

STRETCHING VIBRATIONS OF THE V(O₂) GROUP AND STRUCTURE OF VANADIUM(V) PEROXO COMPLEXES*

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The infrared spectra of some vanadium(V) peroxo complexes were measured and supplemented with published data (a total of 33 complexes) to seek for relations between the stretching vibrations of the V(O₂) group and the structure of the complexes. While no such relation could be established in the region of 9·10—800 cm⁻¹, in the 660—490 cm⁻¹ range the spectral patterns were found sensitive to the composition and structure of the coordination polyhedron, thus making it possible to discriminate between complexes of different types.

The aim of the majority of works dealing with the vibrational spectra of complexes with a coordinated O₂ group¹⁻⁷ has been assignment of the ν(O—O) and ν(M—O_p) stretching vibration bands (O_p stands for oxygen in the O₂ ligand), discrimination of the type of bonding of the O₂ ligand ($M \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$, M—O—O—M, M—O—O, etc.) and discussion of the electron density transfer between the central atom and the O₂ ligand. Little attention has been so far paid to relations between the position and/or intensity of the bands of the M(O₂) group stretching vibrations and the composition and structure of the whole coordination sphere of the complex (number of the peroxo groups involved, the coordination number, etc.).

The present work gives a survey of the positions of the bands belonging to the ν(O—O) and ν(V—O_p) stretching vibrations for 33 vanadium(V) peroxo complexes; these data are investigated with a view to finding whether use could be made of the infrared spectral patterns for discriminating between the various types of complexes.

EXPERIMENTAL

The peroxo complexes were prepared according to published procedures (Table I). The K₃·[DV₂O₃(O₂)₄].D₂O and (ND₄)₃[DV₂O₃(O₂)₄] complexes were obtained by multiple recrystallization of K₃[HV₂O₃(O₂)₄].H₂O and (NH₄)₃[HV₂O₃(O₂)₄], respectively, from D₂O. Preparation of Cs[VO(O₂)₂H₂O]: V₂O₅ (0·91 g, 5 mmol) was dissolved under cooling (0°C) in 40% H₂O₂

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25 ml), CsCl (1.68 g, 10 mmol) was added, and the solution was cooled down to -25°C and precipitated with cooled ethanol (-25°C). The light-yellow precipitate formed was washed with ethanol and dried over silica gel in a desiccator accommodated in a refrigerator. Preparation of $\text{N}(\text{CH}_3)_4[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]: \text{V}_2\text{O}_5$ (0.91 g, 5 mmol) was dissolved in a 10% solution of $\text{N}(\text{CH}_3)_4\cdot\text{OH}$ (10 ml), the solution obtained was cooled down to -25°C , H_2O_2 (5 ml) was added, and the system was precipitated with cooled ethanol (-25°C); further was proceeded as above. The synthesis of new fluoro-peroxo complexes will be published elsewhere. The analytical data of the substances obtained were consistent with the formulas.

The infrared spectra were measured in Nujol mulls on Perkin Elmer 567 (U.S.A.) and Spectromaster (Grubb-Parsons, Great Britain) instruments, wavenumber-calibrated by means of a polystyrene foil.

RESULTS AND DISCUSSION

The following conclusions can be drawn from the published data on the $\nu(\text{O}-\text{O})$ stretching vibrations in compounds involving a coordinated O_2 group: The band positions do not correlate with the $\text{O}-\text{O}$ bond lengths (Table II). No information can be derived from the $\nu(\text{O}-\text{O})$ band positions concerning the electron density shift between the central atom and the O_2 group⁸⁻¹⁴. The $\nu(\text{O}-\text{O})$ band position permits a discrimination between the monodentate ($\text{M}-\text{O}-\text{O}$) and the bidentate ($\text{M} \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O} \end{array}$ or $\text{M}-\text{O}-\text{O}-\text{M}$) O_2 ligands¹⁴.

