Crystal Structure and Infrared and Raman Spectra of Tetramethylammonium Di-μ-fluoro-bis[aquadifluoro-oxovanadate(IV)]

By **Peter Bukovec, Svetozar Milićev,* Alojz Demšar,** and **Ljubo Golič,** Department of Chemistry, E. Kardelj University, Ljubljana, Yugoslavia

The title complex, $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$, has been isolated from an aqueous solution of VF_4 and $[NMe_4]F$. The crystal structure has been determined from three-dimensional counter *X*-ray data. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 7.012(1), b = 8.119(1), c = 9.047(1) Å, α = 65.84(1), β = 83.21(1), γ = 73.09(1)°, and Z = 1. Least-squares refinement of the structure based on 1 552 observations led to an R factor of 0.046. The structure consists of dimeric units $[\{VOF_3(OH_2)\}_2]^{2-}$ possessing a centre of inversion, which are linked in chains by short hydrogen bonds [O–H ··· F 2.564(5) Å]. The geometry around vanadium is distorted octahedral with vanadium–fluorine distances ranging from 1.894(4) to 2.173(3), V–O 1.607(5), V–OH_2 2.074(3), V–V 3.292(1) Å, and V–F–V 105.5(1)°. The i.r. (250—4 000 cm^{-1}) and Raman spectra of $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ and its deuteriated and anhydrous derivatives are reported and interpreted according to the structure. The spectrum of the cation shows only influences of the solid-state forces. Stretching vibrations of the V=O bonds appear either in the Raman (980 cm^{-1}) or the i.r. (968 cm^{-1}). Hydrogen bonds give rise to a strong absorption manifesting one of the strongest interactions in hydrates (3 205 and 3 030 cm^{-1}). The shift (ν_H/ν_D = 1.34) and the reduction in band width (factor of 1.8) upon deuteriation have expected values. The spectra of the product of reversible dehydration indicate the absence of a centre of inversion in the anionic portion.

CONSIDERABLE interest has been shown in the study of oxovanadium(IV) complexes.[1] The $[VO]^{2+}$ unit is very stable and capable of persisting in reactions with ligands in the first co-ordination sphere of vanadium. Fluoro-oxovanadates(IV), mostly prepared with alkali and ammonium ions,[2,3] show different stoicheiometries. The basic structural units of the fluoro-anions are $[VOF_5]^{3-}$ octahedra which are found isolated in $M^I_3[VOF_5]$ [2] and $[M^{III}(NH_3)_6][VOF_5]$,[4] connected to *cis* chains in $K_2[VOF_4]$ [5] and $[NH_4]_2[VOF_4]$,[6] or to complex chains [7] in $Cs[VOF_3]\cdot0.5H_2O$. In the case of $Cs_2[VOF_4(OH_2)]$ the structure contains $[VOF_4(OH_2)]^{2-}$ octahedra.[8] The anion $[V_2O_2F_7]^{2-}$, also found with caesium, consists of two $[VOF_5]^{3-}$ octahedra sharing a common face.[9]

EXPERIMENTAL

Preparation.—Vanadium pentaoxide (0.01 mol) was dissolved in 20% hydrofluoric acid (25 cm^3), reduced with sulphur dioxide, and the excess of SO_2 driven off on a water-bath. A solution of tetramethylammonium fluoride (0.02 mol), prepared by neutralisation of the corresponding hydroxide with 40% hydrofluoric acid to pH 5, was added, and the mixture left at room temperature. Within a few days, blue crystals had appeared, which were filtered off, washed with chloroform, and dried under vacuum. The preparation was repeated with NMe_4 : V mol ratios of 3 : 1 and 10 : 1, both in 10 and 5% hydrofluoric acid {Found: F, 26.2; H_2O, 8.5; NMe_4, 34.6; V, 23.1. $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ requires F, 26.35; H_2O, 8.35; NMe_4, 34.3; V, 23.55%}.

