Fluoride Crystal Structures. Part 30.[1] 2,2′-Bipyridylfluorodioxovanadium(V)

By **Anthony J. Edwards** * and **David R. Slim**, Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT
Jacques E. Guerchais and **Jean Sala-Pala**, Laboratoire de Chimie Minérale, Université de Bretagne Occidentale, 29283 Brest-Cedex, France

The structure of the title compound has been determined from *X*-ray diffractometer data and refined by full-matrix least-squares methods to *R* 0.078 for 1 084 reflections. Crystals are monoclinic, space group $P2_1/c$, $a = 6.43$, $b = 15.80$, $c = 13.94$ Å, $\beta = 134.8°$. The vanadium atom has a distorted square pyramidal arrangement and achieves a distorted octahedral co-ordination by weak dimer formation, through asymmetric oxygen bridges. The vanadium–oxygen distances are V–O (terminal) 1.618(8) and V–O (bridge) 1.691(7) and 2.361(7) Å.

ALTHOUGH vanadium trifluoride oxide and vanadium fluoride dioxide have long been known, only recently[2] have derivatives of these species with organic ligands been prepared and characterised. For the title compound spectroscopic measurements did not distinguish between the two structural possibilities of a five-co-ordinate monomer and a six-co-ordinate dimer. The crystal structure was determined to elucidate this problem and to determine whether oxygen or fluorine acted as the bridging atom in the second case. Preliminary results have been briefly reported previously.[3]

EXPERIMENTAL

The preparation and characterisation of the yellow, air-stable crystals have been described.[2] Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

TABLE 1

Atomic positional parameters with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
V	0.184 5(3)	−0.027 7(1)	0.151 3(2)
F	0.406 7(14)	−0.103 6(5)	0.157 4(7)
O(1)	0.210 5(17)	−0.063 1(6)	0.268 4(8)
O(2)	−0.160 9(14)	−0.048 7(5)	0.002 1(7)
N(1)	0.580 9(19)	0.050 6(7)	0.279 7(8)
N(2)	0.059 0(18)	0.094 1(6)	0.161 6(8)
C(1)	0.845 8(22)	0.021 5(10)	0.336 6(11)
C(2)	1.098 7(25)	0.071 8(9)	0.430 1(12)
C(3)	1.081 0(26)	0.150 6(12)	0.463 5(14)
C(4)	0.806 8(26)	0.181 4(10)	0.399 7(13)
C(5)	0.559 7(21)	0.129 4(8)	0.307 0(9)
C(6)	0.260 8(21)	0.156 3(7)	0.237 9(10)
C(7)	0.186 8(29)	0.235 7(10)	0.246 9(13)
C(8)	−0.106 4(31)	0.252 5(9)	0.179 0(14)
C(9)	−0.306 9(25)	0.186 9(9)	0.103 4(12)
C(10)	−0.222 2(22)	0.109 1(8)	0.098 4(10)

Crystal Data.—$C_{10}H_8FN_2O_2V$, $M = 258$, Monoclinic, $a = 6.43(1)$, $b = 15.80(2)$, $c = 13.94(2)$ Å, $\beta = 134.8(3)°$, $U = 1\,004$ Å^3, $D_m = 1.73$ g cm^{-3}, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 520$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 10 cm^{-1}.

Structure Determination.—Intensity data were collected about the *b* axis (layers *h*0—16*l*) with a Stoe two-circle computer-controlled diffractometer as described previously.[4] Within the range $0.1 < \sin\theta/\lambda \leqslant 0.65$, 1 084 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarisation factors but not for absorption.

The structure was solved by conventional Patterson-Fourier techniques. Scattering factors used were those for neutral atoms.[5] Refinement of the positional and isotropic temperature parameters and layer scale factors was carried out by full-matrix least-squares methods, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, with unit weights initially.

TABLE 2

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

(*a*) Intramolecular distances

V–F	1.820(7)	V–N(1)	2.192(9)
V–O(1)	1.618(8)	V–N(2)	2.131(9)
V–O(2)	1.691(7)	V–O(2^{I})	2.361(7)
N(1)–C(1)	1.36(1)	C(1)–C(2)	1.41(2)
C(2)–C(3)	1.36(3)	C(3)–C(4)	1.39(2)
C(4)–C(5)	1.41(2)	C(5)–N(1)	1.34(2)
C(5)–C(6)	1.48(1)	N(2)–C(6)	1.36(1)
C(6)–C(7)	1.38(2)	C(7)–C(8)	1.42(2)
C(8)–C(9)	1.39(2)	C(9)–C(10)	1.37(2)
C(10)–N(2)	1.36(1)	N(1) · · · N(2)	2.58(1)
N(1) · · · F	2.72(1)	F · · · O(2)	2.76(1)
O(2) · · · N(2)	2.76(1)	O(1) · · · N(1)	2.90(1)
O(1) · · · N(2)	2.70(1)	O(1) · · · F	2.67(1)
O(1) · · · O(2)	2.65(1)	O(2^{I}) · · · N(1)	2.79(1)
O(2^{I}) · · · N(2)	2.87(1)	O(2^{I}) · · · F	2.88(1)
O(2^{I}) · · · O(2)	2.61(1)	V · · · V^{I}	3.175(4)

