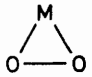
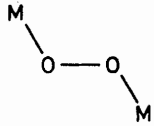
Crystal Structure of Benzyltrimethylammonium μ_2-Peroxo-bis[trichlorodioxouranate(VI)], a Binuclear Uranium Complex containing Dioxygen in a μ_2-Peroxo-linkage.

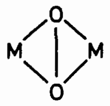
By **Robert Haegele** and **Jan C. A. Boeyens**,*† National Institute for Metallurgy, Applied Structural Chemistry Research Group, Rand Afrikaans University, Johannesburg, South Africa

The interaction in air of benzyltrimethylammonium chloride with uranyl sulphate in methanol solution, containing sulphuric acid, has provided a variety of products one of which we have now characterized as benzyltrimethylammonium μ_2-peroxo-bis[trichlorodioxouranate(VI)], containing one of the first examples of a complex containing a dioxygen molecule, bonding as a μ_2-peroxo-linkage. The crystals are monoclinic, $P2_1/c$, with a = 8.869(5), b = 11.013(5), c = 25.60(1) Å and β = 103.7(1)°. The asymmetric unit contains $[N(PhCH_2)Me_3]_2[UO_2Cl_3(O_2)_{\frac{1}{2}}]$, Z = 4. An automatic Weissenberg diffractometer was used to measure 2 442 independent reflections using Mo-K_α radiation at room temperature. The structure was refined by full-matrix least squares to R = 0.114 and R' = 0.072. The anion consists of two distorted coplanar Cl_3O_2 pentagons. They surround the uranyl groups which lie perpendicular to the plane of the pentagons and which are linked by a bridging oxygen molecule in which both oxygen atoms are equidistant from both uranium atoms.

A RECENT review[1] of dioxygen–metal complexes has categorised the many metal–peroxo linkages known to be formed from interactions of dioxygen into two main groups: (*i*) those compounds containing side-on bonded dioxygen groups (1), and (*ii*) those with a single bridging dioxygen molecule (2). The O–O distance in these compounds is invariably in the range of 1.45—1.50 Å and hence is generally considered to have peroxo-character.


(1)


(2)


(3)

However, in contrast, metal complexes with bridging dioxygen linkages of the type (3) are rare. For uranium all dioxygen compounds, *e.g.*[2] $Na_4[UO_2(O_2)_3]\cdot 9H_2O$, solved structurally to date contain type (1) interaction with average O–O bond distances of 1.51 Å. We have recently investigated reactions of mixed alkylaryl-ammonium cations with uranyl salts in air and have, from the interaction of benzyltrimethylammonium chloride with uranyl sulphate in sulphuric acid, isolated a series of products. One of these we have characterized structurally and we now present the results.

EXPERIMENTAL

From studies on the interactions of benzyltrimethylammonium chloride, $[N(PhCH_2)Me_3]Cl$, with uranyl sulphato-complexes we isolated three crystalline products. The following method of preparation consistently gave the title complex in reasonable yields.

Preparation.—Fairly concentrated solutions of commercial grade $[N(PhCH_2)Me_3]Cl$ (in methanol) and $UO_2SO_4\cdot 3\frac{1}{2}H_2O$ (in water) were mixed in the ratio 2 : 1. About 2% (by volume) of concentrated H_2SO_4 was added and the clear mixture was heated for *ca.* 1 h. When exposed to the air for several days a sulphate complex had formed, and was filtered off. After several more days, plate-like, green crystals, probably of a uranyl chloride complex, appeared and were also removed.

Finally, out of the remaining mother liquor (pH *ca.* 0.5) orange-yellow crystals developed and these were recrystallized from methanol. Though stable in the air when dry, these crystals slowly turned green and changed habit when kept in methanol for several months. The composition of the orange product was not established until the *X*-ray crystal structure analysis had been done, but a subsequent chemical analysis confirmed the formula $[N(PhCH_2)Me_3]_4[UO_2Cl_3O]_2$ (Found: Cl, 15.1; U, 34.0. Calc.: Cl, 15.38; U, 34.37%). The complex is soluble in water, m.p. 189—190 °C. The i.r. spectrum showed, besides the peaks due to the organic cation and to the antisymmetric uranyl vibration at *ca.*[3] 930 cm^{-1}, a strong absorption at *ca.* 905 cm^{-1} which may be assigned to the peroxo O–O stretching frequency, expected[1] in the range of 807—911 cm^{-1}.