The deuteriated compound $[NMe_4]_2[V_2O_2F_6(OD_2)_2]$ was prepared by repeatedly heating $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ to 130 °C at 10^{-3} mbar † for 3 h and then treating it with D_2O. Dehydration and consequent hydration or deuteriation gave products with identical powder diagrams and vibrational spectra (with the exception of the H_2O–D_2O part of the spectrum).

Crystal Data.—$C_8H_{28}F_6N_2O_4V_2$, M = 432.2, Triclinic, a = 7.012(1), b = 8.119(1), c = 9.047(1) Å, α = 65.84(1), β = 83.21(1), γ = 73.09(1)°, U = 449.7 Å^3, D_m (by flotation) = 1.59 g cm^{-3}, Z = 1, D_c = 1.596 g cm^{-3}, $F(000)$ = 222, space group $P\bar{1}$, μ(Mo-K_α) = 10.7 cm^{-1}, λ = 0.710 69 Å.

Preliminary cell dimensions and space-group symmetry were determined from oscillation and Weissenberg photographs (Cu-K_α radiation). Accurate cell parameters were obtained from a least-squares fit of the 2θ values of 75 high-angle reflections. Data were collected from a crystal of dimensions 0.23 × 0.23 × 0.08 mm with an Enraf–Nonius CAD-4 automatic diffractometer in the ω—2θ mode, using graphite-monochromated Mo-K_α radiation. The whole sphere of reflections (5 226 in all) in the range $1.5 < \theta < 30.0°$ was measured. The symmetry-related reflections were averaged (mean discrepancy on I = 4.5%) to yield 2 613 independent reflections of which 1 552 with $I_o > 3\sigma(I_o)$ (obtained from counting statistics) were considered observed and used for the structure analysis. Lorentz-polarization corrections were applied, but no absorption corrections.

The position of the vanadium atom, the oxygen atom of the vanadyl group, as well as the positions of two additional atoms around vanadium were obtained from a three-dimensional Patterson map. The subsequent electron-density maps gave co-ordinates for all the non-hydrogen atoms. At this stage we could not distinguish between fluorine atoms and the oxygen atom of the water molecule. There were three terminal positions at 1.89, 1.92, and 2.07 Å from vanadium, where two fluorine atoms and the water oxygen should be located. Two full-matrix least-squares cycles were calculated with the oxygen atom on one of the three positions and fluorine atoms on the remaining two. The calculations were carried out for all three possible arrangements. By placing the oxygen atom at 2.07 Å away from vanadium the best agreement was obtained (R = 0.093). After three cycles of full-matrix least-squares refinement with anisotropic temperature factors for all the atoms, R was 0.057. The difference electron-density map revealed the positions of the hydrogen atoms of the water molecule. There were several peaks, in the difference electron-density map, around carbon atoms. The most convenient peak, according to C–H bond length and N–C–H

---

† Throughout this paper: 1 bar = 10^5 Pa.

bond angle, was chosen for each carbon atom and the positions of the remaining three hydrogen atoms calculated, so that the C–H bond distance equalled 1.08 Å. Hydrogen atoms were included in the refinement as invariants with isotropic thermal parameters, $U = 0.06$ Å^2. Refinement terminated at R 0.046 $(=\Sigma|\Delta F|/\Sigma|F_o|)$ and R' 0.062 $\{=[\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}\}$. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weighting function $w = W_F W_S$ was determined empirically from $W_F(|F_o| < 5.0) = (|F_o|/5.0)^{2.0}$, $W_F(F_o > 20.0) = (20.0/|F_o|)^{2.0}$, and $W_F(5.0 \leqslant |F_o| \leqslant 20.0) = 1.0$, and $W_S\ (\sin\theta < 0.35) = (\sin\theta/0.35)^{2.0}$, $W_S(\sin\theta > 0.45) = (0.45/\sin\theta)^{2.0}$, and $W_S\ (0.35 \leqslant \sin\theta \leqslant 0.45) = 1.0$. An extinction parameter was included in the refinement with a final value of 1.341×10^{-3}. Atomic scattering factors for H atoms were taken from ref. 10 and for other atoms from ref. 11, those for V, O, F, N, and C being corrected for the effects [12] of anomalous scattering ($\Delta f'$, $\Delta f''$). All the calculations were made on a CDC CYBER 72 computer at RRC Ljubljana using the '*X-RAY '72*' system of crystallographic programs.[13] The atomic thermal parameters and observed and calculated structure amplitudes are available as Supplementary Publication No. SUP 23062 (14 pp.).*

