

# Vibrational Spectra of the Layered Compound $[(VO_2)_2(4,4\text{-bipy})_{0.5}(4,4'\text{-Hbipy})(PO_4)] \cdot H_2O$

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Z. Naturforsch. **58b**, 485–488 (2003); received January 31, 2003

The infrared and Raman spectra of the title complex were recorded and assignments for the  $VO_2^+$ ,  $PO_4^{3-}$  and V–O and V–N skeletal vibrations are proposed. The results are of interest in relation to the vibrational-spectroscopic properties of the active site of vanadium haloperoxidases.

**Key words:**  $VO_2^+$  Complex, Phosphate, IR Spectra, Raman Spectra, Skeletal Vibrations

As part of our research devoted to the spectroscopic characterization of different oxovanadium(IV) and oxovanadium(V) complexes, which may be useful as mimics of naturally occurring vanadium centers of enzymes [1–3], we have now investigated the vibrational (infrared and Raman) spectra of the recently reported title complex [4]. Its asymmetric unit contains two  $V^{5+}$  cations, two distinct 4,4'-bipyridine (bipy) ligands, a  $PO_4^{3-}$  anion, and a water molecule. The bipy molecules are present in two forms: one is neutral and the other one monoprotonated.

As shown schematically in Fig. 1 each  $V^{5+}$  cation has a distorted trigonal bipyramidal coordination in which two equatorial positions are occupied by terminal O-atoms, one axial position is occupied by the N-atom of a bipy ligand, and the remaining positions are occupied by O-atoms of two  $PO_4^{3-}$  anions. The *cis*- $VO_2$  arrangement with two very short V=O bonds (*ca.* 1.62 Å) is a characteristic feature of oxovanadium(V) complexes. Each  $PO_4^{3-}$  ligand coordinates to four different vanadium centers. The described atomic arrangement around vanadium(V) generates an  $O_4VN$  skeleton, which closely resembles that found in the vanadium-dependent haloperoxidases [5, 6].

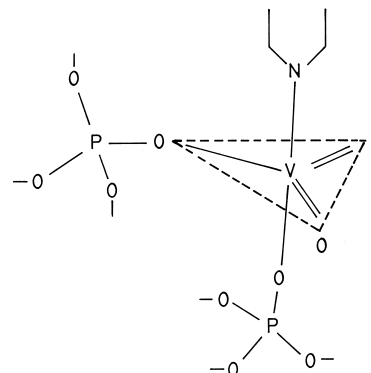


Fig. 1. Schematic drawing showing the distorted trigonal bipyramidal coordination of one of the vanadium(V) centers in  $[(VO_2)_2(4,4\text{-bipy})_{0.5}(4,4'\text{-Hbipy})(PO_4)] \cdot H_2O$ .

The overall structure of the  $[(VO_2)_2(4,4\text{-bipy})_{0.5}(4,4'\text{-Hbipy})(PO_4)] \cdot H_2O$  complex consists of phosphate-bridged vanadium(V) double chains linked through the 4,4'-bipy ligands to form a sheet, the monoprotonated 4,4'-Hbipy<sup>+</sup> ligand being coordinated to the metal atom as a pendent group. The guest water molecules are located within channels in the structure [4].

The complex was synthesized by hydrothermal reaction, as previously described [4] and its purity checked by X-ray diffractometry. The infrared spectra were recorded on a FTIR-Bruker IF 66 spectrophotometer, in the spectral range between 4000 and 250  $cm^{-1}$ , using the KBr pellet technique. Raman spectra were obtained with FRA 106 accessory of the above-mentioned instrument. The 1064 nm-Line of a Nd:YAG laser was used for excitation.

As both spectra are relatively complex we have only attempted to make an analysis and assignment of the  $VO_2^+$  and  $PO_4^{3-}$  vibrations and to identify the skeletal vibrations, as these motions are the most interesting in relation to our studies of vanadium centers of biological interest. This analysis was further complicated by the rather poor quality of the Raman spectra, with relatively unfavorable signal-to-noise ratio. Notwithstanding, these spectra offer some useful information, complementing the IR data and supporting some of the proposed assignments.