Crystallography.—A crystal with the shape of a parallelepiped and approximate dimensions of 0.11 × 0.17 × 0.27 mm was selected for data collection on a two-circle automatic diffractometer (Stoe, Stadi II) equipped with an incident-beam graphite-crystal monochromator, using Mo-$K_{\alpha 1}$ radiation in ω-scan mode and a μ,θ-dependent scan width to compensate for spot elongation. The counting time for each 0.02° step was 1 s, with background counts of 20 s on both sides of the peak. Seven layers, 0—6*kl*, were recorded to maximum θ-values of 30° for the first two, and 20° for the remaining layer lines. Data reduction of the 5 362 measured intensities consisted of a standard Lorentz polarization and an approximate spherical absorption correction, omission of systematically absent reflections, a 2σ cut-off, and merging of symmetry-equivalent reflections.

Crystal Data.—$C_{20}H_{32}Cl_3N_2O_3U$. Monoclinic, $P2_1/c$, a = 8.869(5), b = 11.013(5), c = 25.60(1) Å, β = 103.66(10)°, U = 2 430 Å^3, Z = 4, D_c = 1.89 g cm^{-3}; μ(Mo-K_α) = 103.5 cm^{-1}, $\mu\bar{R}$ = 1.13.

Structure Solution and Refinement.—The structure was solved from 2 442 unique reflections. All computations were done with the program SHELX.[4] The atomic scattering factors of Cromer and Mann[5] for the lighter atoms and of International Tables[6] for uranium were

---

† *Present address:* National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria, South Africa.

[1] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.

[2] N. W. Alcock, *Chem. Comm.*, 1966, **536**; *J. Chem. Soc.* (*A*), 1968, 1588.

[3] 'Complex Compounds of Uranium,' ed. I. I. Chernayev, Moscow, 1964 (English translation, Jerusalem, 1966).

[4] G. M. Sheldrick, personal communication, 1975.

[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1969, **A24**, 321.

[6] International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, Vol. IV, 1974, p. 99.

used together with the anomalous dispersion corrections of Cromer and Libermann.[7] Neutral atom scattering factors were used and refinement was based on F.

The atomic positions were determined by standard Patterson and Fourier methods. The uranyl group, the chlorine atoms, and one $[N(PhCH_2)Me_3]$ cation were easy to locate, but the interpretation of the electron density between symmetry-related neighbouring uranium atoms was more complicated. The best interpretation was provided by introducing a centrosymmetric peroxo-group as a bridging entity. A difference-Fourier map based on this arrangement revealed the second $[N(PhCH_2)Me_3]$ cation. Least-squares refinement of all atomic parameters (U and Cl anisotropic) and interlayer scale factors finally resulted in a conventional R of 0.114, and a simple $1/\sigma(F^2)$ weighting scheme yielded $R' \{= [\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$ of 0.072.

TABLE 1

Fractional atomic co-ordinates and isotropic temperature parameters of the atoms in the asymmetric unit. The error in the last digit(s) is given in parentheses

Atom	x	y	z	U_{iso}
U	0.169 0(2)	0.636 5(1)	0.536 6(1)	
Cl(1)	0.220 6(11)	0.556 2(8)	0.638 4(3)	
Cl(2)	0.401 2(12)	0.795 2(7)	0.580 2(4)	
Cl(3)	0.145 3(11)	0.769 9(8)	0.445 5(3)	
O(1)	0.318 1(24)	0.542 4(17)	0.522 4(7)	0.037 8(48)
O(2)	0.022 6(26)	0.730 6(19)	0.551 5(8)	0.047 9(55)
O(3)	0.011 6(28)	0.469 5(21)	0.526 7(8)	0.057 6(62)
N(1)	0.251 1(34)	0.469 4(25)	0.351 1(10)	0.052 3(73)
C(1)	0.205 6(54)	0.344 8(41)	0.336 5(17)	0.085 8(135)
C(2)	0.396 4(56)	0.502 9(43)	0.332 9(18)	0.090 9(141)
C(3)	0.283 6(55)	0.478 7(43)	0.411 0(18)	0.089 8(140)
C(4)	0.119 0(44)	0.552 9(32)	0.326 1(14)	0.056 6(94)
C(5)	0.070 3(36)	0.548 8(25)	0.265 6(11)	0.035 1(69)
C(6)	−0.041 5(51)	0.466 3(38)	0.239 5(16)	0.076 2(120)
C(7)	−0.084 3(64)	0.468 5(50)	0.183 2(21)	0.107 9(167)
C(8)	−0.021 5(60)	0.539 0(47)	0.153 2(19)	0.097 7(152)
C(9)	0.086 7(53)	0.623 5(40)	0.180 6(17)	0.081 8(125)
C(10)	0.130 8(47)	0.625 5(36)	0.234 5(15)	0.070 7(110)
N(2)	0.332 3(35)	0.357 2(27)	0.050 6(11)	0.060 2(79)
C(11)	0.313 5(41)	0.222 4(30)	0.044 0(12)	0.049 9(86)
C(12)	0.254 2(49)	0.407 3(37)	−0.003 5(15)	0.073 9(115)
C(13)	0.502 4(40)	0.387 5(30)	0.059 6(12)	0.050 2(85)
C(14)	0.262 9(40)	0.398 0(30)	0.095 0(12)	0.051 7(87)
C(15)	0.339 8(39)	0.349 7(28)	0.149 3(12)	0.045 8(81)
C(16)	0.462 0(48)	0.405 9(37)	0.183 2(16)	0.074 2(116)
C(17)	0.534 8(43)	0.360 3(34)	0.232 7(13)	0.058 7(93)
C(18)	0.476 8(46)	0.257 4(34)	0.251 0(15)	0.061 4(98)
C(19)	0.346 5(42)	0.205 4(30)	0.221 9(13)	0.051 3(86)
C(20)	0.277 7(47)	0.249 9(35)	0.171 6(15)	0.066 4(106)

