VIBRATIONAL SPECTRA OF AQUADIOXOTETRA; PEROXODIVANADATES(V) $M_2[V_2O_2(O_2)_4(H_2O)].xH_2O$ (M = N(CH$_3$)$_4$, Cs)

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The infrared and Raman spectra of $M_2[V_2O_2(O_2)_4(H_2O)].xH_2O$ and $M_2[V_2O_2(O_2)_4(D_2O)].xD_2O$ (M = N(CH$_3$)$_4$, Cs) were measured. In the region of the vanadium–oxygen stretching vibrations, the spectra were interpreted based on normal coordinate analysis, employing empirical correlations between the bond lengths and force constants.

Although vanadium(V) peroxo compounds have been investigated for nearly 150 years[1], until recently no consensus existed concerning the structure of the products isolated from weakly acid aqueous solutions of peroxovanadates(V). These products are unstable and mostly X-ray-amorphous. The different formulations of, e.g., $MH_2VO_2(O_2)_2$ (ref.[2]), $MVO_5.aq$ (ref.[3]), or $M_2H_2V_2O_{11}$ (ref.[4]) relied on the results of chemical analysis while lacking any structure verification, by spectral methods at least. The X-ray-amorphous potassium salt has been formulated as $K[VO(O_2)_2.(H_2O)]$ primarily based on the infrared spectra and the assumed structure of the anion in solution[5]. Recently, crystalline peroxovanadates(V) were prepared from weakly acid solutions at our laboratory. X-ray analysis of the tetramethylammonium[6] and potassium[7] salts gave evidence that the substances can be written as $M_2[V_2O_2.(O_2)_4(H_2O)].xH_2O$. The dinuclear complex anion possesses two atypical features, viz. asymmetry (the two coordination polyhedra are different) and a tridentate μ-peroxo group (Fig. 1).

The vibrational spectra of monomeric vanadium(V) peroxo complexes have been interpreted by using the Wilson GF approach employing empirical correlations between the bond length and the force constant[8-10]; a satisfactory fit to the experimental data has been thereby achieved.

In the present work, this procedure is applied to more complex species. The asymmetric $[V_2O_2(O_2)_4(H_2O)]^{2-}$ anion, with a variable V—O bond length, is a suitable object for testing the applicability of the above approach.

EXPERIMENTAL

Substances. $(N(CH_3)_4)_2[[V_2O_2(O_2)_4(H_2O)].2\ H_2O$ was prepared following the procedure[6]. $Cs_2[V_2O_2(O_2)_4(H_2O)].H_2O$ was synthesized by dissolving 0·58 g (2·5 mmol) of $CsVO_3$ in 5 ml of water and 5 ml of 30% H_2O_2 at 0°C. After filtering, 3 ml of cool ethanol and several drops

TABLE I

Experimental and calculated vibrational wavenumbers for $[V_2O_2(O_2)_4H_2O]^{2-}$

$\tilde{\nu}_{exp}$ [a] cm^{-1}	ν_{calc} cm^{-1}	PED[b] %			Assignment
973	979	88(16)			$\nu(V{=}O)$
960	968	98(8)			
	903	92(3)			$\nu(O_p{-}O_p)$
885	885	92(14)			
867	884	91(6)			
859	880	94(11)			
	666	51(4),	24(5),	17(7)	$\nu(V{-}O_p)$
642	639	32(10),	29(15),	26(13)	
619	613	32(12),	25(13),	23(15)	
	604	40(7),	23(5),	19(2)	
533	546		41(12),	32(13)	
523	536	32(7),	29(2),	27(4)	
	496	24(5),	22(10),	16(15)	
495	495	24(10),	20(5),	17(2)	
403	408	73(9),		15(1)	$\nu(V{-}OH_2)$
392[c]	397[c]	48(9)[c],		43(1)[c]	$\nu(V{-}OD_2)$
376	385		72(1)		$\nu(V{-}O_p)_b$

[a] Infrared spectra; [b] potential energy distribution, contributions being higher than 15%, numbers of internal coordinate according to Fig. 1 are given in parentheses; [c] data for $[V_2O_2(O_2)_4D_2O]^{2-}$.

FIG. 1

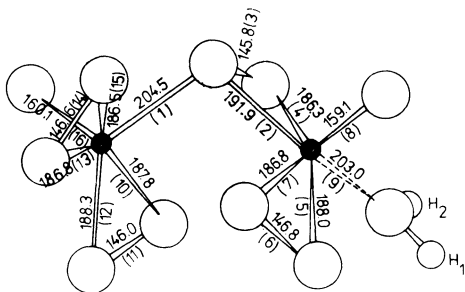Structure of anion in the $(N(CH_3)_4)_2.$ $.[V_2O_2(O_2)_4(H_2O)].2\ H_2O$ complex. The numbers attached to the bonds are bond lengths in pm, the internal coordinate numbering is given in parentheses

of H_2SO_4 ($c = 1$ mol l^{-1}) were added to make the solution clear, and the latter was allowed to crystallize at $-25°C$. In several days, light-yellow hexagonal crystals of the substance were isolated, rinsed with ethanol and dried at $-25°C$. Chemical analysis: calculated: 17·93% V, 22·90% O_2^{2-}; found: 18·07% V, 22·71% O_2^{2-}.

