JOURNAL OF SOLID STATE CHEMISTRY 97, 283–291 (1992)

Synthesis and Crystal Structure of α-$NH_4(VO_2)(HPO_4)$

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Received July 16, 1991

Hydrothermal synthesis starting from β-$NH_4(VO_2)(HPO_4)$ leads to α-$NH_4(VO_2)(HPO_4)$: orthorhombic, space group $Pb2_1a$; $Z = 4$; $a = 6.830(1)$ Å, $b = 9.233(2)$ Å, $c = 8.817(2)$ Å; $R = 0.037$ for 3371 reflections. NH_4^+ cations connect isolated chains of *trans*-corner sharing VO_5 square pyramids running along the *a*-axis. The α-phase transforms irreversibly into the β-form by heating near 200°C. Comparison is made between the two phases.

Introduction

The characterization of any phase in the V–P–O system, catalysts as well as their precursors, is of particular interest owing to the catalytic properties of some oxovanadium phosphates in the maleic anhydride obtainment from C_4 hydrocarbons (*1*, *2*). Advances in the knowledge of the solid state chemistry of some precursors in the V–P–O–H system were recently reviewed (*3*, *4*); the crystal structures of α- and β-$VO_2HPO_4 \cdot 2H_2O$ (*5*, *6*) were determined ab initio from X-ray powder data. Another precursor of the $(VO)_2P_2O_7$ active catalyst is β-$NH_4(VO_2)(HPO_4)$, as shown by Pulvin *et al.* (*7*, *8*); this compound belongs to a family of salts having the general formulation $A(VO_2)(HPO_4)$ ($A = NH_4^+$, K^+, Rb^+, and Cs^+) earlier reported by Preuss and Schug (*9*). We recently reported the crystal structure determination of these salts from X-ray powder data (*10*). The presence of the monohydrogenophosphate group was in fact established at this occasion, since it was previously reported as $A(VOOH)(PO_4)$ (*7*) or $AHVPO_6$ (*9*); its structure (space group $Pbca, Z = 8, a = 6.8064(6)$ Å, $b = 9.2567(7)$ Å, and $c = 17.732(2)$ Å when $A = NH_4^+$) is built up from isolated infinite chains of *trans*-corner sharing VO_5 square pyramids running along the *a*-axis.

We report here on the synthesis and the structure determination, from single crystal X-ray diffraction data, of a new polymorph: α-$NH_4(VO_2)(HPO_4)$.

Experimental

A 1.3-*M* solution of β-$NH_4(VO_2)(HPO_4)$, synthesized as described in (*9*), was evaporated to a smaller volume until incipient

0022-4596/92 $3.00

cloudiness. A 15-cm^3 portion of this suspension was introduced in a hermetic teflon jar placed in a metallic container (PARR bomb) and heated at 200°C for 24 hr. The apparatus was allowed to cool down to room temperature for 48 hr. The resulting yellow crystals were filtered out and washed with small portions of acetone.

The transition α-β-$NH_4(VO_2)(HPO_4)$ was characterized by a DSC experiment (DS2 Perkin–Elmer) realized under a flowing N_2 atmosphere. A crucible containing 4.30 mg of α-$NH_4(VO_2)(HPO_4)$ crystals was heated at 20°C min^{-1} up to 560°C. The differentiation of the phases (from several DSC stopped at the desired temperature) was realized by powder X-ray diffractometry (Siemens D501). The DSC curve presented two endothermic effects: one in the temperature ranges 186–213°C and the other in 294–395°C. The first peak (3.11 cal g^{-1}) was attributed to the α–β irreversible transition and the second one to the elimination of NH_3. After cooling from 560°C to room temperature, the material was amorphous. The $\alpha \rightarrow \beta$ transition also can be induced under mechanical pressure ($\geq$2 Ton cm^{-2}).

