The Crystal Structures of Potassium Triperoxo-(*o*-phenanthroline)niobate Trihydrate and its Hydrogen Peroxide Adduct

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Summary Both the compounds mentioned in the title contain the $[Nb(O_2)_3(C_{12}H_8N_2)]^-$ ion in which the niobium atom is eight-co-ordinate; the water and H_2O_2 molecules form hydrogen bonds with the co-ordinated oxygens.

ALKALI-METAL NIOBATES(V) react in hydrogen peroxide solutions with oxalic acid, bipyridyl, and *o*-phenanthroline to form stable crystalline di- and tri-peroxo-compounds in which niobium is bonded to the corresponding bidendate ligand.[1]

In ammonium diperoxodioxalatoniobate monohydrate the niobium is eight-co-ordinate, the co-ordination polyhedron being a distorted dodecahedron with the two peroxide groups in *cis*-positions.[2]

We have now investigated the structures of potassium triperoxo-(*o*-phenanthroline)niobate trihydrate, $KNb(O_2)_3(C_{12}H_8N_2),3H_2O$ (I), and the corresponding perhydrate $KNb(O_2)_3(C_{12}H_8N_2),3H_2O,H_2O_2$ (II).

Stable crystals of compound (I) were prepared by the method of Djordjević and Vuletić.[1] They are monoclinic needles extended along the *a* axis with $a = 7{\cdot}254 \pm 0{\cdot}005$;

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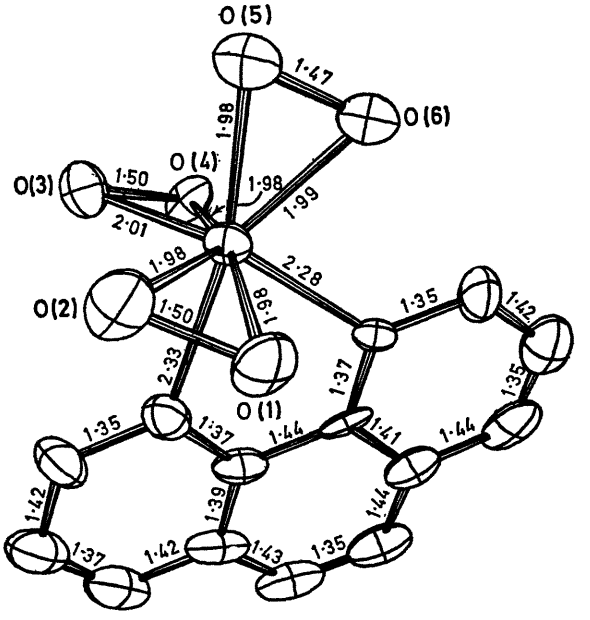
$b = 12{\cdot}62 \pm 0{\cdot}01$; $c = 19{\cdot}22 \pm 0{\cdot}02$ Å; $\beta = 105{\cdot}87° \pm 0{\cdot}10°$; $D_c = 1{\cdot}817$; $D_o = 1{\cdot}79$; $Z = 4$; space group $P2_1/C$.

Crystals of (II) were obtained by crystallising (I) in 35% hydrogen peroxide solution. They are unstable and decompose at ordinary temperature in a few days. They are triclinic with $a = 13{\cdot}83 \pm 0{\cdot}01$; $b = 7{\cdot}345 \pm 0{\cdot}005$; $c = 12{\cdot}91 \pm 0{\cdot}01$ A; $\alpha = 99{\cdot}5° \pm 0{\cdot}2$; $\beta = 135{\cdot}4° \pm 0{\cdot}2$; $\gamma = 94{\cdot}5° \pm 0{\cdot}2$; $D_c = 1{\cdot}891$; $D_o = 1{\cdot}88$; $Z = 2$; space group $P\bar{1}$.



FIGURE

The intensities of 1640 and 2348 independent above-background reflections, for compounds (I) and (II), respectively, were collected on a Pailred diffractometer. Radiations used were Cu-K_α for (I) and Mo-K_α for (II). The intensities have been corrected for absorption effects by the method of Burnham.[3]

The structures have been determined by Patterson and electron-density Fourier methods. Full-matrix anisotropic least-squares refinement[4] on all non-hydrogen atoms led to a discrepancy index of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}049$ for (I) and 0·053 for (II). The weighted factor $R_2 = \{\Sigma\omega[|F_o| - |F_c|]^2/\Sigma\omega|F_o|^2\}^{\frac{1}{2}}$ was 0·051 for (I) and 0·060 for (II).

Both compounds contain the complex anion $[Nb(O_2)_3(C_{12}H_8N_8)]^-$ in which the niobium atom is eight-co-ordinate. A perspective view of this anion is shown in the Figure, Approximate standard deviations are σ(Nb–O) 0·010 ; σ(0–0) 0·015; σ(C–C) 0·020 Å.

Application of the test of Lippard and Russ[5] to the co-ordination polyhedron of the metal shows that it is a distorted dodecahedron. The main distortion is probably due to steric interaction effects between the two O(1)–O(2) and O(3)–O(4) peroxo-groups on one side and the O(5)–O(6) peroxo-group on the other side. The niobium atom is not located in the mean plane of the O(1), O(2), O(3), O(4) oxygen atoms, but 0·34 Å above it, on the same side as the O(5)–O(6) group.

Water and hydrogen peroxide molecules form hydrogen bonds with the oxygen atoms of the $[Nb(O_2)_3(C_{12}H_8N_2)]^-$ anion. The O–O distance of the hydrogen peroxide molecule is 1·45 Å.

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