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Adsorption and Structural Studies of Water in the Layered Compounds $K_3Sb_3M_2O_{14}$, xH_2O (M = P, As)

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The layered compounds $K_3Sb_3M_2O_{14}$, xH_2O (M = P, As) crystallize in the rhombohedral system, space group $R\bar{3}m$, with $a = 7.147(1)$ Å, $c = 30.936(6)$ Å when $M = P$ and $a = 7.232(2)$ Å, $c = 31.606(5)$ Å when M = As. They are isomorphous. Their hydration–dehydration process has been studied using various techniques: adsorption isotherms, thermogravimetric analysis, and thermodiffractometry; it occurs between 30 and 180°C and is completely reversible. At 20°C and for almost the whole range of relative humidity the formulas are $K_3Sb_3P_2O_{14}$, $5H_2O$ and $K_3Sb_3As_2O_{14}$, $4.3H_2O$. The crystal structure of $K_3Sb_3P_2O_{14}$, xH_2O previously described as that of an anhydrous compound has been reexamined and the oxygen atoms of the water molecules located, thus leading to the true composition of the crystal, $K_3Sb_3P_2O_{14}$, $1.32(6)H_2O$. © 1988 Academic Press, Inc.

Introduction

We have recently described the crystal structure of the potassium phosphatoantimonate $K_3Sb_3P_2O_{14}$ (*1*). In this compound, the potassium atoms are situated between the $(Sb_3P_2O_{14}^{3-})_n$ covalent layers and can then be easily ion-exchanged in acidic medium leading to the phosphatoantimonic acid $H_3Sb_3P_2O_{14}$, xH_2O (*2, 3*). This solid acid is a very good ion-exchanger as it was shown by titrations with alkali hydroxide solutions (*2, 3*). All the phases formed upon exchange are hydrated and surprisingly the lattice parameters of the potassium one are identical to those of the phase described in (*1*) and so far considered as anhydrous. In order to elucidate this problem, thermodiffractometry experiments have been undertaken and the crystal structure of "$K_3Sb_3P_2O_{14}$" has been reexamined. Furthermore, the isomorphous potassium arsenoantimonate $K_3Sb_3As_2O_{14}$, xH_2O has been prepared and its thermal behavior studied.

We report here on these different studies. The water content of the title compounds, inferred from thermogravimetry (TG) experiments and adsorption isotherms, is then discussed in connection with structural considerations.

Preparation and X-Ray Study

$K_3Sb_3P_2O_{14}$, xH_2O has been prepared as previously described (*1*). The starting materials for synthesizing $K_3Sb_3As_2O_{14}$, xH_2O

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TABLE I

UNIT CELLS CONSTANTS

$K_3Sb_3P_2O_{14}$, xH_2O	$a = 7.147(1)$ Å,		$c = 30.936(6)$ Å	
$K_3Sb_3As_2O_{14}$, xH_2O	$a = 7.232(3)$ Å,		$c = 31.606(5)$ Å	
$K_3Sb_3P_2O_{14}$	$a = 12.32(2)$ Å,	$b = 7.11(1)$ Å,	$c = 9.05(2)$ Å,	$\beta = 116.0(1)°$
$K_3Sb_3As_2O_{14}$	$a = 12.427(6)$ Å,	$b = 7.199(3)$ Å,	$c = 9.273(6)$ Å,	$\beta = 116.21(5)°$

were KNO_3 (RP grade, Prolabo), $NH_4H_2AsO_4$ (Alfa division), and Sb_2O_3 (GR grade, Merck). The reactants were weighed out in the stoichiometric ratio and the mixture was heated in a platinum crucible at 1173 K for 24 hr. The bulk of the crystals obtained are hexagonal-shaped platelets. Single-crystal X-ray study indicates that the arsenic compound is of rhombohedral symmetry (space group $R\bar{3}m$) and is isotypic with the phosphorus phase. Its cell parameters (Table I) were refined by a least-squares procedure from powder diffraction data collected with a Guinier camera (Guinier–Nonius FR552, quartz crystal monochromator, $\lambda CuK\alpha_1 = 1.54056$ Å, $Pb(NO_3)_2$ as standard).