Structure Determination

A small yellow platelet limited by 100/010/001 faces was selected for the structure determination. The data were collected on a Siemens AED2 four-circle diffractometer. Table I gathers the conditions of the experiment. The cell parameters were refined from 28 reflections well distributed in the reciprocal space at $\approx$30°2θ. The observed conditions limiting possible reflections were consistent with the *Pbma* and $Pb2_1a$ space groups (this non-standard representation was chosen in order to facilitate the comparison with β-$NH_4(VO_2)(HPO_4)$ which is described using the *Pbca* space group). All the calculations were made with the SHELX-76 program (*11*); atomic scattering factors and anomalous dispersion correction were taken from the International Tables for X-Ray Crystallography (*12*). The *E* statistic was clearly in favor of the acentric $Pb2_1a$ space group ($\langle E^2-1\rangle = 0.746$), however, we first tried to solve the structure using the centric *Pbma* space group. A starting set of atomic coordinates with V and P on 4*d* sites was obtained from the direct methods. Successive refinements and Fourier difference syntheses did not allow us to complete a fully credible structure model: some interatomic distances and thermal motions were unrealistic, the minimal *R*-factor was 0.17. Refinements using the $Pb2_1a$ space group converged well, starting from the previous set of positions. With all V, P, N, and O atoms, the *R*-factor decreased to 0.084 in the isotropic thermal motion approximation (36 parameters refined). Refinements with anisotropic thermal motion lead to the residual $R = 0.040$. At this stage, five independent hydrogen atoms on general position were located from a $\sin \theta_{max} = 0.4$ limited Fourier difference synthesis. Refinements of their coordinates together with a common isotropic *B*-factor lead to the final residuals listed Table I. Refinements after changing all *y* coordinates into $-y$ lead to $R = 0.046$, $R_w = 0.053$, confirming the absolute configuration choice. α-$NH_4(VO_2)(HPO_4)$ really shows an important deviation from a centrosymmetric description in the *Pbma* space group, since it would have required at least V and P atoms to be on the special position 4*d* with the same $y = \frac{1}{4}$ coordinate.

The atomic coordinates and thermal parameters are gathered in Table II; selected bond lengths and angles are listed in Table III. The list of structure factors may be obtained on request to the authors.

Description of the Structure and Discussion

The structure of α-$NH_4(VO_2)(HPO_4)$ is built up from VO_5 square pyramids linked by *trans*-vertices through the O(1) atoms, in

TABLE I

CRYSTALLOGRAPHIC DATA FOR α-$NH_4(VO_2)(HPO_4)$

Formula weight	196.96
Space group	$Pb2_1a$
Z	4
Calculated density	2.353
Radiation	Mo$K\alpha$
Monochromator	graphite
μ (cm^{-1}), Mo$K\alpha$	19.7
Crystal size (mm)	0.120 × 0.247 × 0.027
Lattice constants	$a(Å) = 6.830(1)$
	$b(Å) = 9.233(2)$
	$c(Å) = 8.817(2)$
	$V(Å^3) = 556.01$
Scan type	$w - 2\theta$
T	20°C
Angular range (°2θ)	4.4 − 90.0
Learn profile data collection	
Isotropic line width $w = (A + B\mathrm{tg}\theta)°$	$A = 0.76$
	$B = 0.33$
Maximum h, k, l	13, 18, 17
Data examined	8068
Unique reflections ($m2m$)	4342
R average	0.031
Merged data retained $I > 3\sigma_{(I)}$	3371
Absorption correction	Gauss method
Min. and Max. transmission factors	0.779, 0.932
No extinction correction	
Weighting scheme	$w = 1.1/[\sigma^2(\lvert F_o\rvert) + 0.0020F_o^2]$
Discrepancy factors	$R = 0.037$, $R_w = 0.044$
Parameters refined	97
Max. Shift/esd	0.001
Max. and Min. electron density in final Fourier difference map	1.40, −0.97 $eÅ^{-3}$