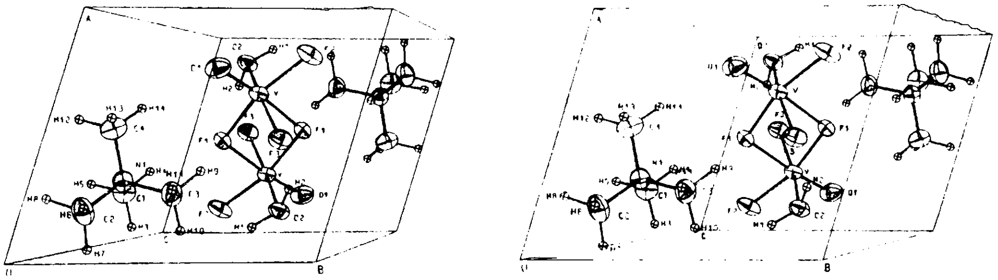

FIGURE 1 Stereoscopic view of the unit cell and numbering scheme used for $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$

Spectroscopy.—Infrared spectra were recorded on a Perkin-Elmer model 521 spectrophotometer as Nujol and perfluorobutadiene mulls. Raman spectra were recorded at the Department for Fluorochemistry, Institute Josef Stefan, Ljubljana, using a SPEX-1401 double monochromator and 4 880 Å and 5 145 Å exciting radiations of a Coherent Radiation CR-3 Ar$^+$ ion laser.

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
V	0.683 12(10)	0.492 35(11)	0.369 14(9)
F(1)	0.476 51(33)	0.364 55(33)	0.477 59(28)
F(2)	0.848 87(40)	0.656 11(40)	0.314 14(33)
F(3)	0.482 90(37)	0.678 92(39)	0.216 98(30)
N(1)	0.689 23(54)	0.811 44(51)	0.797 65(42)
O(1)	0.786 79(50)	0.364 41(57)	0.269 89(44)
O(2)	0.835 27(42)	0.323 18(44)	0.585 60(37)
C(1)	0.743 61(74)	0.889 85(71)	0.621 61(53)
C(2)	0.805 11(86)	0.861 61(78)	0.893 80(61)
C(3)	0.737 86(75)	0.602 66(64)	0.857 76(60)
C(4)	0.470 64(74)	0.887 98(80)	0.816 44(66)
H(1)	0.977 2	0.216 9	0.603 9
H(2)	0.735 0	0.318 7	0.662 5
H(3)	0.901 3	0.832 8	0.603 6
H(4)	0.658 2	0.854 2	0.552 2
H(5)	0.712 2	1.010 0	0.573 0
H(6)	0.783 2	0.789 4	1.021 9
H(7)	0.936 6	0.824 4	0.866 8
H(8)	0.757 2	1.012 0	0.863 1
H(9)	0.647 4	0.554 6	0.803 2
H(10)	0.892 7	0.547 5	0.838 3
H(11)	0.713 5	0.545 0	0.988 3
H(12)	0.432 5	1.039 0	0.771 8
H(13)	0.429 9	0.833 1	0.944 3
H(14)	0.395 6	0.848 0	0.750 8

RESULTS AND DISCUSSION

Crystal Structure.—The crystal structure consists of tetramethylammonium cations and discrete dimeric anions. A stereoscopic view of the unit cell is shown in Figure 1. Atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2. Octahedral co-ordination of vanadium has been found in all structurally characterized fluoro-oxovanadates(IV), however the dimeric unit $[\{VOF_3(OH_2)\}_2]^{2-}$ is observed here for the first time. The V_2F_2 bridging group is exactly planar because of the crystallographic centre of inversion.

