A Structural Explanation for the Polymorphism of the α Form of Anhydrous Vanadyl Phosphate

M. TACHEZ AND F. THEOBALD

Laboratoire de Chimie-Physique, Université de Franche-Comté, 25030 Besançon Cedex, France

AND E. BORDES

Département de Génie Chimique, Université de Technologie de Compiègne, B.P. 233 - 60206 Compiègne Cedex, France

According to the method of preparation of α-VOPO$_4$, the X-ray powder patterns and the cell parameters are different. A structural distinction between α_I- and α_{II}-VOPO$_4$ is proposed which is based on the relative positions of the vanadium and phosphorus atoms: in the case of α_I-VOPO$_4$ (as for α-VOSO$_4$), prepared by dehydration of VOPO$_4 \cdot$ 2 H$_2$O, these atoms are on the same side of the equatorial chain V–O(2)–P–O(2)–V; therefore, its characteristic layered texture is reinforced. In the α_{II} form, these atoms are on alternate sides of that chain.

Two structural forms, α and β, are generally known for the oxysalts $MOXO_4$ (M = V, Nb, Ta, Mo; X = P, As, S, Mo). In the particular case of α-VOPO$_4$, there is some discrepancies between the results obtained by Bordes and Courtine (*1*) and Jordan and Calvo (*2*); since two varieties, called respectively α_I and α_{II}, seem to exist, the purpose of this paper is to present a structural model for the form α_I-VOPO$_4$.

Preparation and X-Ray Diffraction

α_I-VOPO$_4$ has been prepared by Bordes *et al.* by dehydration of VOPO$_4 \cdot$ 2 H$_2$O near 400°C under p_{O_2} = 1 atm (*1*) or by decomposition of NH$_4$ VOOHPO$_4$ at 500°C

(p_{O_2} = 1 atm) (*3*); α_I-VOPO$_4$ transforms into β-VOPO$_4$ at 810°C before melting.

α_{II}-VOPO$_4$ has been synthesized at 850°C by Jordan and Calvo (*2*) from equal molar amounts of P$_2$O$_5$ and V$_2$O$_5$ in a platinum crucible and they determined its crystal structure (a = 6.014(7) Å, c = 4.434(2) Å, space group $P4/n$). Its melting point has been found to be more than 1140°C, and less than 1% V^{4+} species was detected by ESR (*2*). We could obtain the form α_{II} only by dehydration of a mixture made of VOPO$_4 \cdot$ 2 H$_2$O + 1% MoO$_3$ at 580°C (p_{O_2} = 1 atm) or by decomposition of NH$_4$VOOH PO$_4$ at 600°C under nitrogen atmosphere (p_{O_2} = 5 × 10^{-5} atm). Since the presence of V^{4+} has been detected in both preparations

described in this paragraph by diffuse reflectance spectroscopy, this species is assumed to stabilize form α_{II}.

X-Ray diffraction experiments ($CuK\alpha_1$ radiation) have been performed with a Seeman-Bohlin chamber at 18°C and with a diffractometer equipped with a heating chamber (oxygen atmosphere) from 18 to 400°C. The powder pattern of α_I-$VOPO_4$ has been indexed in the space group $P4/n$ with $a = 6.20$ Å and $c = 4.11$ Å (*1*), following the hypothesis that on dehydration the $hk0$ lines are retained. The indexing of the electron diffraction patterns of $VOPO_4 \cdot 2 H_2O$, $VOPO_4 \cdot H_2O$, and α_I-$VOPO_4$ has confirmed that the mean value of a is 6.2 Å instead of 6.014(7) Å in α_{II}-$VOPO_4$.

The X-ray powder pattern of α_{II}-$VOPO_4$, prepared by the method just described, can be indexed satisfactorily with the parameters found by Jordan and Calvo (*2*) (Table I).

