3496 *Inorg. Chem.* **1991**, *30*, 3496-3499

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China, and Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

Hydrothermal Synthesis and Structural Characterization of Two Layered Mixed-Valence Vanadyl Phosphate Hydrates $Na_{0.50}VOPO_4\cdot 2.0H_2O$ and $K_{0.50}VOPO_4\cdot 1.5H_2O$

S. L. Wang,*,[†] H. Y. Kang,[†] C. Y. Cheng,[†] and K. H. Lii*,[‡]

Received December 17, 1990

The single crystals of two mixed-valence vanadium phosphates $A_{0.50}VOPO_4\cdot xH_2O$ (A = Na, $x = 2.0$; A = K, $x = 1.5$) were grown hydrothermally. Their structures were characterized by single-crystal X-ray diffraction and thermogravimetric analysis. For $Na_{0.50}VOPO_4\cdot 2.0H_2O$, triclinic, $P\bar{1}$, $a = 6.2851$ (7) Å, $b = 6.284$ (1) Å, $c = 13.262$ (2) Å, $\alpha = 80.30$ (1)°, $\beta = 87.434$ (9)°, $\gamma = 89.94$ (1)°, $V = 515.7$ (1) Å^3, $Z = 4$, and $R = 0.0351$, $R_w = 0.0480$ for 2413 unique reflections. For $K_{0.50}VOPO_4\cdot 1.5H_2O$, triclinic, $P\bar{1}$, $a = 6.282$ (2) Å, $b = 6.285$ (1) Å, $c = 6.679$ (2) Å, $\alpha = 89.11$ (2)°, $\beta = 72.84$ (2)°, $\gamma = 89.98$ (2)°, $V = 251.9$ (1) Å^3, $Z = 2$, and $R = 0.0309$, $R_w = 0.0369$ for 1030 unique reflections. Both structures contain layers of distorted vanadium octahedra and phosphate tetrahedra with the water molecules and alkali-metal cations between the layers. The layer is a 4-connected net in which corner-sharing vanadium and phosphorus polyhedra alternate. These two structures are discussed along with the parent $VOPO_4\cdot 2H_2O$.

Introduction

We have recently synthesized and structurally characterized a large number of new structures in the alkali-metal vanadium phosphate system.[1-10] These phosphates are of interest for their complex tetrahedral–octahedral network structures. Potentially, the study of these compounds allows for the better understanding of the factors affecting their crystal structures. Our synthetic approaches were 2-fold, namely solid-state reactions and hydrothermal methods. The hydrothermal method is particularly suited for the synthesis of low-temperature phases and is also useful for the growth of single crystals.

In 1983, Johnson and Jacobson prepared a series of compounds $A_xVOPO_4\cdot yH_2O$ by redox intercalation reactions of $VOPO_4\cdot 2H_2O$ with iodides in aqueous solution.[11] These are the first intercalation reactions in which the charge transfer proceeds chemically and not electrochemically. Further investigation on these interesting compounds appeared in two other reports.[12,13] On the basis of powder X-ray diffraction, it was reported that the basic tetragonal structure of $VOPO_4\cdot 2H_2O$ was essentially maintained and cations were incorporated into the interlayer spaces. Detailed structural information has been unavailable due to the lack of suitable single crystals for X-ray analysis. We have now found that crystals of $A_xVOPO_4\cdot yH_2O$ can be grown under hydrothermal conditions. In this work, we report the hydrothermal synthesis and structural characterization of two layered mixed-valence vanadyl phosphate hydrates $Na_{0.50}VOPO_4\cdot 2.0H_2O$ and $K_{0.50}VOPO_4\cdot 1.5H_2O$.

