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# The Chemistry of Uranium.
# Part 25. The Structure and Properties of Tetrakis-(trisdimethylamidophosphine oxide) Dioxouranium-(VI) Triiodide

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Compounds of the type $UX_4tdpo_2$, where X = Cl and Br and tpdo = tris(dimethylamido)phosphine oxide, have been well studied and characterised [1–7]. The greater degree of tetragonal distortion of these *trans* octahedral complexes in going from the chloride to the bromide, *i.e.* U–X bond lengthening and U–O bond shortening, is of special interest [6, 8]. The differences between bromide and iodide, with reference to ionic size and nature of bonding with other elements, are even bigger than between chloride and bromide. Very few iodo complexes of uranium(IV) are known [9]. The only U(IV)–I bondlength reported thus far is that of $UI_4$, which was done recently [10].

Efforts have therefore been made to isolate $UI_4tdpo_2$ by reacting one equivalent of uranium metal with four equivalents of iodine in a methyl cyanide solution containing two equivalents of tdpo in a nitrogen atmosphere [11]. The violet colour of the iodine disappeared, but an undefined brown material was produced from which $UI_4tdpo_2$ could not be isolated. When the above mixture was exposed to air large brown-red non-hygroscopic crystals were formed from the solution. These were suspected to be the iodo analogue of $UO_2X_2tdpo_2$ (X = Cl or Br) [9] in view of the infrared peak at 917 $cm^{-1}$ typical of dioxouranium(VI). Since U(VI)–I bondlengths have not been reported in the literature and the crystals were of good quality, a crystal structure determination was undertaken even before analytical problems regarding the determination of iodide had been solved and in spite of the fact that the original aim was not achieved.

The absence of symmetry in Weissenberg and precession photographs indicated that the crystals belong to the triclinic system. Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.7107 Å) and a spherically-ground crystal. Refined cell dimensions are $a$ = 13.790(7), $b$ = 13.953(7), $c$ = 8.506(4) Å, $\alpha$ = 93.10(2), $\beta$ = 94.37(2), $\gamma$ = 117.02(2)°. The intensities of 2690 reflections were measured in the range $3° < \theta < 20°$ ($\omega - 2\theta$ scan mode: scan width 1.2°$\theta$, speed 0.04° $\theta s^{-1}$). Three reference reflections were monitored periodically. During an eight hour period midway during data collection (45 h) these intensities showed a decline, but remained fairly constant thereafter. The range corresponded to a variation of ±3.6% about the mean intensities, but no re-scaling of the data was attempted. Lorentz-polarization corrections were applied to the 2344 reflections with $I_o > 2\sigma(I_o)$. For the specimen used (average radius 0.125 mm) transmission factors ranged from 0.33 to 0.38 ($\mu$ = 58.1 $cm^{-1}$). In view of the outcome of the analysis (see below), improvement of the data by re-scaling and correction for absorption were regarded as unwarranted.

With $D_m$ = 2.06 g $cm^{-3}$ and $M_r$ = 882.2 g $mol^{-1}$ for the assumed formula $UO_2I_2(tdpo)_2$, the calculated $Z$ is 2.03, an acceptable indication that $Z$ = 2 molecules per unit cell. Initial attempts to interpret a three-dimensional Patterson map on this basis failed in both space groups $P1$ and $P\bar{1}$. This was followed by an unbiased approach in space group $P1$, assuming no chemical information other than the presence of U and I atoms in the cell. After several calculations, a model was eventually obtained which revealed two parallel linear triatomic arrays equidistant from the assigned U position. All coordinates were then referred to space group $P\bar{1}$ with U at 0, 0, 0. Subsequent difference maps confirmed an ionic structure with the formula $UO_2(tdpo)_4^{2+}$-$2I_3^-$ ($M_r$ = 1748.2 g $mol^{-1}$). In retrospect, the main difficulties which hampered a rapid solution were attempts to reconcile the Patterson map with a U:I atomic ratio of 1:2 compared with that ultimately found, *viz.* 1:6, and the inability to distinguish between I–I and U–I bonds whose lengths are practically identical (triodide I–I, 2.904–2.934 Å [12], U–I (terminal) in $UI_4$, 2.92(2) Å [10]).