In all the peroxo complexes listed in Table I except $\text{K}_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4]\cdot 2\text{H}_2\text{O}$, the peroxide anion can be assumed to bond exclusively as the bidentate ($\text{V} \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O} \end{array}$) ligand; the $\text{K}_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4]\cdot 2\text{H}_2\text{O}$ complex involves probably also a bridge O_2 group. The $\text{V} \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O} \end{array}$ group is characterized by three normal vibrations; one of them is predominantly $\text{O}-\text{O}$ stretching, the other two are essentially $\text{V}-\text{O}_p$ stretchings (the problem of the $\nu(\text{O}-\text{O})$ and $\nu(\text{V}-\text{O}_p)$ vibrational coupling has been discussed in ref.⁸); all the three vibrations are infrared-active.

In all of the vanadium(V) peroxo complexes, the $\nu(\text{O}-\text{O})$ vibration gives rise to one or several bands in the $910-800\text{ cm}^{-1}$ range. No relation could be traced between the $\nu(\text{O}-\text{O})$ band positions and intensities and the composition and structure of the complexes. In the $660-490\text{ cm}^{-1}$ region, on the other hand, the spectrum is to an extent sensitive to changes in the coordination polyhedron of the complex.

In the case of diperoxo complexes in which the central vanadium atom possesses the coordination number 6, there are two characteristic regions in the spectra, *viz.* the 630 and 520 cm^{-1} ranges. Characteristic is not only the band position, but also the intensity: bands in the 630 cm^{-1} range are very strong, whereas those in the 520 cm^{-1} range are weak or medium. Such bands are typical of monomeric as well as dimeric complexes of the group (Table I).

TABLE I

Positions (cm^{-1}) of the infrared bands of the $\nu(\text{O}-\text{O})$ $\nu(\text{V}-\text{O}_p)$ stretching vibrations in vanadium(V) peroxo complexes

Complex	$\nu(\text{O}-\text{O})$	$\nu(\text{V}-\text{O}_p)$		Δ^b	Ref. S/IR ^c
		A	B		
$\text{K}[\text{V}(\text{O}_2)_4] \cdot 2 \text{H}_2\text{O}$	851 vs	623 m	561 s	62	15/d
$\text{K}_4[\text{V}_2\text{O}_3(\text{O}_2)_4] \cdot 2 \text{H}_2\text{O}$	887 s	627 vs	548 m	79	16/d
	879 s				
	869 s				
	866 vs				
	875 vs	629 vs	544 m	85	17/d
$(\text{NH}_4)_4\text{V}_2\text{O}_3(\text{O}_2)_4$	865 vs				
$\text{K}_3[\text{HV}_2\text{O}_3(\text{O}_2)_4] \cdot \text{H}_2\text{O}$	884 vs	640 s	522 m	109	18/d
	866 vs	620 sh	508 w		
	879 w	612 s			
	860 vs				
$\text{K}_3[\text{DV}_2\text{O}_3(\text{O}_2)_4] \cdot \text{D}_2\text{O}$	884 vs	641 s	527 sh	104	d/d
	867 vs	611 s	516 m		
	878 w				
$(\text{NH}_4)_3[\text{HV}_2\text{O}_3(\text{O}_2)_4]$	885 vs	641 s	521 sh	113	19/d
	869 vs	611 s	505 m		
$(\text{ND}_4)_3[\text{DV}_2\text{O}_3(\text{O}_2)_4]$	885 vs	638 s	518 m	114	d/d
	868 vs	611 s	505 w		
	860 vs				
$\text{Cs}_3[\text{HV}_2\text{O}_3(\text{O}_2)_4]$	886 vs	630 sh	505 w	114	19/19
	870 vs	608 vs			
$\text{Cs}_3[\text{DV}_2\text{O}_3(\text{O}_2)_3]$	890 vs	605 vs	510 w	95	19/19
	871 vs				
$\text{K}[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]$	892 s	629 s	499 w	130	20/20
	872 s				
$\text{Cs}[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]$	890 s	624 s	522 w	118	d/d
	876 s		490 w		
$\text{N}(\text{CH}_3)_4[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]$	898 s	652 s	526 m	98	d/d
	877 s	630 s	518 m		
	861 s	602 s			
	853 s	595 s			
$\text{NH}_4[\text{VO}(\text{O}_2)_2\text{NH}_3]$	87 vs	633 s	531 m	112	1/1
		623 s	500 sh		
$\text{ND}_4[\text{VO}(\text{O}_2)_2\text{NH}_3]$	876 s	635 vs	531 m	119	1/1
			500 sh		
$\text{K}_2[\text{VO}(\text{O}_2)_2\text{F}]$	897 s	634 vs	535 m	101	21, 22/d
	876 vs		531 m		
$(\text{NH}_4)_2[\text{VO}(\text{O}_2)_2\text{F}]$	881 vs	641 s	518 m	108	24/d
		611 s			