$(N(CH_3)_4)_2[V_2O_2(O_2)_4(D_2O).2\ D_2O]$ and $Cs_2[V_2O_2(O_2)_4(D_2O)].D_2O$ were prepared likewise using D_2O_2 and D_2SO_4 in D_2O, and also C_2D_5OD (Isocommerz, G.D.R.).

Spectral measurements. Infrared spectra were scanned over the 4 000—200 cm^{-1} region on a Specord M-80 grating spectrophotometer (Carl Zeiss, Jena, G.D.R.). The substances were measured in Nujol mulls using KBr (4 000—400 cm^{-1}) and polyethylene (500—200 cm^{-1}) windows.

Raman spectra of the solid complexes were measured on a JEOL JRS 1 instrument equipped with a He–Ne laser (monochromatic power at sample 18 mW).

Normal coordinate analysis of the $[V_2O_2(O_2)_4(H_2O)]^{2-}$ anion in the tetramethylammonium complex (dihydrate) was performed in terms of the Wilson GF matrix method in the point

TABLE II
Vibrational spectra of $(N(CH_3)_4)_2[V_2O_2(O_2)_4A_2O].2\ A_2O$ (A = H, D)

IR		Raman		Assignment
H	D	H	D	
973 s	975 s	977 s	978 s	$\nu(V{=}O)$
960 s	959 s	958 sh	952 sh	
937 vs	936 vs	931 s	934 s	*a*
885 s	886 s	889 s	891 s	$\nu(O_p–O_p)$
867 vs	870 vs	875 sh	873 sh	
859 sh	860 w	859 sh	864 w	
		753 m	755 m	*a*
642 s	639 s			$\nu(V–O_p)$
619 s	621 vs	624 m	627 m	
609 m	427 w	608 m		$\varrho_w(A_2O)$
533 w	535 sh	532 vs	533 vs	$\nu(V–O_p)$
523 m	529 m			
495 w	496 w	492 m	496 m	
469 w	470 w			*a*
460 m	461 m	459 m	461 m	*a*
403 w	392 w			$\nu(V–OA_2)$
376 w	373 w	371 w	373 w	$\nu(V–O_p)_b$
332 m	333 m	328 s	328 s	deformation
310 sh	310 sh			vibrations
247 m	248 m	261 m	263 m	
226 w	227 w	223 m	224 m	

a Vibrational bands of cation.

model approximation for H_2O (D_2O). The G matrix was calculated using the structure data from ref.[6]. Only the internal stretching coordinates were considered; their numbering and bond lengths are shown in Fig. 1.

The force constants for the V–O and O–O bonds were derived based on the empirical correlations between the bond length and the force constant[8] and were used in the treatment without further refinement. From among the interaction force constants, only the $f(VO_p, VO_p)$ and $f(VO_p, O_pO_p)$ bond–bond interactions (O_p is peroxide oxygen) were taken into account. Negative values, corresponding to the assumed electron density transfer from the O_2^{2-} ligand to the central atom[8], were used for these force constants in the anion studied, as was the case with other peroxovanadates(V) too.

The values of the force constants, in N m^{-1}, were as follows (the bond numbers in Fig. 1 are given in parentheses): $f(V{=}O)$ 665 (8), 650 (16); $f(V{-}O_p)$ 280 (4), 270 (7, 13, 15), 260 (5, 10, 12), 220 (2); $f(O_p{-}O_p)$ 370 (3), 360 (6, 11, 14); $f(V{-}O_p)_b$ 135 (1); $f(V{-}OH_2)$ 145 (9); $f(VO_p{-}VO_p)$ −20; $f(VO_p{-}O_pO_p)$ −20.