Adsorption Isotherms and TG Studies

When left in air at room temperature, $K_3Sb_3M_2O_{14}$ (M = P, As) compounds become hydrated. Their water content has been determined on powdered samples from adsorption isotherms at 20°C and TG experiments.

The different partial pressures of water vapor were obtained over P_2O_5 (Relative humidity Rh $\simeq$ 0%) and sulfuric acid solutions with densities varying between 1.70 (Rh = 3.2%) and 1.05 (Rh = 97.5%). The thermal analyses were performed on a Perkin–Elmer Model TGS-2 TGA system (heating rate 120 K/hr).

For the arsenic phase the dehydration process is similar to that of the phosphorus one. It begins at 30°C and the anhydrous compound is obtained at 180°C. The formulas calculated from the weight loss are $K_3Sb_3P_2O_{14}$, $5H_2O$ and $K_3Sb_3As_2O_{14}$, $4.3H_2O$. They remain constant for almost the whole range of relative humidity as can be seen from the adsorption isotherms represented in Fig. 1.

Thermodiffractometric Study

The Guinier powder patterns were registered between 20 and 200°C using a high-temperature Guinier–Lenne camera (Nonius FR503G, $\lambda CuK\alpha_1 = 1.54056$ Å, heating rate 10 K/hr). For both compounds the thermodiffractometry experiments have been performed in the following way: the temperature is first raised up to 200°C (heating rate 10 K/hr) and maintained at this level for several hours in order to get the powder pattern of the anhydrous compound. The furnace is then switched off and the powder pattern is registered so as to check the reversibility of the process. The X-ray powder patterns obtained in this way

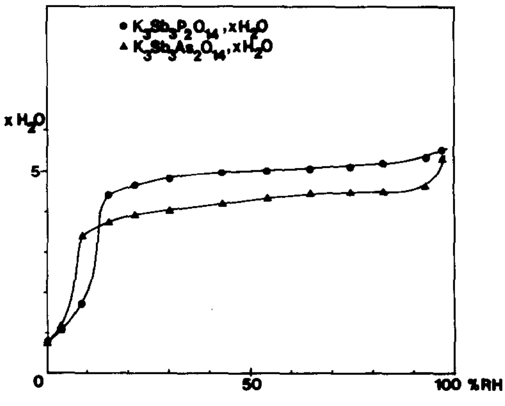

FIG. 1. Adsorption isotherms at 20°C for (●) $K_3Sb_3P_2O_{14}$, xH_2O and (▲) $K_3Sb_3As_2O_{14}$, xH_2O.

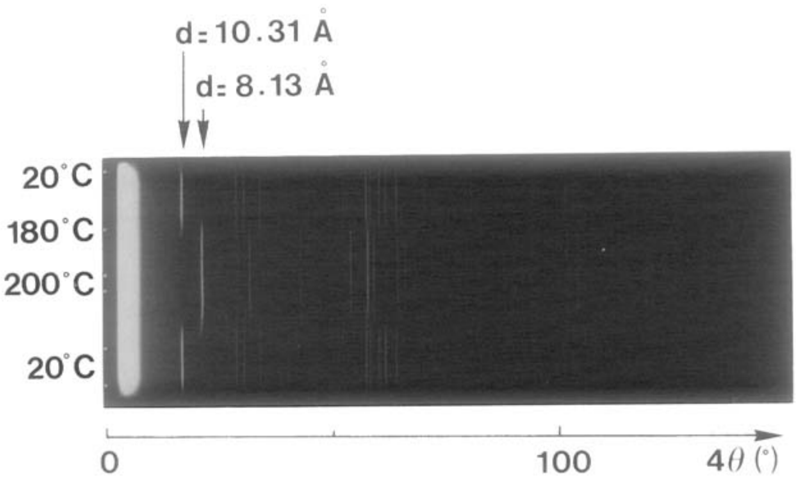

FIG. 2. High-temperature Guinier powder spectra for $K_3Sb_3P_2O_{14}$, xH_2O.

are represented in Fig. 1, for the phosphorus compound (those concerning the arsenic phase are very similar and then not given).

One can observe in Fig. 2 that:

—the dehydration process is reversible;

—the powder spectrum remains the same as long as the dehydration process continues and changes only when reaching the fully dehydrated state.

