are therefore totally different.

The ν_1 symmetrical stretching frequencies of the linear O=M=O group observed for sodium actinide(V) carbonate solid compounds decrease linearly with the increase in the atomic number, but surprisingly these frequencies are higher than those corresponding to the aqueous MO_2^+ ion (ν_1 for NpO_2^+(aq) and AmO_2^+(aq) are the only data available). These results can be compared with the IR spectra of certain neptunium solid compounds published in the literature. Vodovatov et al.[36c] showed that the value of the ν_3 asymmetrical stretch of NpO_2^+ depends on the number of water molecules present in the solid compounds studied; for example, ν_3 is found to be 727 cm^{-1} for $NpO_2ClO_4(H_2O)_3$ and 795 cm^{-1} for anhydrous $KNpO_2CO_3$. Vodovatov et al.[36c] explained these results by a possible hydrogen bond between the oxygen of NpO_2^+ and water molecules. Thus, the position of the ν_1 band of MO_2^+ for a given actinide(V) depends not only on the nature and number of ligands present in the equatorial plane of the ion but also on a possible hydrogen bond between water

molecules and the oxygen of the actinyl. This interpretation may also explain the behavior of actinide(V) solutions in acidic noncomplexing and carbonate media. Additional Raman data on the complexation of actinide(V) ions by different ligands may provide for a better understanding of the identity of these species in aqueous solutions.

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Intercalation into NbOPO4·3H2O and Comparison with VOPO4·2H2O

K. BENEKE and G. LAGALY*

Hydrated niobium phosphate, NbOPO4·3H2O (basal spacing 8.04 Å), is a layered host compound with {NbO(H2O)PO4} layers. It intercalates different types of guest molecules, in particular, different types of amines. Long-chain alkylamines $C_nH_{2n+1}NH_2$ form bilayers with a chain orientation of 60° ($n \leq 10$) or 90° ($n > 10$). Many guest molecules suitable for layered host structures (Me2SO, FA, NMFA, ethylene glycol, etc.) are not intercalated. They dehydrate NbOPO4·3H2O to the monohydrate (basal spacing 6.17 Å) or to interstratified structures with spacings between 6.17 and 8.04 Å. VOPO4·2H2O (basal spacing 7.41 Å) is more reactive than NbOPO4·3H2O. Both phosphates intercalate phosphoric and sulfuric acid. The dehydration of NbOPO4·3H2O to NbOPO4·H2O is reversible. VOPO4·2H2O is reversibly dehydrated to VOPO4·H2O (basal spacing 6.3 Å) and even to VOPO4 ("basal spacing" 4.1 Å); in water the lattice expands to 10.5 Å (about VOPO4·5H2O). The transition between the different forms is distinctly sharper than for niobium phosphate. A new hydrated niobium phosphate with stoichiometry Nb2O5·1.5P2O5·5.9H2O probably contains {Nb2(OH)2(HPO4)(PO4)2} layers and is more reactive than NbOPO4·3H2O. In particular, it should be mentioned that alkanol molecules are intercalated with ease.

Introduction

Niobium phosphate forms an anhydrous compound, NbOPO4, and two hydrates, NbOPO4·H2O and NbOPO4·3H2O.[1–3] A layer structure is proposed for the hydrates and is deduced from NbOPO4 by cleaving the three-dimensional network of [NbO6] octahedra and [PO4] tetrahedra perpendicular to the *c* axis. The vacancies in the coordination environment of Nb are filled by H2O molecules. The puckered layers {NbO(H2O)PO4} thus formed consist of [NbO6] octahedra connected in the equatorial planes by [PO4] tetrahedra. The layers are electrically neutral and are held together by hydrogen bonds (Figure 1; note that the schematic representation of the structure in ref 4 is misleading). In the monohydrate all water molecules belong to the distorted octahedra around Nb. In the fully hydrated form additional water molecules (about four per unit cell) are enclosed between the layers.

