alteration in *p* character the C–C–C angles at C(10) and C(30) decrease and increase at C(20) and C(40). The mean values of the C–C bond lengths in the cyclobutadiene moiety are 1·465 in (1), 1·463 in (2) and 1·467 Å in the unsubstituted parent compound (3); with reference to these – within experimental error – no influence of the substituents on bond lengths is detectable. (1) and (2) are characterized by two more common structural features.

The three *exo* bonds of the cyclobutadiene, C(20)–C(21), C(40)–C(41) and C(30)–Si(30), are distorted out of the plane of the four-membered ring in the direction opposite to the Co atom [C(21): 0·088 (5), C(41): 0·12 (5), Si(30): 0·333 (6) Å for (1) and 0·154 (6), 0·130 (6), 0·371 (7) Å for (2)], while C(10)–Si(10) is in this plane [Si(10): −0·010 (5) for (1) and −0·030 (7) Å for (2)]. This difference between the positions of Si(10) and Si(20), relative to the cyclobutadiene plane, is probably caused by the different environment of the two atoms in the unit cell and shows an external influence on the molecular structure by packing effects.

Two of the three methyl groups of both trimethylsilyl substituents are orientated in directions such that their steric interference with the two – with respect to the cyclobutadiene plane – distorted phenyl rings is a minimum. The only significant differences in the structures of (1) and (2) are the angles between the planes of the phenyl rings and cyclobutadiene: they are 40·5 (3) and 32·5 (4)° in (1), lower than 45·2 (5) and 41·6 (5)° found in (2).

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Structure of $[N(CH_3)_4][VOF_3(H_2O)]$

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Abstract. Tetramethylammonium aquatrifluorooxovanadate(IV), $[N(CH_3)_4][VOF_3(H_2O)]$, $M_r = 216·1$, triclinic, $P\bar{1}$, $a = 7·000$ (3), $b = 8·120$ (4), $c = 9·050$ (4) Å, $\alpha = 65·85$ (2), $\beta = 83·08$ (3), $\gamma = 72·97$ (3)°, $V = 448·8$ (4) Å^3, $Z = 2$, $F(000) = 222$, $D_x = 1·59$, $D_m = 1·60$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10·4$ mm^{-1}, room temperature, $R = 4·7\%$ for 1638 independent reflections. The vanadyl ion VO^{2+} [V–O bond distance 1·598 (3) Å] is coordinated to four fluorine atoms and to one H_2O molecule occupying a *cis* position relative to the vanadyl oxygen. These octahedra share one F–F edge forming discrete $[V_2O_2F_6(H_2O)_2]^{2-}$ dimers that are connected by hydrogen bonds.

Introduction. The investigation of the system CsF–VO_2–HF (aq.) showed the existence of compounds in which V atoms constitute discrete units or isolated chains (Waltersson, 1978, 1979*a*,*b*). Up to now no crystallographic investigation has been made on systems in which CsF is replaced by tetramethylammonium fluoride. The aim of this study was therefore to prepare corresponding compounds, the substitution of Cs^+ ions by $N(CH_3)_4^+$ ions being supposed to favour formation of magnetic entities or isolated magnetic chains.

The starting materials were tetramethylammonium fluoride tetrahydrate, $[N(CH_3)_4]F.4H_2O$ (p.a. Fluka), V_2O_5 (p.a. Merck) and V_2O_3 obtained by reduction of V_2O_5 with hydrogen. A 1:1 (molar) mixture of V_2O_5 and V_2O_3 was first dissolved in a 40% HF solution. The fluoride was added to the solution in the ratio $N(CH_3)_4/V = 1$. Upon evaporating the solution at room temperature blue crystals are obtained which are characteristic of V^{IV}.