order to form infinite isolated chains running along the a-axis. The PO_4 tetrahedra alternate along the chain and link to the remaining *trans*-vertices of the pyramids (namely O(2), O(3)). Figure 1 shows that two $[(VO_2)(HPO_4)]_n^{n-}$ chains are stacked along the b-axis in such a way that the free apices (O(5) oxygen atoms) of the square pyramids, which are always pointing in the same b-direction, would build VO_6 octahedron by completion of the square pyramids of the next chain. The resulting V–O(5) distance (3.110 Å) is too long to be considered as representative of a normal bond, however, the topology is consequently near that of isolated perovskite planes parallel to the ab-plane. One may consider that α-$NH_4(VO_2)(HPO_4)$ presents a superstructure since, without the opposite tilting which differentiates two adjacent chains stacked on the ac-plane, the b-axis would have been divided by a factor 2. The NH_4^+ ion links the chains by a clear hydrogen bonding scheme. Two hydrogen atoms fix the NH_4^+ ion to one given chain through H(4)· · ·O(1) and H(1)· · ·O(6) bonds; the two remaining hydrogen atoms are connected to two other different chains: one neighboring chain in

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS ($U_{ij} \times 10^4$)[a] FOR α-$NH_4(VO_2)(HPO_4)$, e.s.d. IN PARENTHESES

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}(Å^2) or B
V	0.02856(4)	0	0.51851(3)	91(1)	191(1)	120(1)	8(1)	1(1)	0(1)	1.06(1)
P	0.31578(7)	0.06376(7)	0.80033(5)	117(2)	160(2)	109(1)	−13(2)	0(1)	−7(2)	1.02(1)
N	0.7796(4)	0.2582(3)	0.8059(3)	257(9)	263(9)	219(8)	−39(7)	33(7)	−51(8)	1.94(7)
O(1)	0.2944(2)	0.0538(2)	0.4470(2)	108(4)	304(8)	151(5)	42(6)	3(4)	2(5)	1.48(4)
O(2)	0.4845(2)	0.0085(2)	0.7000(2)	149(5)	279(7)	130(4)	−7(7)	10(4)	56(6)	1.47(4)
O(3)	0.1256(2)	0.0763(3)	0.7077(2)	128(5)	420(9)	163(5)	−53(7)	−15(4)	41(6)	1.87(5)
O(4)	0.2842(3)	0.9486(2)	0.9282(2)	316(9)	242(7)	180(6)	42(6)	7(6)	−99(7)	1.94(6)
O(5)	0.0320(4)	0.8288(3)	0.5418(3)	322(9)	214(7)	302(9)	63(7)	10(7)	37(7)	2.20(7)
O(6)	0.3712(3)	0.2026(2)	0.8785(2)	235(7)	167(6)	229(7)	−43(5)	−29(6)	0(5)	1.66(5)
H(1)	0.650(9)	0.259(6)	0.808(7)	379(68)						3.0(5)
H(2)	0.824(9)	0.226(7)	0.908(7)	379(68)						3.0(5)
H(3)	0.836(9)	0.327(7)	0.781(7)	379(68)						3.0(5)
H(4)	0.793(9)	0.211(7)	0.722(7)	379(68)						3.0(5)
H(5)	0.241(9)	0.866(7)	0.912(6)	379(68)						3.0(5)

[a] Vibrational U_{ij} coefficients relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12})]$.

the *b*-direction through H(3)· · ·O(2) and one neighboring chain in the *c*-direction through H(2)· · ·O(6). The H(5) hydrogen atom of the HPO_4 group also links two chains by connecting two neighboring PO_4 tetrahedra in the *b*-direction through P–O(4)–H(5)· · ·O(6)–P bond. The terminal O(6) oxygen atom of the HPO_4 group is consequently involved in three hydrogen bonds.