Chernorukov et al.[3] mentioned a "one-dimensional intracrystalline swelling by inclusion of neutral molecules" but reported no details. Later, Chernorukov et al.[5] described the formation of NbOPO4·2H3PO4·5H2O (basal spacing 11.2 Å) by inserting H3PO4 and water molecules between the layers during the synthesis.

Experimental Section

Preparation of Niobium Phosphates. For the procedure described by Chernorukov et al.[3] different products were obtained. They often had admixtures of phases with basal spacings of 10–11 Å (=NbOPO4·2H3PO4·5H2O or interstratified products).

We prepared NbOPO4·3H2O by dissolving 5 g of metallic niobium in a mixture of 50 mL of hydrofluoric acid (40%) and 5 mL of concentrated nitric acid. Then, 50 g of H3PO4 (85%) was added. The clear solution was heated on the water bath until a crystalline product precipitated, which was filtered off and resuspended in 200 mL of 5 M HNO3. After filtration, the product was washed with 100 mL of water and 100 mL ethanol and air-dried.

For the preparation of NbOPO4·2H3PO4·5H2O it should be noted that, as water removes the interlayer H3PO4, the washing procedure

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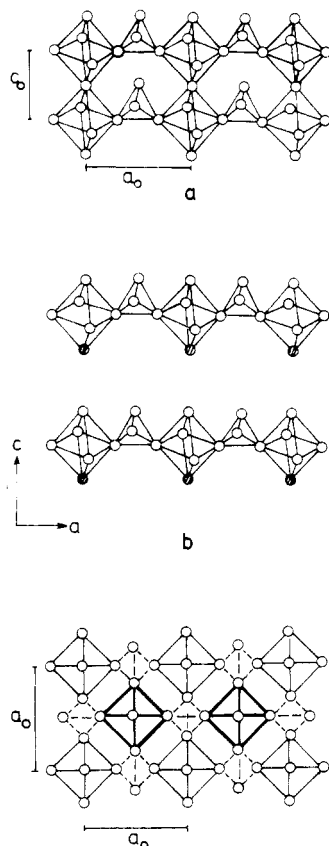
Figure 1. {NbOPO$_4$} layers in NbOPO$_4$ (a,c) and {NbO(H$_2$O)PO$_4$} layers in NbOPO$_4$·H$_2$O (b), (shown schematically; the [NbO$_6$] octahedra and [PO$_4$] tetrahedra in NbOPO$_4$ are distorted): (O) oxygen; (●) water. Nb and P are not shown.

decisively affects the reproducibility. Thus, suspending the precipitates in no more than 40 mL of water/g of starting metallic Nb and air-drying after filtration gives NbOPO$_4$·2H$_3$PO$_4$·5H$_2$O with basal spacings of 11–11.2 Å. Using this procedure instead of the method of Chernorukov et al.,[5] we obtained reproducible results.

The hydrated niobium phosphate with stoichiometry Nb$_2$O$_5$·1.5P$_2$O$_5$·5.9H$_2$O was obtained by a two-step procedure. A 30-g quantity of niobium metal was dissolved in hydrofluoric acid (40%) in the presence of nitric acid. To the clear solution was added 300 g of phosphoric acid (85%). One-third of this solution was heated on a water bath until a fine crystalline material began to precipitate. Immediately the remaining two-thirds of the solution was added and again heated on the water bath. A fine white crystalline material precipitated and was washed with 100 mL of 5 M HNO$_3$, 200 mL of water, and 100 mL of ethanol and air-dried.

VOPO$_4$·2H$_2$O was prepared by the method of Ladwig.[6]

Characterization of the Products. The chemical composition was determined by the precipitation of niobium as the cupferron complex and by calorimetric analysis of phosphorus as the molybdophosphate.

The basal spacings of the phosphates were measured under different conditions: after air-drying, after drying under high vacuum or over P$_4$O$_{10}$, in contact with water, after rehydration of the dried samples, etc.