Full-matrix least-squares refinement [13] with anisotropic temperature factors assigned to all non-hydrogen atoms converged at $R$ = 0.044, $R_w$ = 0.041 with $w \propto 1/\sigma^2$. Hydrogen atoms were geometrically placed with isotropic temperature factors fixed at reasonable values. The final difference map contained residual electron-density in the vicinity of the triiodide ion (max. height 2.2 $eÅ^{-3}$.

Structure factor tables and anisotropic thermal parameters have been deposited. Atomic coordinates for the non-hydrogen atons are listed in Table I.

The structure consists of centrosymmetric $UO_2(tdpo)_4^{2+}$ ions and symmetrical, nearly linear

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TABLE I. Fractional Atomic Coordinates $(\times 10^4)$ for non-hydrogen Atoms with Estimated Standard Deviations in Parenthesis.

| Atom | x | y | z |
|---|---|---|---|
| U | 0 | 0 | 0 |
| I1 | 1732(1) | 5922(1) | 6924(2) |
| I2 | 3508(1) | 6764(1) | 4943(1) |
| I3 | 5157(1) | 7476(1) | 2742(2) |
| P1 | 1935(3) | −806(3) | 2257(4) |
| P2 | 2053(3) | 2922(3) | 986(4) |
| O1 | 1090(7) | −619(7) | 1270(10) |
| O2 | 1392(7) | 1737(6) | 587(10) |
| O3 | −518(7) | 103(7) | 1779(10) |
| N1 | 1666(10) | −2065(10) | 2252(14) |
| N2 | 1990(10) | −403(10) | 4081(13) |
| N3 | 3092(10) | −157(10) | 1577(15) |
| N4 | 1314(11) | 3438(9) | 1699(16) |
| N5 | 3085(10) | 3182(9) | 2276(14) |
| N6 | 2506(9) | 3441(10) | −610(15) |
| C11 | 2105(17) | −2554(15) | 1145(20) |
| C12 | 711(16) | −2806(15) | 2906(26) |
| C21 | 1804(14) | 551(14) | 4494(18) |
| C22 | 2377(17) | −800(15) | 5466(18) |
| C31 | 3154(16) | −28(16) | −148(23) |
| C32 | 4145(14) | 119(17) | 2514(24) |
| C41 | 1336(16) | 4427(14) | 1352(21) |
| C42 | 657(21) | 2946(17) | 2955(31) |
| C51 | 3792(14) | 2704(17) | 1952(22) |
| C52 | 3469(18) | 3977(16) | 3632(22) |
| C61 | 2003(15) | 2926(14) | −2206(19) |
| C62 | 3474(14) | 4486(15) | −607(25) |

$I_3^-$ counterions in the ratio 1:2. The molecular configuration of the cation and the atomic numbering of the asymmetric unit are shown in Fig. 1 [14]. Selected bond lengths and angles are listed in Table II. Bond angles involving the uranium atom indicate that the coordination is octahedral, with the linear uranyl group normal to the equational plane containing the four tdpo oxygen donor atoms.

Chemically-equivalent bond lengths in the cation are in close agreement and fall within the expected ranges.

