. The three water molecules coordinated to V(1) and the water molecule coordinated to V(2) all project out into the interlayer space. The layers are connected through an extensive hydrogen bonding network. The details of the spe-

TABLE I

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS ($Å^2 \times 10^3$)

	x	y	z	U(eq)
V(1)	7723(1)	1274(1)	5079(1)	13(1)
V(2)	5230(1)	−2849(1)	7580(1)	9(1)
P(1)	5867(1)	−349(1)	6445(1)	8(1)
P(2)	7776(1)	−3397(1)	7220(1)	8(1)
C(1)	6943(2)	−55(3)	7185(2)	12(1)
O(11)	5761(2)	2459(3)	4995(2)	26(1)
O(12)	6742(2)	873(2)	3819(1)	15(1)
O(13)	8278(2)	455(3)	5068(2)	25(1)
O(14)	7299(2)	2065(2)	6263(1)	15(1)
O(15)	7875(2)	2868(2)	4565(2)	24(1)
O(16)	6267(2)	−116(2)	5497(1)	14(1)
O(21)	5302(2)	−4234(2)	6479(2)	23(1)
O(22)	6781(2)	−3170(2)	7751(1)	12(1)
O(23)	5188(2)	−1789(2)	8355(1)	17(1)
O(24)	3690(2)	−2780(2)	7281(1)	13(1)
O(25)	5491(2)	−1709(2)	6531(1)	12(1)
O(26)	4990(2)	578(2)	6690(1)	13(1)
H(1)	6752	−327	7767	50
H(2)	7514	−526	6893	50
H(11B)	5589	2639	5565	50
H(11A)	5393	2512	4494	50
H(12A)	6597	1512	3491	50
H(12B)	6245	276	3701	50
H(15B)	8005	2904	3994	50
H(15A)	8063	3613	4878	50
H(21B)	5111	−5051	6487	50
H(21A)	5689	−4105	6033	50

Note. Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. Hydrogen atom values of *U* were not refined.

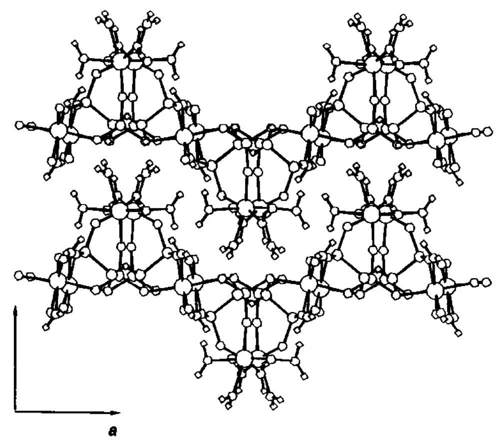

FIG. 1. View of the *ac* plane showing the vanadium phosphonate layers in the compound $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$. Large circles represent vanadium atoms.

cific hydrogen bonding interactions are given in Table III. The intralayer connectivity is dominated by the V(2) atoms and the methylenediphosphonate ions. The layer can be viewed as made up from V(2)—O(24)—P(2)—C(1)—P(1)—O(26) six-membered rings. These rings are connected by O(22) in the *a* direction and O(25) in the *b* direction, see Fig. 2. The coordination sphere of the V(2) atom is a distorted octahedron typical of V^{4+}. The distance of the apical oxygen O(23) to V(2) is 1.619(2) Å with an oxygen O(21) from a coordinated water molecule *trans* to it at a distance of 2.215(2) Å. Of the four equatorial oxygens, two of them, O(24) and O(26), are from the same $[O_3PCH_2PO_3]^{4-}$ group with bond distances of 2.025(2) and 2.014(2) Å, respectively. The remaining two oxygen atoms, O(22) and O(25), are from two different $[O_3PCH_2PO_3]^{4-}$ groups, and their distances to V(2) are 2.030(2) and 2.015(2) Å. Bond valence calculations (*5*) gave a total V(2) valence of 3.91. V(1) atoms are also six-coordinated by oxygen atoms, of which O(14) and O(16) are from the same $[O_3PCH_2PO_3]^{4-}$ group at V—O distances of 1.970(2) and 2.016(2) Å, respectively, while O(11), O(12), and O(15) are water oxygen atoms. Their distances to V(1) are 2.257(3), 2.037(2), and 2.036(3) Å (Fig. 3). The distance betweenV(1) and O(13) is 1.606(3) Å, indicating V═O character. The vanadyl oxygen O(13) is *trans* to the longest of the three bonds to coordinated water molecules. The calculated bond valence of V(1) is 4.00. The V(1) atom environment has not been observed in other vanadyl organophosphonates $VORPO_3 \cdot _xH_2O$ (*1–4*) but the coordination is very similar to that of vanadium in $VOSO_4 \cdot 3H_2O$ (*6*).