Experimental Section

Synthesis. VO_2 (99.5%) and V_2O_5 (99.9%), which were obtained from Cerac Inc., were used as received. H_3PO_4 (85%, ISO), NaOH (GR, ACS), and KOH (GR, ACS) were obtained from Merck. The title compounds are difficult to prepare as single crystals. Due to the layered nature, crystals of the compounds are prone to flaking. A suitable reaction condition for the crystal growth of the Na compound consisted of a mixture of 0.402 g of VO_2, 0.205 g of V_2O_5, 0.203 g of NaOH, 1.5 mL of 85% H_3PO_4, and 10 mL of H_2O in a 23-mL Teflon-lined autoclave (Parr Instruments). The reaction vessel was maintained at 230 °C and autogenous pressure for 5 days before slow cooling at 10 °C/h to room temperature. The crystal growth of the K compound was achieved under similar conditions. The products were filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. It was found that, in addition to the dark green plate crystals of the title compounds, a very small amount of blue-green crystals also crystallized from the reaction mixtures. Separation from the title compounds was performed easily because of the differences in color, crystal habit, and size. The amounts of Na (or K), V, and P in single-phase products of the title compounds were determined by using an ICP-AE spectrometer after dissolving the samples in aqua regia. Anal. Calcd for $Na_{0.50}VOPO_4\cdot 2.0H_2O$: Na, 5.489; V, 24.32; P, 14.79. Found: Na, 5.64; V, 23.8; P, 15.5. Calcd for $K_{0.50}VOPO_4\cdot 1.5H_2O$: K, 9.377; V, 24.43; P, 14.86. Found: K, 8.48; V, 23.8; P, 15.7. The experimental result for K was a little lower than the theoretical value. However, the single-crystal X-ray diffraction analysis suggested full occupancy at the K atom site.

Single crystals of the Li and Cs analogues have not been obtained despite numerous attempts at crystal growth. Preliminary work on a crystal of the Rb analogue of reasonable quality showed that it was isostructural with the K compound.

Thermal Analysis. Thermogravimetric (TG) analyses, using a SEIKO TG system, were performed on crushed samples of manually selected crystals of the title compounds. The experiments were performed in flowing Ar at 50 mL/min with a heating rate of 5 °C/min.

Single-Crystal X-ray Diffraction. Peak profile analysis (ω scan) of the dark green crystals of the title compounds using a Nicolet R3m/V diffractometer indicated that most of them were not single crystals. Many had to be selected before a satisfactory crystal was obtained. Finally, a piece of each of the title compounds was chosen. The crystals used were dark green prisms of dimensions 0.12 × 0.15 × 0.52 and 0.06 × 0.10 × 0.48 mm for the Na and K compounds, respectively. Indexing and intensity data collection were done on the same diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters and orientation matrices were determined by a least-squares fit of 18 (the Na compound) and 25 (the K compound) peak maxima with 2θ ranging from 10 to 31°. Axial oscillation photographs taken along the c axis of the Na compound showed a couple weak but sharp superlattice reflections. The actual repeat distance in the c direction of the Na compound is 3 times of that reported in this work. The superstructure of the Na compound is still under investigation. Of the 3487 and 1263 reflections collected ($2\theta_{max} = 60$ and 55°, scan mode $2\theta/\theta$), 2413 and 1030 unique reflections were considered observed ($I > 3.0\sigma(I)$) after Lp and empirical absorption corrections for the Na and K compounds, respectively. Corrections for absorption were based on ψ scans of a few suitable reflections with χ values close to 90°.[14] On the basis of intensity statistics and successful solution and refinement of the structures, the space group was determined to be $P\bar{1}$ for both compounds.

The structure of the K compound was solved by direct methods and successive Fourier syntheses. Phase solutions for the Na compound were attempted but were unsuccessful, and the coordinates of V and P atoms in the K compound were used to derive its structure model. The hydrogen atoms of the Na compound were located by careful scrutiny of a difference Fourier map and were included in the refinement. The hydrogen atoms of the K compound could only be partially located, since

---

[†] National Tsing Hua University.
[‡] Academia Sinica.