The IR spectrum in the most interesting region for this analysis, between 1200 and 250  $cm^{-1}$ , is shown in Fig. 2 and a brief discussion of the vibra-

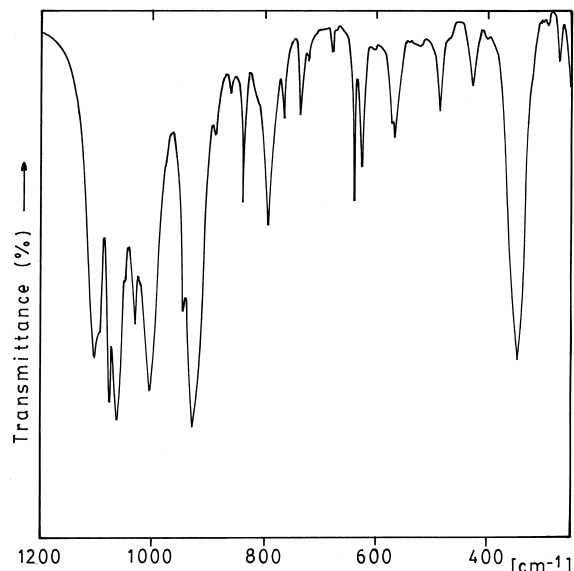


Fig. 2. FTIR spectrum of  $[(\text{VO}_2)_2(4,4\text{-bipy})_{0.5}(4,4'\text{-Hbipy})(\text{PO}_4)] \cdot \text{H}_2\text{O}$  between 1200 and 200  $\text{cm}^{-1}$ .

Table 1. Phosphate,  $\text{VO}_2^+$ , and skeletal vibrations of the compound (band positions in  $\text{cm}^{-1}$ ).

	Infrared	Raman	Assignment
Phosphate modes			
	1101 s/1092 sh	1114 w	$\nu_3(\text{PO}_4)$
	1076 s	1084 m	
	1062 vs/1053 sh	1070 m	$\nu_1(\text{PO}_4)$
	1029 m/1002 vs	1022s/1010 w	
	570 sh/564 m	568 vw	$\nu_4(\text{PO}_4)$
	427 m	429 m	$\nu_2(\text{PO}_4)$
$\text{VO}_2^+$ modes			
	943 w	939 vs	$\nu_s(\text{V-O})$
	919 vs	905 m	$\nu_{\text{as}}(\text{V-O})$
		325 w	$\delta(\text{VO}_2)$
Skeletal modes			
	521 w/400 vw	525 w	$\nu(\text{V-O})$
	345 vs	342 w	$\nu(\text{V-N})$

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

tional modes related to the groups of interest, also summarized in Table 1, is given below.

#### Phosphate groups

The assignment of the typical vibrational modes of the tetrahedral  $\text{PO}_4^{3-}$  moiety is relatively straightforward and can be done by comparison with solution data and those known for a large number of crystalline salts containing this anion [7].

The triply degenerated antisymmetric stretching mode ( $\nu_3$ ) appears clearly split into its components in both spectra. Interestingly, in the IR spectrum two of these components present additional weak shoulders (1092 and 1053  $\text{cm}^{-1}$ ) suggesting the presence of correlation field effects [7, 8]. Also the symmetric stretching mode ( $\nu_1$ ) is split in both spectra.

The shifts of the two stretching vibrations to higher frequencies, in comparison with the values measured in solution for the “free”  $\text{PO}_4^{3-}$  anion ( $\nu_1 = 938 \text{ cm}^{-1}$ ;  $\nu_3 = 1017 \text{ cm}^{-1}$  [7]), is a direct consequence of the strongly strained nature of the oxo-anion in the present structure, in which it shares oxygen atoms with four different metal centers.

The deformational modes ( $\nu_2$  and  $\nu_4$ ) are more difficult to identify as they have relatively low intensities. Although they are also expected to split in the structure, only one or two components could be identified for each of these modes.

#### $\text{VO}_2^+$ -units

This cation also presents absorptions in typical spectral ranges, at relatively high frequencies, due to the presence of short and strong metal-oxygen bonds. The  $\text{VO}_2^+$ -moiety present in this compound may be compared with that found in the sodium salt of the anion  $[\text{VO}_2\text{Q}_2]^-$  ( $\text{Q} = 8\text{-hydroxyquinolate}$ ) [9, 10]. In this case, the two expected  $\text{VO}_2^+$  vibrations have been found at 913 and 888  $\text{cm}^{-1}$  in the IR spectrum and at 915 and 885  $\text{cm}^{-1}$  in the Raman spectrum [10]. In the title complex they are found in the same region, but at somewhat higher energies (*cf.* Table 1), despite the fact that the V=O bond lengths are practically identical in both compounds [4, 9].