Experimental. Precession and Weissenberg photographs: triclinic Enraf–Nonius CAD-3 diffractometer with Mo $K\alpha$ radiation. Crystal size 0·25 × 0·2 × 0·15 mm. Unit

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters with estimated standard deviations*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} a_i^* a_j^* U_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)*
V	1831 (1)	−77 (1)	−1307 (1)	2·11 (2)
F(1)	−172 (4)	1793 (4)	−2837 (3)	2·94 (3)
F(2)	3481 (4)	1568 (4)	−1849 (3)	3·53 (3)
F(3)	238 (3)	1346 (3)	225 (3)	2·37 (3)
O(*W*)	3353 (5)	−1761 (5)	848 (4)	2·73 (3)
O	2863 (5)	−1347 (5)	−2298 (4)	3·51 (3)
N	1897 (5)	3101 (5)	2978 (4)	2·49 (3)
C(1)	2372 (9)	1027 (7)	3583 (7)	3·29 (3)
C(2)	−272 (8)	3883 (9)	3167 (8)	3·92 (3)
C(3)	2432 (9)	3895 (8)	1220 (6)	3·33 (3)
C(4)	3048 (10)	3616 (9)	3935 (7)	3·56 (3)
H(1)	2623 (69)	−1687 (62)	1475 (54)	2 (1)
H(2)	4343 (91)	−1671 (8)	1290 (70)	5 (1)
H(3)	3677 (90)	484 (80)	3447 (68)	4 (1)
H(4)	1971 (84)	580 (79)	4695 (73)	4 (1)
H(5)	1724 (88)	638 (82)	2952 (71)	5 (1)
H(6)	−541 (83)	3397 (79)	4230 (72)	4 (1)
H(7)	−626 (74)	5229 (77)	2741 (60)	3 (1)
H(8)	−948 (95)	3578 (89)	2555 (78)	6 (1)
H(9)	1924 (74)	5333 (75)	821 (59)	3 (1)
H(10)	3709 (98)	3449 (88)	1157 (75)	5 (1)
H(11)	1735 (77)	3420 (71)	620 (63)	4 (1)
H(12)	2631 (80)	5048 (82)	3535 (65)	4 (1)
H(13)	2871 (84)	3060 (81)	4962 (73)	4 (1)
H(14)	4415 (102)	3016 (90)	3824 (76)	6 (1)

* Isotropic thermal parameters for H atoms.

cell: least squares on 15 reflections, $2\theta > 23°$. Density: hydrostatic pressure method (Rabardel, Pouchard & Hagenmuller, 1971). Intensity measurements by θ–2θ scans with $\theta < 30°$ ($-9 \le h \le 4$, $-11 \le k \le 11$; $-12 \le l \le 12$). Five standards for count and orientation every 200 reflections; no appreciable trends. 1638 independent reflections with $I > 3\sigma(I)$. Only Lorentz–polarization corrections. All subsequent calculations by *SHELX*76 (Sheldrick, 1976). Computer used: IBM 870. V position from Patterson map. N, C, O and F positions from $\Delta\rho$ maps initially in V position and, after several cycles of least squares (to $R = 0{\cdot}08$), refinement on F magnitudes. H positions from $\Delta\rho$ map. Scattering factors: Cromer & Mann (1968), f' and f'' values (Cromer & Liberman, 1970). Final cycle of anisotropic least squares on V, N, C, O and F, H positions isotropic; $R = wR = 0{\cdot}047$ (unit weights). Subsequent $\Delta\rho$ excursions $<0{\cdot}5$ e Å^{-3}. $(\Delta/\sigma)_{max} = 0{\cdot}8$.

Discussion. Final fractional atomic coordinates are given in Table 1 and bond distances and angles in Table 2.* The projection of the structure on (001) is given in Fig. 1. Each V atom is coordinated to six ligands forming a distorted octahedron with one short metal–ligand distance of 1·598 (3) Å. It was assumed at an early stage of the refinement that this ligand is an oxygen atom. The observed distance is characteristic of a V=O double bond in a vanadyl ion, VO^{2+}. It is in fair agreement with those observed in the vanadate(IV) in $2CsVOF_3.H_2O$ (Waltersson, 1979*b*). The other ligands at distances of 1·894 to 2·163 Å from the V atom correspond to four fluorine atoms and to one water molecule. This can be confirmed by comparison with observed V—O and V—F distances in several closely related vanadium(IV) compounds (Waltersson, 1979*a*). As often observed the largest distance corresponds to a *trans* position relative to the O atom of the vanadyl ion (Waltersson, 1979*b*). The water molecule is in a *cis* position. Two octahedra share an F(3)—F(3^i) edge forming a discrete dimeric $[V_2O_2F_6(H_2O)_2]$ unit [symmetry code: (i) $-x, -y, -z$]. These dimers are connected to each other by hydrogen bonding (Fig. 1). The O(*W*)—H(2)···F(2^i) hydrogen-bond distance is in fair agreement with those found in other hydrates (Simonov & Bukvetsky, 1978).