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Intramolecular distances and angles in $[V_2O_2F_6(OH_2)_2]^{2-}$			
V–F(1)	1.960(3)	F(2)–V–O(1)	101.42(18)
V–F(2)	1.894(4)	F(2)–V–O(2)	90.88(13)
V–F(3)	1.917(2)	F(3)–V–O(1)	100.36(16)
V–F(1$^{\mathrm{I}}$)	2.173(3)	F(3)–V–O(2)	160.83(13)
V–O(1)	1.607(5)	O(1)–V–O(2)	97.62(16)
V–O(2)	2.074(3)	F(1$^{\mathrm{I}}$)–V–F(1)	74.54(11)
F(1)–V–F(2)	160.38(15)	F(1$^{\mathrm{I}}$)–V–F(2)	85.98(13)
F(1)–V–F(3)	87.52(11)	F(1$^{\mathrm{I}}$)–V–F(3)	81.55(11)
F(1)–V–O(1)	97.95(18)	F(1$^{\mathrm{I}}$)–V–O(1)	172.23(16)
F(1)–V–O(2)	83.46(11)	F(1$^{\mathrm{I}}$)–V–O(2)	79.76(11)
F(2)–V–F(3)	92.02(12)		
(*b*) Intramolecular distances and angles in NMe_4^+			
N(1)–C(1)	1.502(6)	C(1)–N(1)–C(3)	109.05(41)
N(1)–C(2)	1.494(9)	C(1)–N(1)–C(4)	109.22(33)
N(1)–C(3)	1.496(6)	C(2)–N(1)–C(3)	108.95(36)
N(1)–C(4)	1.495(6)	C(2)–N(1)–C(4)	110.18(45)
C(1)–N(1)–C(2)	110.16(41)	C(3)–N(1)–C(4)	109.26(40)
(*c*) Atomic contacts			
O(2)–H(1) ··· F(2$^{\mathrm{II}}$)	2.564(5)	V–V($^{\mathrm{I}}$)	3.292(1)
O(2)–H(2) ··· F(3$^{\mathrm{I}}$)	2.686(4)		

Symmetry code: I, $1 - x$, $1 - y$, $1 - z$; II, $2 - x$, $1 - y$, $1 - z$.

The observed V–O distance in the vanadyl group is in the range characteristic for the V–O double bond, *e.g.* 1.602 Å in $Cs_2[VOF_4(OH_2)]$,[8] 1.583 and 1.595 Å in $Cs[VOF_3]\cdot0\cdot5H_2O$,[7] and 1.612 Å in $[NH_4]_2[VOF_4]$.[6] There are two different V–F(1) bond distances of the bridging

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

fluorine atoms. This difference could be explained by the *trans* influence of vanadyl oxygen, an effect which is characteristic of fluoro-oxovanadates(IV) and has been observed in the complexes mentioned previously. The V–V separation is 3.292(1) Å and the V–F–V bridging angle is 105.5(1)°.

The anions are linked together by hydrogen bonds, O(2)–H(1) • • • F(2^{II}) 2.564(5) Å. This is one of the shortest hydrogen bonds observed in hydrates.[14] In this way, chains are formed parallel to the *a* axis. There is also an intramolecular hydrogen bond O(2)–H(2) • • • F(3^{I}) of 2.686(4) Å.

The bond lengths and angles of the cation are close to the reported values.[15] The cations and anions are well separated from one another with the shortest C • • • F distance being 3.313 Å.