Thermal dehydration was studied by heating 100-mg samples from 65 to 1000 °C. The isothermal changes of the water content were studied by equilibrating 100-mg samples over standard solutions for humidity control at 25 °C. In both cases the changes were also followed by basal spacing measurements.

Debye–Scherrer cameras with diameters of 11.46 cm (Cu Kα radiation) were used for all X-ray investigations.

Intercalation. Small amounts of the niobium phosphates were placed in contact with various organic compounds (e.g., formamide, dimethyl sulfoxide, glycol, glycerol, alkanols, and alkyl- and arylamines) for 1 day and, if they did not react, for more days up to several months at 65 °C and then X-rayed in the presence of the organic compounds.

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Table I. Lattice Expansion of NbOPO$_4$·3H$_2$O by Butylamines and Some Other Amines

amine	basal spacing, Å
butylamine	17.1
di-*n*-butylamine	21.6
2-aminobutane	22.0
(3-methylbutyl)amine	19.0
methylbutylamine	22.4
methyl-*sec*-butylamine	21.3
methyl-isobutylamine	22.1
dimethylbutylamine	21.7
4-amino-2-butanol	6.2
ephedrine	24.8
cyclohexylamine	14.7
piperazine	7.8
aniline	26.0
pyridine	7.0

The long-chain alkanols and alkylamines were obtained from Fluka, Switzerland, in "purissimum" or "purum" quality.

The intercalation products were characterized by their basal spacings. In general, only the low-order basal reflections, in particular the intense (001) and the (002) reflections, could be observed. Any interstratification is therefore difficult to detect. However, the powder patterns of the complexes with long-chain alkanols and alkylamines show rational series of basal reflections, and the absence of interstratification could be clearly established.

As usual, the ratio guest molecules/host compound could not be obtained with high reliability because the niobium phosphate desorbs the intercalated molecules if the adhering excess of guest compounds is removed. The alkylamine complexes are relatively stable, and the adherent excess of amine could be largely removed by small amounts of ethanol. A slight decrease of the basal spacings (≤2 Å), however, indicated some alkylamine to be removed from the interlayer region. The approximate composition was obtained from C and N combustion analyses.

Results and Discussion

Intercalation of Short-Chain Amines. The lattice constants, in particular the value of c_0, change if hydrated niobium phosphate is reacted with several organic compounds. The variation specifies an intracrystalline reactivity with remarkable particularities. The reactivity is not as pronounced as for zirconium phosphate, H$_2$Zr(PO$_4$)$_2$·H$_2$O[7,8] or the highly condensed crystalline silicic acids.[9] Like HMnAsO$_4$·H$_2$O[10] hydrated niobium phosphate preferentially intercalates amines. The spacings can be much increased even by relatively small molecules such as aniline and ephedrine (Table I). After intercalation of aniline the spacings exceed those for bilayer arrangements. The aniline molecules are aggregated to multilayers. Multilayer formation is seldom observed in intercalation chemistry and reveals strong intermolecular interactions by forming distinct liquid structures.[11,12] The lattice collapses to 14.7 Å if aniline is displaced by cyclohexylamine.

Intercalation of Long-Chain Alkylamines. A large lattice expansion characterizes the intercalation of long-chain alkylamines. The composition approximately is 1.5C$_n$H$_{2n+1}$NH$_2$/NbO(H$_2$O)PO$_4$ ($n \leq 10$). The spacings d_L in the presence of alkylamines C$_n$H$_{2n+1}$NH$_2$ increase linearly with the alkyl chain length for $n \leq 10$ (Figure 2). The increase $\Delta d_L/\Delta n = 1.10$ Å indicates bilayers of alkylamine molecules (Figure 3). The chains are tilted in angles of about 60° to the {NbO(H$_2$O)PO$_4$} layers.