The methylenediphosphonate group is

TABLE II

BOND DISTANCES (Å) AND ANGLES (°) IN $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$

V(1)–O(11)	2.257(3)	V(2)–O(21)	2.215(2)
–O(12)	2.037(2)	–O(22)	2.030(2)
–O(13)	1.606(3)	–O(23)	1.619(2)
–O(14)	1.970(2)	–O(24)	2.025(2)
–O(15)	2.036(3)	–O(25)	2.015(2)
–O(16)	2.016(2)	–O(26A)	2.014(2)
P(1)–C(1)	1.797(3)	P(2)–C(1A)	1.793(3)
–O(16)	1.535(2)	–O(22)	1.523(2)
–O(25)	1.525(2)	–O(14A)	1.523(2)
–O(26)	1.537(2)	–O(24A)	1.537(2)
O(11)–V(1)–O(12)	79.3(1)	O(21)–V(2)–O(22)	86.7(1)
O(11)–V(1)–O(13)	176.1(1)	O(21)–V(2)–O(23)	177.5(1)
O(12)–V(1)–O(13)	97.6(1)	O(22)–V(2)–O(23)	93.3(1)
O(11)–V(1)–O(14)	81.7(1)	O(21)–V(2)–O(24)	84.2(1)
O(12)–V(1)–O(14)	160.8(1)	O(22)–V(2)–O(24)	170.7(1)
O(13)–V(1)–O(14)	101.4(1)	O(23)–V(2)–O(24)	95.9(1)
O(11)–V(1)–O(15)	81.9(1)	O(21)–V(2)–O(25)	78.7(1)
O(12)–V(1)–O(15)	86.8(1)	O(22)–V(2)–O(25)	92.1(1)
O(13)–V(1)–O(15)	95.7(1)	O(23)–V(2)–O(25)	98.8(1)
O(14)–V(1)–O(15)	88.3(1)	O(24)–V(2)–O(25)	88.1(1)
O(11)–V(1)–O(16)	85.4(1)	O(21)–V(2)–O(26A)	82.3(1)
O(12)–V(1)–O(16)	87.3(1)	O(22)–V(2)–O(26A)	86.0(1)
O(13)–V(1)–O(16)	96.9(1)	O(23)–V(2)–O(26A)	100.2(1)
O(14)–V(1)–O(16)	93.4(1)	O(24)–V(2)–O(26A)	90.8(1)
O(15)–V(1)–O(16)	166.8(1)	O(25)–V(2)–O(26A)	161.0(1)
C(1)–P(1)–O(16)	106.9(1)	C(1)–P(1)–O(25)	110.7(1)
O(16)–P(1)–O(25)	109.7(1)	C(1)–P(1)–O(26)	107.5(1)
O(16)–P(1)–O(26)	111.3(1)	O(25)–P(1)–O(26)	110.6(1)
O(22)–P(2)–C(1A)	109.7(1)	O(22)–P(2)–O(14A)	113.1(1)
C(1A)–P(2)–O(14A)	107.4(1)	O(22)–P(2)–O(24A)	108.3(1)
C(1A)–P(2)–O(24A)	106.2(1)	O(14A)–P(2)–O(24A)	111.9(1)
P(1)–C(1)–P(2A)	110.0(2)	V(1)–O(14)–P(2A)	135.6(1)
V(1)–O(16)–P(1)	127.6(1)	V(2)–O(22)–P(2)	141.1(1)
V(2)–O(24)–P(2B)	128.2(1)	V(2)–O(25)–P(1)	133.3(1)
P(1)–O(26)–V(2A)	139.6(1)		

TABLE III

BOND DISTANCES (Å) AND ANGLES (Å) INVOLVING HYDROGEN BONDING

Donor	Hydrogen	Acceptor	D ··· A	D–H	H ··· A	D–H ··· A
[a]O(11)	H(11A)	O(25)	2.909	0.890	2.092	152.14
O(11)	H(11B)	O(23)	2.876	0.906	1.999	163.60
[a]O(12)	H(12A)	O(24)	2.669	0.858	1.813	175.27
[a]O(12)	H(12B)	O(26)	2.820	0.831	2.022	157.05
O(15)	H(15A)	O(16)	2.780	0.950	1.847	166.49
[a]O(15)	H(15B)	O(22)	2.781	0.875	1.910	173.48
O(21)	H(21A)	O(13)	2.814	0.844	2.019	156.58
O(21)	H(21B)	O(23)	2.789	0.899	1.895	172.47

[a] Hydrogen bonding between the atoms in the adjacent layers.