Vibrational Spectra.—The observed frequencies of $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$, its deuteriated and dehydrated analogues, and their assignments are given in Table 3. Only values below 1 000 cm^{-1} are shown, since the observed spectrum of the cation is almost identical with the spectra of its halides. Small shifts may be primarily caused by packing forces, as suggested for tetramethylammonium halides.[16] The spectrum is assigned according to the literature.[16,17]

TABLE 3

Observed i.r. and Raman bands (in cm^{-1}) and assignments for $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$, (A), and its deuteriated, (B), and dehydrated, (C), derivatives

(A)		(B)		(C)		
I.r.	Raman[a]	I.r.	Raman[a]	I.r.	Raman[a]	Assignment
	980 (10)		974 (10)	995s	992 (10)	ν(V=O)
968vs		970vs		970vs	970 (4)	
950s	952 (3)	955s	950 (2)	957s—m	951 (3)	ν_{18}[b]
	948 (sh)			950 (sh)		
910vw	925 (0.5)	927w			930 (0.5)	$2\nu_{19}$
890vw		890w		850vw		
805m	796 (?)	610m—s				H_2O wag
	752 (3)		748 (2)		753 (3)	ν_3
	748 (sh)		743 (sh)			
660m		650m				ν(V–OH_2)
					606 (0.2)	$\nu_{asym.}$(VF)
				565vs	566 (0.2)	
				545vs	549 (0.2)	
				530 (sh)	534 (0.1)	
				520 (sh)		ν_{sym}(VF)
				475s	486 (0.5)	
558 (sh)	555 (?)					(A_u)
532s	532 (?)	530s				$\nu(VF_t)$[c] (A_g)
	513 (1)		508 (0.5)			(A_u)
493vs		500vs				(A_g)
	488 (1)		486 (1)			
478 (sh)	477 (?)	480s				ν_{19}
	475 (?)					
450s	459 (2)	455s	455 (2)	460s	461 (1)	
	449 (?)				453 (0.2)	
412w		405w				ν_8
	382 (1)		378 (0.5)			
				377m	381 (2)	V=O rock
	355 (1)		350 (0.5)	345m—w	350 (0.5)	
312s		310s		321m		
					314 (0.5) (br)	
302 (sh)				308 (sh)		
				283w		
					270 (0.2)	δ_{sym} (VF)
					240 (2)	
					235 (1)	
					222 (1)	
	296 (3)		293 (2)			(A_g)
	262 (0.1)		262 (0.2)			$\nu(VF_b)$[d] (A_u)
	243 (1)		240 (0.5)			(A_g)
	220 (0.5)		219 (0.2)			(A_u)
					194 (2)	δ_{asym}(VF)
					172 (0.5)	
					159 (1)	
	205 (2)		205 (1)			(A_g)
	189 (2)		187 (1)			$\delta(VF_t)$[c] (A_g)
	174 (0.5)		172 (0.5)			and lattice (A_g)
	143 (1)		141 (1)			modes (A_g)

[a] Relative intensities are given in parentheses. [b] Assignment for NMe_4^+ ion from refs. 16 and 17. [c] Subscript t denotes terminal fluorine. [d] Subscript b denotes bridging fluorine.

The point group of the dimeric anion, its site symmetry (Wyckoff notation *h*), and the factor-group symmetry are identical (C_i). There is one dimeric anion in the unit cell and we may expect only Raman- (A_g) or i.r.-active (A_u) vibrations. There should be 42 vibrations of the anion, approximately described as the group vibrations of the V=O bond ($3A_g$ and $3A_u$), the V–H_2O group ($9A_g$ and $9A_u$), and the V–F framework, which may be subdivided into stretching ($2A_g$ and $2A_u$) and bending ($4A_g$ and $4A_u$) modes of the terminal fluorine atoms and stretching ($2A_g$ and $2A_u$) and in-plane (A_g) and out-of-plane (A_u) bending modes of the fluorine bridge. The description is necessarily very rough, since the angle at the bridging fluorine atom is 105° and the in-plane stretchings cannot be separated from in-plane bendings.