A valence bond analysis (Table IV) is in agreement with the proposed hydrogen bonding scheme. The analysis was carried out using the Zachariasen law for the V–O and P–O bonds ($s = \exp[(R_0 - R)/B]$ with $R_0 = 1.62$, $B = 0.36$ for P, and $R_0 = 1.79$, $B = 0.319$ for V (*13*)); owing to the large uncertainty in the observed N–H and O–H distances, we attributed, somewhat arbitrarily, 0.75 valence units (v.u.) to N–H and O–H bonds and 0.25 v.u. to H· · ·O bonds. From the results presented Table IV, one must conclude that the repartition of the 1^+ charge of NH_4 ions through the four H· · ·O bonds, each corresponding to 0.25 v.u., is a very imperfect model: in fact, the three different oxygen atoms contributing to O· · ·H–N bonds (namely O(1), O(2), O(6)) show all an excess of nearly 0.1 v.u.; at variance the O(3), O(4) and O(5) oxygen atoms, which may be considered as belonging to the NH_4 coordination sphere (see distances Table III), show a nearly 0.1 v.u. deficit. Nevertheless, the V and P calculated valences match fairly well the expected values of 5 v.u. in both cases; this allows us to confirm that V–O and P–O distances are quite normal in this structure.

The occurence of two very short V–O distances (1.594 and 1.702 Å) must be emphasized, although this is not uncommon for V^{5+} in square pyramid coordination (for instance in V_2O_5 (*14*), the V–O distances are 1.577, 1.779, 1.878 × 2, and 2.017 Å). The shortest V–O distance is characteristic of the double V=O bond; the other short distance corresponds to the connection between two VO_5 pyramids. Very similar results were observed in the case of β-$NH_4(VO_2)(HPO_4)$ (*10*), in spite of the medium accuracy which characterizes its structure determined and refined from X-ray powder data.

The structural relationship between α- and β-$NH_4(VO_2)(HPO_4)$ becomes obvious when Fig. 2 is compared to Fig. 1. One can see that the fundamental building block, defined by the whole $[(VO_2)(HPO_4)]_n^{n-}$ infinite chain, is common to the two phases. The

TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR α-$NH_4(VO_2)(HPO_4)$, e.s.d. IN PARENTHESES

V Square pyramid ⟨V–O⟩ = 1.832

V	O(5)	O(1)	O(3)	O(2)	O(1)
O(5)	**1.594(2)**	2.638(3)	2.788(2)	2.721(2)	2.868(2)
O(1)	106.3(2)	**1.702(1)**	2.650(2)	2.615(2)	3.541(2)
O(3)	104.2(2)	93.5(1)	**1.928(1)**	3.774(3)	2.580(2)
O(2)	99.7(2)	91.1(2)	153.2(2)	**1.952(1)**	2.517(2)
O(1)	106.0(2)	147.5(1)	82.5(2)	79.5(1)	**1.985(1)**

P Tetrahedron ⟨P–O⟩ = 1.537

P	O(6)	O(3)	O(2)	O(4)
O(6)	**1.504(2)**	2.538(2)	2.507(1)	2.459(2)
O(3)	113.1(2)	**1.539(1)**	2.531(2)	2.519(2)
O(2)	110.9(1)	110.6(2)	**1.540(1)**	2.495(2)
O(4)	106.5(2)	108.5(2)	107.0(2)	**1.565(1)**

