Vibrational spectra of vanadium(V) compounds
VI. Raman spectra of vanadium(V) oxodiperoxo complexes

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Dedicated to Professor RNDr. J. Masár, CSc., in honour of his 60th birthday

Raman spectra of seven vanadium(V) oxodiperoxo complexes have been measured. On the basis of interpretation of the spectra a reassignment of the vanadium—ligand stretching vibrations has been proposed. The sensitivity of the vanadium—peroxo oxygen stretching vibrations to changes in the coordination polyhedron has been confirmed.

Измерены спектры Рамана семи оксо-дипероксокомплексов ванадия(V). На основе интерпретации спектров было предложено изменение в отнесении валентных колебаний связей ванадий—лиганд. Полученные результаты подтвердили чувствительность валентных колебаний связи ванадий—перекисный кислород к изменениям в координационном полиэдре.

As it follows from interpretation of infrared spectra for a series of peroxo complexes of vanadium(V) the vanadium—peroxo oxygen stretching modes are sensitive to changes in the composition and geometry of the coordination sphere [1]. The spectra enable to distinguish among monoperoxo complexes, pentagonal-pyramidal and pentagonal-bipyramidal diperoxo complexes of vanadium(V).

The aim of this study was to verify the correlation between geometry of coordination sphere and spectral properties of oxodiperoxo complexes of vanadium(V) by means of interpretation of Raman spectra of the complexes with the known crystal structure.

Experimental

The complexes were prepared according to published methods: $K_2[VO(O_2)_2F]$ [2], $(NH_4)_2[VO(O_2)_2F]$ [3], $(NH_4)_3[VO(O_2)_2F_2]$ [4], $K_3[VO(O_2)_2CO_3]$ [5], $K_3[VO(O_2)_2C_2O_4] \cdot H_2O$ [6], $(NH_4)_3[HV_2O_3(O_2)_4]$ [7], $(ND_4)_3[DV_2O_3(O_2)_4]$ [2]. Raman spectra of crystalline

samples were measured on Jeol JRS 1 and Ramalog 3 Spex spectrophotometers using He-Ne laser. Decomposition was observed even for relatively stable complexes, *e.g.* $K_3[VO(O_2)_2CO_3]$, when the Ar^+ laser was used.

Results and discussion

Oxodiperoxovanadate ions have a low symmetry, therefore all vibrations corresponding to the site symmetry of the anions are active both in infrared and Raman spectra. However, Raman spectra are more suitable for investigation of the $v(V=O)$, $v(V-O_p)$ (O_p — peroxo oxygen), and $v(O-O)$ vibrations, because the corresponding bands are intensive in comparison with the bands which correspond to the bending vibrations of ligands. Similarly the V—X stretching modes (X is a donor atom of the further ligand (Fig. 1)) are observed in Raman spectra mostly as weak bands*.
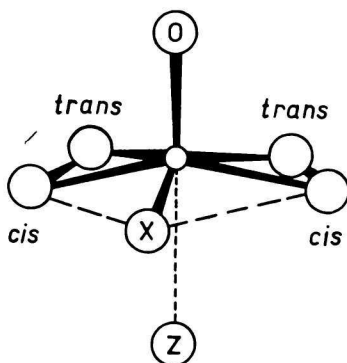

Fig. 1. Model of diperoxovanadate ion. *Cis* and *trans* positions of peroxo oxygen atoms are related to the X atom in the pentagonal plane.

When the correlation splitting is not considered, four bands corresponding to normal vibrations involving predominantly vanadium—peroxo oxygen stretching vibrations (v_1, v_2, v_3, and $v_4(V-O_p)$) can be expected for the $(O_2)V(O_2)$ group. For pentagonal-pyramidal complexes** the v_1 and $v_2(V-O_p)$ vibrations occur at approximately $\tilde{v} = 630\,cm^{-1}$ (the bands are intensive in the IR spectrum and weak or medium in the Raman spectrum). The v_3 and $v_4(V-O_p)$ vibrations occur at about $\tilde{v} = 520\,cm^{-1}$ (weak or medium bands in the IR spectrum, one band very strong, the second band medium in the Raman spectrum) (Table 1). This assignment was confirmed for $NH_4[VO(O_2)_2NH_3]$ by

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* It is true especially for the $v(V-F)$ vibrations [8].

** There are only three vanadium(V) diperoxo complexes for which pentagonal-pyramidal structure has been proved by X-ray analysis: $NH_4[VO(O_2)_2NH_3]$, $K_2[VO(O_2)_2F]$, $Cs_2[VO(O_2)_2F]$. The fourth will be probably $N(CH_3)_4[VO(O_2)_2H_2O]$, the structure of which is being solved.