(1) Lii, K. H.; Wang, Y. P.; Wang, S. L. *J. Solid State Chem.* **1989**, *80*, 127.
(2) Lii, K. H.; Tsai, H. J.; Wang, S. L. *J. Solid State Chem.* **1990**, *87*, 396.
(3) Lii, K. H.; Wang, S. L. *J. Solid State Chem.* **1989**, *82*, 239.
(4) Lii, K. H.; Wang, Y. P.; Chen, Y. B.; Wang, S. L. *J. Solid State Chem.* **1990**, *86*, 143.
(5) Wang, Y. P.; Lii, K. H.; Wang, S. L. *Acta Crystallogr.* **1989**, *C45*, 673.
(6) Wang, Y. P.; Lii, K. H. *Acta Crystallogr.* **1989**, *C45*, 1210.
(7) Lii, K. H.; Lee, C. S. *Inorg. Chem.* **1990**, *29*, 3298.
(8) Lii, K. H.; Tsai, H. J. *J. Solid State Chem.* **1991**, *90*, 291.
(9) Lii, K. H.; Li, C. H.; Chen, T. M.; Wang, S. L. *Z. Kristallogr.*, in press.
(10) Lii, K. H.; Tsai, H. J. *Inorg. Chem.* **1991**, *30*, 446.
(11) Johnson, J. W.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 412.
(12) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782.
(13) Casan, N.; Amoros, P.; Ibanez, R.; Martinez-Tamayo, E.; Beltran-Porter, A.; Beltran-Porter, D. *J. Incl. Phenom.* **1988**, *6*, 193.
(14) Alcock, N. W. *Acta Crystallogr.* **1974**, *A30*, 332.

0020-1669/91/1330-3496$02.50/0

Table I. Crystallographic and Experimental Parameters for $Na_{0.50}VOPO_4{\cdot}2.0H_2O$ (I) and $K_{0.50}VOPO_4{\cdot}1.5H_2O$ (II)

	I	II
formula	$H_4Na_{0.5}O_7PV$	$H_3K_{0.5}O_{6.5}PV$
fw	209.436	208.482
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.2851 (7)	6.282 (2)
b, Å	6.284 (1)	6.285 (1)
c, Å	13.262 (2)	6.679 (2)
α, deg	80.30 (1)	89.11 (2)
β, deg	87.434 (9)	72.84 (2)
γ, deg	89.94 (1)	89.98 (2)
V, Å^3	515.7 (1)	251.9 (1)
Z	4	2
ρ_{calcd}, g/cm^3	2.697	2.748
μ, cm^{-1}	21.8	25.9
transm coeff	0.661–0.723	0.767–0.849
T, °C	24	
radiation (λ, Å)	Mo Kα (0.71073)	
R	0.0351	0.0309
R_w	0.480	0.0369

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^2) for $Na_{0.50}VOPO_4{\cdot}2.0H_2O$

atom	x	y	z	U_{eq}[a]
Na	0.5858 (2)	0.9874 (2)	0.2518 (1)	3.76 (5)
V(1)	0.75876 (5)	0.26412 (6)	0.45331 (3)	0.71 (1)
V(2)	0.24548 (5)	0.23951 (6)	0.04728 (3)	0.71 (1)
P(1)	0.25181 (8)	0.25122 (8)	0.49825 (5)	0.72 (2)
P(2)	0.24922 (8)	0.75209 (9)	−0.00195 (5)	0.72 (2)
O(1)	0.7492 (3)	0.2191 (3)	0.5746 (2)	1.72 (6)
O(2)	0.7771 (3)	0.5805 (3)	0.4310 (1)	1.30 (5)
O(3)	0.7377 (3)	0.9669 (3)	0.4297 (1)	1.16 (5)
O(4)	0.0677 (3)	0.2584 (3)	0.4248 (1)	1.26 (5)
O(5)	0.4540 (3)	0.2942 (3)	0.4286 (1)	1.51 (5)
O(6)	0.5496 (3)	0.2114 (3)	0.0733 (1)	1.25 (5)
O(7)	−0.0635 (3)	0.2458 (3)	0.0733 (1)	1.30 (5)
O(8)	0.2553 (3)	0.2926 (3)	−0.0736 (2)	1.72 (5)
O(9)	0.2574 (3)	0.5378 (3)	0.0742 (1)	1.22 (5)
O(10)	0.2247 (3)	0.9263 (3)	0.0658 (2)	1.58 (5)
O(11)[b]	0.7556 (3)	0.3275 (3)	0.2747 (1)	1.80 (5)
H(11A)[c]	0.6595	0.4320	0.2666	8.0
H(11B)	0.8270	0.3236	0.2239	8.0
O(12)[b]	0.2310 (3)	0.1446 (3)	0.2279 (2)	1.80 (5)
H(12A)	0.1695	0.2303	0.2603	8.0
H(12B)	0.1493	0.0338	0.2484	8.0
O(13)[b]	0.9383 (3)	0.8288 (3)	0.2467 (2)	2.69 (6)
H(13A)	0.9268	0.7150	0.2962	8.0
H(13B)	0.9828	0.7680	0.2022	8.0
O(14)[b]	0.4488 (3)	0.6360 (3)	0.2493 (2)	2.23 (6)
H(14A)	0.3992	0.5710	0.2955	8.0
H(14B)	0.3897	0.6050	0.2008	8.0