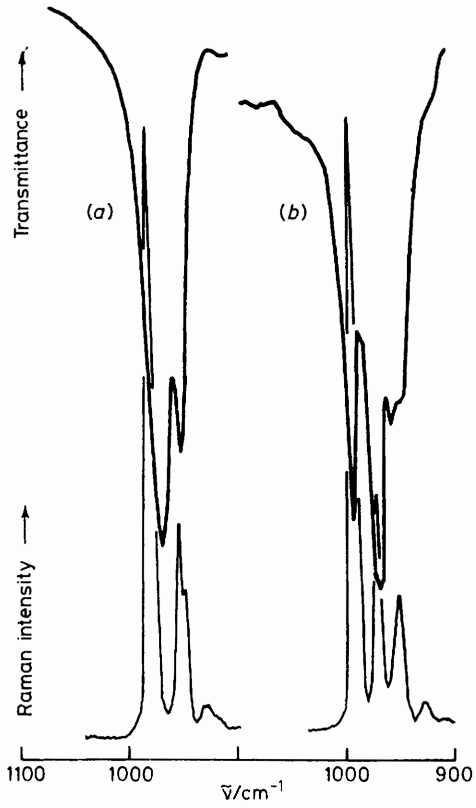

FIGURE 2 Infrared and Raman spectra (in the region of V=O stretching modes) of (a) $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ and (b) the anhydrous derivative

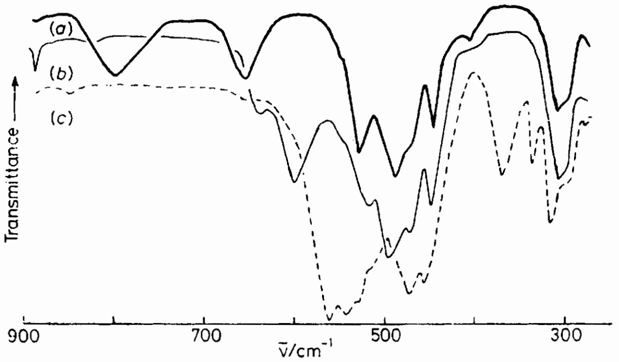

FIGURE 3 Infrared spectra (250—900 cm^{-1}) of (a) $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$, (b) $[NMe_4]_2[V_2O_2F_6(OD_2)_2]$, and (c) the anhydrous derivative

Reversible dehydration leaves a product with spectra that show two very strong bands in the V=O stretching mode region,[18] both in the Raman and i.r. spectra, but with alternate intensity (Figure 2). The V–F stretching bands [18c,19,20] are somewhat shifted to higher frequencies and four bands appear in the i.r. and in the Raman spectra in the region of rocking modes [18c,19] of the V=O bond (Figure 3). Fluorine bridges in $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ are very asymmetric (approximate bond-order ratio is 1 : 0.6, estimated from equations of Siebert [21] and Herschbach and Laurie [22]), and we infer that the removal of co-ordinated water molecules leaves deformed $[VOF_3]^-$ ions coupled to some extent and with no centre of symmetry between them. The spectra are therefore tentatively assigned by comparison with each other and with the published data on VOF_3 [19] and similar vanadium compounds,[18,20] considering the effects of different oxidation state, charge, co-ordination number, and symmetry. Simpler spectra with higher frequencies should be expected in VOF_3 (vapour) and simpler spectra with lower frequencies in the hydrated complex than in the dehydrated complex.

Stretching vibrations of the V=O bonds in $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$, coupled over the centre of symmetry, appear with great intensity at 980 cm^{-1} (Raman, A_g) and at 968 cm^{-1} (i.r., A_u). There is a first overtone at 1 940 cm^{-1} in the i.r. Small splittings tally with weak coupling through heavy vanadium atoms and weak fluorine bridges.