N Tetrahedron ⟨N–H⟩ = 0.880

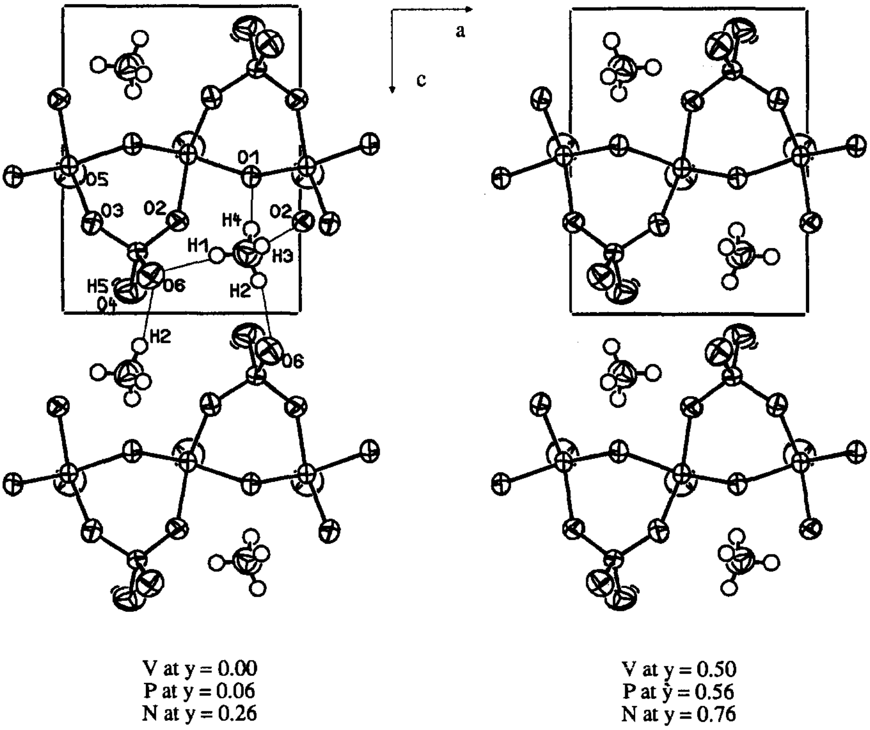
N	H(3)	H(4)	H(1)	H(2)
H(3)	**0.77(6)**	1.23(8)	1.44(8)	1.46(6)
H(4)	97(9)	**0.86(6)**	1.31(8)	1.66(9)
H(1)	120(9)	97(9)	**0.88(6)**	1.51(8)
H(2)	110(9)	126(9)	107(9)	**0.99(6)**

Hydrogen bonding scheme

O/N–H···O	O/N–H	H···O	O/N–H···O	O/N–O
O(4)–H(5)···O(6)	0.83(6)	1.72(6)	174(7)	2.545(2)
N–H(1)···O(6)	0.88(6)	2.07(6)	157(6)	2.908(3)
N–H(2)···O(6)	0.99(6)	2.09(5)	166(6)	2.898(3)
N–H(3)···O(2)	0.77(6)	2.20(6)	175(6)	2.968(3)
N–H(4)···O(1)	0.86(6)	2.08(6)	165(6)	2.923(3)

N–O Distances

N–O(6)	2.898(3)
N–O(6)	2.908(3)
N–O(1)	2.923(3)
N–O(4)	2.963(3)
N–O(2)	2.968(3)
N–O(3)	3.026(3)
N–O(2)	3.202(3)
N–O(5)	3.221(4)
N–O(5)	3.388(4)