The deviation of the spacings for longer chain alkylamines from the solid line in Figure 2 agrees with observations on other

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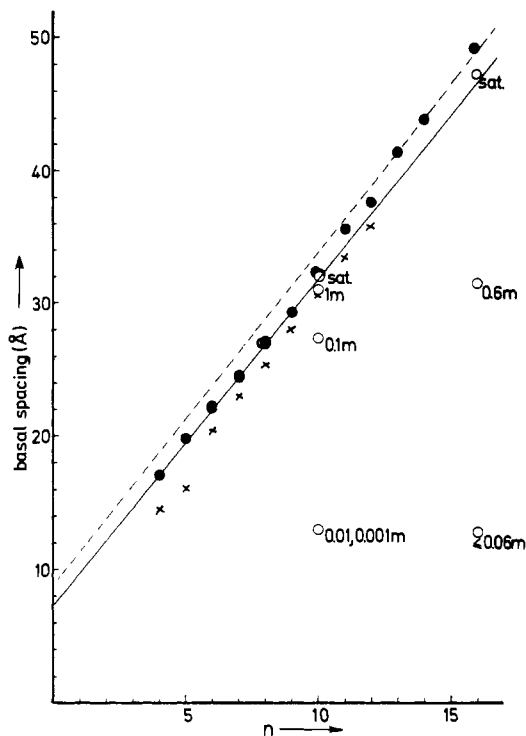(8) D. Behrendt, K. Beneke, and G. Lagaly, *Angew. Chem., Int. Ed. Engl.*, **15**, 544 (1976).
(9) G. Lagaly, *Adv. Colloid Interface Sci.*, **11**, 105 (1979).
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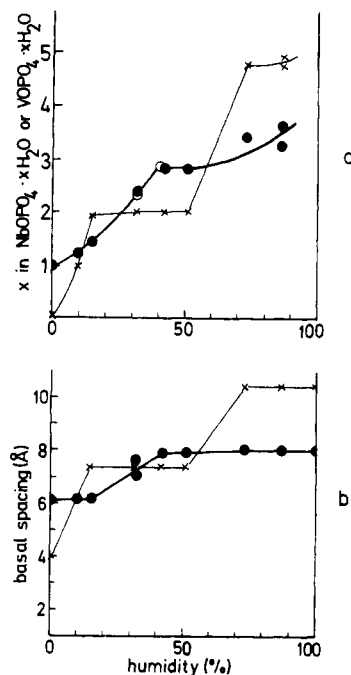
Figure 2. Basal spacings of $NbOPO_4 \cdot 3H_2O$ and $VOPO_4 \cdot 2H_2O$ after intercalation of alkylamines $C_nH_{2n+1}NH_2$: (●) $NbOPO_4 \cdot 3H_2O$, pure alkylamines; (O) $NbOPO_4 \cdot 3H_2O$, alkylamines from ethanolic solution; (×) $VOPO_4 \cdot 2H_2O$, pure alkylamines. The solid line denotes a 60° chain orientation and the dashed line a perpendicular chain orientation.
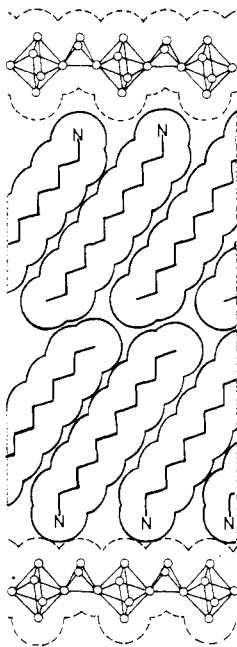
Figure 3. Alkylamine bilayers between {NbO(H₂O)PO₄} layers.

layered host compounds.[9,10,13] With increasing chain length the amines tend to assume the perpendicular orientation. Extrapolation to $n = 0$ gives $d_L(n = 0) = 7.3$ Å ($n \leq 10$, solid line) and 9.0 Å ($n > 10$, dashed line). The value of 7.3 Å specifies close contacts between the amine end groups and the niobium phosphate layers. Likely, this causes the tilting of the chains. In the perpendicular orientation the chains are sufficiently close packed only if the amine groups (or a part of them) lose their close contacts to the surface.