TABLE I
(Continued)

Complex ^a	$\nu(\text{O}=\text{O})$	$\nu(\text{V}-\text{O}_p)$		Δ^b	Ref. S/IR ^c
		A	B		
$(\text{NH}_4)_3[\text{V}_2\text{O}_2(\text{O}_2)_4\text{F}]$	897 s	646 sh	536 w	101	24/d
	891 s	635 s	517 w		
	876 s	600 s			
	856 s				
$\text{K}_3[\text{VO}(\text{O}_2)_2\text{CO}_3]$	877 m	626 m	586 m	40	20/20
	859 s				
	851 s				
$\text{K}_3[\text{VO}(\text{O}_2)_2\text{C}_2\text{O}_4] \cdot \text{H}_2\text{O}$	878 s	628 m	584 s	44	8/d
	858 vs				
$\text{K}_3[\text{VO}(\text{O}_2)_2\text{C}_2\text{O}_4]$	898 s	632 s	591 s	39	20/20
	880 vs	628 s			
	875 vs				
$(\text{NH}_4)_3[\text{VO}(\text{O}_2)_2\text{C}_2\text{O}_4] \cdot 2 \text{H}_2\text{O}$	870 s	636 m	588 m	48	8/8
	850 vs				
$\text{Na}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 5 \text{H}_2\text{O}$	895 m	623 m	588 s	35	8/8
	872 vs				
$\text{K}[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 5 \text{H}_2\text{O}$	875 s	621 m	582 s	39	8/8
	856 vs				
$\text{NH}_4[\text{VO}(\text{O}_2)_2\text{bpy}] \cdot 4 \text{H}_2\text{O}$	870 s	622 m	585 s	37	8/8
	858 vs				
$\text{Na}[\text{VO}(\text{O}_2)_2\text{phen}] \cdot \text{B} \text{H}_2\text{O}$	880 s	628 m	588 s	40	8/8
	858 vs				
$\text{K}[\text{VO}(\text{O}_2)_2\text{phen}] \cdot 3 \text{H}_2\text{O}$	870 s	635 m	590 m	45	8/8
	854 vs				
$\text{NH}_4[\text{VO}(\text{O}_2)_2\text{phen}] \cdot 2 \text{H}_2\text{O}$	870 s	636 m	588 m	48	8/8
	850 vs				
$\text{K}_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot s \text{H}_2\text{O}$	903 s	617 s	585 s	e	24/d
	894 s				
	869 m				
$\text{NH}_4[\text{VO}(\text{O}_2)\text{dipicH}_2\text{O}] \cdot x \text{H}_2\text{O}$	839 m	610 m	670 s	40	11/12
$\text{K}_3[\text{VO}(\text{O}_2)(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$	904 m	554 m	549 m	5	20/20
$\text{K}_3[\text{VO}(\text{O}_2)\text{EDTA}] \cdot 2 \text{H}_2\text{O}$	869 s		555 w	—	23/23
$\text{Na}_3[\text{VO}(\text{O}_2)\text{EDTA}] \cdot 3 \text{H}_2\text{O}$	869 s		55 w	—	23/23
$(\text{NH}_4)_3[\text{VO}(\text{O}_2)\text{EDTA}] \cdot 3 \text{H}_2\text{O}$	880 s		555 w	—	23/23

^a Ligand abbreviations: bpy — 2,2'-bipyridine, phen — 1,10-phenanthroline, dipic — pyridine-2,6-dicarboxylate. In the $[\text{VO}(\text{O}_2)_2\text{L}]^{n-}$ complex anions (L is the CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, bpy, or phen bidentate ligand) the vanadium atom possesses the coordination number 7, in the remaining diperoxo complexes the coordination number can be assumed to be 6; ^b $\Delta\nu(\text{V}-\text{O}_p)$, calculated as the difference of the $\nu(\text{V}-\text{O}_p)$ bands A and B; ^c S — synthesis, IR — infrared spectra of the complexes; ^d this work; ^e the vibrations of the bridge and the side-on-bonded O_2 group cannot be so far discriminated.