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Water oxygen atom. [c] The atomic coordinates and thermal parameters for all H atoms are fixed.

the water oxygen O(7) was disordered. Both structures were refined by full-matrix least-squares refinement based on F values. All of the non-hydrogen atoms were refined with anisotropic temperature factors. The atomic positions and isotropic thermal parameters for the hydrogen atoms were fixed. The multiplicities of Na, K, and the O atoms of water molecules were all allowed to vary but did not deviate significantly from full occupancy. The final difference maps were flat to less than ±0.99 and ±0.74 e/Å^3 for the Na and K compounds, respectively. Calculations were performed on a DEC MicroVAX II computer system using SHELXTL-PLUS programs.[15] Neutral-atom scattering factors and corrections for anomalous dispersion were from common sources.[16]

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^2) for $K_{0.50}VOPO_4{\cdot}1.5H_2O$

atom	x	y	z	U_{eq}[a]
K	0	0	0	6.87 (7)
V	0.28783 (7)	0.75387 (7)	0.40273 (8)	0.69 (2)
P	0.2497 (1)	0.2502 (1)	0.4955 (1)	0.85 (3)
O(1)	0.2876 (4)	0.0615 (3)	0.3452 (4)	1.37 (7)
O(2)	0.6090 (3)	0.7685 (3)	0.3519 (4)	1.46 (7)
O(3)	0.3118 (4)	0.4480 (3)	0.3531 (4)	1.76 (7)
O(4)	−0.0085 (3)	0.7439 (4)	0.3623 (4)	1.67 (7)
O(5)[b]	0.3850 (4)	0.7608 (4)	0.0398 (4)	2.62 (9)
H(5A)[c]	0.4924	0.7205	−0.0175	8.0
H(5B)[c]	0.2852	0.6425	0.0225	8.0
O(6)	0.2130 (4)	0.7579 (4)	0.6513 (4)	1.95 (8)
O(7)[b]	0	$^1/_2$	0	6.3 (2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Water oxygen atom. [c] The atomic coordinates and thermal parameters for all H atoms are fixed.

Table IV. Bond Distances (Å) and Bond Valence Sums ($\sum s$) for $Na_{0.50}VOPO_4{\cdot}2.0H_2O$

Na–O(3)	2.568 (2)	Na–O(6)	2.562 (2)
Na–O(11)	2.460 (2)	Na–O(12)	2.450 (2)
Na–O(13)	2.431 (2)	Na–O(14)	2.377 (2)
$\sum s$(Na) = 0.99			
V(1)–O(1)	1.584 (2)	V(1)–O(2)	1.963 (2)
V(1)–O(3)	1.951 (2)	V(1)–O(4)	1.963 (2)
V(1)–O(5)	1.961 (2)	V(1)–O(11)	2.335 (2)
$\sum s$(V(1)) = 4.66,[a] 4.43[b]			
V(2)–O(6)	1.960 (2)	V(2)–O(7)	1.959 (2)
V(2)–O(8)	1.579 (2)	V(2)–O(9)	1.968 (2)
V(2)–O(10)	1.946 (2)	V(2)–O(12)	2.366 (3)
$\sum s$(V(2)) = 4.68,[a] 4.44[b]			
P(1)–O(2)	1.533 (2)	P(1)–O(3)	1.536 (2)
P(1)–O(4)	1.541 (2)	P(1)–O(5)	1.534 (2)
$\sum s$(P(1)) = 4.98			
P(2)–O(6)	1.539 (2)	P(2)–O(7)	1.534 (2)
P(2)–O(9)	1.543 (2)	P(2)–O(10)	1.532 (2)
$\sum s$(P(2)) = 4.96			
O(11)–H(11A)	0.89	O(11)–H(11B)	0.80
O(12)–H(12A)	0.83	O(12)–H(12B)	0.86
O(13)–H(13A)	0.89	O(13)–H(13B)	0.80
O(14)–H(14A)	0.73	O(14)–H(14B)	0.81
H(11A)···O(14)	1.84	H(11B)···O(7)	2.21
H(12A)···O(4)	2.28	H(12B)···O(13)	1.85
H(13A)···O(2)	2.03	H(13B)···O(8)	2.40
H(13B)···O(10)	2.39	H(14A)···O(5)	2.30
H(14B)···O(9)	2.01		

[a] The formula for V^{5+}–O was used. [b] The formula for V^{4+}–O was used.