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Figure 4. Intercalation of water into $NbOPO_4 \cdot H_2O$ and $VOPO_4$ as a function of relative humidity at 25 °C: (a) x in $NbOPO_4 \cdot xH_2O$ (●) and $VOPO_4 \cdot xH_2O$ (×), from the weight increase; (b) Basal spacings of $NbOPO_4 \cdot H_2O$ (●) and $VOPO_4 \cdot xH_2O$ (×).

Washing the alkylamine complexes with ethanol/water (1:1) and air-drying reduces the spacings by about 2 Å. The dried samples intercalate other long-chain molecules, for instance decanol. The increase of the spacings, 3.9 Å for decanol, shows that the intercalated molecules complete the bilayers and make the perpendicular chain orientation possible.

Alkylamines are also intercalated from diluted ethanolic solution. In 0.001 and 0.01 M solutions of decylamine the basal spacing is 13 Å (Figure 2). The chains of the bilayers lie parallel to the niobium phosphate layers (the van der Waals thickness of alkyl chain bilayers is 8 Å and of the niobium phosphate layer is 5 Å; thus we expect for the bilayer complex 8 + 5 = 13 Å). At concentrations ≥0.1 M the spacings strongly increase and approach the values observed in the presence of pure amines.

Small Polar Molecules. Some of the organic compounds that are suitable guest molecules for many layered host compounds decrease the spacings of $NbOPO_4 \cdot 3H_2O$ to 7–8 Å (for instance NMFA 7.8 Å, urea 7.2 Å, N-methylurea 7.4 Å). Instead of being intercalated, the liquids absorb water from the interlayer spaces. In most cases, the dehydration to the monohydrate is incomplete, and an interstratified structure of the trihydrate with the monohydrate is formed. The interstratification often causes a broadening of the (001) reflection. If salts such as KSCN, $NaNO_3$, Na_2SO_4, and KI are dissolved in the organic liquids (e.g. DMFA and Me_2SO), the trihydrate is completely dehydrated to the monohydrate.

6-Å and 7-Å Phases. Chernorukov et al.[3] postulated the dehydration of the trihydrate (basal spacing 8.04 Å) to a monohydrate with a spacing of 7.14 Å. Spacings of 7–7.5 Å are often observed in dehydration experiments, in particular by water-soluble organic liquids (NMFA, DMFA, Me_2SO, etc.). However, a structure with a spacing of 7.1 Å is too bulky to be considered as the true monohydrate. The volumes of the unit cells (lattice constants from ref 3) are as follows: 167 Å³ for $d_L = 4.1$ Å (=NbOPO₄); 293 Å³ for $d_L = 7.14$ Å, and 300 Å³ for $d_L = 8.04$ Å (=NbOPO₄·3H₂O).

Dehydration over P_4O_{10} (Figure 4), careful thermal dehydration at 85–150 °C, or removal of the interlayer water by solutions of inorganic salts in organic liquids give the mono-

hydrate as a distinct phase with a spacing of 6.17 Å. The 7-Å form has an approximate composition $NbOPO_4 \cdot 2H_2O$ and evidently appears as an intermediate during the dehydration.

Between 15 and 42% relative humidity (Figure 4) the 6.17-Å phase transforms into the 8-Å hydrate. The transition starts with a broadening of the 6.2-Å reflection at 15% humidity. At 32%, a phase with a spacing of 7.05 Å occurs besides other phases. At higher humidity (42%) a sharp and intense 7.94-Å reflection appears, which increases to 8.04 Å at humidities >50%. The lattice expansion from 7.94 to 8.04 Å is accompanied by a distinct weight increase, which demonstrates the filling up of the interlayer space by water molecules.

Disordered Phases. In many cases, spacings between 7 and 7.5 Å do not indicate a distinct hydrate but result from interstratification of the 6.14-Å form with the fully hydrated 8.04-Å form. The interstratification is often revealed by a broadening of the (001) reflection. It cannot be analyzed in detail because of the low number of observable basal reflections.