The region around 500 cm^{-1} is assigned to terminal fluorine stretching modes and the bands below 300 cm^{-1} to bridging modes, deformation of terminal fluorine atoms, and lattice vibrations. Asymmetric deformation modes of terminal fluorine atoms and bending modes of the fluorine bridge are not identified.

The strong and broad absorption due to the stretching modes of OH bonds of the co-ordinated water (Figure 4; 3 180 and 3 010 cm^{-1} for the hydrated and 2 400 and 2 260 cm^{-1} for the deuteriated complex) is rather low for crystalline hydrates. If the shift in stretching frequencies of OH bonds, relative to free water molecules,

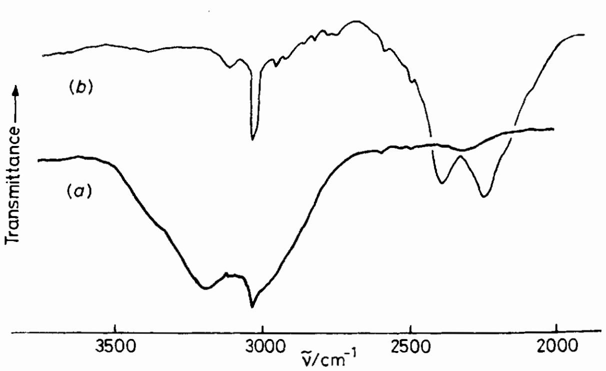

FIGURE 4 Infrared spectra (in the region of OH stretching modes) of (a) $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$ and (b) $[NMe_4]_2[V_2O_2F_6(OD_2)_2]$

is assumed to be proportional to hydrogen-bond enthalpies, the Badger–Bauer relation [23] predicts values from 29 to 46 kJ mol^{-1} which are remarkably larger than those expected in some other hydrates.* This is in agreement with the short hydrogen bond. Upon deuteriation the centre of absorption shifts by the usual factor [26] of 1.34 and the band width is reduced from 470 to 260 cm^{-1} (factor of 1.8).[27] There is a combination band of the deformation mode and libration of water at 2 308 cm^{-1}.[28] The band at 660 cm^{-1} gradually disappears with drying and reappears on deuteriation, shifted to 650 cm^{-1} (Figure 3). This is assigned to the stretching vibration of co-ordinated water,† the magnitude of the shift being of the expected order.[30]

The financial support of The Research Council of Slovenia is gratefully acknowledged.

[1/057 *Received*, 14*th January*, 1981]

---

* Stretching frequencies of OH bonds in inorganic hydrates [24] appear mostly between 3 300 and 3 600 cm^{-1}. The ethalpies estimated from shifts in the i.r. spectra are, for example, 8—12 kJ mol^{-1} for chlorates,[23] perchlorates, and nitrates,[25] 17—34 kJ mol^{-1} for sulphates,[25] and 34—38 kJ mol^{-1} for phosphates.[25]

† The stretching vibration of co-ordinated water is predicted by normal co-ordinate analysis [29] to be at 673 cm^{-1} but is found in most hydrates at appreciably lower frequencies (from 250 to 490 cm^{-1}).[30,31]

REFERENCES

[1] J. Selbin, *Chem. Rev.*, 1965, **65**, 153.

[2] G. Pausewang, *Z. Anorg. Allg. Chem.*, 1971, **381**, 189; G. Pausewang and W. Rüdorff, *ibid.*, 1969, **364**, 69.

[3] M. C. Chakraworti and A. R. Sarkar, *J. Fluorine Chem.*, 1977, **9**, 315; A. E. Baker and H. M. Haendler, *Inorg. Chem.*, 1962, **1**, 127; J. Selbin and L. H. Holmes jun., *J. Inorg. Nucl. Chem.*, 1962, **24**, 1111; J. Selbin, *ibid.*, 1969, **31**, 433; P. L. Davidovich, L. G. Kharlamova, and L. V. Samarec, *Koord. Khim.*, 1977, **3**, 850.

