Fluoride Crystal Structures. Part 33.[1] Tetraethylammonium μ-Fluoro-bis[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 2 417 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to *R* 0.044. Crystals are monoclinic, space group *C*2/*c*, with unit cell dimensions a = 18.55(2), b = 12.43(2), c = 14.17(2) Å, and β = 119.1(3)°. In the structure each molybdenum atom has a pentagonal-bipyramidal co-ordination, with the centrosymmetric binuclear anions formed by axially linking two units, through a symmetric fluorine bridge. The Mo–F distance of 2.135 Å is very long, due to the *trans* effect of the oxide ligand (Mo–O 1.659 Å) and to the bridging role of the fluorine atom.

SUBSTITUTION of the labile water molecule in the molecular peroxo-complexes [Mo(O_2)(pydca)(OH_2)] (M = Mo or W; pydca = pyridine-2,6-dicarboxylate) by fluoride ion in the presence of $[NH_4]^+$ produces a mononuclear anion.[2] In contrast, in the presence of other univalent cations a binuclear anion is formed. We recently reported a structural analysis of the ammonium salt[3] and here describe our analysis of the $[NEt_4]^+$ salt, which has provided a comparison of the mono- and bi-nuclear anions.

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.—$C_{22}H_{26}FMo_2N_3O_{14}$, M = 767, Monoclinic, a = 18.55(2), b = 12.43(2), c = 14.17(2) Å, β = 119.1(3)°, U = 2 855 Å^3, D_m = 1.81 g cm^{-3} (by flotation), Z = 4, D_c = 1.78 g cm^{-3}, $F(000)$ = 1 536. Space group *C*2/*c* (C^6_{2h}, no. 15) or *Cc* (C^4_s, no. 9) from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$, and $0k0$ when $k \neq 2n$. The centrosymmetric space group *C*2/*c* was confirmed by the successful structure refinement. Mo-K_α radiation (λ 0.710 7 Å; μ 9 cm^{-1}).

Structure Determination.—Intensity data were collected about the b axis (layers $h0$—$12l$) with a Stoe two-circle computer-controlled diffractometer as described previously.[4] A total of 2 417 independent reflections having $I > 3\sigma(I)$ were observed within the range $0.1 < (\sin\theta)/\lambda < 0.65$, and intensities 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] 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 achieved by full-matrix least-squares methods, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, with unit weights initially, and weights derived from the counting statistics in the final stages. Scattering factors were assigned on geometrical grounds, since the light atoms could not be distinguished by X-ray means in the presence of the molybdenum atom.

The refinement converged at R 0.089 and was continued with layer scale factors held constant, and with the introduction of anisotropic thermal parameters, for all atoms, of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Refinement of the large number of parameters was now performed in blocks. Final parameter shifts were <0.1 σ and the final R was 0.044. 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 $|F_o|$.

TABLE 1

Final atomic positional parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Mo	0.126 46(2)	0.195 06(3)	−0.058 91(3)
F	$\frac{1}{4}$	$\frac{1}{4}$	0
O(1)	0.030 4(2)	0.149 5(4)	−0.124 6(3)
O(2)	0.125 5(3)	0.291 2(3)	0.046 5(4)
O(3)	0.155 8(2)	0.186 7(3)	0.091 3(3)
O(4)	0.180 0(2)	0.047 6(3)	−0.022 8(3)
O(5)	0.230 6(3)	−0.094 1(3)	−0.070 7(4)
O(6)	0.103 0(2)	0.331 2(3)	−0.148 5(3)
O(7)	0.116 4(3)	0.422 5(4)	−0.273 5(4)
N(1)	0.158 5(2)	0.158 8(3)	−0.180 7(2)
N(2)	0	0.283 8(4)	$\frac{1}{4}$
C(1)	0.202 0(3)	−0.003 6(4)	−0.086 1(4)
C(2)	0.193 0(3)	0.063 8(4)	−0.179 5(4)
C(3)	0.219 3(3)	0.039 7(4)	−0.254 4(4)
C(4)	0.212 7(4)	0.124 9(5)	−0.327 5(4)
C(5)	0.181 6(3)	0.220 2(4)	−0.323 1(4)
C(6)	0.153 5(3)	0.237 8(4)	−0.248 8(3)
C(7)	0.120 9(3)	0.339 4(4)	−0.224 5(4)
C(8)	−0.068 6(3)	0.353 3(5)	0.163 5(4)
C(9)	−0.044 3(4)	0.417 4(5)	0.090 1(5)
C(10)	−0.015 2(5)	0.136 8(6)	0.112 8(7)
C(11)	0.042 8(3)	0.217 0(5)	0.201 2(5)

Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22684 (17 pp.) † and the final positional parameters with their estimated standard deviations are in Table 1. Interatomic distances and angles are given in Table 2.

