Fluoride Crystal Structures. Part 31.[1] Ammonium Fluoro-oxoperoxo(pyridine-2,6-dicarboxylato)molybdate(VI)

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The structure of the title compound has been determined by the heavy-atom method from 1 350 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to *R* 0.046. Crystal are orthorhombic, space group *Pbca*, with *a* = 11.15(2), *b* = 26.25(4), and *c* = 7.56(1) Å. In the structure the monomeric anions have a pentagonal-bipyramidal co-ordination, with the bidentate peroxo-group and terdentate pyridine-2,6-dicarboxylate group filling the equatorial positions, and the oxide and fluoride ligands in the axial positions. There is a very long Mo–F distance (2.058 Å), which can be correlated with the *trans* effect of the oxide ligand (Mo–O 1.661 Å).

MOLECULAR peroxo-complexes of molybdenum and tungsten of formula $[MO(O_2)(pydca)(OH_2)]$ (M = Mo or W; pydca = pyridine-2,6-dicarboxylate) have been shown to contain a labile water molecule.[2] This lability has been attributed to the position of the water molecule *trans* to a multiple M–O bond, in the axial positions of a pentagonal-bipyramidal arrangement. This water molecule can be rather easily substituted by fluoride or chloride ion, in the presence of a univalent cation to preserve charge neutrality. Although in the presence of the cations Cs^+, Rb^+, K^+, Na^+, $[NMe_4]^+$, and $[N(C_2H_3)_4]^+$ dimeric anions are formed, in the presence of $[NH_4]^+$ a monomeric anion results. We here describe our structural analysis of this product which has confirmed its monomeric formulation and supports the previous proposal to account for the lability of the water molecule in the precursor.

EXPERIMENTAL

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

Crystal Data.—$C_7H_7FMoN_2O_7$, $M = 346$, Orthorhombic, $a = 11.15(2)$, $b = 26.25(4)$, $c = 7.56(1)$ Å, $U = 2\,213$ Å^3, $D_m = 2.08$ g cm^{-3} (by flotation), $Z = 8$, $D_c = 2.08$ g cm^{-3}, $F(000) = 1\,368$. Space group *Pbca* (D_{2h}^{15}, no. 61) from systematic absences: $0kl$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$. Mo-K_α radiation (λ 0.710 Å; μ 12 cm^{-1}).

Structure Determination.—Intensity data were collected about the *c* axis (layers $hk0$—8) with a Stoe two-circle computer-controlled diffractometer as described previously.[3] Within the range $0.1 < \sin\theta/\lambda < 0.65$, 1 350 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,[4] with corrections for the effects of anomalous dispersion applied to those for molybdenum. 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, followed by weights derived from the counting statistics. Fluorine scattering factors were applied for the single terminal atom furthest from molybdenum, since it could not be distinguished from oxygen directly, and the Mo–F distance is expected to be greater than the Mo–O(multiple bond) distance.

The refinement converged at *R* 0.107 and was continued with layer-scale factors held constant, and with the introduction of anisotropic thermal parameters, for all atoms, of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. 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 $B = 6.0$ Å, were included in the structure-factor calculations. Final parameter shifts were $< 0.1\sigma$ and the final *R* was 0.046. The weighting scheme was found to be appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$.

Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22054 (8 pp.) * and the final positional parameters with their estimated standard deviations are in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Mo	0.438 4(1)	0.153 4(0)	0.193 6(1)
F	0.572 9(4)	0.190 8(2)	0.327 3(5)
O(1)	0.333 1(5)	0.114 8(3)	0.115 2(7)
O(2)	0.387 7(7)	0.219 4(3)	0.109 6(11)
O(3)	0.477 6(7)	0.195 6(3)	−0.004 6(8)
O(4)	0.575 2(5)	0.109 8(2)	0.096 3(7)
O(5)	0.695 1(7)	0.042 6(3)	0.129 7(9)
O(6)	0.335 2(5)	0.173 2(2)	0.407 4(8)
O(7)	0.277 1(6)	0.156 4(3)	0.681 8(8)
N(1)	0.486 9(5)	0.102 2(2)	0.398 2(8)
N(2)	0.173 6(6)	0.266 2(3)	0.380 0(8)
C(1)	0.621 4(8)	0.072 6(4)	0.185 2(12)
C(2)	0.577 6(8)	0.069 9(3)	0.375 3(11)
C(3)	0.623 8(8)	0.041 3(3)	0.508 2(13)
C(4)	0.572 4(9)	0.047 1(4)	0.675 4(11)
C(5)	0.474 8(8)	0.079 8(4)	0.700 2(10)
C(6)	0.435 5(8)	0.106 9(3)	0.557 2(10)
C(7)	0.339 3(8)	0.148 0(4)	0.556 9(12)

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

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

[4] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. 3, p. 202.