On the basis of arguments advanced by Taguchi *et al.* [11], the vibration at highest frequency should be assigned to the symmetric stretching of this  $\text{VO}_2^+$ -moiety. In the present case, this proposal is additionally supported by the higher intensity of this band in the Raman spectrum, leading to the assignment proposed in Table 1.

Regarding the  $\text{VO}_2^+$  deformational mode, we have assigned a weak Raman band located at 325  $\text{cm}^{-1}$  to this vibration, also by comparison with the value determined for this mode in the  $[\text{VO}_2\text{Q}_2]^-$  salt [10]. In the IR spectrum this vibration could not be found because it is overlapped by the strong band at 345  $\text{cm}^{-1}$  assigned to one of the skeletal vibrations.

#### Skeletal vibrations

(V–O) and (V–N) stretching modes were also assigned by comparison with values measured in the  $[\text{VO}_2\text{Q}_2]^-$  salt [10] and in related oxovana-

dium(V) and oxovanadium(IV) 8-hydroxyquinoline complexes [12–14]. V–O stretching modes usually appear at higher frequencies than corresponding V–N vibrations [12–15]. In  $[\text{VO}_2\text{Q}_2]^-$  the  $\nu_s\text{VO}$  vibration was found at  $523\text{ cm}^{-1}$  whereas the corresponding  $\nu_{as}\text{VO}$  mode lies at  $400\text{ cm}^{-1}$  and this assignment was corroborated by pre-resonance Raman measurements. For the V–N motions only one Raman band, located at  $353\text{ cm}^{-1}$ , was found [10]. In  $\text{VO}^{2+}$  8-hydroxyquinoline complexes and some of its halogenated derivatives  $\nu(\text{VO})$  bands are found in the ranges between  $528\text{--}603$  and  $406\text{--}496\text{ cm}^{-1}$ , whereas  $\nu(\text{VN})$  modes are found between  $342$  and  $359\text{ cm}^{-1}$  [13]. In all these cases always only one  $\nu(\text{VN})$  band could be identified, suggesting that the other one does not attain enough intensity or lies at very low energies [13].

In the present case, the two skeletal vibrations are clearly found to lie in the expected ranges although in the Raman spectrum only one V–O vibration could be identified with certainty. Besides, the unusual high intensity of the  $345\text{ cm}^{-1}$  IR band, assigned to the one of the  $\nu(\text{VN})$  modes (*cf.* Fig. 2), suggests an overlapping with other vibrational modes, located at the same energy.

#### Other bands

Only brief comments on some characteristic 4,4'-bipyridine bands shall be made. Most of these bands appeared doubled, in agreement with the fact that two different bipy ligands are present in this structure. In the IR spectra a series of bands that can be assigned to complex motions involving the  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  vibrations are found at

$1612$  (vs),  $1527$  (w),  $1492$  (s) and  $1413$  (s)  $\text{cm}^{-1}$ , in the same region as in the free ligand [16]. For 4,4'-bipy a band located at  $611\text{ cm}^{-1}$ , which is very sensitive to coordination, usually shifting to higher frequency after bonding to a metal center [17, 18], has been assigned to a C–H bending mode. In the present case the medium intensity doublet at  $639/626\text{ cm}^{-1}$  (*cf.* Fig. 2) is assigned to this mode in the two different ligands present in the lattice.

To conclude, the performed analysis allowed to attain a good insight into the spectroscopic behavior of the vanadium(V) environment in this new compound, and this information can be directly transferred to the active site of vanadium-dependent haloperoxidases. In the case of the chloroperoxidase of the fungus *Curvularia inaequalis*, the active site of which has been investigated in detail [5, 6, 19], the vanadium coordination is also trigonal bipyramidal. Three non-protein oxygen atoms occupy the equatorial plane (bond lengths at about  $1.65\text{ Å}$ ), one N atom of an histidine residue (bond length  $1.96\text{ Å}$ ) resides on one apical position whereas the other one is occupied by another O-atom, probably a OH-group (bond length  $1.93\text{ Å}$ ) [19]. In the present case, three equatorial V–O bonds (two at about  $1.62\text{ Å}$  and the other one at  $1.94\text{ Å}$ ) are also present, whereas at the apical positions there are a V–N bond ( $2.23\text{ Å}$ ) and a V–O bond ( $1.95\text{ Å}$ ) [4].

#### Acknowledgements

This work has been supported by CONICET and ANPCyT (PICT 06-06148) from Argentina. E. J. B. is a member of the Research Career from CONICET.

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