The cell parameters of the anhydrous phase (Table I) were refined by a least-squares procedure from powder diffraction data collected at 200°C with a Guinier camera. These data indicate a distortion of the rhombohedral lattice. It can be accounted for with a monoclinic unit cell which simply derives from the hexagonal one in the following way:

$$\mathbf{a}_m \simeq -\mathbf{a}_h + \mathbf{b}_h \qquad (a_m \simeq a_h\sqrt{3})$$
$$\mathbf{b}_m \simeq \mathbf{a}_h + \mathbf{b}_h$$
$$\mathbf{c}_m \simeq (\mathbf{a}_h - \mathbf{b}_h - \mathbf{c}_h)/3.$$

Reexamination of the Crystal Structure of $K_3Sb_3P_2O_{14}$

It is clear from the thermal study that as long as, or as soon as, there is some water molecules between the $(Sb_3M_2O_{14}^{3-})_n$ layers the interlayer distance is that of the corresponding fully hydrated phase and the symmetry is rhombohedral. The crystal structure determination reported by us in (*1*) must then be that of a slightly hydrated form of $K_3Sb_3P_2O_{14}$.

Coming back to the final stage of the crystal structure determination, the last difference Fourier map has been examined carefully. The highest peak indicates a small amount of electron density, 1.0 $eÅ^{-3}$, at the middle of the shortest P–O bond and then is of no particular significance. On the other hand the next highest peak, which is 0.9 $eÅ^{-3}$, is situated half-way between the layers and could be due to a partial occupancy of a 18 g position (x, 0, $\frac{1}{2}$, with $x \simeq 0.27$) by oxygen atoms of water molecules. A refinement including the positional parameter, the isotropic temperature factor, and the occupancy of this new oxygen position was undertaken. After three refinement cycles the R index is reduced from 0.033 to 0.029, the R_w index from 0.042 to 0.037, and the occupancy of the 18 g position is stabilized at 0.22(1). The decrease of this R_w value allows us to check the validity of the hypothesis using the Hamilton test. It

TABLE II

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	Occupancy	x	y	z	B (Å^2)
Sb	9e	1	$\frac{1}{2}$	0	0	0.565(7)*
K(1)	6c	0.882(6)	0	0	0.4360 (1)	2.87 (5)*
K(2)	6c	0.618(6)	0	0	0.0522 (3)	4.6 (2)*
P	6c	1	0	0	0.25309(8)	0.79 (2)*
O(1)	18h	1	0.4641(3)	−0.4641(3)	0.3174 (1)	0.99 (5)*
O(2)	18h	1	0.5488(3)	−0.5488(3)	0.0621 (1)	1.05 (4)*
O(3)	6c	1	0	0	0.2050 (3)	1.43 (9)*
O(4)	18g	0.22 (1)	0.275 (5)	0	$\frac{1}{2}$	3.6 (5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0.00258(6)	0.00210(8)	0.00025(1)	0.00210(8)	−0.00001(3)	−0.00002(3)
K(1)	0.0222 (6)	0.0222 (6)	0.00056(3)	0.0222 (6)	0	0
K(2)	0.0125 (7)	0.0125 (7)	0.0026 (1)	0.0125 (7)	0	0
P	0.0043 (3)	0.0043 (3)	0.00027(2)	0.0043 (3)	0	0
O(1)	0.0039 (3)	0.0039 (3)	0.00040(3)	0.0014 (8)	0.0005 (1)	−0.0005 (1)
O(2)	0.0078 (3)	0.0078 (3)	0.00027(3)	0.0106 (8)	−0.0001 (1)	0.0001 (1)
O(3)	0.011 (1)	0.011 (1)	0.00022(5)	0.011 (1)	0	0

Note. Expression for anisotropic temperature factors: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$.

* $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

shows that the result is significant at a level higher than 99.5%. The occupancy of this new oxygen position leads to the following formula: $K_3Sb_3P_2O_{14}$, $1.32(6)H_2O$. Table II presents the final atomic coordinates and thermal parameters. The water content of the crystal studied is small compared with that of the powder and we must assume that the hydration process is much slower for crystals than for a powder.