DISCUSSION

The structural unit (illustrated in Figure 1) consists of separate $[NH_4]^+$ cations and monomeric seven-co-ordinate anions. In the anion the molybdenum atom is at the centre of a distorted pentagonal bipyramid, with the bidentate peroxo-group and terdentate pyridine-2,6-carboxylate group filling the equatorial positions, and the oxide and fluoride ligands in axial positions. In the equatorial plane this arrangement gives a close approach to the theoretical angle of 72° for the two ' bites ' of the terdentate ligand (73.6 and 74.2°) and accommodates the very small ' bite ' of the peroxo-group (O–Mo–O 44.7°) with an increase in the interligand angles of 10° [O(3)–Mo–O(4) 82.6 and O(2)–Mo–O(6) 82.4°].

TABLE 2

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

(*a*) Distances			
Mo–O(1)	1.661(5)	N(1)–C(2)	1.33(1)
Mo–F	2.058(4)	N(1)–C(6)	1.34(1)
Mo–O(2)	1.930(7)	C(2)–C(3)	1.36(1)
Mo–O(3)	1.914(6)	C(3)–C(4)	1.40(1)
Mo–N(1)	2.119(6)	C(4)–C(5)	1.40(1)
Mo–O(4)	2.044(6)	C(5)–C(6)	1.37(1)
Mo–O(6)	2.051(6)	C(1)–C(2)	1.52(1)
O(2)–O(3)	1.46(1)	C(6)–C(7)	1.52(1)
C(1)–O(4)	1.29(1)	C(7)–O(6)	1.31(1)
C(1)–O(5)	1.21(1)	C(7)–O(7)	1.19(1)
O(1) · · · O(2)	2.81(1)	F · · · O(2)	2.74(1)
O(1) · · · O(3)	2.81(1)	F · · · O(3)	2.73(1)
O(1) · · · O(6)	2.69(1)	F · · · O(6)	2.76(1)
O(1) · · · O(4)	2.71(1)	F · · · O(4)	2.75(1)
O(1) · · · N(1)	2.76(1)	F · · · N(1)	2.57(1)
O(2) · · · O(6)	2.62(1)	O(3) · · · O(4)	2.62(1)
N(1) · · · O(4)	2.49(1)	N(1) · · · O(6)	2.52(1)
O(4) · · · O(5)	2.23(1)	O(6) · · · O(7)	2.22(1)
(*b*) Angles			
O(1)–Mo–O(2)	102.9(3)	F–Mo–O(2)	86.9(2)
O(1)–Mo–O(3)	103.6(3)	F–Mo–O(3)	86.7(2)
O(1)–Mo–O(4)	93.3(3)	F–Mo–O(4)	84.3(2)
O(1)–Mo–O(6)	92.3(3)	F–Mo–O(6)	84.3(2)
O(1)–Mo–N(1)	93.0(3)	F–Mo–N(1)	76.0(2)
O(2)–Mo–O(3)	44.7(3)	O(1)–Mo–F	169.1(2)
O(3)–Mo–O(4)	82.6(3)	O(2)–Mo–O(6)	82.4(3)
O(4)–Mo–N(1)	73.6(2)	O(6)–Mo–N(1)	74.3(2)
O(6)–C(7)–O(7)	124.7(9)	O(4)–C(1)–O(5)	125.5(9)
O(7)–C(7)–C(6)	122.7(9)	O(5)–C(1)–C(2)	121.0(9)
O(6)–C(7)–C(6)	112.6(7)	O(4)–C(1)–C(2)	113.5(7)
N(1)–C(6)–C(5)	121.7(8)	N(1)–C(2)–C(3)	123.0(8)
C(6)–C(5)–C(4)	117.6(7)	C(2)–C(3)–C(4)	117.1(9)
C(5)–C(4)–C(3)	120.5(8)	C(2)–N(1)–C(6)	120.1(7)
C(7)–C(6)–N(1)	111.5(7)	C(1)–C(2)–N(1)	109.7(7)
(*c*) Contacts <3.5 Å			
N(2) · · · O(2)	3.37(1)	N(2) · · · O(2^{I})	3.42(1)
N(2) · · · O(6)	3.04(1)	N(2) · · · F^{II}	2.73(1)
N(2) · · · F^{I}	2.76(1)	N(2) · · · O(7^{III})	2.78(1)
N(2) · · · O(3^{I})	3.02(1)	N(2) · · · O(2^{III})	2.98(1)

Roman numerals as superscripts refer to atoms in the positions:

I $-\frac{1}{2}+x, y, \frac{1}{2}-z$ II $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
III $x, \frac{1}{2}-y, -\frac{1}{2}+z$

The O–O separation (1.46 Å) in the peroxo-group is the same as that in other transition-metal peroxo-complexes, and the Mo–O(peroxo) distances, which are not significantly different from each other (mean 1.922 Å), are similar to such distances reported previously.[5]

The geometry of the pyridine-2,6-carboxylate ligand is unremarkable and the Mo–N and Mo–O co-ordination distances are those expected by comparison with other complexes. Thus the mean Mo–O(carboxylate) distance (2.047 Å) is similar to the range (2.08—2.18 Å) reported in the structures of some oxalatomolybdenum complexes.[6] The Mo–N distance (2.119 Å) is shorter than that in several molybdenum complexes with histidine and cysteine [7] (2.23—2.25 Å), but only slightly longer than the value [8] (2.109 Å) in $[Mo\{N(H)NC(CO_2Et)COH\}(\eta\text{-}C_5H_5)(CO)_2]$, where multiple bonding is considered to be present, and therefore probably reflects some multiple-bond character in the present case.

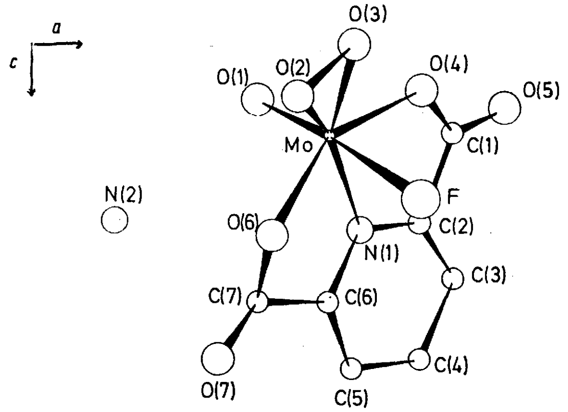

FIGURE 1 Projection of the structural unit down [010] showing the atom numbering

The short Mo–O (terminal) distance (1.661 Å) is close to the value (1.65 Å) which has been assigned by Cotton and Wing [9] to a molybdenum-to-oxygen multiple bond with a bond order of three. The molybdenum atom is displaced 0.18 Å from the equatorial plane of the bipyramid towards this terminal atom, as is generally found for such interactions. The bond *trans* to the terminal oxygen atom is that for Mo–F (2.058 Å), which is very long for a terminal bond to fluorine, and can be compared with values of 1.83 Å in [10] MoF_4O and 1.88 Å in [11] $K[MoF_5O]\cdot H_2O$. This lengthening, and presumably weakening, can be ascribed to the effect of the multiply bonded oxygen atom in the *trans* position, and can be compared with the corresponding lengthening to 2.03 Å of the Mo–F distance *trans* to the oxygen ligand in $K[MoF_5O]\cdot H_2O$. The longer distance in the present complex may be due to a general lengthening of the M–F distance, in the presence of ligands other than fluoride or oxide, as we have previously noted [1] for (2,2′-bipyridyl)fluorodioxovanadium(V).

The packing arrangement in the structure is illustrated

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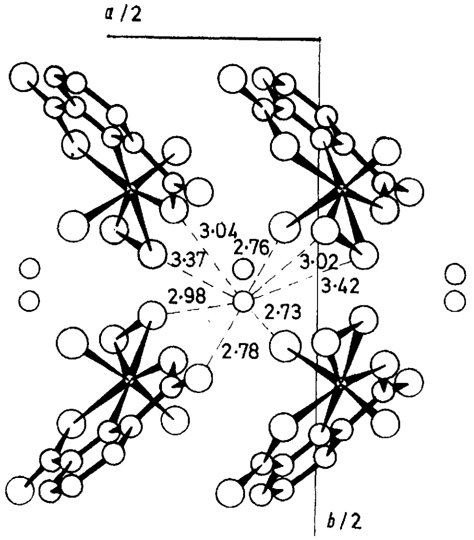

Figure 2 Projection of the structure down [001] showing the packing arrangement and the co-ordination of the cation

in Figure 2. The only close contacts (<3.5 Å) between units are those between the nitrogen atom of the ammonium cation and fluorine and oxygen atoms of surrounding anions. There are eight such contacts, three of which are in the range normally associated with hydrogen bonding. These comprise two short N · · · F distances (2.73 and 2.76 Å) and a N · · · O distance (2.78 Å). Thus each fluorine atom appears to be involved in two hydrogen bonds to separate ammonium cations, and double layers of anions perpendicular to the *b* axis are linked together by the cations. The double layers are presumably held by weak van der Waals forces since there are no contacts between them at <3.5 Å.

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