A disordered form of the hydrated phosphate was investigated by Deulin et al.[4] Their X-ray patterns show very poor basal reflections and a broadening of most of the other reflections. The authors conclude from infrared and Raman spectra that this form contains hydrogen phosphate groups formed by proton transfer from the water molecules in the coordination spheres of Nb to the $[PO_4]^{3-}$ groups. The data of Deulin make evident that the protonation of the phosphate groups not only destroys the regular layer packing but also renders more difficult the dehydration of the trihydrate to the monohydrate. The critical dehydration temperature of the disordered trihydrate largely exceeds that of the well-ordered form. The monohydrate then formed still shows some disorder, but the infrared and Raman spectra give evidence that the structure contains $[PO_4]^{3-}$ groups and water molecules coordinated to Nb.

Hydrated Niobium Phosphates with P/Nb > 1. In $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O^5$ phosphoric acid molecules are intercalated between $\{NbO(H_2O)PO_4\}$ layers (basal spacing 11.2 Å). Similar compounds can be obtained by reacting $NbOPO_4 \cdot 3H_2O$ with concentrated phosphoric acid. (Among other mineral acids only sulfuric acid (25–100%) is intercalated. The highly disordered intercalation complex has a spacing of about 20 Å, which collapses to 13.7 Å by slight washing and air drying.)

The phosphoric and sulfuric acid complexes are more reactive than the original niobium phosphate and intercalate typical guest compounds. The intercalation, however, has to compete with the desorption of H_3PO_4 from the interlayer spaces. Transition into the 8-Å phase or even more dehydrated forms is often observed. Washing with water or ethanol removes the interlayer H_3PO_4.

The niobium phosphate with stoichiometry $Nb_2O_5 \cdot 1.5 P_2O_5 \cdot 5.9H_2O$ (Anal. Calcd: Nb, 31.8; P, 15.9. Found: Nb, 31.7; P, 15.9.) represents a quite different type, probably $Nb_2(OH)_2(HPO_4)(PO_4)_2 \cdot 4.4H_2O$. The basal spacing of the air-dried product is 13.1 Å and increases to 13.3 Å in water. Thermal dehydration collapses the structure to 11.8 Å. The weight loss up to 700 °C (12%) is much lower than for $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$ (about 45%[5]).

The P/Nb ratio, the basal spacings, and the thermal behavior make it probable that pairs of $\{Nb(OH)_2PO_4\}$ layers are condensed by H_3PO_4 molecules. The composition of the layer would be $\{Nb_2(OH)_2(HPO_4)(PO_4)_2\}$, but likely the layers contain some additional water molecules (about 1.2). The thermal dehydration indicates 3.2 interlayer water molecules.

The layers should be thicker by about 6 Å ($\sim a_0$ in $NbOPO_4$ and its hydrates) then the $\{NbO(H_2O)PO_4\}$ layers (6.17 Å)

Table II. Intracrystalline Reactivity of $NbOPO_4 \cdot 3H_2O$ (I) and $Nb_2(OH)_2(HPO_4)(PO_4)_2 \cdot 4.4H_2O$ (II) with Some Selected Guest Molecules

guest molecules	basal spacing, Å	
	I	II
formamide	...^{a}	14.8
dimethylformamide	...	14.8
dimethyl sulfoxide	...	18.8
ethylene glycol	...	14.1
glycerol	...	14.8
trimethylamine N-oxide	15.0	16.5
ephedrine	24.8	22.9
butylamine	17.1	19.9
decylamine	32.4	36.8
butanol	...	21.0
decanol	...	36.5

conditions	basal spacing, Å	
	I	II
air-dried	7.6–7.8	13.1
in water	8.04	13.3
heated to 100 °C	6.17	12.2
heated to 400 °C	4.5	11.8

^{a} No reaction; spacings of 7.6–8.0 Å.

in $NbOPO_4 \cdot H_2O$. The estimated value 6.2 + 6 = 12.2 Å agrees with the experimental layer thickness (11.8 Å, from thermal dehydration). In the fully hydrated state the observed spacing (13.3 Å) is again as expected (8.0 + 6 = 14 Å).