TABLE 2

Anisotropic temperature parameters of uranium and chlorine atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0.046 6(7)	0.036 4(6)	0.056 7(8)	0.002 0(7)	0.004 4(6)	−0.000 5(42)
Cl(1)	0.059 3(25)	0.066 1(52)	0.052 5(45)	−0.010 7(49)	0.005 9(46)	0.011 6(45)
Cl(2)	0.064 8(28)	0.033 8(40)	0.095 8(62)	−0.006 7(45)	−0.008 4(57)	0.003 0(41)
Cl(3)	0.056 5(24)	0.057 8(46)	0.055 1(45)	−0.001 6(47)	0.003 1(45)	0.017 8(41)

The U_{ij} are coefficients in the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Observed and calculated structure factors are given in Supplementary Publication No. SUP 21930 (16 pp., 1 microfiche).* The refined parameters are in Table 1. Figure 1 shows part of the structure in (010) projection to illustrate the atomic numbering scheme.

The stereoscopic diagram of Figure 2 shows one unit cell viewed along [010] and a similar view of the dinuclear anion is shown in Figure 3. Bond lengths and angles are in Table 3.

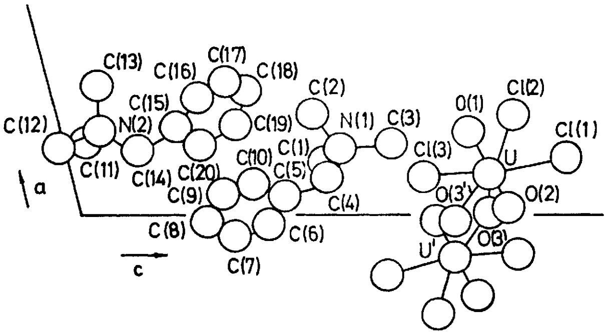


FIGURE 1 Projection along [010] to illustrate the atomic numbering scheme

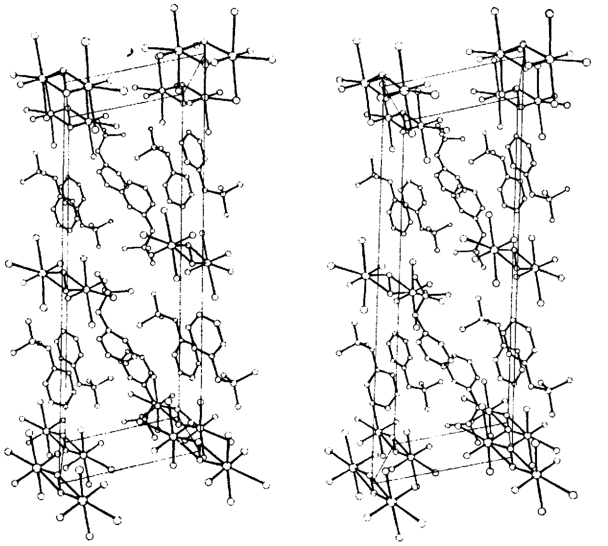


FIGURE 2 Stereoscopic drawing of one unit cell viewed along [010]

DISCUSSION

The structure of the uranyl salt consists of puckered sheets of binuclear $[Cl_3O_2U\text{-}(\mu_2\text{-}O_2)\text{-}UO_2Cl_3]^{4-}$ anions parallel to (001) and interleaved by $[N(PhCH_2)Me_3]$ cations. The polar ends of two neighbouring and crystallographically independent $[N(PhCH_2)Me_3]$ molecules point in opposite directions towards the anions, thus keeping their polar phenyl fragments together.