(*b*) Angles

N(1)–V–N(2)	73.3(3)	N(2)–V–O(2)	91.6(3)
N(1)–V–F	84.9(4)	O(2)–V–F	103.7(3)
O(1)–V–N(1)	97.9(4)	O(1)–V–N(2)	91.1(4)
O(1)–V–F	101.8(4)	O(1)–V–O(2)	106.6(4)
O(2^{I})–V–N(1)	75.4(4)	O(2^{I})–V–N(2)	79.3(3)
O(2^{I})–V–F	86.0(4)	O(2^{I})–V–O(2)	78.4(4)
V–O(2)–V^{I}	101.6(4)	V–N(2)–C(6)	120.8(7)
V–N(1)–C(5)	117.7(7)	N(2)–C(6)–C(5)	112.9(10)
N(1)–C(5)–C(6)	115.3(9)	C(5)–N(1)–C(1)	119.1(10)
N(1)–C(1)–C(2)	120.4(13)	C(1)–C(2)–C(3)	120.8(12)
C(2)–C(3)–C(4)	118.4(12)	C(3)–C(4)–C(5)	119.1(14)
C(4)–C(5)–N(1)	122.0(10)	C(5)–C(6)–C(7)	125.0(11)
C(4)–C(5)–C(6)	122.6(11)	C(7)–C(8)–C(9)	117.1(12)
C(6)–C(7)–C(8)	119.4(12)	C(9)–C(10)–N(2)	121.3(11)
C(8)–C(9)–C(10)	121.3(11)		
C(10)–N(2)–C(6)	118.8(9)		

One of the single-atom near neighbours was further from vanadium than the other two and was tentatively assigned as fluorine. Refinement was continued with the layer-scale factors held constant, and with the introduction of anisotropic thermal parameters for all atoms of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

---

[1] Part 29, J. C. Dewan, A. J. Edwards, J. Y. Calves, and J. E. Guerchais, *J.C.S. Dalton*, preceding paper.

[2] J. Sala-Pala and J. E. Guerchais, *J. Mol. Structure*, 1974, **20**, 169.

[3] A. J. Edwards, D. R. Slim, J. Sala-Pala, and J. E. Guerchais, *Compt. rend.*, 1973, **276C**, 1377.

[4] J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J.C.S. Dalton*, 1975, 2171.

[5] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. III, p. 202.

Subsequently hydrogen atoms, with positions calculated from the molecular geometry, assuming a C–H bond length of 1.08 Å, and with a temperature factor of $B = 6.5$ Å^2, were included in the structure-factor calculations. In the final stages of refinement weights derived from the counting statistics were found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$. Final parameter shifts were $<0.1\sigma$ and the final R was 0.078.

Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22003 (11 pp., 1 microfiche) and the final positional parameters with their estimated standard deviations in Table 1. Interatomic distances and angles are given in Table 2.

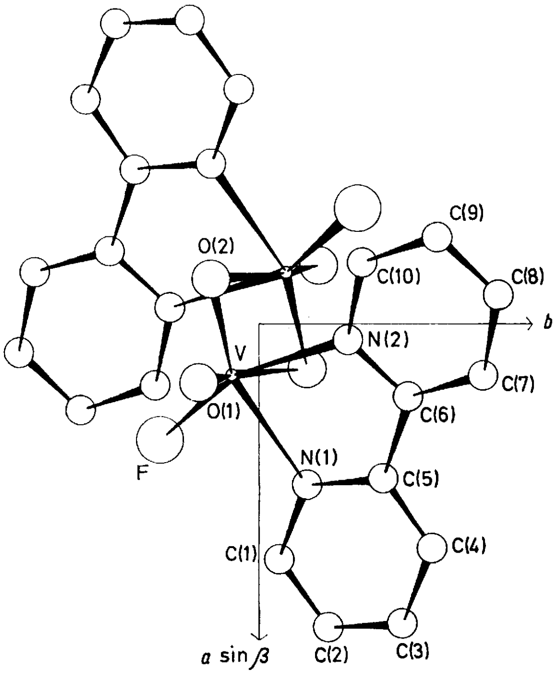

FIGURE 1 The dimer unit in projection down [001] showing the atom numbering

DISCUSSION

The structure consists of pairs of five-co-ordinate molecular units, weakly linked into dimers through asymmetric oxygen bridges, to give a distorted octahedral arrangement around each vanadium atom (Figure 1). The oxygen and fluorine atom ligands could not be distinguished directly by X-ray methods and were assigned from the co-ordination geometry. The two shorter distances (1.618 and 1.691 Å) were assumed to be V–O bonds and that of 1.820 Å a V–F bond. In vanadium trifluoride oxide[6] the V–O and V–F(terminal) distances are 1.57 and 1.70 Å respectively, giving a V–F/V–O ratio of 1.08. Although the present distances are greater, the V–F/V–O(1) ratio of 1.12 is similar [V–O(2) is lengthened by the bridging interaction]. The lengthening of the metal–fluorine bond in a co-ordination complex containing an organic ligand, in comparison with that in a simple fluoride or oxide fluoride, has also been found in niobium and molybdenum systems that we have investigated[7] and may be due to the *trans* effects of ligands other than fluorine.