Treatment with water shows the different bonding of the additional phosphate as compared with that of $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$. The latter compound loses the interlayer phosphoric acid molecules in contact with water, and the spacings collapse to ≤ 8 Å. In the case of $Nb_2(OH)_2 (HPO_4)(PO_4)_2 \cdot 4.4H_2O$ intensive washing or extraction with boiling water removes only small amounts (≤ 0.15 mmol/g) of phosphoric acid. Titration with NaOH shows 1.6 mmol/g of acidic protons to be present in the structure (theoretical value 1.7 mmol/g).

The niobium phosphate intercalates many guest molecules (Table II). The increased reactivity clearly distinguishes this phosphate from $NbOPO_4 \cdot 3H_2O$ and its H_3PO_4 intercalation products. The basal spacings of the alkylamine derivatives increase with the alkyl chain length in a similar way as for $NbOPO_4 \cdot 3H_2O$. The larger absolute spacings reflect the increased thickness of the niobium phosphate layers. Particularly, it should be mentioned that alkanols are intercalated with ease.

$VOPO_4 \cdot 2H_2O$. The layer structure of hydrated vanadium phosphate $VOPO_4 \cdot 2H_2O$ proposed by Ladwig[6] was confirmed by a crystal structure determination.[14] The structure consists of infinite sheets of distorted $[VO_6]$ octahedra and $[PO_4]$ tetrahedra linked by shared oxygen atoms.

Vanadium phosphate reversibly forms a monohydrate (basal spacing 6.3 Å), a dihydrate (spacing 7.4 Å), and in contact with water, a highly hydrated 10.5-Å phase (about $VOPO_4 \cdot 5H_2O$) (Figure 4). The dehydration to anhydrous $VOPO_4$ is reversible, even at dehydration temperatures of 200 °C. The rehydration requires a cleavage of the V–O–V bonds in $VOPO_4$. As illustrated in Figure 4, the transition between the different hydrates is sharper than for $NbOPO_4 \cdot xH_2O$.

Vanadium phosphate reacts with guest compounds more easily than $NbOPO_4 \cdot 3H_2O$. N-Methylformamide expands the lattice to 13.1 Å; other acid amides dehydrate $VOPO_4 \cdot xH_2O$ ($x > 1$) to $VOPO_4 \cdot H_2O$. Ladwig[6] described the intercalation of phosphoric acid, ethanol, NH_3, and butylamine. Long-chain alkylamines ($n > 4$) are easily intercalated and form bimo-

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

lecular complexes as with niobium phosphate. The spacings for amines $C_nH_{2n+1}NH_2$ with $n > 5$ plotted vs. n (Figure 2) follow a straight line. The increase $\Delta d_L/\Delta n = 1.3$ Å indicates a nearly perpendicular chain orientation. The absolute spacings are slightly smaller than those for $NbOPO_4\cdot3H_2O$; the amine end groups are packed closer to the {$VO(H_2O)PO_4$} layers than to the {$NbO(H_2O)PO_4$} layers. In equilibrium with diluted ethanolic solutions (≤ 0.05 M) the interlayer amines lie flatly on the vanadium phosphate layers.