Table 2. *Bond distances* (Å) *and angles* (°) *with estimated standard deviations*

V–O	1·598 (3)	C(1)–H(5)	0·96 (6)
V–F(1)	1·922 (3)	C(2)–H(6)	0·90 (6)
V–F(2)	1·894 (3)	C(2)–H(7)	0·96 (5)
V–F(3^i)	1·955 (3)	C(2)–H(8)	0·91 (6)
V–O(*W*)	2·068 (3)	C(3)–H(9)	1·03 (5)
V–F(3)	2·163 (3)	C(3)–H(10)	0·87 (6)
V–V^i	3·280 (1)	C(3)–H(11)	1·01 (5)
N–C(1)	1·486 (6)	C(4)–H(12)	1·03 (6)
N–C(2)	1·483 (6)	C(4)–H(13)	0·86 (6)
N–C(3)	1·497 (6)	C(4)–H(14)	0·95 (7)
N–C(4)	1·496 (6)	O(*W*)–H(1)	0·73 (5)
C(1)–H(3)	0·91 (6)	O(*W*)–H(2)	0·88 (6)
C(1)–H(4)	0·96 (6)		

O–V–F(1)	100·0 (2)	N–C(2)–H(6)	107 (4)
O–V–F(2)	101·9 (2)	N–C(2)–H(7)	111 (3)
O–V–F(3^i)	98·0 (2)	N–C(2)–H(8)	108 (4)
O–V–O(*W*)	97·8 (2)	N–C(3)–H(9)	107 (3)
O–V–F(3)	172·2 (2)	N–C(3)–H(10)	106 (4)
F(1)–V–F(3^i)	87·6 (1)	N–C(3)–H(11)	108 (3)
F(1)–V–O(*W*)	161·1 (1)	N–C(4)–H(12)	108 (3)
F(1)–V–F(3)	81·9 (1)	N–C(4)–H(13)	111 (4)
F(1)–V–F(2)	91·9 (1)	N–C(4)–H(14)	106 (4)
F(2)–V–F(3^i)	159·9 (1)	H(3)–C(1)–H(4)	112 (15)
F(2)–V–O(*W*)	90·7 (1)	H(3)–C(1)–H(5)	101 (5)
F(3^i)–V–O(*W*)	83·6 (1)	H(4)–C(1)–H(5)	112 (5)
F(3)–V–F(3^i)	74·5 (1)	H(6)–C(2)–H(7)	111 (5)
F(2)–V–F(3)	85·6 (1)	H(6)–C(2)–H(8)	114 (5)
O(*W*)–V–F(3)	79·7 (1)	H(2)–C(2)–H(8)	106 (5)
C(2)–N–C(1)	109·6 (4)	H(9)–C(3)–C(10)	116 (6)
C(1)–N–C(3)	109·8 (4)	H(9)–C(3)–H(11)	110 (4)
C(3)–N–C(4)	110·1 (4)	H(10)–C(3)–H(11)	109 (5)
C(4)–N–C(1)	109·3 (4)	H(12)–C(4)–C(13)	113 (5)
C(3)–N–C(2)	108·8 (4)	H(12)–C(4)–H(14)	118 (5)
C(2)–N–C(4)	109·3 (4)	H(13)–C(4)–H(14)	101 (5)
N–C(1)–H(3)	113 (4)	H(1)–O(*W*)–V	105 (4)
N–C(1)–H(4)	107 (3)	H(1)–O(*W*)–H(2)	97 (5)
N–C(1)–H(5)	112 (3)	H(2)–O(*W*)–V	132 (4)

1	2	3	d_{13}	d_{23}	∠123
O(*W*)–H(1)···F(1^i)			2·687 (5)	1·99 (5)	162 (1)
O(*W*)–H(2)···F(2^{ii})			2·563 (5)	1·70 (7)	169 (2)