[4] A. Demšar and P. Bukovec, *Inorg. Chim. Acta*, 1977, **25**, L121.

[5] K. Waltersson and B. Karlsson, *Cryst. Struct. Commun.*, 1978, **7**, 459.

[6] P. Bukovec and L. Golič, *Acta Crystallogr., Sect. B*, 1980, **36**, 1925.

[7] K. Waltersson, *J. Solid State Chem.*, 1979, **28**, 121.

[8] K. Waltersson, *J. Solid State Chem.*, 1979, **29**, 195.

[9] K. Waltersson, *Cryst. Struct. Commun.*, 1978, **7**, 507.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem., Phys.*, 1956, **42**, 3175.

[11] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

[12] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[13] J. M. Stewart, G. J. Kruger, H. L. Amon, C. Dickinson, and S. R. Hall, *X*-Ray System, Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

[14] V. I. Simonov and B. V. Bukvetsky, *Acta Crystallogr., Sect. B*, 1978, **34**, 355.

[15] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3, p. 275.

[16] G. L. Bottger and A. L. Geddes, *Spectrochim. Acta*, 1965, **21**, 1701.

[17] T. Edsall, *J. Chem. Phys.*, 1937, **5**, 225; C. W. Young, J. S. Koehler, and D. S. Kinney, *J. Am. Chem. Soc.*, 1947, **69**, 1410; E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.

[18] (*a*) D. N. Sathyanarayana and C. C. Patel, *J. Inorg. Nucl. Chem.*, 1968, **30**, 207; (*b*) O. Piovesana and J. Selbin, *ibid.*, 1969, **31**, 433; (*c*) H. Rieskamp and R. Mattes, *Z. Naturforsch., Teil B*, 1976, **31**, 357.

[19] R. J. H. Clark and P. D. Mitchell, *J. Chem. Soc., Dalton Trans.*, 1972, 2429; I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc. A*, 1970, 1210; H. Selig and H. H. Claassen, *J. Chem. Phys.*, 1966, **44**, 1404.

[20] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762; F. E. Dickson, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2636.

[21] H. Siebert, *Z. Anorg. Allg. Chem.*, 1953, **272**, 170.

[22] H. S. Johnston, *J. Am. Chem. Soc.*, 1964, **86**, 1643.

[23] G. Brink and M. Falk, *Can. J. Chem.*, 1970, **48**, 2096; G. Brink, *Appl. Spectrosc.*, 1976, **30**, 630.

[24] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 1962, **24**, 1253; J. Lecomte, *J. Chim. Phys. Phys.-Chim. Biol.*, 1953, **50**, 53; C. Duval and J. Lecomte, *ibid.*, p. 61; I. Gamo, *Bull. Chem. Soc. Jpn.*, 1961, **34**, 760; 764; 1430; 1433.

[25] A. V. Karjakin and G. A. Muradova, *Zh. Fiz. Khim.*, 1968, **42**, 2735.

[26] G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' W. H. Freeman and Co., San Francisco and London, 1960, p. 111.

[27] S. Detoni, D. Hadzi, R. Smerkolj, J. Hawranek, and L. Sobczyk, *J. Chem. Soc. A*, 1970, 2851.

[28] E. Hartert and O. Glemser, *Z. Elektrochem.*, 1956, **60**, 746.

[29] G. Sartori, C. Furlani, and A. Damiani, *J. Inorg. Nucl. Chem.*, 1958, **8**, 119.

[30] D. M. Adams and P. J. Lock, *J. Chem. Soc. A*, 1971, 2801.

[31] G. Brun, *Rev. Chim. Minerale*, 1968, 899.