DISCUSSION

The structure consists of separate tetraethylammonium cations and binuclear anions. In the anion each molybdenum atom has a distorted pentagonal-bipyramidal co-ordination, with pairs of bipyramids linked through the fluorine atom at a centre of symmetry as

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

shown in Figure 1. This fluorine atom and the oxide ligand are in axial positions and the bidentate peroxo-group and terdentate pyridine-2,6-carboxylate group fill the equatorial positions.

The dimensions of the pentagonal-bipyramidal arrangement are virtually identical with those in the mononuclear anion, found in the ammonium salt,[3] apart from the Mo–F distance which is lengthened by 0.077 Å.

This lengthening can be correlated with a decrease in the angles between the Mo–F bond and the bonds in the equatorial girdle, averaging 2°, and an increase in the displacement of the molybdenum atom from the equatorial plane, from 0.18 Å in the mononuclear to 0.30 Å in the binuclear ion. This increase in the displacement is independent of the Mo–O multiple bond, since the Mo–O(terminal) distance of 1.659 Å is the same within experimental error as that of 1.661 Å in the mononuclear ion. Thus the lengthening (and presumably weakening) of the Mo–F bond has no corresponding shortening effect on the bond *trans* to it and merely leads to a slight adjustment of angular parameters.

TABLE 2

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

(*a*) Distances

Mo–O(1)	1.659(3)	N(1)–C(2)	1.34(1)
Mo–F	2.135(1)	N(1)–C(6)	1.35(1)
Mo–O(2)	1.919(4)	C(2)–C(3)	1.40(1)
Mo–O(3)	1.927(4)	C(3)–C(4)	1.44(1)
Mo–N(1)	2.129(3)	C(4)–C(5)	1.33(1)
Mo–O(4)	2.030(3)	C(5)–C(6)	1.40(1)
Mo–O(6)	2.031(4)	C(1)–C(2)	1.51(1)
O(2)–O(3)	1.43(1)	C(6)–C(7)	1.51(1)
C(1)–O(4)	1.31(1)	C(7)–O(6)	1.28(1)
C(1)–O(5)	1.22(1)	C(7)–O(7)	1.22(1)
N(2)–C(8)	1.53(1)	N(2)–C(11)	1.53(1)
C(8)–C(9)	1.54(1)	C(10)–C(11)	1.55(1)
O(1) · · · O(2)	2.82(1)	F · · · O(2)	2.74(1)
O(1) · · · O(3)	2.84(1)	F · · · O(3)	2.75(1)
O(1) · · · O(6)	2.73(1)	F · · · O(6)	2.70(1)
O(1) · · · O(4)	2.74(1)	F · · · O(4)	2.78(1)
O(1) · · · N(1)	2.85(1)	F · · · N(1)	2.55(1)
O(2) · · · O(6)	2.63(1)	O(3) · · · O(4)	2.55(1)
N(1) · · · O(4)	2.49(1)	N(1) · · · O(6)	2.51(1)
O(4) · · · O(5)	2.25(1)	O(6) · · · O(7)	2.22(1)

(*b*) Angles

F–Mo–O(2)	84.9(1)	O(1)–Mo–O(2)	103.6(2)
F–Mo–O(3)	84.9(1)	O(1)–Mo–O(3)	104.6(2)
F–Mo–O(4)	83.6(2)	O(1)–Mo–O(4)	95.4(2)
F–Mo–O(6)	80.9(1)	O(1)–Mo–O(6)	95.0(2)
F–Mo–N(1)	73.4(1)	O(1)–Mo–N(1)	96.9(2)
O(2)–Mo–O(3)	43.8(2)	O(1)–Mo–F	170.2(2)
O(3)–Mo–O(4)	80.3(2)	O(2)–Mo–O(6)	83.6(2)
O(4)–Mo–N(1)	73.6(2)	O(6)–Mo–N(1)	74.3(1)
O(6)–C(7)–O(7)	124.9(5)	O(4)–C(1)–O(5)	125.2(5)
O(7)–C(7)–C(6)	120.0(5)	O(5)–C(1)–C(2)	121.6(5)
O(6)–C(7)–C(6)	115.0(5)	O(4)–C(1)–C(2)	113.1(4)
N(1)–C(6)–C(5)	120.3(4)	N(1)–C(2)–C(3)	121.3(4)
C(6)–C(5)–C(4)	120.1(5)	C(2)–C(3)–C(4)	116.6(5)
C(5)–C(4)–C(3)	120.5(4)	C(2)–N(1)–C(6)	121.2(4)
C(7)–C(6)–N(1)	110.0(4)	C(1)–C(2)–N(1)	110.5(4)
C(8)–N(2)–C(11)	110.9(5)	C(8)–N(2)–C(8$^{\mathrm{I}}$)	111.5(5)
C(8)–N(2)–C(11$^{\mathrm{I}}$)	104.8(5)	C(11)–N(2)–C(11$^{\mathrm{I}}$)	114.1(5)
N(2)–C(8)–C(9)	115.4(4)	N(2)–C(11)–C(10)	113.9(4)

