

The infrared spectrum of $\alpha\text{-(NH}_4\text{)}_2\text{(VO)}_3\text{(P}_2\text{O}_7\text{)}_2$

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Vanadium phosphates exhibit a wide range of structures partly due to the different oxidation states which this metal adopts and the variety of ways in which phosphate tetrahedra and vanadium-oxygen polyhedra can be interlinked. Interest in these compounds arises from the fact that most of them are potentially useful as catalysts or precursors of catalysts for selective oxidations [1–6]. On the other hand, these systems also have some interest from the point of view of vanadium/phosphate interactions in biological systems [7–9].

A detailed physicochemical characterization of these materials is important to attain a better insight into their stability, bond properties, redox behavior, etc.

Recently, the structural characteristics of some ammonium vanadium diphosphates were investigated by means of X-ray powder diffractometry, an *ab-initio* structure determination and Rietveld refinement [10]. Using this information, and in order to extend the structural information, we have analyzed the vibrational spectroscopic behavior of one of these compounds, namely $\alpha\text{-(NH}_4\text{)}_2\text{(VO)}_3\text{(P}_2\text{O}_7\text{)}_2$.

The compound was prepared from $\text{V}_2\text{O}_5\text{/(NH}_4\text{)}_2\text{-HPO}_4$ mixtures which were firstly heated up to 200 °C. The fused product was homogenized and further heated at 325 °C for 2 h, in air. The final product was washed several times with water and with acetone and finally dried in air.

The infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet technique.

The compound belongs to the orthorhombic space group *Pnma* with $Z=4$ and consists of a highly condensed three-dimensional framework of corner sharing VO_5 pyramids, VO_6 octahedra and PO_4 tetrahedra. The NH_4^+ cations are located in intersecting channels originated along the *b* and *c* axes. There are three crystallographic different VO_x polyhedra: VO_5 square pyramids, stretched VO_6 octahedra and chains of VO_6 octahedra [10]. The vanadium atom is displaced from the center in all these coordination polyhedra due to the double bond to one of the oxygen atoms forming the vanadyl group. These short apical bonds have a length of about 160 pm, whereas the other V–O bonds are in the range between 193 and 207 pm. Alternate short and long bonds are found in the octahedral VO_6 chains.

The infrared spectrum of the compound is shown in Fig. 1 and the proposed assignment presented in Table I.

To facilitate the discussion of these results the analysis is divided into the three constituent groups of the structure: the diphosphate anion, the VO_x -polyhedra and the NH_4^+ cations.

1. $\text{P}_2\text{O}_7^{4-}$ vibrations. The antisymmetric stretching vibration of the terminal PO_3 groups is found as a very well defined and strong band multiplet between 1189 and 1085 cm^{-1} , whereas the corresponding symmetric stretching is observed as a weak band at 1054 cm^{-1} . The stretching motions corresponding to the P–O–P bridges are located at 938 and 744 cm^{-1} . The presence of an i.r. active ν_s (POP) stretching indicates a bent bridge conformation for the diphosphate group [11]. All diphosphate vibrations lie in similar ranges than in $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ [12, 13] and in some heavy metal diphosphates [14]. The bending and torsion modes of the PO_3 groups are more difficult to assign although the band multiplet between 622 and 485 cm^{-1} is surely related to vibrations of these types.

2. VO_x vibrations. As stated above, all these polyhedra contain one short V=O bond which stretching motion is expected in the range $900\text{--}1000\text{ cm}^{-1}$. From the previous investigation of other highly condensed

TABLE I Assignment of the infrared spectrum of $\alpha\text{-(NH}_4\text{)}_2\text{(VO)}_3\text{(P}_2\text{O}_7\text{)}_2$ (band positions in cm^{-1})^a