Discussion

Since the values of a and c obtained for α_I-$VOPO_4$ are very close from the parameters of α-$VOSO_4$ (*4*) ($a = 6.263$ Å, $c = 4.101$ Å, space group $P4/n$), their structures are assumed to be identical.

On the other hand, the main difference lying between the structure of α-$VOSO_4$ and α_{II}-$VOPO_4$ can be seen by examining the z coordinates for atoms in the chain $O(2)$–V–$O(2)$–X–$O(2)$–V, where $X = P$ or S (Table II) (*2, 4*). The positions of the vanadium and sulfur or phosphorus atoms can be compared with those of the oxygen $O(2)$ atoms in the same sheet; i.e., oxygen atoms

being shared by vanadium coordination octahedra and sulfur or phosphorus coordination tetrahedra. It is seen that in α-$VOSO_4$, the vanadium and sulfur atoms are situated on the same side of the equatorial square of the octahedron (z coordinates for V and S are both smaller than those of $O(2)$), whereas in α_{II}-$VOPO_4$ the vanadium and phosphorus atoms lie on alternate sides of

TABLE I

INDEXATION OF THE X-RAY PATTERN OF α_{II}-$VOPO_4^a$

$I/I_{0\,obs}$	d_{obs} (Å)	hkl	d_{calc} (Å)
20	4.42	001	4.434
15	4.24	110	4.252
94	3.562	101	3.567
85	3.066	111	3.069
100	3.006	200	3.007
37	2.296	211	2.299
25	2.215	002	2.217
33	2.125	220	2.126
40	1.963	112	1.966
55	1.900	310	1.902
60	1.826	301	1.827
52	1.748	311	1.748
22	1.711	212	1.711
40	1.562	321	1.561
45	1.503	400	1.503
61	1.442	312	1.443
5	1.437	330	1.435
12	1.417	330	1.417
30	1.385	411	1.385
48	1.344	420	1.345
10	1.327	203	1.326
25	1.212	223	1.213

Note. $a = 6.014(7)$, $c = 4.434(2)$, $P4/n - C_{4h}^3$ (*2*).

^{a} Seeman–Bohlin chamber, $CuK\alpha$ radiation, quartz as internal standard.

TABLE II

z COORDINATES FOR $VOXO_4$

	$O(2)$	V	$O(2)$	X	$O(2)$	V
α-$VOSO_4$	0.715(3)	0.618(1)	0.715(3)	0.5	0.715(3)	0.618(1)
α_{II}-$VOPO_4$	0.701(2)	0.786(1)	0.701(2)	0.5	0.701(2)	0.786(1)

that square (the z coordinate is larger for V than for O(2) and is smaller for P).

If the z coordinates for O(2) and for P are considered to be unchanged from α_I-VOPO$_4$ to α_{II}-VOPO$_4$, the difference in structure can be attributed to a difference in the position of the vanadium atom inside the octahedron: it is on the same side as the phosphorus atom in α_I and on the other side in α_{II} (Fig. 1). The longest V–O bond increases from 2.53 Å in α_I to 2.85 Å in α_{II}, whereas the edge of the square decreases from 2.65 Å in α_I to 2.52 Å in α_{II}-VOPO$_4$. Furthermore the distance between the vanadium atom and the equatorial plane O(2) is slightly larger in α_{II}-VOPO$_4$ (0.398 Å) than in α-VOSO$_4$ (0.378 Å).