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Table 1

Raman spectra of diperoxo complexes of vanadium(V) ($\tilde{\nu} = 200$—$1000\ cm^{-1}$)

$\tilde{\nu}(NH_4[VO(O_2)_2NH_3])^a$ cm^{-1}	$\tilde{\nu}(K_2[VO(O_2)_2F])$ cm^{-1}	$\tilde{\nu}((NH_4)_2[VO(O_2)_2F])$ cm^{-1}	Assignment
1000 m			$\nu(V=O)$
957 vs	950 vs	909 vs	
884 s	896 s	881 s	$\nu(O-O)$
	873 m		
	637 w	635 sh	$\nu_1(V-O_p)$
623 m	626 m	619 m	$\nu_2(V-O_p)$
533 vs	529 vs	511 vs	$\nu_3(V-O_p)$
503 m	489 m	485 w	$\nu_4(V-O_p)$
446 m			$\nu(V-N)$
322 s	339 vs	352 s	Bending
287 m	302 m	298 w	vibrations,
	276 s	251 m	$\nu(V-Z)$
230 w		232 w	

$\tilde{\nu}((NH_4)_3[VO(O_2)_2F_2])$ cm^{-1}	$\tilde{\nu}(K_3[VO(O_2)_2CO_3])$ cm^{-1}	$\tilde{\nu}(K_3[VO(O_2)_2C_2O_4]\cdot H_2O)$ cm^{-1}	Assignment
961 sh			$\nu(V=O)$
945 vs	934 vs	924 vs	
890 s	881 s	876 s	$\nu(O-O)$
865 m		859 w	
	740 vw		*b*
	693 vw?		
638 m	630 m	631 m	$\nu_1(V-O_p)$
592 m	593 s	584 s	$\nu_2(V-O_p)$
505 vs	484 vs	485 vs	$\nu_3(V-O_p)$
484 sh	446 vw?	472 sh	$\nu_4(V-O_p)$
		520 s	*c*
448 vw			$\nu(V-F)$
	387 m	379 m	Bending
349 s	332 s	346 s	vibrations,
297 w	296 m	307 w	$\nu(V-Z)$
268 vw	254 vw?	257 vw	
230 w	228 vw?	233 vw	

Table 1 (Continued)

$\tilde{v}((NH_4)_3[HV_2O_3(O_2)_4])^d$ cm^{-1}	$\tilde{v}((ND_4)_3[DV_2O_3(O_2)_4])^d$ cm^{-1}	Assignment
967 vs	971 vs	$v(V{=}O)$
942 s	942 s	
881 vs	884 s	$v(O{-}O)$
864 w	858 sh	
?	?	$v_1(V{-}O_p)$
608 s	607 s	$v_2(V{-}O_p)$
519 vs	519 vs	$v_3(V{-}O_p)$
483 sh	?	$v_4(V{-}O_p)$
370 w	365 w	Bending
324 m	321 m	vibrations,
271 m	271 m	$v(V{-}Z)$

a) According to [9]; *b*) bending vibrations of the coordinated carbonato group; *c*) vibration of the coordinated oxalato group; *d*) worse quality spectra.

means of isotopical substitutions NH$_3$—ND$_3$ and ^{14}NH$_3$—^{15}NH$_3$, as well as by normal coordinate analysis [9].

The original assignment for pentagonal-bipyramidal complexes was published by *Vuletic* and *Djordjevic* [6]. According to their interpretation only two strong infrared bands at about $\tilde{v} = 630\,\text{cm}^{-1}$ and $590\,\text{cm}^{-1}$ were assigned to the $v(V{-}O_p)$ vibrations*. But an analysis of the structural data and a normal coordinate analysis [10] show that there is no reason why the wavenumber region of the $v(V{-}O_p)$ vibrations should be more narrow for pentagonal-bipyramidal complexes than for pentagonal-pyramidal complexes. Raman spectra strongly support this view: intensity ratio for bands assigned to vanadium—peroxo oxygen stretching modes is characteristic of and similar for all diperoxo complexes under study. Analogically to NH$_4$[VO(O$_2$)$_2$NH$_3$] a very strong band at about $\tilde{v} = 500\,\text{cm}^{-1}$ was assigned to $v_3(V{-}O_p)$ for all listed diperoxo complexes (Table 1, Fig. 2). Assignment of the $v_4(V{-}O_p)$ vibration is more problematic and not unambiguous. It seems that corresponding band is weak in Raman as well as in IR spectra and the coupling of the $v_4(V{-}O_p)$ and $v(V{-}X)$ vibrations can be expected.