Symmetry code: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43363 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

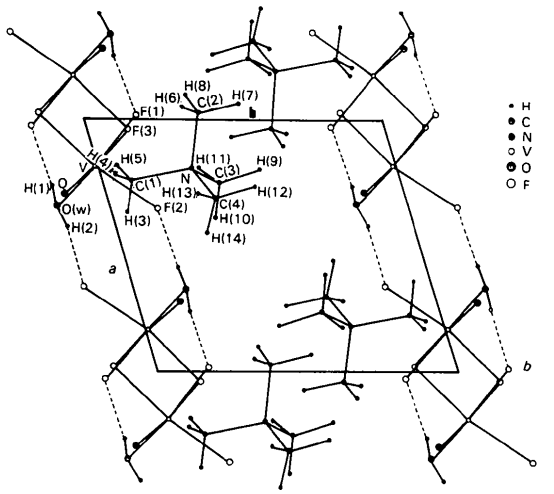

Fig. 1. Schematic structure of $[N(CH_3)_4][VOF_3(H_2O)]$ viewed along **c**.

The tetramethylammonium ions and the dimeric units are held together by a three-dimensional network of hydrogen bonds. The magnetic behaviour of $[N(CH_3)_4][VOF_3(H_2O)]$ will be analysed in terms of binuclear magnetic units such as $Cs_3V_2O_2F_7$ which contains similar groups (Darriet, Bonjour, Beltran-Porter & Drillon, 1984).

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Intramolecular Hydrogen Bonding in Dichlorotetrakis(pyrazole-N^2)nickel(II) as Studied by Low-Temperature Neutron Diffraction, X-ray Diffraction and Infrared Spectroscopy

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Abstract. $[NiCl_2(C_3H_4N_2)_4]$, $M_r = 401{\cdot}9$, monoclinic, $C2/c$, $Z = 4$. (I) $T = 100$ K, $a = 13{\cdot}857$ (6), $b = 9{\cdot}182$ (5), $c = 14{\cdot}096$ (8) Å, $\beta = 117{\cdot}10$ (4)°, $V = 1596{\cdot}7$ (9) Å^3, $D_x = 1{\cdot}67$ g cm^{-3}, $\lambda = 1{\cdot}304$ Å, $\mu = 2{\cdot}31$ cm^{-1}, $F(000) = 9{\cdot}52$, final $R = 0{\cdot}036$ for 1771 neutron data. (II) $T = 295$ K, $a = 13{\cdot}881$ (4), $b = 9{\cdot}255$ (4), $c = 14{\cdot}417$ (8) Å, $\beta = 116{\cdot}85$ (3)°, $V = 1652{\cdot}4$ (1) Å^3, $D_x = 1{\cdot}62$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 15{\cdot}17$ cm^{-1}, $F(000) = 824$, final $R = 0{\cdot}028$ for 2210 X-ray data. The structural results of the X-ray and neutron studies agree well with each other and with a previous structure determination [Reimann, Mighell & Mauer (1967). *Acta Cryst.* **23**, 135–141]. Ni–N, 2·09 Å, and Ni–Cl distances, 2·50 Å, are in agreement with the tetragonal ligand-field spectra. The long Ni–Cl distances correspond to strong N–H···Cl interactions, N···Cl 3·09–3·12 Å. H-atom positions determined by neutron diffraction confirm the presence of these hydrogen bonds (H···Cl = 2·31–2·36 Å).

Introduction. An early structure determination of the title compound (Reimann, Mighell & Mauer, 1967) showed that an unusually long Ni–Cl bond occurs in comparison with other NiN_4Cl_2 chromophores. This long Ni–Cl contact was attributed to hydrogen bonding between the Cl^- ions and N–H groups of two pyrazole ligands (Reimann, 1969). Infrared spectra of related compounds, M(5-methylpyrazole)$_4X_2$ (M = metal, X = Cl, Br), strongly indicated that relatively strong hydrogen bonding is indeed responsible for the long Ni–X bonds and – as a consequence – the weak axial ligand field (Reedijk, 1970). However, a detailed study was not possible because the positions of the H

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