Results and Discussion

Thermal Analysis. The TG analyses show water loss in two steps for both compounds. The first weight loss is at ~120 °C and corresponds to the loss of water molecules that are bound to the alkali metals and weakly linked by hydrogen bonding. The second weight loss, which occurs at ~220 °C, is due to the loss of water molecules that are coordinated to the V atoms (vide infra). The observed total weight differences between room temperature and 650 °C agree well with those calculated from the formulas. $Na_{0.50}VOPO_4{\cdot}2.0H_2O$: calcd, 17.20%; found, 16.64%. $K_{0.50}VOPO_4{\cdot}1.5H_2O$: calcd, 12.96%; found, 13.85%.

Structural Description. Table I lists the crystallographic data. Final atomic coordinates and U_{eq} values are listed in Tables II and III. Selected interatomic distances and bond order sums[17] are given in Tables IV and V.

The crystal structures of the title compounds are closely related to that for $VOPO_4{\cdot}2H_2O$. The compound $VOPO_4{\cdot}2H_2O$ crystallizes in the tetragonal space group $P4/nmm$ with a = 6.202 (2) Å, c = 7.410 (1) Å, and Z = 2.[18] The structure contains layers

---

(15) Sheldrick, G. M. *SHELXTL-PLUS Crystallographic System*, release 4.11; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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

Table V. Bond Distances (Å) and Bond Valence Sums ($\sum s$) for $K_{0.50}VOPO_4 \cdot 1.5H_2O$

K–O(1)	3.349 (3) (2×)[a]	K–O(2)	3.188 (2) (2×)
K–O(4)	2.872 (3) (2×)	K–O(5)	2.923 (3) (2×)
K–O(6)	2.793 (2) (2×)	K–O(7)	3.142 (1) (2×)
$\sum s(K) = 1.16$			
V–O(1)	1.965 (2)	V–O(2)	1.946 (2)
V–O(3)	1.954 (2)	V–O(4)	1.959 (2)
V–O(5)	2.318 (2)	V–O(6)	1.587 (2)
$\sum s(V) = 4.69$,[b] 4.45[c]			
P–O(1)	1.538 (2)	P–O(2)	1.540 (2)
P–O(3)	1.532 (2)	P–O(4)	1.534 (2)
$\sum s(P) = 4.98$			
O(5)–H(5A)	0.72	O(5)–H(5B)	1.00
H(5B)···O(7)	2.05		

[a] Number of times the distance occurs per formula unit. [b] The formula for V^{5+}–O was used. [c] The formula for V^{4+}–O was used.

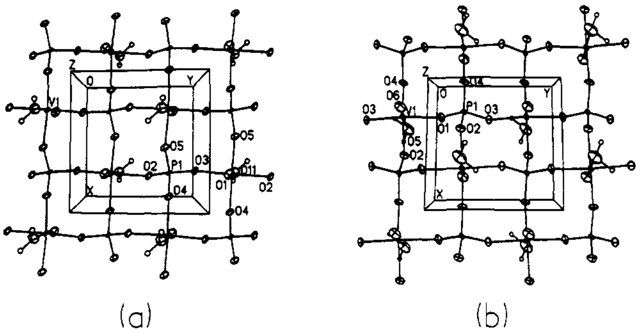

Figure 1. Section of a 4-connected net in (a) $Na_{0.50}VOPO_4 \cdot 2.0H_2O$ and (b) $K_{0.50}VOPO_4 \cdot 1.5H_2O$. Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms are represented by small open circles.