The shift of the vanadium atom from one side of the equatorial plane to the other, the increase of the height of the octahedron (along z) and the shortening of the edge of the equatorial square may be related to the fact that in the structures of all the known
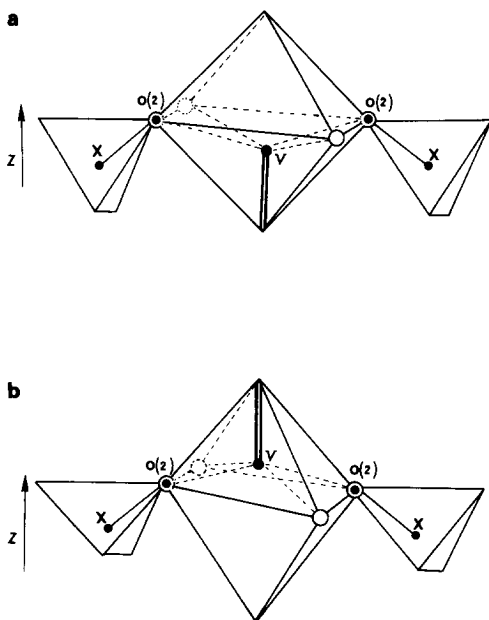
tetragonal structures of MoXO$_4$ oxysalts, the anisotropic thermal factor U_{33} of the M atom is about ten times larger than U_{11}: this means that the vibration amplitude of V atom along z is much larger than in the other directions, so the V atom can change its position inside the octahedron before the arrangement of the octahedron and tetrahedra in the sheets is disturbed. This assumes that the transformation of α_I into α_{II} is a displacive reaction.

Once again it is worth noting the importance of the method of preparation: the α_{II}-VOPO$_4$ type includes the structure of MoOPO$_4$ (5), NbOPO$_4$ (6), VOMoO$_4$ (7), TaOPO$_4$ (8), all of which are prepared by heating a mixture of two oxides at high temperature (and pressure for TaOPO$_4$) in the range 800–1200°C. On the contrary, α-VOSO$_4$ and α_I-VOPO$_4$ are obtained by decomposition at low temperature (below 220°C) of a hydrate that has a structure belonging to the same space group as the product. This is the case for VOPO$_4$ · 2 H$_2$O (1) as well as for VOSO$_4$ · 2 H$_2$O and VOPO$_4$ · 2 D$_2$O (9); consequently it is assumed that the loss of water molecules initially located between the layers of [VOXO$_4$]$_\infty$ type brings simply these layers together without a noticeable disturbance of the lattice. Moreover, the layered texture is significantly reinforced in the case of α_I-VOPO$_4$, where the longest V–O bond length is close to the value 2.78 Å found in V$_2$O$_5$ (10).

FIG. 1. Chain $-$X$-$O(2)$-$V$-$O(2)$-$X$-$: (a) for compounds of the α-VOSO$_4$ type: α_I-VOPO$_4$, VOPO$_4$ · 2 D$_2$O, VOSO$_4$ · 2 H$_2$O; (b) for compounds of the α_{II}-VOPO$_4$ type: MoOPO$_4$, NbOPO$_4$, VOMoO$_4$, TaOPO$_4$.

References

1. E. BORDES, P. COURTINE, ET G. PANNETIER, Ann. Chim. 8, 105 (1973).
2. B. D. JORDAN AND C. CALVO, Can. J. Chem. 51, 2621 (1973).
3. S. PULVIN, E. BORDES, M. RONIS, ET P. COURTINE, J. Chem. Res. (S), 29 (1981); J. Chem. Res. (M), 362 (1981).
4. J. M. LONGO AND R. J. ARNOTT, J. Solid State Chem. 1, 394 (1970).

5. P. KIERKEGAARD AND M. WESTERLUND, *Acta Chem. Scand.* **18,** 2217 (1964).

6. J. M. LONGO AND P. KIERKEGAARD, *Acta Chem. Scand.* **20,** 72 (1966).

7. H. A. EICK AND L. KIHLBORG, *Acta Chem. Scand.* **20,** 722 (1966).

8. J. M. LONGO, J. W. PIERCE, AND J. A. KAFALAS, *Mater. Res. Bull.* **6,** 1157 (1971).

9. M. TACHEZ, F. THEOBALD, AND A. W. HEWAT, submitted for publication.

10. H. G. BACHMANN, F. R. AHMED, AND W. H. BARNES, *Z. Kristallogr.* **115,** 110 (1961).