Although the symmetric Mo–F(bridge) distance of 2.135 Å is extremely long, it can be compared with the Mo–F(bridge) distances of 2.27 and 1.96 Å in the structure[6] of MoF_4O. This bridge is asymmetric, with a Mo–F bond *trans* to the shorter, and a multiple Mo–O bond *trans* to the longer distance, but the average Mo–F distance is 2.12 Å, close to the value in the present case. The presence of two multiple Mo–O bonds *trans* to the fluorine bridge does not therefore appear to have an excessive lengthening effect.

The structures of the two salts containing the mono- and bi-nuclear anions provide a direct comparison of terminal and bridging fluorine atoms, with almost identical environments. The formal charge per molybdenum atom has changed from -1 to $-\frac{1}{2}$, but this should have a negligible effect, as is confirmed by the similarity of the other bond distances in the two cases. The ratio of bridge to terminal distances for fluorine bonds has been used previously[7] in an attempt to correlate the strengths of bridging interactions. In the present case this ratio is 1.03 : 1, for a lengthening of 0.08 Å in the bond. This value is low compared with values for the symmetrically bridged pentafluorides. For example, in rhodium pentafluoride[8] (for which the most accurate results are known) the ratio is 1.11 : 1 and the lengthening of the bridge bond 0.19 Å. This may reflect the fact that the present work gives a comparison of virtually identical environments, whereas in the pentafluorides the lengthening of the bridge bonds may result in a concomitant shortening of the terminal bonds in the same unit. However, it is more likely that the effect of the terminal Mo–O multiple bond in a *trans* position may so weaken the bond to the fluorine atom, that in both the mono- and bi-nuclear anions the major contribution to the bond is from a fluoride ion, weakly co-ordinated to one or two neutral molybdenum complexes, with little change in interaction on going from monomer to dimer. This would invalidate any comparison with fluoride systems not containing *trans* oxygen atoms.

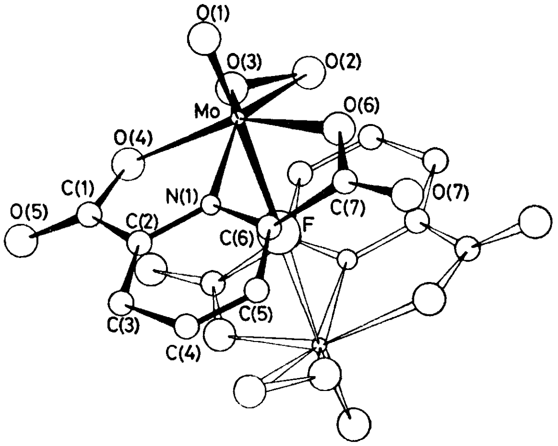

FIGURE 1 The binuclear anion $[\{MoO(O_2)(pydca)\}_2F]^-$ showing the atom numbering. Atoms in the cation, on the two-fold axis, are numbered N(2), C(8)—C(11)

Further evidence for a weak interaction and therefore a predominantly ionic fluoride in the dimer is provided by the recently reported structure[9] of the parent aquacomplex [$MoO(O_2)(pydca)(OH_2)$]. The dimensions within the pentagonal-bipyramidal unit are the same as in the present work, the displacement of the molybdenum atom from the pentagonal plane is 0.28 compared with 0.30 Å, and the Mo–OH_2 distance of 2.287 Å, for the weakly bonded water molecule, is comparable with the Mo–F distance of 2.135 Å.

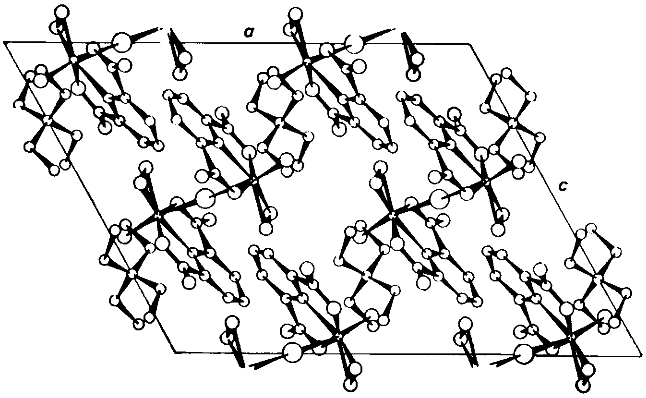

FIGURE 2 Projection of the structure down [010]

The geometry of the tetraethylammonium cation, which lies on the two-fold axis, is unremarkable and Figure 2 shows the packing arrangement, with no close contacts between the ions.

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