SPECTROSCOPIC AND THERMAL BEHAVIOR OF Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O

C. I. Muglia, E. G. Ferrer and E. J. Baran[*]

Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina

Abstract

The electronic (absorption and reflectance) as well as the infrared and Raman spectra of Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O were recorded and discussed. Its thermal behavior was investigated by means of TG and DTA measurements. After a two-step dehydration, the compound melts at 464°C and, apparently, depolymerization takes place during this process. The characteristics of the pyrolysis residues, collected at different temperatures, were spectroscopically investigated.

Keywords: spectroscopic behavior, thermal behavior, trimeric oxovanadium(IV) diphosphate

Introduction

Vanadium phosphates exhibit a wide range of structures partly due to the different oxidation states that this metal adopts and the variety of ways in which phosphate tetrahedral and vanadium–oxygen polyhedra can be interlinked. Interest on these compounds arises from the fact that most of them are potentially useful as catalysts or precursors of catalysts for selective oxidations [1–8].

On the other hand, interaction of vanadium cations with different kind of phosphates are also of biological significance [9–11] and generated renewed interest in the last years in relation to similar processes occurring in natural systems, in which phosphate groups form part of more complex structures or ligands [12].

In order to attain a wider insight into the peculiarities of some complex vanadium phosphates in this paper we present results on the spectroscopic and thermal behavior of a solid oxovanadium(IV) diphosphate trinuclear species, Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O, which has been briefly mentioned in literature [13, 14] but has never been characterized in detail.

---

[*]   Author to whom all correspondence should be addressed.

Experimental

$VO(ClO_4)_2$ solution were obtained by reactions between equimolecular aqueous solutions of $VOSO_4$ and $Ba(ClO_4)_2$ as described earlier [15]. To 40 mL of a 0.1 M solution of this salt, 40 mL of an 0.1 M solution of sodium diphosphate were dropwise added, under continuous stirring. The resultant solution was reduced to half volume by evaporation on a water bath. After cooling, 40 mL of absolute ethanol was added. The blue precipitate was filtered off, washed several times with ethanol and finally dried during 24 h at 60°C. The content of vanadium was determined by the tungstophosphovanadic method [16], typical values for different samples ranged between 15.3–15.7% (calculated, V=15.49%). Previous reports on this complex suggest the presence of eighteen [13] or twelve [14] molecules of water. The difference with the now reported stoichiometry probably arises from different precipitation and/or drying conditions of the material.

Electronic absorption spectra were recorded with a Hewlett-Packard 8452 diode-array spectrophotometer, using 10 mm quartz cells. The reflectance spectra were obtained with a Shimadzu UV-300 spectrophotometer, using MgO as a reference. Infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained with a Bruker IF6 66 FTIR instrument provided with a FRA 106 Raman accessory and using the 1064 nm line of a Nd:YAG laser for excitation. ESR spectra were measured at 25°C with a Bruker-300 spectrometer, using 34.01 GHz (Q-band).

Thermogravimetric (TG) and differential thermoanalytical (DTA) measurements were performed with a Shimadzu system (models TGA-50 and DTA-50), working under a constant O_2 flow (50 mL min^{-1}) and at a heating rate of 5°C min^{-1}. Al_2O_3 was used as a DTA standard. Sample quantities ranged between 15 and 20 mg.

Results and discussion

Electronic spectra

The electronic absorption spectrum of an aqueous solution of the complex shows bands at 810 (ε=43.3 L mol^{-1} cm^{-1}) and 595 nm (ε=18.2 L mol^{-1} cm^{-1}) and a shoulder at ca 370 nm (ε=9 L mol^{-1} cm^{-1}), located on the tail of a strong charge transfer band situated in the UV region. These are the three typical electronic transitions expected for the complexed VO^{2+} cation under C_{4v}-symmetry, i.e. $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ respectively [17].

A comparison with the spectrum of the $[VO(H_2O)_5]^{2+}$ species [17] shows a slight displacement of the higher intensity band to lower energies in the phosphate complex (from 760 to 810 nm), whereas for the second transition a reverse displacement is observed (from 625 to 595 nm), indicating a somewhat higher 10 Dq value in the present case. Also, the band intensities are appreciable higher in the phosphato than in the aqua complex.

The electronic reflectance spectrum of the powdered solid is practically identical to the solution spectrum, confirming the presence of the same complex species in both phases. It shows the bands at 815, 605 and 375 nm.

