The Structure of the Uranyl Triperoxide Ion

By N. W. Alcock

(*University Chemical Laboratory, Cambridge*)

Recent work on the peroxides of uranium[1] has suggested that the uranyl group can combine with up to three peroxide ions. Complexes are also found in which some of the peroxide has been replaced by acetate, carbonate, oxalate, or other ligands. These compounds have been claimed to show replacement of a peroxide group by one bidentate or two monodentate ligands, suggesting that the peroxide group is itself behaving as a bidentate ligand. This is in complete contrast to the normal behaviour of peroxide groups replacing monodentate ligands, *e.g.*, O^{2-} in peroxychromates. The characterisation of these compounds has been largely spectrophotometric with some cryoscopic work. An *X*-ray investigation has therefore been undertaken to throw more light on their structures.

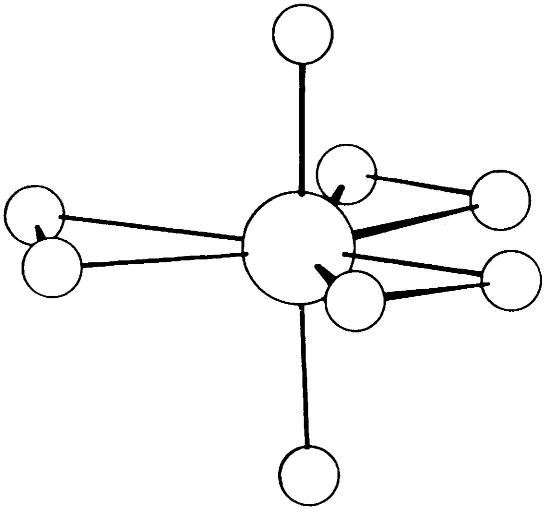
In solutions of high pH the ratio of combined peroxide to uranium is 3 : 1 and the compounds formed are believed to contain the $UO_2(O_2)_3{}^{4-}$ ion. Crystals of the sodium salt of this ion were prepared by the reaction of uranium tetroxide with an excess of hydrogen peroxide in 10M-sodium hydroxide.

Crystal data: $Na_4UO_8,9H_2O$. Monoclinic, $a = 6{\cdot}41$, $b = 17{\cdot}29$, $c = 14{\cdot}18$ Å, $\beta = 98{\cdot}5°$. $Z = 4$, space group $P2_1/C$. 1331 reflections were recorded by the Weissenberg technique, with visual estimation of intensities. The position of the uranium atom was readily found from a Patterson synthesis, and the light atoms were located in several stages by difference syntheses. The structure was refined initially by differential synthesis, and then by full-matrix least-squares analysis, with anisotropic temperature factors ($R = 11{\cdot}5\%$). The standard deviations of uranium oxygen distances are $\sim 0{\cdot}04$ Å, and of oxygen–oxygen distances $\sim 0{\cdot}06$ Å.

The structure of the $UO_8{}^{4-}$ ion is shown in the Figure. There is a linear UO_2 group, with mean U–O distance 1·88 Å, surrounded equatorially by three peroxide groups, mean U–O distance 2·27 Å, mean O–O in the peroxide groups 1·51 Å.

This structure is extremely similar to those of other uranyl compounds which have linear uranyl groups with four, five or most frequently six oxygen atoms in a plane.[2–4] The uranyl U–O distance is rather long, *cf.* 1·71 Å in uranyl acetate.[2] The peroxide U–O is short, *cf.* 2·49 Å in uranyl acetate, 2·40 and 2·52 Å in uranyl nitrate.[3] This may indicate that the peroxide oxygens are bound more strongly than those of other ligands, while the uranyl oxygen atoms are more loosely held. The peroxide O–O length is similar to that in $W_2O_{11}{}^{2-}$, 1·50 Å,[5] and in the free peroxide ion, 1·49 Å.

The crystal-structure determination confirms the stoicheiometry and nature of the complex as deduced from other evidence. The close similarity



FIGURE

of the structure to that of uranyl acetate shows how mixed peroxy-acetates, *etc.*, could be formed by simple substitution of a bidentate ligand for a peroxide group. The position of the peroxide groups side-on to the uranium atom is the same as that found in other peroxide complexes.

The unusual behaviour of the peroxide as a ligand in this complex is presumably due to the nature of the orbitals to which it is donating. In complexes such as uranyl acetate the uranyl group is likely to have available six equatorial orbitals of σ-symmetry separated by angles of about 60°. These will be sufficiently close together for a single peroxide ion to donate to two of them. On the other hand for octahedrally co-ordinated metal atoms the available σ-orbitals are separated by 90°, and for tetrahedral co-ordination by 109°, and a single peroxide ion can only donate to one such orbital.

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