of distorted vanadium octahedra and phosphate tetrahedra with the water molecules between the layers. The layer is a 4-connected net in which corner-sharing vanadium and phosphorus polyhedra alternate. Each vanadium octahedron shares its four equatorial oxygen atoms with four different PO_4 groups. The two remaining axial oxygens consist of a vanadyl oxygen and a water molecule coordinated trans to it. The second water molecule is located between two phosphate groups and is linked by hydrogen bonds to two layers simultaneously. Along the [110] direction the vanadyl oxygens alternately point up and down relative to a layer. The incorporation of alkali-metal cations such as K^+ and Na^+ into the interlayer spaces not only leads to reduction of partial V^{5+} to V^{4+} but also alters the water content or the way in which the layers pack in the lattice. Both the sodium and potassium compounds have a triclinic symmetry. A comparison of the powder patterns of the samples prepared by the hydrothermal method with those prepared by the redox intercalation reaction shows that the previously reported compounds appear to have higher symmetry.[12] It is also noted that their samples show a large effect of preferred orientation. The interlayer separations for the sodium and potassium compounds prepared hydrothermally are respectively 6.53 and 6.38 Å, which are the same as those for the compounds prepared by the intercalation reaction. The interlayer separations for both compounds are considerably shorter than that in $VOPO_4 \cdot 2.0H_2O$. On intercalation, the layers become negatively charged and are brought closer together by electrostatic interaction with the interlayer alkali-metal cations. As shown in Figure 1, the intralayer structural features in these compounds are essentially the same. The V atoms have a common environment, which is a gross distortion of an octahedron; one short V–O bond length is 1.58 Å, which is about 0.38 Å shorter than the four equatorial V–O bonds, but the sixth bond is much longer, ~2.3 Å. This kind of geometry often occurs with compounds containing oxovanadium(IV) or oxovanadium(V) groups. Bond order sums of V–O bonds for both compounds are in good accord with their average formal oxidation states (+4.5). The V^{4+} and V^{5+} ions are probably disordered inside the layers. The difference in size between V^{4+} and V^{5+} can be correlated to the large U_{33} values for V and some of the other atoms.

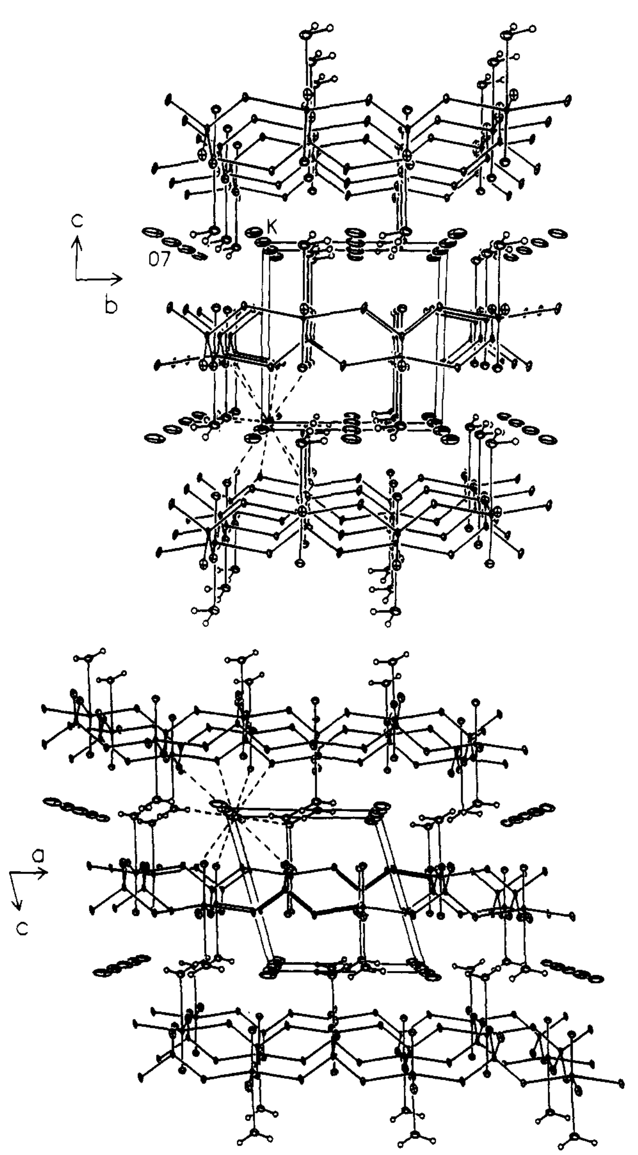

Figure 2. $K_{0.50}VOPO_4 \cdot 1.5H_2O$ structure as viewed (a, top) along the *a* axis and (b, bottom) along the *b* axis. Thermal ellipsoids are shown at the 50% probability level. Thermal ellipsoids with shaded segments are K atoms. Small open circles are H atoms. The K–O bonds are represented by dashed lines.