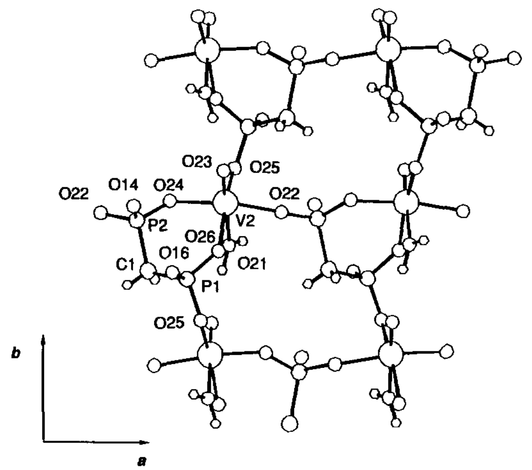

FIG. 2. View of the *ab* plane illustrating the V(2)–O(24)–P(2)–C(1)–P(1)–O(26) six-membered rings connected by O(22) in the *a* direction and O(25) in the *b* direction. V(1) coordination spheres are omitted.

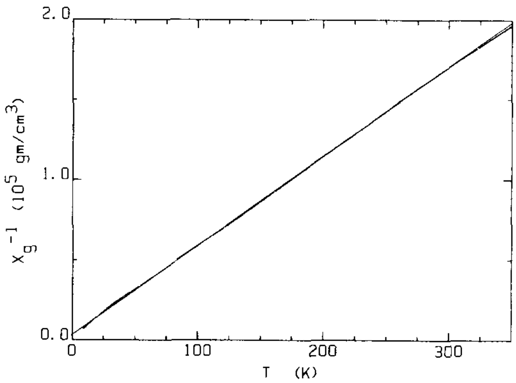

FIG. 4. Inverse magnetic susceptibility as a function of temperature for $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$.

connected to three V(2) atoms and one V(1) atom as shown in Fig. 3. The diphosphonate group acts as a bidentate ligand for V(1) and one of the V(2) atoms and a monodentate ligand for the other two V(2) atoms. The average P—O distance is 1.532(3) Å for P(1) and 1.527(3) Å for P(2). The phosphorus atoms are bound to the methylene carbon atom with average P—C distance of 1.795(3) Å. The P(1)—C(1)—P(2) angle is 110.0(2)°, which is slightly smaller than the corresponding angle (117.2(1)°) in the parent compound $CH_2(PO_3H_2)_2$ (*7, 8*).

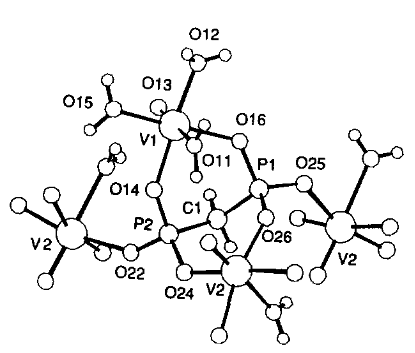

FIG. 3. The coordination of the $[O_3PCH_2PO_3]^{4-}$ group and the V(1) atom in $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$.

The magnetic susceptibility of $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$ was measured as a function of temperature using a George Associates Faraday magnetometer with an applied magnetic field of 6.2kG. The results are shown in Fig. 4. The data were fitted in the temperature range 50–300 K using the formula $\chi = \chi_0 + C/(T - \theta)$ with $\chi_0 = -9.839 \times 10^{-7}$ g/cm^3, C = 1.792×10^{-3} g/cm$^3 \cdot$ K, and $\theta = -5.6$ K. The μ_{eff} value calculated from the Curie constant is 1.65 BM per vanadium, close to the spin-only value of 1.71 BM for one unpaired electron and consistent with the bond valence calculations.

The diphosphonate group in $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$ has an unusual coordination environment serving both as a chelating ligand to V(1) and V(2), as well as a monodentate ligand to two additional V(2) atoms to link the structure in two dimensions. In the complex cation $Co(NH_3)_4[CH_2(PO_3H)_2]^+$ (*9*), the diphosphonate $(O_3PCH_2PO_3)^{4-}$ acts as a bidentate ligand resulting in a M—O—P—C—P—O six-membered ring. However, to our knowledge, all of the characterized extended lattice compounds containing methylenediphosphonate ligands

($Tl_4[CH_2(PO_3)_2]$ (*10*), $Tl_2H_2[CH_2(PO_3)_2]$ and $(NH_4)_2H_2[CH_2(PO_3)_2]$ (*11*)) have isolated $[O_3PCH_2PO_3]^{4-}$ units. The structural complexity of $(VO)_2[CH_2(PO_3)_2] \cdot 4H_2O$ arises because of the versatility of the methylenediphosphonate ion as a connecting unit for the vanadyl ions.

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