The Crystal Structure of Ammonium Dioxotrifluoromolybdate

By L. O. ATOVMYAN,* O. N. KRASOCHKA, and M. YA. RAHLIN

(*Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Verobyevskoye chaussée*, 2b, *Moscow, V-334, U.S.S.R.*)

Summary An *X*-ray crystal study of $NH_4MoO_2F_3$ has shown that $MoO_2F_3^{-1}$ anions exist in infinite chains formed by fluorine bridging atoms; in each MoO_2F_4 octahedron two terminal oxygen atoms are *cis*-related and the bridging fluorine atoms are *trans* to the oxygen atoms.

BROAD absorption in the region 700—800 cm^{-1} was observed[1,2] in Raman and i.r. spectra of crystalline $MMoO_2F_3$(M = K,NH_4,Rb) as well as absorbtion bands assigned to ν(Mo–O) and ν(Mo–F). The 700—800 cm^{-1} absorption band was assigned to the vibrations of Mo–O–Mo[1] and Mo–F–Mo[2,3] bridging groups. However, spectral studies did not define either the nature of bridge atom or the anion structure. In the i.r. spectrum of $CsMoO_2F_3$ no analogous

broad band is apparent indicating the presence of either a five-co-ordinate anion structure or a polymer structure with assymetric bridges.[3] An *X*-ray study of $CsMoO_2F_3$[4] confirmed the first assumption.

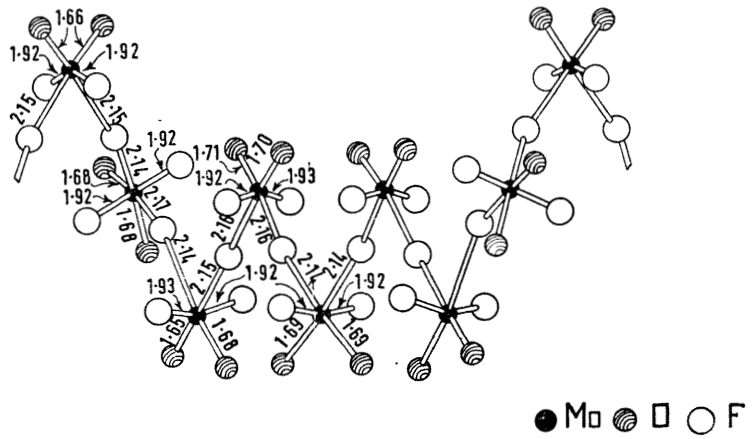

FIGURE. *The structure of* $MoO_2F_3^{-1}$ *in* $NH_4MoO_2F_3$.
Standard deviations; Mo–O 0·04, Mo–F(bridge) 0·05, and Mo–F 0·03 Å.

To clarify the structure of dioxo-fluorides of the type $MMoO_2F_3$(M = K,NH_4,Rb) an *X*-ray crystal study of $NH_4MoO_2F_3$ has been carried out.

$NH_4MoO_2F_3$ *crystal data*: $M = 203$, $a = 8{\cdot}47(2)$, $b = 13{\cdot}70(4)$, $c = 16{\cdot}22(5)$ Å, $\beta = 94{\cdot}3(5)°$, $U = 1876$ Å^3, $D_0 = 2{\cdot}87$, $D_c = 2{\cdot}80$, $Z = 16$. Space group C_2.

Using unfiltered Mo-radiation, intensities of 1380 independent non-zero reflections were estimated visually, covering the sets $hk0$,$hk1$, $0kl$, $h0$—$6l$. Absorption corrections were considered unnecessary ($\mu = 11{\cdot}9$ cm^{-1}). The crystal structure was refined by full-matrix least-squares methods using isotropic temperature factors, to $R = 0{\cdot}099$.

The structure contains $MoO_2F_3^-$ units, linked into infinite chains by fluorine bridges (see Figure). Each Mo atom is surrounded by four fluorine and two (*cis*-related) oxygen atoms, constituting a distorted octahedron. Two octahedra have their Mo atom in special positions on two-fold axes; three other octahedra are in general positions.

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