

Oxygen as a Di- μ -peroxo Bridge; Synthesis and Crystal Structure of Benzyltrimethylammonium-di- μ -peroxohexachlorouranyl(VI)

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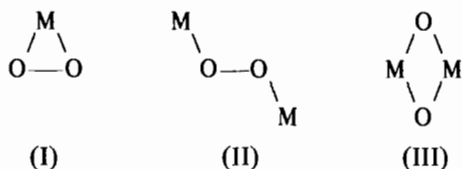
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Introduction

A recent review [1] on dioxygen-metal complexes has classed all metal-peroxo type species into two general groups, namely (I) and (II), and to date no complexes containing a linkage of type (III) appear



to have been characterized. We have been investigating the interaction of mixed alkyl-aryl ammonium cations with uranyl salts, and from one of these have structurally characterized a complex containing probably the first example of a metal di- μ -peroxo bridge.

A 2:1 mixture of BTMA Cl (in methanol) and $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (in water) was treated with 2 per cent (by volume) of concentrated H_2SO_4 and left standing in air. Several compounds crystallized from the solution over a period of days, one of which, an

orange-yellow product analysed for $\text{C}_{40}\text{H}_{64}\text{Cl}_6\text{N}_4\text{O}_6\text{U}_2$ and has been characterized crystallographically. *Crystal data:* $\text{C}_{20}\text{H}_{32}\text{Cl}_3\text{N}_2\text{O}_3\text{U}$. Monoclinic, $P2_1/c$, $a = 8.869(5)$, $b = 11.013(5)$, $c = 25.60(1)$ Å, $\beta = 103.66(10)^\circ$, $Z = 4$, $D_c = 1.89$ g cm $^{-3}$.

Cell constants and three-dimensional intensities were measured on an automatic Weissenberg diffractometer (Stoe, Stadi 2), with $\text{MoK}\alpha_1$ radiation. The structure was solved by Fourier methods and the non-hydrogen positions were refined by full-matrix least squares to $R = 0.114$, $R_w = 0.072$; using 2442 non-zero intensities.

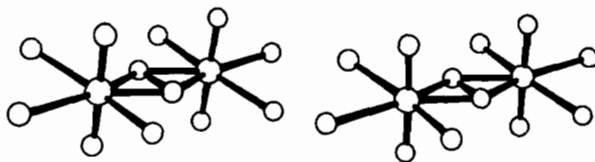


Figure. A stereoscopic view of the anion.

The figure shows a stereoscopic drawing of the $[\text{UO}_2\text{Cl}_3\text{-O}_2\text{-Cl}_3\text{UO}_2]^{4-}$ anion. This is the first known example of an oxygen molecule bonding as a di- μ -peroxo linkage (Structure III). The O-O distance of 1.49(3) Å is typical of peroxo bonds [1] and in keeping with the $\nu_{\text{O-O}}$ observed at 905 cm $^{-1}$. The mean U-O (peroxy) distance of 2.30 Å agrees within the limits of error with the 2.27 Å found [2] in $\text{Na}_4[\text{UO}_2(\text{O}_2)_3] \cdot 9\text{H}_2\text{O}$. The mean U-O (uranyl) and U-Cl distances are 1.78(1) and 2.71(2) Å respectively and agree with those found in other uranyl compounds.

References

- 1 L. Vaska, *Acc. Chem. Res.*, in the press.
- 2 N. W. Alcock, *Chem. Comm.*, 15, 536 (1966); *J. Chem. Soc. (A)*, 1588 (1968).