---

* For details see Notices to Authors, *J.C.S. Dalton*, 1976, Index issue.

[7] D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.

The U···N distances are all in the range of 5.10—5.93 Å.

The average geometries of both [N(PhCH$_2$)Me$_3$] groups are as expected.[8] The deviation of the N–C–C angles (115°) on the methylene groups from the tetrahedral value is probably real and due to steric factors.

TABLE 3

Important distances (Å) and angles (°) in the structure of [N(PhCH$_2$)Me$_3$]$_4$[Cl$_3$O$_2$U-(μ_2-O$_2$)-UO$_2$Cl$_3$]. The error in the last digit(s) is given in parentheses

U–U′	4.35(4)	U′–U–O(1)	88.8(7)
U–O(1)	1.78(3)	U′–U–O(2)	91.8(8)
U–O(2)	1.77(3)	O(1)–U–O(2)	179.3(1.0)
U–O(3)	2.29(3)	O(3)–U–Cl(3)	76.8(6)
U–O(3′)	2.31(3)	Cl(3)–U–Cl(2)	84.4(4)
U–Cl(1)	2.69(1)	Cl(2)–U–Cl(1)	82.8(4)
U–Cl(2)	2.73(3)	Cl(1)–U–O(3)	78.6(6)
U–Cl(3)	2.77(1)	O(3′)–U–O(3)	37.9(8)
O(3′)–O(3)	1.49(3)	Cl(1)–O(3′)–O(3)	128.0(1.5)
O(3)–Cl(1)	3.17(3)	O(3′)–O(3)–Cl(3)	127.8(1.5)
Cl(1)–Cl(2)	3.58(3)	O(3)–Cl(3)–Cl(2)	93.4(5)
Cl(2)–Cl(3)	3.66(3)	Cl(3)–Cl(2)–Cl(1)	95.6(4)
Cl(3)–O(3)	3.14(3)	Cl(2)–Cl(1)–O(3′)	94.0(5)
N(1)–C(1)	1.45(5)	C(1)–N(1)–C(2)	110.8(3.0)
N(1)–C(2)	1.52(5)	C(1)–N(1)–C(3)	107.6(3.0)
N(1)–C(3)	1.50(5)	C(1)–N(1)–C(4)	109.0(2.7)
N(1)–C(4)	1.51(5)	C(2)–N(1)–C(3)	109.1(2.9)
C(4)–C(5)	1.51(4)	C(2)–N(1)–C(4)	110.7(2.7)
C(5)–C(6)	1.39(5)	C(3)–N(1)–C(4)	109.6(2.7)
C(6)–C(7)	1.40(7)	N(1)–C(4)–C(5)	115.0(2.7)
C(7)–C(8)	1.31(7)	C(4)–C(5)–C(6)	120.7(2.9)
C(8)–C(9)	1.41(6)	C(4)–C(5)–C(10)	121.9(2.9)
C(9)–C(10)	1.34(6)	C(6)–C(5)–C(10)	117.4(3.0)
C(10)–C(5)	1.36(5)	C(5)–C(6)–C(7)	118.1(3.7)
		C(6)–C(7)–C(8)	124.1(4.7)
		C(7)–C(8)–C(9)	116.1(4.4)
		C(8)–C(9)–C(10)	121.3(4.0)
		C(9)–C(10)–C(5)	122.5(3.5)
N(2)–C(11)	1.50(4)	C(11)–N(2)–C(12)	104.2(2.6)
N(2)–C(12)	1.50(5)	C(11)–N(2)–C(13)	108.5(2.5)
N(2)–C(13)	1.51(4)	C(11)–N(2)–C(14)	109.3(2.5)
N(2)–C(14)	1.48(4)	C(12)–N(2)–C(13)	106.7(2.5)
C(14)–C(15)	1.49(4)	C(12)–N(2)–C(14)	114.3(2.7)
C(15)–C(16)	1.37(5)	C(13)–N(2)–C(14)	113.4(2.5)
C(16)–C(17)	1.37(5)	N(2)–C(14)–C(15)	115.1(2.6)
C(17)–C(18)	1.37(5)	C(14)–C(15)–C(16)	123.3(3.0)
C(18)–C(19)	1.35(5)	C(14)–C(15)–C(20)	121.2(2.9)
C(19)–C(20)	1.38(5)	C(16)–C(15)–C(20)	115.0(3.0)
C(20)–C(15)	1.41(5)	C(15)–C(16)–C(17)	123.3(3.5)
		C(16)–C(17)–C(18)	119.0(3.3)
		C(17)–C(18)–C(19)	120.3(3.4)
		C(18)–C(19)–C(20)	119.9(3.3)
		C(19)–C(20)–C(15)	121.8(3.2)