Vibrational spectra

The infrared spectrum of the compound in the range between 1300 and 300 cm^{-1} is shown in Fig. 1. The Raman spectra were rather poor due to strong fluorescence effects, which generate a high background. Notwithstanding a number of characteristic Raman lines, which show good reproducibility in different measured samples, were also useful for the vibrational analysis. The proposed assignment is presented in Table 1, and is briefly commented as follows:

– The vibration of the water molecules (not shown in Fig. 1) are found as rather strong and broad bands between 3600–3200 cm^{-1} (O–H stretchings) and at 1652 cm^{-1} (OH-bending).
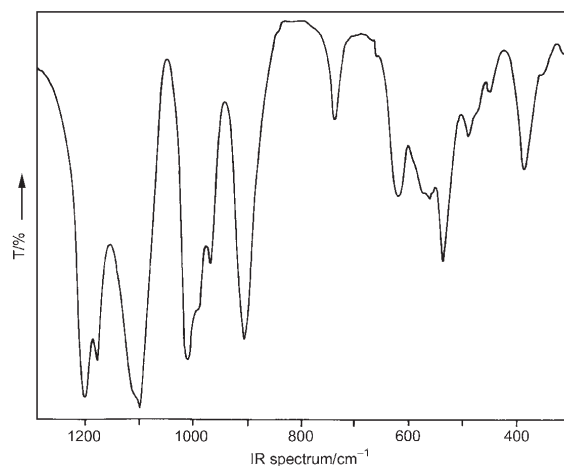
Fig. 1 Infrared spectrum of Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O, between 1300 and 300 cm^{-1}

– The internal vibrations of the P$_2$O$_7^{4-}$ moieties are found in similar ranges than in Na$_4$P$_2$O$_7$ [18, 19] and in some heavy metal diphosphates [20], but lie at lower frequencies than in (VO)$_2$P$_2$O$_7$ [19].

– An important splitting of the ν_{as}(PO$_3$) vibration is observed, which is surely generated by the cyclic structure that involves coordination of two of the oxygen atoms to the metal center, with a concomitant decrease of the strength of these two P–O bonds and the reinforcement of the remaining (non-coordinated) P–O bond.

– The separation of the two P–O–P bridge stretchings ($\Delta\nu$=163 cm^{-1}) is smaller than that found in most of the other investigated diphosphates [18, 20]. This is also a consequence of the cyclic structure.

– The characteristic ν(V=O) stretching is the most intense line in the Raman spectrum (968 cm^{-1}) and is found in the same position in the infrared spectrum, partially overlapped by the components of the ν_s(PO$_3$) mode (Fig. 1).

– The spectral range below 650 cm^{-1} is more difficult to assign. In this region, one expects deformational and torsional modes of the PO$_3$ groups. The bending mode of the P–O–P bridges probably lies out of the measured range [20]. Besides, the V–O bands are expected in this region. Such metal-to-ligand vibrations are often found to lie between 600 and 400 cm^{-1} [21–23]. A comparison of our infrared spectrum with that of Na$_4$P$_2$O$_7$·10H$_2$O, suggests that the weak band at 453 cm^{-1} could be assigned to one of these modes.

Table 1 Assignment of the vibrational spectrum of Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O

Infrared/cm^{-1}	Raman/cm^{-1}	Assignment
3525 s		
3430 vs		ν(OH)
3240 m		
1652 m		δ(HOH)
1199 vs		
1176 m	1180 m	
1110 sh	1138 m	ν_{as}(PO$_3$)
1093 vs	1092 m	
1007 vs, 990 sh	1038 s	ν_s(PO$_3$)
968 m	968 vs	ν(V=O)
904 vs	890 w	ν_{as}(POP)
741 s	753 m	ν_s(POP)
622 s	631 w	
577 w	585 w	
561 w		PO$_3$-deformations
538 vs		and torsions
522 sh	520 w	(see tex)
493 w, 477 sh		
453 w		ν(V–O) (?)
386 s, 357 sh	352 m	

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

To conclude, the vibrational spectroscopic results are in agreement with the previously reported ESR data [11, 13, 14] that suggested the formation of a cyclic structure in which each diphosphate anion acts as a bidentate bridging ligand (also [24]).