TABLE III

Vibrational spectra of $Cs_2[V_2O_2(O_2)_4A_2O].A_2O$ (A = H, D)

IR		Raman		Assignment
H	D	H	D	
993 m	993 s	994 vs	993 vs	$\nu(V{=}O)$
978 vs	980 vs			
960 s	961 vs	966 m	970 m	
893 s	895 vs	896 s	895 s	$\nu(O_p{-}O_p)$
885 m	883 s	885 m	882 s	
875 w	874 m			
855 vs	855 vs	860 m	862 m	
675 sh				$\varrho_w(H_2O)$?
645 s	643 s	644 sh	644 sh	$\nu(V{-}O_p)$
625 sh	626 sh	626 sh	628 sh	
619 m	616 m	610 s	612 s	
608 vs	607 vs			
520 m	520 m	530 vs	530 vs	
		484 m	483 m	
464 s	464 s	462 s	462 s	
401 w	400 w	403 s	400 s	$\nu(V{-}O_p)_b$
347 m	348 m	350 sh	350 sh	deformation
340 sh	338 m	340 s	342 s	vibrations
302 m	304 m	320 m	320 m	
280 sh	280 w	286 w	284 w	
256 m	256 m	256 w	256 w	
		239 w	240 w	
		208 sh	209 sh	

RESULTS AND DISCUSSION

The calculated and observed vibrational wavenumbers, along with the potential energy distribution data, are given in Table I. The satisfactory agreement between the experimental and calculated data gives evidence that the empirical correlations between the bond lengths and force constants suit well for estimating the stretching vibration wavenumbers in vanadium(V) peroxo complexes. A good agreement was also achieved for the $\nu(V\text{---}OH_2)$ stretching vibrations, where the correctness of the assignment was confirmed by the band shift accompanying the $H \to D$ isotopic substitution; the experimental and calculated shifts are both about $10\ cm^{-1}$. The lower shift as compared to the expected value of $20\ cm^{-1}$ (ref.[11]) is apparently related with the different contribution of the $\Delta(V\text{---}O_p)_b$ internal coordinate (Fig. 1, coordinate No. 1) to the potential energy for this normal vibration, viz. 15% for $[V_2O_2(O_2)_4(H_2O)]^{2-}$ and 43% for the perdeuterated analogue (Table I).

The vibrational spectra over the $1\ 000-200\ cm^{-1}$ range (Tables II and III, Figs 2 and 3) contain a relatively high number of bands, which is consistent with the asym-
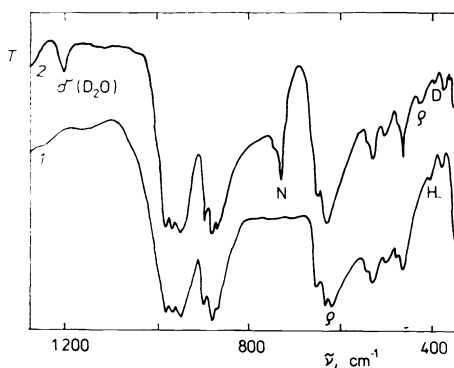

FIG. 2

Infrared spectra of $(N(CH_3)_4)_2[V_2O_2(O_2)_4.(H_2O)].2\ H_2O$ (1) and $(N(CH_3)_4)_2[V_2O_2.(O_2)_4(D_2O)].2\ D_2O$ (2). **N** Nujol, ϱ $\varrho_w(A_2O)$, **H** $\nu(V-OH_2)$, **D** $\nu(V-OD_2)$
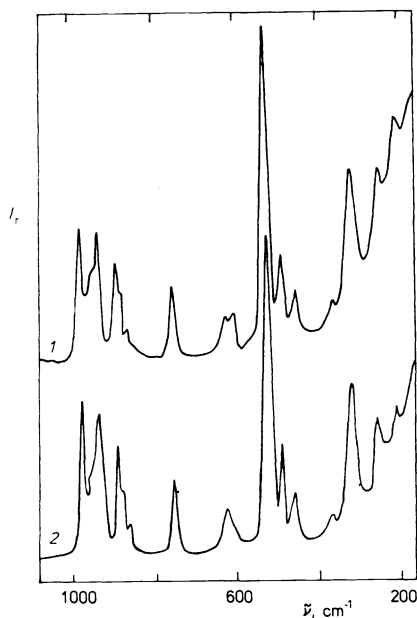
FIG. 3

Raman spectra of solid $(N(CH_3)_4)_2[V_2O_2.(O_2)_4(H_2O)].2\ H_2O$ (1) and $(N(CH_3)_4)_2.[V_2O_2(O_2)_4(D_2O)].2\ D_2O$ (2)

metric structure of the anion. In addition to the $v(V{=}O)$, $v(O_p{-}O_p)$, $v(V{-}O_p)$ and $v(V{-}OH_2)$ bands, the spectra exhibit many bending vibration bands; the tetramethylammonium complex displays also bands belonging to the cation. The spectra contain besides the $v(V{-}OH_2)$ band an additional band which is shifted on deuteration (from 609 to 427 cm^{-1} for the tetramethylammonium complex); this band can be attributed to a bending vibration of coordinated water $(\varrho_w?)$ or to a libration of crystal water.

The bands of the $N(CH_3)_4^+$ cation occur where they have been expected (see e.g., ref.[12]).

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