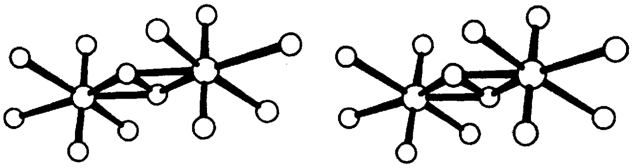


FIGURE 3 Stereoscopic view of the anion [Cl$_3$O$_2$U-(μ_2-O$_2$)-UO$_2$Cl$_3$]$^{4-}$

The benzyl groups are both planar with a maximum deviation from planarity of 0.04 Å.

The binuclear anion consists of two identical, distorted pentagonal bipyramids sharing the peroxo-group as a common edge. This arrangement of side-on bridging by a peroxo-group (structure 3) is not discussed by Vaska[1] and no other examples could be found in the literature. Each uranium atom lies in the plane through its five equatorial ligand atoms. The maximum deviation from the best plane through the uranium, the three chlorine atoms, and the peroxo-group is 0.14 Å. The linear uranyl group is arranged roughly perpendicular to this plane to complete a seven-co-ordination shell around the uranium. The linearity of the uranyl is not required by the space group. The O–O distance (1.49 Å) in the peroxo-group is within the expected range,[1] and the mean U–O(peroxo) distance (2.30 Å) agrees within the limits of error with that found[2] in Na$_4$UO$_8$·9H$_2$O (2.27 Å). The mean U–O(uranyl) and U–Cl distances (1.778 and 2.713 Å respectively) are in good agreement with those determined in other uranyl and uranyl–chlorine compounds.[3,9]

The large standard deviations in the atomic positions, and hence in the distances between them, are mainly due to the relatively strong scattering power of uranium in the presence of the much lighter atoms. This renders the precise positioning of the latter very difficult and the choice of uranium scattering factors is therefore of crucial importance. In addition to those examples cited before the scattering factors of Cromer and Waber[10] for neutral U and for U^{6+} were also tried, either with or without different corrections for anomalous dispersion, *e.g.* those used by Roof.[11] This gave no improvement and neither did the introduction of a refineable extinction parameter. The difference-Fourier maps persistently showed some residual electron density around the U positions at a distance of <1 Å. The maximum electron density in these peaks was 2.5 e Å^{-3} compared to the 4.5 e Å^{-3} at the position of the peroxo-oxygen atom. This could not be accounted for by thermal motion and probably reflects an inadequate description of the scattering by uranium atoms.

The formation of the peroxo-complex can only be due to interaction with atmospheric oxygen. A similar oxygenation occurs[12] in the case of [(NH$_3$)$_5$Co-(μ-O$_2$)-Co(NH$_3$)$_5$][NO$_3$]$_5$ and some earlier work[13] reports the formation of a uranyl peroxo-carbonate complex in the presence of alcohol. An attempt to prepare the present compound directly from dioxygen and a 4 : 1 [N(PhCH$_2$)Me$_3$] : UO$_2$Cl$_2$ mixture has so far been unsuccessful and further studies are underway to establish the reaction mechanism.

The chemical analysis was done by the Analytical Division of the National Institute for Metallurgy and most computations were carried out on the IBM 370/115 at the Computer Centre of the Rand Afrikaans University. We thank Jannie Pretorius for the ORTEP drawings and Eric Singleton for helpful discussions.

[6/1289 *Received, 5th July*, 1976]

---

[8] 'Molecular Structures and Dimensions,' ed. O. Kennard, Oosthoek's Uitgewers, Utrecht, Netherlands, 1972, p. S2.

[9] C. Bois, N. Q. Dao, and N. Rodier, *J. Inorg. Nuclear Chem.*, 1976, **38**, 755.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **A18**, 104.

[11] R. Roof, *Acta Cryst.*, 1961, **14**, 934.

[12] E. Bayer and P. Schretzmann, *Structure and Bonding*, 1967, **2**, 181.

[13] J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 279.