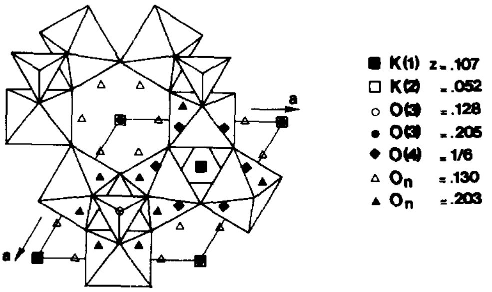

FIG. 3. [001] View of the structure of $K_3Sb_3P_2O_{14}$ showing the oxygen sites of water molecules in the interlayer space. The $(Sb_3P_2O_{14}^{3-})_n$ layer represented is located at $z = 0$.

The new oxygen position O(4) is 2.79(2) Å from K(1) and 2.88(2) Å from O(3) (Fig. 3). Nevertheless, its occupancy cannot be more than 50% since O(4) equivalent sites at the same z level (Fig. 3) are too close to each other (O(4)–O(4) = 1.96(3) Å). According to this restriction, the fully hydrated state should be $K_3Sb_3P_2O_{14}$, $3H_2O$. At this level, the structural study does not allow us to account for the water content inferred from the adsorption isotherm and TG experiments. Consequently, two possibilities are now to be considered:

—When the O(4) site is occupied, there exists in the interlayer space one or several other sites which can accommodate water molecules simultaneously.

—When the water content increases from $1.3H_2O$ per formula unit (as in the

TABLE III

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA

Sb–O(1) × 4	1.944(1)	O(1)–Sb–O(1) × 2	180.0(1)		
–O(2) × 2	2.014(3)	O(1)–Sb–O(1) × 2	87.7(1)		
		O(1)–Sb–O(1) × 2	92.3(1)		
		O(1)–Sb–O(2) × 4	92.8(1)		
		O(1)–Sb–O(2) × 4	87.2(1)		
		O(2)–Sb–O(2)	180.0(1)		
P–O(2) × 3	1.563(2)	O(2)–P –O(2) × 3	107.9(1)		
–O(3)	1.486(6)	O(2)–P –O(3) × 3	111.0(1)		
K(1)–O(1) × 3	3.132(4)	K(1)–O(2) × 3	2.947(2)	K(1)–O(3)	4.202(5)
K(1)–O(4) × 6	2.79 (2)				
K(2)–O(1) × 3	2.748(5)	K(2)–O(2) × 6	3.637(1)	K(2)–O(3)	4.727(5)
K(2)–O(4) × 6	4.40 (2)				
K(1)–K(1)	3.964(6)	K(1)–K(2)	4.411(3)	K(2)–K(2)	3.230(2)
O(1)–O(1)	2.803(3)	O(1)–O(1)	2.695(3)	O(1)–O(2)	2.867(3)
O(1)–O(2)	2.731(3)	O(2)–O(2)	2.527(3)	O(2)–O(3)	2.513(6)
O(3)–O(4)	2.87 (2)				
K(1)–O_n	2.95	K(2)–O_n	2.92	O(2)–O_n	2.92
O(3)–O_n	2.85	O(3)–O_n	2.83	O_n–O_n	2.85

crystal studied) to 5 (as inferred from TG and isotherm studies) the O(4) atom moves toward a new site O_n capable of accounting for the fully hydrated state.

From geometrical considerations it appears that the second possibility is the only reasonable one. A single site O_n can accommodate simultaneously 6 water molecules per formula unit. It is a 36i position, with $x \simeq y \simeq 0.23$ and $z \simeq 0.13$ (Fig. 3); its occupancy cannot be more than 50% because the O_n–O_n distances are too short (Fig. 3). Distances between this site O_n and its neighbors (K(1), K(2), O(2), and O(3)) are given in Table III.

References

1. Y. PIFFARD, A. LACHGAR, AND M. TOURNOUX, *J. Solid State Chem.* **58,** 253 (1985).
2. M. TOURNOUX AND Y. PIFFARD, French Patent 85-01839.
3. Y. PIFFARD, A. VERBAERE, A. LACHGAR, S. DENIARD-COURANT, AND M. TOURNOUX, *Rev. Chim. Miner.* **23,** 1 (1986).