The different reactivities of vanadium and niobium phosphate may be related to differently distorted [MO_6] octahedra. It should be noted that the distortion of the [VO_6] octahedra in $VOPO_4\cdot2H_2O$ is maintained during thermal dehydration (below 220 °C) to α_{II}-$VOPO_4$. This compound differs from α_I-$VOPO_4$ (obtained by heating of the mixtures of the oxides) by the position of the vanadium atoms within the octahedra.[15]

The ease with which vanadium phosphate $VOPO_4\cdot2H_2O$ and niobium phosphate $Nb_2(OH)_2(HPO_4)(PO_4)_2\cdot4.4H_2O$ intercalate long-chain alkanol molecules distinguishes both phosphates from nearly all other layered host compounds, even

from α-$H_2[Zr(PO_4)_2]\cdot H_2O$.[16]

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

(16) G. Alberti and U. Costantino in "Intercalation Chemistry", M. S. Whittingham and A. J. Jacobson, Eds., Academic Press, New York, 1982, p 147.

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Preparation and Structure of the Bridged Form of $Mo_2Cl_4[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$. Dependence of the Mo_2 Quadruple Bond Length on Torsional Angle

F. ALBERT COTTON* and GREGORY L. POWELL

The reaction of $Mo_2Cl_4(PEt_3)_4$ with $(CH_3)_2PCH_2CH_2P(CH_3)_2$, dmpe, in toluene gave a ca. 90% yield of the red-brown bridged (β) form of $Mo_2Cl_4(dmpe)_2$, as well as a small amount of a blue solid presumed to be the chelated (α) form. The bridged form was characterized by X-ray crystallography. It crystallizes in space group $P2_12_12$ with two molecules in a unit cell of the following dimensions: $a = 12.743$ (3) Å, $b = 11.497$ (2) Å, $c = 8.553$ (2) Å, $V = 1253.0$ (8) Å³. The molecule has a rigorous twofold symmetry axis that is a perpendicular bisector of the Mo–Mo bond, but two other noncrystallographic twofold axes (one collinear with the Mo–Mo bond) are present, giving virtual D_2 molecular symmetry. The most significant features of the structure are a mean twist angle about the Mo–Mo axis of 40.0 (1)° and an Mo–Mo bond length of 2.183 (3) Å. When these data are combined with results for $Mo_2Cl_4(dppm)_2$ and $Mo_2Br_4(arphos)_2$, it is found that a linear relationship exists between cos (2χ) (where χ is the angle of twist away from the perfectly eclipsed conformation) and the Mo–Mo distance. The extrapolated Mo–Mo distance for $\chi = 45°$ is 2.193 ± 0.001 Å.

Introduction

There are relatively few occasions in chemistry where bonding theory reliably predicts a simple relationship between one structure parameter and another and where it is also feasible to obtain experimental confirmation of the relationship, free of other, complicating factors. This report is concerned with one such case.

From the established description of the $\sigma^2\pi^4\delta^2$ quadruple bond[1] it is straightforwardly predictable that the δ^2 contribution to the bond strength is sensitive to the angle of internal rotation, while the $\sigma^2\pi^4$ contribution is invariant with respect to this angle. Moreover, since the magnitude of the δ overlap varies as the cosine of 2χ, χ being the angle of rotation away from an eclipsed conformation, it is reasonable to expect a monotonic (perhaps even linear) relationship between the Mo–Mo distance and cos (2χ).

With the preparation and structural characterization of the title compound, $Mo_2Cl_4(dmpe)_2$, we now have sufficient data to test this prediction experimentally and to establish quantitatively the relationship between the bond length and the internal twist angle under conditions where there is no significant interference from any other factor.

Experimental Section

General Procedures. All manipulations were carried out in an atmosphere of dry, oxygen-free argon. Toluene was purified by distillation from sodium–potassium/benzophenone under argon.

Starting Materials. $Mo_2Cl_4(PEt_3)_4$ was prepared according to a previously reported procedure.[2] Bis(1,2-dimethylphosphino)ethane (dmpe) was purchased from Strem Chemicals and used without further purification.

Preparation. $Mo_2Cl_4(PEt_3)_4$, 2.57 g (3.19 mmol), and 1.00 g (6.66 mmol) of dmpe were dissolved in 150 mL of toluene to give a deep blue solution. Overnight (12 h) reflux resulted in a reddish brown

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Chapters 1 and 8.

(2) Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.