When in the diperoxo complexes the coordination around the vanadium atom is completed to pentagonal-bipyramidal (coordination number 7), the position and intensity of the $\nu(\text{V—O}_p)$ bands vary. The infrared spectra of complexes of this type exhibit two bands at about 625 and 585 cm^{-1} , with an approximately equal (usually medium) intensity.

In the case of monoperoxo complexes, no splitting of the $\nu(\text{V—O}_p)$ band usually occurs. The slight splitting (5 cm^{-1}) found for the $\text{K}_3[\text{VO}(\text{O}_2)(\text{O}_3)_2] \cdot 2\text{ H}_2\text{O}$ com-

TABLE II

Bond lengths $d(\text{O—O})$ and wavenumbers of the infrared bands of the $\nu(\text{O—O})$ stretching vibration for some complexes involving an $\text{M}(\text{O}_2)$ group

Compound ^a	$d(\text{O—O})$ pm	$\nu(\text{O—O})$ cm^{-1}	Ref.
$[\text{Ir}(\text{bpy})_2(\text{O}_2)]\text{Cl}$	162.5	845	9
$\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$	147.2	876	10, 1
$[\text{Pt}(\text{PPh}_3)_2(\text{O}_2)] \cdot 1.5\text{ C}_6\text{H}_6$	145	815	9
$\text{NH}_4[\text{VO}(\text{O}_2)(\text{dipic})\text{H}_2\text{O}] \cdot x\text{ H}_2\text{O}$	144.1	839	11, 12
$\text{K}_3[\text{VO}(\text{O}_2)_2(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$	144.1	878, 858	13, 8
$[\text{IrClCO}(\text{PPh}_3)_2(\text{O}_2)]$	130.0	856	9

^a Abbreviations: bpy — 2,2'-bipyridine, Ph — phenyl, dipic — pyridine-2,6-dicarboxylate.

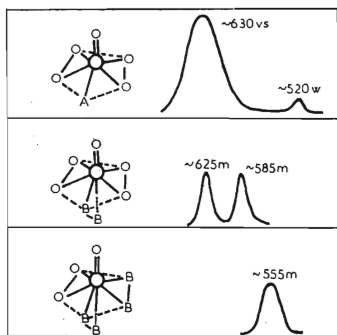


FIG. 1

Discrimination of three types of vanadium(V) peroxo complexes based on the infrared bands of the $\nu(\text{V—O}_p)$ stretching vibrations. A monodentate ligand, B—B bidentate ligand in the case of monoperoxo complexes, two B—B ligands can be replaced by a tetradentate ligand or by a combination of a tridentate and a monodentate ligand

plex may be a result of the correlation effect; the splitting observed in the spectrum of the pyridine-2,6-dicarboxylate complex calls for a detailed investigation. The discrimination between some types of vanadium(V) peroxo complexes based on the $\nu(\text{V}-\text{O}_p)$ bands is shown schematically in Fig. 1. (All the monoperoxo complexes given in Table I have probably the coordination number 7, and so the relation between the coordination number of the complex and its spectral patterns cannot be examined. Similarly, additional data will have to be obtained for the tetraperoxo and triperoxo-divanadate(V) complexes.)

The wavenumber differences $\Delta\nu(\text{V}-\text{O}_p)$ for diperoxo complexes with the coordination number 6 are about 100 cm^{-1} , for diperoxo complexes with the coordination number 7, about 40 cm^{-1} , and for monoperoxo complexes they are very low indeed. This fact supports the assumption that the $\Delta\nu(\text{V}-\text{O}_p)$ difference is essentially a consequence of the interaction of two $\text{V}(\text{O}_2)$ groups⁸.

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