# The Crystal Structures of Ammonium Oxotrioxalatoniobate Monohydrate and Ammonium Diperoxodioxalatoniobate Monohydrate

By G. MATHERN, R. WEISS,* and R. ROHMER

(*Laboratoire de Cristallochimie associé au C.N.R.S., Institut de Chimie, B.P. 296 R/8, 67, Strasbourg, France*)

AMMONIUM OXALATONIOBATE $(NH_4)_3NbO(C_2O_4)_3,H_2O$ (I), has been prepared by a method given by Russ.[1] Ammonium peroxalatoniobate $(NH_4)_3Nb(O_2)_2(C_2O_4)_2,H_2O$ (II), was prepared by dissolving ammonium oxalatoniobate in 30% hydrogen peroxide.

We have established the crystal structure of these two compounds in order to study the stereochemistry of the niobium and the Nb–O bonding.

In compound (I), the niobium is seven-co-ordinate, and the co-ordination polyhedron is a pentagonal bipyramid (see Figure 1). The five oxygen atoms in equatorial positions deviate from mean plane positions by a maximum of 0·06 Å. The niobium atom is situated on the same side of the mean plane as the terminal oxygen atom, at a distance of 0·18 Å. The Nb–O bond distance is 1·71 Å for the terminal oxygen. The O–Nb–O' angle is significantly greater in the (C) oxalate group, than in the (A) and (B) groups.

In compound (II), the niobium is eight-co-ordinate, and the co-ordination polyhedron is a distorted dodecahedron (see Figure 2). The two peroxide groups are *cis*. Such an arrangement has not previously been observed in the crystal structure of diperoxo-compounds of transition metals.[2] The two oxalate groups are planar, and the planes containing them are perpendicular. The angle between the plane containing niobium and the first peroxide group, and the plane containing niobium and the second peroxide group is 103°.

Approximate standard deviations on interatomic distances and angles are $\sigma(Nb–O) = 0·010$ Å; $\sigma(O–O) = 0·015$ Å; $\sigma(O–Nb–O) = 0·2°$.

*Crystal data*: (I) $(NH_4)_3NbO(C_2O_4)_3,H_2O$; $M = 445$;

triclinic; $a = 9 \cdot 23 \pm 0 \cdot 02$; $b = 13 \cdot 56 \pm 0 \cdot 03$; $c = 7 \cdot 71$ $\pm 0 \cdot 02$ Å; $\alpha = 94 \cdot 0° \pm 0 \cdot 5$; $\beta = 123 \cdot 3° \pm 0 \cdot 5$; $\gamma = 107 \cdot 3°$ $\pm 0 \cdot 5$; $U = 734$ Å³; $D_c = 2 \cdot 01$; $D_m = 1 \cdot 99$; $Z = 2$; space group $P\bar{1}$ (No. 2); $\lambda = 0 \cdot 7107$ Å. (II) $(NH_4)_3Nb(O_2)_2$- $(C_2O_4)_2,H_2O$; $M = 470$; monoclinic; $a = 12 \cdot 09 \pm 0 \cdot 03$; $b = 7 \cdot 85 \pm 0 \cdot 02$; $c = 14 \cdot 30 \pm 0 \cdot 03$ Å; $\beta = 94 \cdot 7° \pm 0 \cdot 5$;
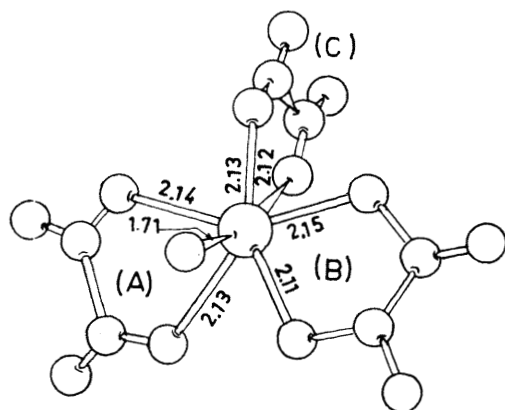


FIGURE 1

$U = 1352$ Å³; $D_c = 1 \cdot 99$; $D_o = 1 \cdot 99$; $Z = 4$; space group $P2/C$ (No. 13); $\lambda = 0 \cdot 7107$ Å;

Intensities of 1122 and 1978 independent nonzero reflexions, respectively, for the compounds (I) and (II), were recorded on a Pailred diffractometer, using Mo-$K_\alpha$ radiation.

The dimensions and shapes of the crystals used for intensities measurements were:

(I)   parallelepiped $0 \cdot 1 \times 0 \cdot 15 \times 2 \cdot 0$ mm.

(II)  sphere          $0 \cdot 31$ mm. radius.

No absorption corrections were applied.

$\mu(I) = 8 \cdot 4$ cm.$^{-1}$; $\mu(II) = 9 \cdot 5$ cm.$^{-1}$
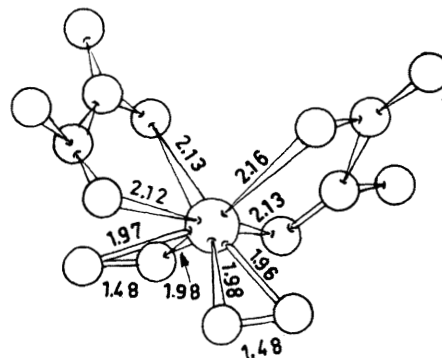


FIGURE 2

The structures were derived by Patterson and Fourier techniques and refined to $R = 0 \cdot 045$ for (I) and $0 \cdot 040$ for (II) by anisotropic full-matrix least-squares refinement.

[1] F. Russ, *Z. anorg. Chem.*, 1902, **31**, 90.

[2] R. Stromberg, *Arkiv Kemi*, 1965, **23**, 401; 1964, **22**, 49; 1965, **24**, 47; 1964, **22**, 29; 1965, **24**, 111; *Acta Chem. Scand.*, 1968, **22**. 1076; A. Mitschler, J. M. Le Carpentier, and R. Weiss, *Chem. Comm.*, 1968, 1260; F. W. B. Einstein and B. R. Penfold, *Acta Cryst*, (suppl.), 1963, **16**, A35.