More detailed assignment of bands in the region of bending vibrations of the O=V(O$_2$)$_2$ group is not possible. However, it can be supposed that the bands which are present in the spectra of (NH$_4$)$_2$[VO(O$_2$)$_2$F] and (NH$_4$)$_3$[VO(O$_2$)$_2$F$_2$]

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* In our previous papers [1, 2, 5] we accepted this assignment.

and which are missing in the spectrum of $K_2[VO(O_2)_2F]$ correspond to normal modes, which involve stretching vibrations of the long axial V—Z bonds with the Z atom *trans* to the double-bonded oxygen. Such a bond is the V···O bond ($d = 0.2505$ nm) which in $(NH_4)_2[VO(O_2)_2F]$ connects two neighbouring units $VO(O_2)_2F$ into a chain O=V···O=V···O=V··· [11] or the V—F bond ($d = 0.2306$ nm) in $(NH_4)_3[VO(O_2)_2F_2]$ [12]*.
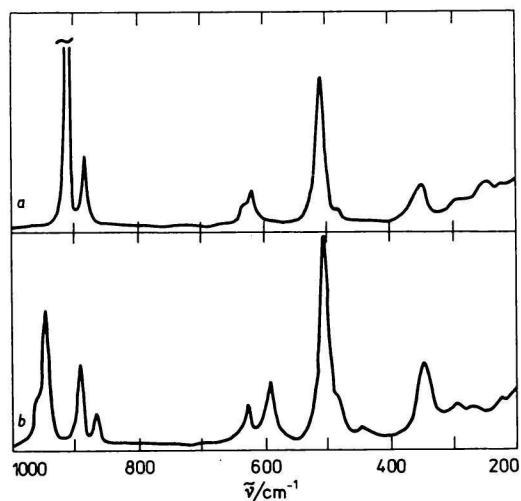
Fig. 2. Raman spectra of $(NH_4)_2[VO(O_2)_2F]$ (*a*) and $(NH_4)_3[VO(O_2)_2F_2]$ (*b*).

In a previous paper [1] a criterion for distinguishing between vanadium(V) diperoxo complexes with the coordination number 6 and 7 by means of the infrared spectra, was suggested. Although in the mentioned paper the original assignment of the V—O_p stretching vibrations was used, *e.g.* without v_3 and v_4(V—O_p), the main conclusions are still valid. These conclusions with respect to reassignment of some bands can be summarized in the following way: *a*) The bands in the region of the V—O_p stretching vibrations are the most sensitive to changes in the coordination sphere. *b*) When the V—Z bond length is decreasing, the asymmetry of the $V(O_2)_2$ group, *e.g.* the difference between bond lengths of two V—O_p bonds in one $V(O_2)$ group, is increasing. An increase of asymmetry demonstrates itself in the shift of the band corresponding to v_3(V—O_p) to lower wavenumbers, but especially in the increase of separation of the bands

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* Other possibility is that these bands correspond to librations of the NH_4^+ ion.

corresponding to the $\nu_1(V—O_p)$ and $\nu_2(V—O_p)$ vibrations (Table 2). The wavenumber difference $\Delta\tilde{\nu} = \tilde{\nu}_1(V—O_p) - \tilde{\nu}_2(V—O_p)$ can be thus considered as a quantity which enables to distinguish between pentagonal-pyramidal ($\Delta\tilde{\nu} \sim 10\,\mathrm{cm}^{-1}$) and pentagonal-bipyramidal ($\Delta\tilde{\nu} \sim 40\,\mathrm{cm}^{-1}$) complexes.

Table 2

Selected structural and spectral data for diperoxo complexes of vanadium(V)

Complex	CN^a	$\dfrac{d(V—Z)}{nm}$	$\left(\dfrac{\tilde{\nu}_1 - \tilde{\nu}_2}{\mathrm{cm}^{-1}}\right)^b$	$\dfrac{\tilde{\nu}_3}{\mathrm{cm}^{-1}}$	Ref.^{c}
$NH_4[VO(O_2)_2NH_3]$	6	—	0	533	[13]
$K_2[VO(O_2)_2F]$	6	—	11	529	[14]
$(NH_4)_3[HV_2O_3(O_2)_4]$	6—7	0.2520	0	519	[15]
$(ND_4)_3[DV_2O_3(O_2)_4]$	6—7		0	519	
$(NH_4)_2[VO(O_2)_2F]$	6—7	0.2505	16	511	[11]
$(NH_4)_3[VO(O_2)_2F_2]$	7	0.2306	36	505	[12]
$K_3[VO(O_2)_2CO_3]$	7	0.2301	37	484	[16]
$K_3[VO(O_2)_2C_2O_4]\cdot H_2O$	7	0.2250	47	485	[17]

a) CN — the coordination number of vanadium atom. The coordination number 6—7 is given for pseudopentagonal-bipyramidal coordination [15]. *b)* From Raman spectra. *c)* References for structural data.

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