The five nearest neighbours of the vanadium atom form a distorted square-pyramidal arrangement, with an oxygen atom in the apical position. The V–O(apical) distance (1.618 Å) is within the range[8] (1.57—1.68 Å) found for such bonds. The vanadium atom is displaced from the basal plane of the square pyramid by 0.31 Å towards the apical atom. A similar displacement is found in other oxovanadium systems, for example[9] 0.30 Å in bis(acetylacetonato)oxovanadium(IV).

The bipyridyl ligand occupies two co-ordination positions in the basal plane. The two V–N distances (2.192 and 2.131 Å) are significantly different and this difference can be correlated with the presence of either oxygen or fluorine atoms in the *trans* positions in the basal plane. Thus the long V–N(1) distance is *trans* to a multiply bonded oxygen atom, and this is considered to produce a lengthening and weakening effect in bonds *trans* to it.[10] Conversely the unusually long V–F distance may result from some weakening effect of the nitrogen atom in the *trans* position. The lengthening of the V–O(2) distance (1.691 Å), by 0.073 Å compared with V–O(1), may be partly due to the reverse effect of the nitrogen atom *trans* to it, although it must be mainly due to the bridging interaction between the pairs of molecular units.

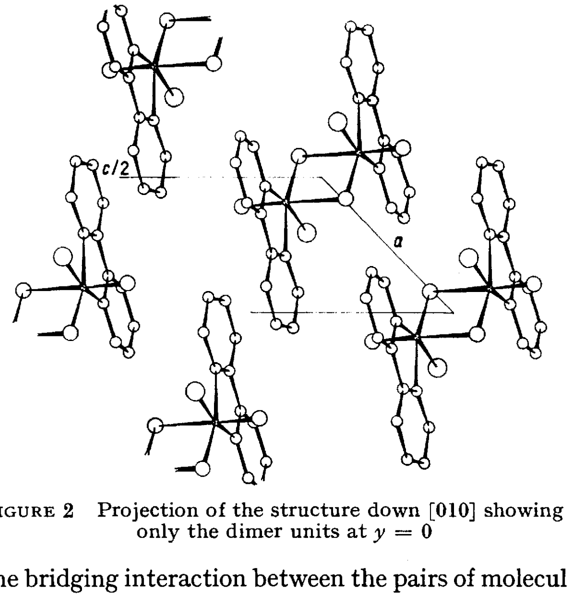

FIGURE 2 Projection of the structure down [010] showing only the dimer units at $y = 0$

The bridging interaction completes a distorted octahedral co-ordination around each vanadium atom, filling the sixth co-ordination position *trans* to the apical

---

* For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[6] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1970, 1474.

[7] Unpublished data.

[8] R. J. H. Clark, ' The Chemistry of Titanium and Vanadium,' Elsevier, Amsterdam, 1968, p. 198.

[9] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.

[10] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.

oxygen atom with the basal oxygen atom from the paired molecular unit. The asymmetry of the bridge (V–O 1.691 and 2.361 Å) can be ascribed to the presence of the apical oxygen atom in a *trans* position. Although the linking through a di-μ-oxo-bridge system is different from the fluorine bridging in the structures of vanadium trifluoride oxide[6] and chromyl fluoride,[7] the effect of the *trans* oxygen atoms is similar. Thus, the fluorine bridges *trans* to terminal oxygen atoms are asymmetric (V–F 1.813, 2.340; Cr–F 1.787, 2.259, and 1.855, 2.090) and the longer bridge distances are similar to the longer V–O distance in the present structure.

Although the bridging interaction is weak it is obviously significant. The separation of the oxygen atoms involved, O(2) and O(2^{I}), (2.61 Å) is less than that (2.65 Å) for O(1) and O(2), bonded to the same vanadium atom. The vanadium atom separation (3.175 Å) is comparable to that (3.09 Å) in the symmetric di-μ-fluoro-bridge system in vanadium trifluoride oxide.

The geometry of the bipyridyl ligand is the same as that in bipyridyl itself[11] and in bipyridyl complexes such as[12] [Nb(O)Cl_2(OC_2H_5)(bipy)]. Both rings are planar and almost co-planar, with an angle of twist of 5.6°. The packing of the dimers is shown in Figure 2. There are no close contacts between the dimer units and no evidence for hydrogen bonding.

We thank the S.R.C. for financial support (to D. R. S.), and Dr. T. A. Hamor for his amended version of the computer programmes FORDAP, ORFLS, and ORFFE. All calculations were carried out on an ICL 1906A computer, and we thank the staff at Birmingham University Computer Centre for their assistance.

[6/1685 *Received, 3rd September*, 1975]

---

[11] L. L. Merritt and E. D. Schroeder, *Acta Cryst.*, 1956, **9**, 801.

[12] B. Kamenar and C. K. Prout, *J. Chem. Soc.* (*A*), 1970, 2379.