Views of the $K_{0.50}VOPO_4 \cdot 1.5H_2O$ structure along the *a* and *b* axes are shown in Figure 2a,b respectively. Each K ion is coordinated by twelve oxygen atoms including four water oxygens (two O(5) and two O(7) atoms). The water molecule $H_2O(5)$ is coordinated to the V atom. The other water molecule $H_2O(7)$, which corresponds to the water molecule located between two phosphate groups in $VOPO_4 \cdot 2H_2O$, shifts to the 1c special position of the triclinic space group in order to accommodate the K ions. The layer stacking is not the same as that in the parent $VOPO_4 \cdot 2H_2O$. Two adjacent layers are displaced with respect to each other in one direction to form large cavities where the K ions and $H_2O(7)$ water molecules are located (Figure 2b). The K ions run in rows parallel to the *a* axis and alternate along *b* with rows of $H_2O(7)$ molecules (Figure 2a). Atoms K and O(7) have large U_{11} and U_{22} values, indicative of positional disorder. This compound appears to have lower potassium content than that of the compound produced by redox intercalation with KI(aq) (0.50 vs 0.64).[12] Both compounds have the same water content.

---

(18) Tietze, H. R. *Aust. J. Chem.* **1981**, *34*, 2035.

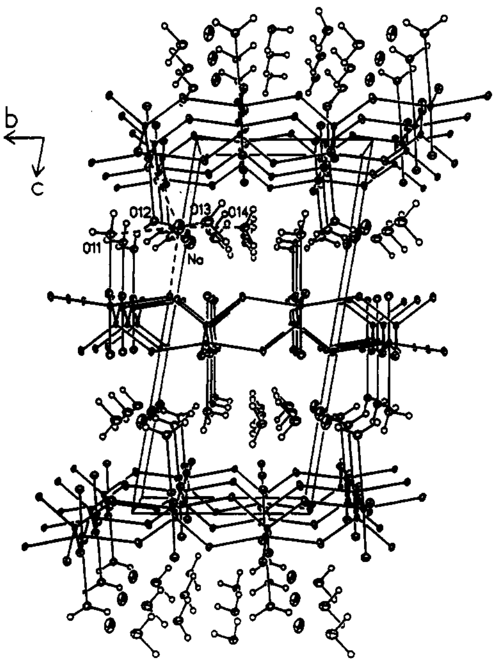

Figure 3. $Na_{0.50}VOPO_4{\cdot}2.0H_2O$ structure as viewed along the *a* axis. Thermal ellipsoids are shown at the 50% probability level. Thermal ellipsoids with shaded segments are Na atoms. Small open circles are H atoms. The Na–O bonds are represented by dashed lines.

In $Na_{0.50}VOPO_4{\cdot}2.0H_2O$, each Na ion is octahedrally coordinated, though in a highly distorted fashion, with the coordination consisting of four water oxygens and two phosphate oxygens (Figure 3). The water molecules, $H_2O(11)$ and $H_2O(12)$, are coordinated to the V atoms. The other water molecules, $H_2O(13)$ and $H_2O(14)$, are weakly held by hydrogen bonding. The Na ion and all the water oxygens reside at general positions. Although the sodium and potassium compounds have similar layer stackings, the *c* axis of the former is 2 times as long as *c* in the latter, since the K ions and $H_2O(7)$ water molecules are at special positions. The size of the alkali-metal cation plays an important role in the arrangement of the metal cations and water molecules between the layers. The compound $Na_xVOPO_4{\cdot}2.0H_2O$ produced by intercalation with NaI(aq) has three different composition ranges, namely, $x < 0.2$ (range I), $0.2 < x < 0.32$ (range II), and $0.35 < x < 0.46$ (range III).[12] In range III, the samples are all two-phase mixtures of phase I and phase II. The compound from the hydrothermal synthesis has $x = 0.5$, which is the upper limit for phase I.