Thermal behavior

The thermogravimetric (TG) and differential thermal analysis (DTA) traces are shown in Fig. 2.
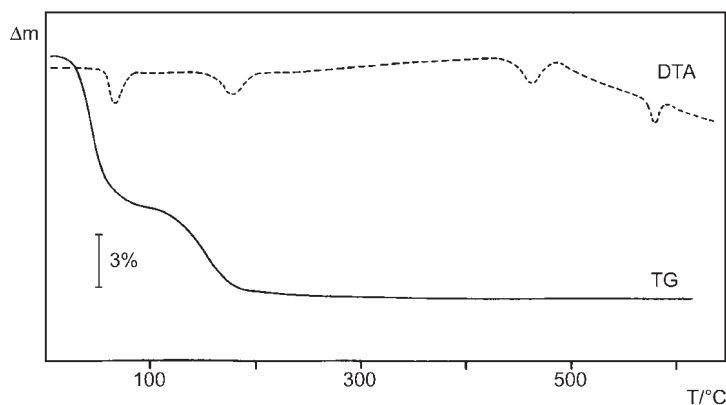
Fig. 2 TG and DTA traces for the thermal decomposition of Na$_6$[(VO)$_3$(P$_2$O$_7$)$_3$]·7H$_2$O

The figure presents two clearly defined steps; the first one between 20 and 66°C, related to a mass loss of 7.5%, and the second, which extends up to 180°C and implies a mass diminution of 5.3%. In the range between 180 and 300°C, usually another small mass loss of about 0.5–0.7% is observed. The analysis of the two principal steps shows that the first implies a loss of four H$_2$O molecules (calcd 7.29%), whereas the three remaining water molecules are lost in the second step (calcd 5.47%). This behavior suggests that the first four molecules are crystalline hydration water where-as the other three are probably coordinated to the metal centers.

Four weak DTA-signals located respectively at 66, 185, 464 and 585°C accompanies the degradation. The first two are clearly related to the two dehydration steps. The third one could be related to the melting of the anhydrous solid, as confirmed by independent studies in a crucible furnace, using greater amounts of the complex. The last signal cannot be explained with certainty.

Fused products, collected from furnace experiments at temperatures of 460 and 600°C, show a dramatic color change, presenting a dark green tint.

In order to analyze more deeply the characteristics of these products, we have recorded its IR and electronic spectra. The IR spectra of the blue powders collected after heating at 200 and 350°C and corresponding to the anhydrous product are similar to that shown in Fig. 1, but the fine structure of the bands is practically lost. Additionally, in the samples collected after heating at 350°C the higher energy band (ca 1200 cm^{-1}) shows a notable intensity diminution.

In the spectra of the green products collected after the thermal treatments at 460 and 600°C some other important changes are observed, as it can be seen in Fig. 3. The first two bands, appear collapsed in one unique and broad feature centered at about
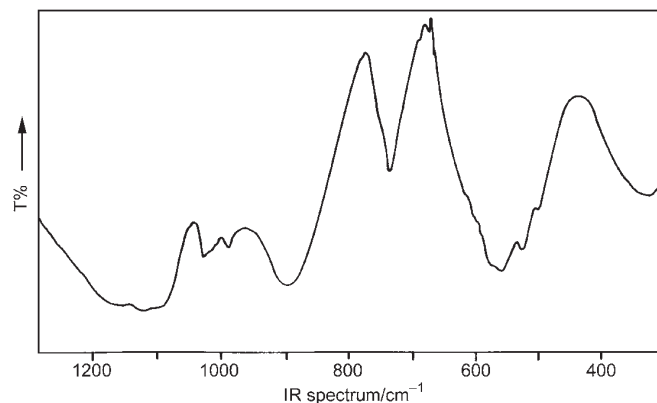
Fig. 3 Infrared spectrum of the thermolysis product of the complex, collected at 600°C, between 1300 and 300 cm^{-1}

1120 cm^{-1} (with shoulders at 1150 and 1090 cm^{-1}), whereas the intensity of the next group of bands diminishes dramatically, presenting two peaks, of medium and weak intensity at 1030 and 990 cm^{-1} respectively. The following two bands are centered at 895 and 734 cm^{-1}, whereas the last block of band also shows important changes in respect to that of the original species. In general, these spectra suggest the presence of mixtures of Na$_4$P$_2$O$_7$ and (VO)$_2$P$_2$O$_7$ [19]. Therefore, one can assume that during the melting, depolymerization of the cyclic anhydrous complex takes place probably generating a mixture of the type:

$$2Na_6[(VO)_3(P_2O_7)_3] \rightarrow 3Na_4P_2O_7 + 3(VO)_2P_2O_7$$
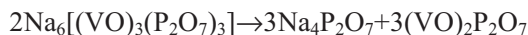
If this proposal is correct, the last observed DTA signal (585°C) is probably related to a phase transformation or to a new ligand rearrangement of the vanadyl diphosphate. This speculation is supported by the electronic spectra of these green materials. The spectra of these phases, collected after heating at 460 and 600°C, although similar, show some differences. That obtained at the melting temperature presents absorption bands at 796 (ε=40), 615 (ε=26) and 402 nm (ε=20 L mol^{-1} cm^{-1}), whereas that collected at 600°C shows the bands at 804, 625 and 408 nm, with similar intensities as those found above. These differences, although small, point out changes on the coordination sphere of the VO^{2+} cation.

We have attempted to attain a wider insight into the characteristics and eventual differences between the initial blue complex and the green material collected after melting, by ESR spectroscopy. Although the signals are very broad, the two spectra show some differences, confirming the existence of two different complex species. The green species presents the typical hyperfine splitting of VO^{2+} (8 lines). From this spectrum we estimate an A value of 195 Gauss (176·10^{-4} cm^{-2}) and g=1.934, values which are similar to those found in some monomeric species in the VO^{2+}/P$_2$O$_7^{4-}$ system [11] supporting our proposal of a depolymerization process during the fusion of

the material. The spectrum of the original trimeric species is much broader, and its hyperfine structure is more difficult to analyze.

* * *

References

 1 P. L. Gay and K. Kourtakis, Sciencs, 267 (1995) 661.
 2 E. Bordes and P. Courtine, J. Catal., 57 (1979) 236.
 3 A. Martin, B. Lücke, H. Seeboth, G. Ladwig and E. Fischer, React. Kinet. Catal. Lett., 38 (1989) 33.
 4 J. W. Johnson, D. C. Johnston, A. J. Jacobson and J. F. Brody, J. Am. Chem. Soc., 106 (1984) 8123.
 5 E. Bordes, P. Courtine and J. W. Johnson, J. Solid State Chem., 55 (1984) 270.
 6 G. Centi, Catal., Today, 5 (1993) 16.
 7 C. C. Torardi, Z. G. Li, H. S. Horowitz, W. Liang and M. H. Whangbo, J. Solid State Chem., 119 (1995) 349.
 8 J. Kalousová, J. Votinsky, L. Benes, K. Melanova and V. Zima, Collect. Czech. Chem. Comm., 63 (1998) 1.
 9 P. A. M. Williams and E. J. Baran, Biol. Trace Elem. Res., 36 (1993) 143.
10 E. J. Baran, in Metal Ions in Biological Systems (H. Sigel, A. Sigel, Eds.), Vol. 21, Dekker, New York 1995, p. 129.
11 P. Buglyó, T. Kiss, E. Alberico, G. Micera and D. Dewaele, J. Coord. Chem., 36 (1995) 105.
12 J. J. R. Fraústo da Silva and R. J. P. Williams, The Biological Chemistry of the Elements, Clarendon Press, Oxford 1991.
13 C. C. Parker, R. R. Reeder, L. B. Richards and P. H. Rieger, J. Am. Chem. Soc., 92 (1970) 5230.
14 A. Hasegawa, Y. Yamada and M. Miura, Bull. Chem. Soc. Jpn., 42 (1969) 846.
15 K. M. Jones and F. Larsen, Acta Chem. Scand., 19 (1965) 1205.
16 H. Onishi, Photometric Determination of Trace Metals, part 2, 4th Ed., Wiley, New York 1984.
17 A. B. P. Lever, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam 1984.
18 E. Steger and B. Kässner, Z. Anorg. Allg. Chem., 355 (1967) 131.
19 I. Kanesaka, K. Ozaki and I. Matsuura, J. Raman Spectr., 26 (1995) 997.
20 E. Steger and B. Kässner, Spectrochim. Acta, 24A (1968) 447.
21 E. J. Baran, A. H. Jubert and A. L.Rocha, J. Raman Spectr., 20 (1989) 801.
22 P. Kögerler, E. G. Ferrer and E. J. Baran, Monatsh. Chem., 127 (1996) 801.
23 A. C. González-Baró and E. J. Baran, Monatsh. Chem., 128 (1997) 323.
24 G. Micera and D. Sanna, in Vanadium in the Environment (J. O. Nriagu, Ed.), Part 1, Wiley, New York 1998, p. 131.