V at y = 0.00
P at y = 0.06
N at y = 0.26

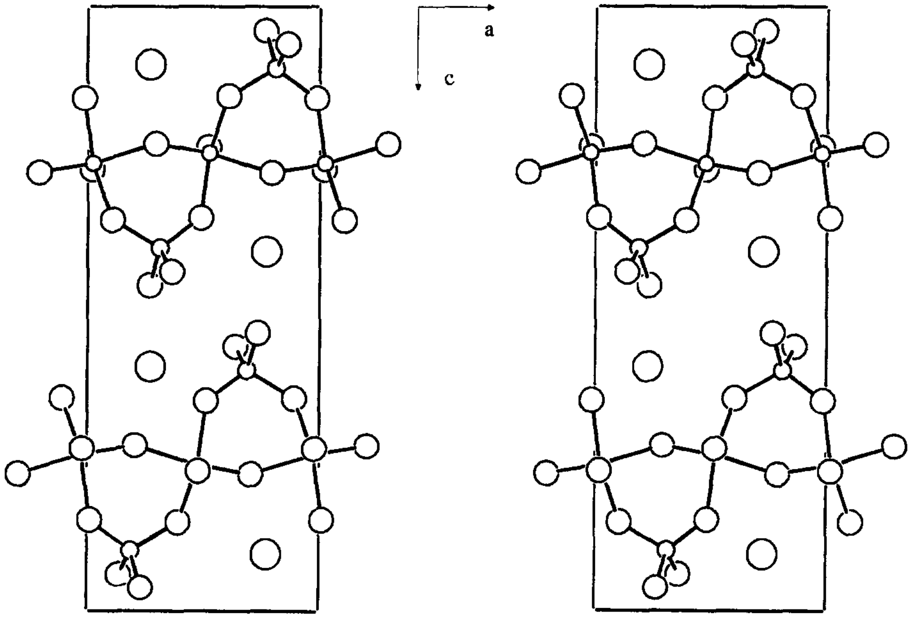
V at y = 0.50
P at y = 0.56
N at y = 0.76

FIG. 1. Projections along *b* of α-$NH_4(VO_2)(HPO_4)$. The hydrogen bonding scheme is shown on the left part of the figure. The O(4)–H(5)· · ·O(6) are almost superimposed and bonds are not marked. Note that the free apices (O(5)) of the VO_5 square pyramids are all situated behind the vanadium atoms. ORTEP drawing (*15*), ellipsoids scaled to include 90% probability, thermal motion of H atoms reduced by a factor of 10.

TABLE IV

VALENCE BOND ANALYSIS FOR α-$NH_4(VO_2)(HPO_4)$

	V	P	H(1)	H(2)	H(3)	H(4)	H(5)	Σ
O(1)	1.32 0.54					0.25		2.11
O(2)	0.60	1.25			0.25			2.10
O(3)	0.65	1.25						1.90
O(4)		1.17					0.75	1.92
O(5)	1.85							1.85
O(6)		1.38	0.25	0.25			0.25	2.13
N			0.75	0.75	0.75	0.75		3.00
Σ	4.96	5.05	1.00	1.00	1.00	1.00	1.00	



V at y = ±0.54
P at y = ±0.60
N at y = ±0.19

V at y = ±0.04
P at y = ±0.10
N at y = ±0.31

FIG. 2. Projections along b of β-$NH_4(VO_2)(HPO_4)$. Note that the free apices of the VO_5 square pyramids are situated behind the vanadium atoms for $0 < z < \frac{1}{2}$ and the contrary for $\frac{1}{2} < z < 1$. ORTEP drawing (*15*).

stacking of the chains along the b-axis is also identical: the main difference is that the c-axis is doubled in the β-phase where the chains at $z \approx \frac{1}{4}$ show significantly different y-coordinates than those at $z \approx \frac{3}{4}$ (the shift is $\Delta y \approx 0.1$); moreover, the apex of the VO_5 pyramids at $z \approx \frac{1}{4}$ and $z \approx \frac{3}{4}$ point toward opposite directions along the b-axis due to the presence of an inversion center. Hydrogen atoms could not be located in the β-phase, but from the fact that the cell of the β-phase is built up from two cells of the α-phase stacked along the c-axis and related by an inversion center, it can be proposed that the hydrogen bonding scheme of the two phases is the same with the exception of the unique hydrogen bond along the c-axis (H(2)· · ·O(6) in the α-phase). Such similitudes suggest that the $\alpha \rightarrow \beta$ transition mechanism is topotactic. In this hypothesis, the reorganization could be realized by a shear, parallel to the ab-plane, of α-blocks of infinite size along a_α and b_α and of thickness equal to the c_α-axis. The displacement of each block is quite small: approximately 0.4 Å in opposite direction along the b_α-axis; however, in half such blocks, the double bond V = O(5) must be formally broken and reinstalled in the opposite direction along the b_α-axis. This operation consists in a weak displacement of O(5') and a shift of the vanadium atom from one side of the equatorial plane to the other. Crystallographically, there is no objection to such a topotactic transitional model: the $Pb2_1a$ space group of the α-phase belongs to the maximal non-isomorphic subgroups of the $Pbca$ space group of the β-phase. The main