The layered mixed oxide hydrates $A_xVOPO_4{\cdot}yH_2O$ were originally prepared by redox intercalation reactions of $VOPO_4{\cdot}2H_2O$ with iodides in aqueous solution. The structural data for these compounds were derived from powder X-ray diffraction, and the lattice constants in the tetragonal and orthorhombic systems were reported. The phases reported herein crystallize in the triclinic space group $P\bar{1}$, although their alkali-metal and water contents are similar to those of the previous work. This study shows the detailed structural features of these interesting layered compounds. Since the hydrothermal method is a useful technique for growth of single crystals, the synthesis from cations in place of Na^+ or K^+ is currently under investigation.

Acknowledgment. Support for this study by the National Science Council and the Institute of Chemistry, Academia Sinica, is gratefully acknowledged.

Supplementary Material Available: Tables of crystal and refinement data, anisotropic thermal parameters, and bond angles and Figures S1 and S2, showing TG curves for both compounds and a view of the sodium compound along the *b* axis, respectively (7 pages); tables of observed and calculated structure factors for both compounds (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Inorganic Chemistry,
University of Sydney, Sydney 2006, Australia

Redetermination of the Crystal Structure of Hexaamminecobalt(II) Chloride

Janet M. Newman, Malcolm Binns, Trevor W. Hambley, and Hans C. Freeman*

Received January 3, 1991

The crystal structure of $[Co(NH_3)_6]Cl_2$ has been redetermined at ambient and low temperatures. The compound forms cubic crystals, $a = 10.1342\ (7)$ Å at 294 K, with $Z = 4$. The structure has been refined in space group $Fm\bar{3}m$ with allowance for the rotationally disordered ammine ligands ($R = 0.025$, $R_w = 0.021$, 165 *F*'s [$>5\sigma(F)$]). The Co^{II}–N bond length is 2.170 (2) Å. Diffraction measurements at 128 K yielded similar but less precise results [$a = 10.012\ (4)$ Å; Co^{II}–N = 2.164 (4) Å].

Introduction

The hexaamminecobalt(II/III) couple occupies a pivotal position in the development of our understanding of electron transfer among coordination compounds. The fact that electron transfer between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ is unusually slow was cited during the discussion of a paper by Libby in 1952;[1] Libby responded that a slow electron self exchange rate would be explained if it were eventually found that the cobalt-ligand distances are appreciably different in the two oxidation states; and Libby's hypothesis appeared to receive immediate support when another speaker[2] cited Co(II)–N and Co(III)–N bond lengths of 2.5 and 1.9 Å, which had been derived by Stoll in 1926 from X-ray powder diffraction data.[3,4] The subsequent measurements and interpretation of the $Co(NH_3)_6^{2+/3+}$ self-exchange rate have been the subject of an authoritative review by Geselowitz and Taube.[5] We restrict our present comments to the dimensional changes associated with the reaction.

During the early 1960's, standard texts continued to cite the lengths of Co(II)–N and Co(III)–N bonds as 2.5 and 1.9 Å, respectively. One contemporary author used slightly different values whose origin is not clear (2.4 and 2.05 Å),[6,7] but there was no evidence to contradict the hypothesis that the difference between the bond lengths was substantial. In 1966, it became clear that the difference between the Co(II)–N and Co(III)–N bond

---

(1) Libby, W. F. *J. Phys. Chem.* **1952**, *56*, 863–868.

(2) Brown, H. C. *J. Phys. Chem.* **1952**, *56*, 868.

(3) Stoll, P. Dissertation Eidgenossische Technische Hochschule, Zürich, Switzerland, 1926.

(4) Bilt, W. Z. *Anorg. Chem.* **1927**, *164*, 245–255.

(5) Geselowitz, D.; Taube, H. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Academic Press: London, 1982; Vol. 1, 391–407.

(6) Stranks, D. R. *Faraday Soc. Discuss.* **1960**, *29*, 73–79.

(7) Biradar, N. S.; Stranks, D. R.; Vaidya, M. S. *Trans. Faraday Soc.* **1962**, *58*, 2421–2432.