3262 m, br	$\nu_{\text{as}}/\nu_{\text{s}}(\text{NH}_4^+)$
1635 vw	$\delta_{\text{s}}(\text{NH}_4^+)$
1427 s	$\delta_{\text{as}}(\text{NH}_4^+)$
1189 sh	
1175 vs	$\nu_{\text{as}}(\text{PO}_3)$
1180 vs	
1085 sh	
1054 w	$\nu_{\text{s}}(\text{PO}_3)$
1004 m	$\nu(\text{V=O})/\text{VO}_5$
978 s	$\nu(\text{V=O})/\text{VO}_6\text{-chains}$
938 vs	$\nu_{\text{as}}(\text{POP})$
915 w	$\nu(\text{V=O})/\text{VO}_6$
744 m	$\nu_{\text{s}}(\text{POP})$
622 sh	
601 m	
568 s	$\delta(\text{PO}_3) + (\text{see text})$
643, 527 sh	$\tau(\text{PO}_3)$
485 s	
411 w	see text
385 s, br	
326 m	

^avs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

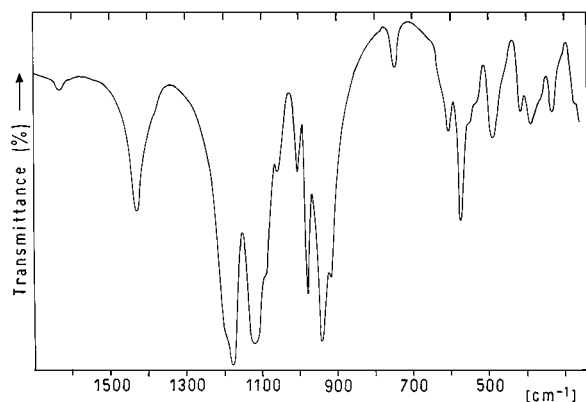


Figure 1 Infrared spectrum of α -(NH₄)₂(VO)₃(P₂O₇)₂ between 1700 and 250 cm⁻¹.

materials containing different VO_x arrangements [14–20] we conclude that the V=O bond belonging to the VO₅ square-pyramids should absorb at somewhat higher energies than those present in the VO₆ octahedra. Therefore, we have assigned the medium intensity band located at 1004 cm⁻¹ to the short vanadium oxygen bond of the pyramidal groups. In [Ni(H₂O)₄][VOPO₄]₂ and in RbVOPO₄ in which similar VO₅ polyhedra are found, this band is located at 990 and 1005 cm⁻¹ respectively [16, 19]. For the octahedral polyhedra, we assume that, due to the condensation effect, the double bonds present in the VO₆ chains should absorb at somewhat higher energies than the isolated octahedra. Therefore, we have assigned the strong band at 978 cm⁻¹ to the vibration of the short bond in the octahedral chains. As shown earlier, the position of this vibration is highly sensitive to the V=O bond distance [18, 20]. On the basis of this argument, we conclude that in the present case this distance lies between 157 and 158 pm. Finally, the weak band found at 915 cm⁻¹ can be assigned to the short V=O bond of the isolated stretched VO₆ octahedra. Vibrations related to the other (longer) V–O bonds are difficult to identify. They lie probably below 400 cm⁻¹ somewhat mixed with the external (lattice) vibrations.

3. NH₄⁺ vibrations. In the high frequency region (not shown in Fig. 1) only a medium intensity and broad band at 3262 cm⁻¹, assigned to the antisymmetric stretching vibration of the cation, is observed. The corresponding symmetric stretching, which is usually very weak, probably remains overlapped under this band. The two bending vibrations could be clearly identified. The fact that neither the antisymmetric stretching, nor the antisymmetric bending vibrations are split, together with the spectral position of the first of these bands, confirms that the NH₄⁺ cations rotate relatively freely [21] in the channels in which they are

located, as was also suggested by the structural analysis [10].

Finally, and using the “two masses” model [22], we have made an estimation of the force constants of the three short V=O bonds found in this structure. The obtained figures are 723, 685 and 600 N/m for the VO₅ pyramids, the VO₆ chains and the VO₆ groups, respectively. They are comparable with those found in the related materials [14–20].

Acknowledgments

This work has been supported by CONICET and CIC-PBA (Argentina). E.J.B. is a member of the research career of CONICET.

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Received 18 March

and accepted 23 June 1999