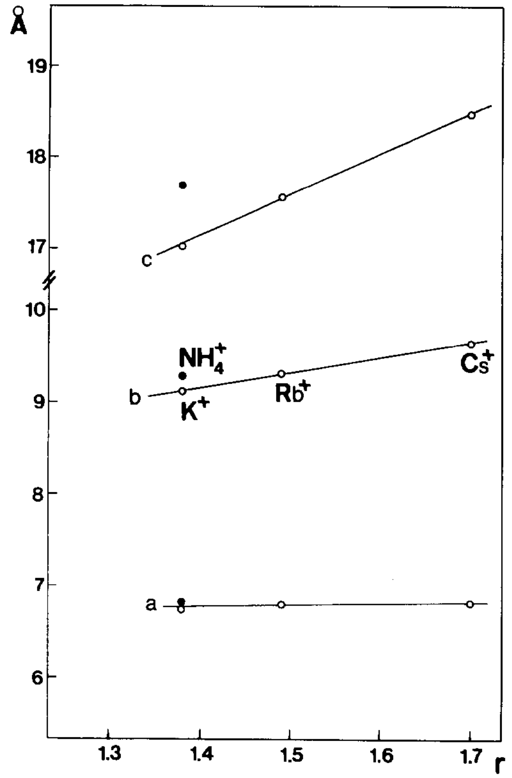


FIG. 3. Cell parameters vs ionic radii plot for the β-$A(VO_2)(HPO_4)$ (A^+ = NH_4^+, K^+, Rb^+, Cs^+) compounds (*r*: ionic radii for sixfold coordination).

difference between the α_I- and α_{II}-$VOPO_4$ forms (*16*) is due to such shifts of the vanadium atoms, however, no phase transition has been pointed out.

Conclusion

The non-existence of either sodium and lithium compounds with the stoichiometry $A(VO_2)(HPO_4)$ (A^+ = Na^+, Li^+) or alkaline compounds showing the α-$NH_4(VO_2)(HPO_4)$ structure-type can be now explained in the light of the structural analysis of the two ammonium polymorphs.

Only the NH_4^+ cation shows the two polymorphic (α and β) varieties of the $A(VO_2)(HPO_4)$ salts. The structure of both polymorphs is well described as formed by polymerization of *cis*-VO_2^+ units by μ-(O, O')–[$HOPO_3$] groups. The differences are due to the different packing between these chains and the NH_4^+ cations. It seems that the capability of the NH_4^+ ions to form such a similar network of directed bonds through its hydrogen atoms allows the existence of both α- and β-phases. This indirectly would justify the failure in the preparation of the α-phase in the case of such spherical cations as K^+, Rb^+, and Cs^+.

Electrostatic interactions involving nonspheric cations such as the ammonium are less effective in order to give close-packed lattices. In fact, the cell volume of β-polymorphs with spherical cations of similar ionic radius as K^+ or even larger than NH_4^+ as Rb^+ are significantly smaller than the cell volume measured for β-$NH_4(VO_2)(HPO_4)$.

On the other hand, failure in the prepara-

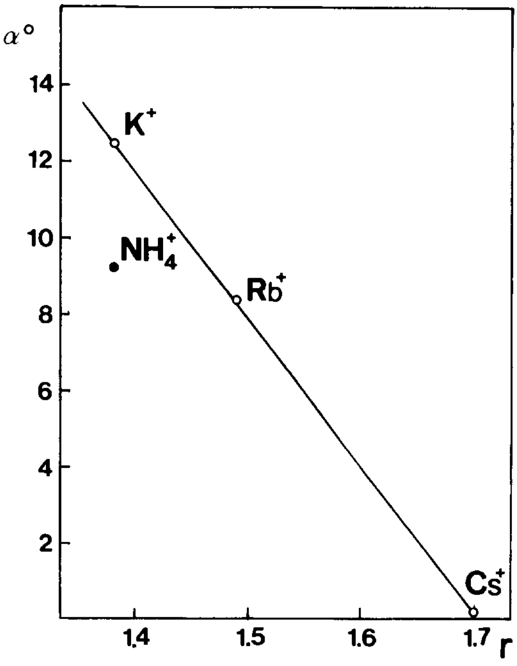


FIG. 4. Variation of the tilting angle in the β-phases vs the ionic radii.

tion of both β- and α-phases of lighter alkaline metals can be easily explained from the structural data. Thus from Figs. 3 and 4, a good correlation is found between cell parameters or tilting angle (observed between the medium planes defined by the four basal oxygen atoms of the VO_5 pyramids) and the ionic radii (*17*) of alkaline cations in the β-phases. Extrapolation down smaller cations such as Na^+ would imply very strong repulsion among chains resulting in a compression of approximately 0.30 and 0.75 Å in the [010] and [001] directions, respectively, and very distorted topology of the bridging HPO_4 groups due to the higher expected value of the tilting angle (26.6°).

Acknowledgments

The authors are very indebted to Dr. M. Leblanc (Université du Maine) for the X-ray data collection and Dr. D. Beltran (Universitat de Valencia) for helpful discussion.

References

1. G. Centi, F. Trifiro, J. R. Ebner, and V. M. Franchetti, *Chem. Rev.* **88,** 55 (1988).

2. B. L. Hodnett, *Catal. Rev. Sci. Eng.* **27,** 373 (1985).

3. D. Beltran, P. Amoros, R. Ibanez, E. Martinez, A. Beltran, A. Le Bail, G. Ferey, and G. Villeneuve, *Solid State Ionics* **32/33,** 57 (1989).

4. D. Beltran, A. Beltran, P. Amoros, R. Ibanez, E. Martinez, A. Le Bail, G. Ferey, and G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* **28,** 131 (1991).

5. A. Le Bail, G. Ferey, P. Amoros, and D. Beltran, *Eur. J. Solid State Inorg. Chem.* **26,** 419 (1989).

6. A. Le Bail, G. Ferey, P. Amoros, D. Beltran, and G. Villeneuve, *J. Solid State Chem.* **79,** 169 (1989).

7. S. Pulvin, E. Bordes, M. Ronis, and P. Courtine, *J. Chem. Res. Miniprint*, 362 (1981).

8. S. Pulvin, E. Bordes, M. Ronis, and P. Courtine, *J. Chem. Res. Synop.*, 362 (1981).

9. F. Preuss and H. Schug, *Z. Naturforsch B: Anorg. Chem. Org. Chem.* **30,** 334 (1975).

10. P. Amoros, D. Beltran, A. Le Bail, G. Ferey, and G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* **25,** 599 (1988).

11. G. M. Sheldrick, SHELX76, A Program for Crystal Structure Determination, Univ. of Cambridge, England (1976).

12. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, (1974).

13. I. D. Brown, *in* "Structure and Bonding in Crystals" (M. O'Keefe and A. Navrotsky, Eds.), Vol. 2, p. 1, Academic Press, New York (1981).

14. R. Enjalbert and J. Galy, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **42,** 1467 (1986).

15. C. K. Johnson, Ortep, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1965).

16. M. Tachez, F. Theobald, and E. Bordes, *J. Solid State Chem.* **40,** 280 (1981).

17. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25,** 925 (1969).