It is of interest to compare the cation configurations in the tri-iodide (this study) and perchlorate [15] salts. In the latter compound the uranium atom displays the same coordination but occupies a general position in the unit cell (space group *Pbca*, $Z = 8$). Principal bond lengths in the cations of the two salts compare favourably, although the e.s.d.s and the scatter in chemically-equivalent bond lengths are somewhat larger in the case of the perchlorate, for reasons stated in the original reference [15]. While the $UO_6$ octahedra are geometrically indistinguishable in the two salts, significant conformational differences exist owing to the flexibility of the U–O–P bond angles and the possibility of rotation of the tdpo moieites about the U–O and P–O bonds. For related complexes, values for U–O–P in the range 159.8 to 178.5° have been reported [16]. In the tri-iodide salt, the two independent U–O–P angles are similar and resemble those reported for $UCl_4(tppo)_2$ (163.7°) [6] whereas in the perchlorate salt, the four U–O–P angles range from 152(3) to 164(3)°. The two unique O3–U–O–P torsion angles are −71.1° and −57.4° in the $I_3^-$ salt, with the result that atoms P1 and P2 are situated above the equational plane (deviations +0.10, +0.20 Å respectively) with $P1^i$ and $P2^i$ correspondingly below the plane ($i = -x, -y, -z$). This is in contrast to the $ClO_4^-$ salt for which the analogous O–U–O–P torsion angles are 16.4, 163.1, 6.7 and 177.1° (proceeding cyclically around U), resulting in corresponding deviations

TABLE II. Selected Bond Lengths and Angles (E.s.d.s in Parenthesis).

| | | | |
|---|---|---|---|
| *(a) Bond lengths* (Å) | | | |
| U–O1 | 2.281(7) | P1–N3 | 1.61(1) |
| U–O2 | 2.300(8) | P2–N4 | 1.62(1) |
| U–O3 | 1.750(9) | P2–N5 | 1.63(1) |
| P1–O1 | 1.512(8) | P2–N6 | 1.62(1) |
| P2–O2 | 1.488(8) | | |
| P1–N1 | 1.62(1) | I1–I2 | 2.904(1) |
| P1–N2 | 1.61(1) | I2–I3 | 2.909(2) |
| *(b) Bond angles* (°) | | | |
| O2–U–O1 | 88.9(8) | O1–P1–N1 | 114.4(5) |
| O3–U–O1 | 89.9(3) | O1–P1–N2 | 109.5(6) |
| O3–U–O2 | 90.3(3) | O1–P1–N3 | 107.4(6) |
| U–O1–P1 | 168.9(5) | O2–P2–N4 | 110.5(6) |
| U–O2–P2 | 165.3(5) | O2–P2–N5 | 110.2(6) |
| I1–I2–I3 | 175.2(1) | O2–P2–N6 | 107.6(6) |

*(continued on facing page)*

TABLE II. *(continued)*

*Anisotropic thermal parameters* ($Å^2 \times 10^3$) *of the form* $T = \exp|-2\pi^2\Sigma\Sigma_{a_i}a_jh_ih_jU_{ij}|$ *for Tetrakis-(trisdimethylamidophosphine oxide) dioxouranium(VI) triodide.*

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| U | 41(1) | 36(1) | 39(1) | 4(0) | 0(0) | 20(0) |
| I1 | 166(2) | 167(2) | 119(1) | 60(1) | 60(1) | 115(1) |
| I2 | 80(1) | 69(1) | 81(1) | −7(1) | −13(1) | 44(1) |
| I3 | 82(1) | 119(1) | 156(1) | 37(1) | 31(1) | 47(1) |
| P1 | 57(2) | 55(2) | 51(2) | 10(2) | 2(2) | 35(2) |
| P2 | 49(2) | 41(2) | 64(3) | 6(2) | 6(2) | 16(2) |
| O1 | 63(6) | 64(6) | 56(6) | 6(5) | −8(5) | 40(5) |
| O2 | 58(6) | 38(6) | 72(6) | 0(5) | 3(5) | 16(5) |
| O3 | 77(7) | 60(6) | 49(6) | 7(5) | −1(5) | 28(5) |
| N1 | 73(9) | 61(8) | 78(9) | 14(7) | −3(7) | 37(8) |
| N2 | 92(9) | 73(9) | 51(8) | 7(6) | −1(7) | 44(8) |
| N3 | 64(9) | 86(9) | 80(9) | 29(7) | 30(7) | 39(7) |
| N4 | 90(10) | 47(8) | 108(11) | 10(7) | 35(9) | 32(7) |
| N5 | 60(8) | 62(8) | 79(9) | −3(7) | −12(7) | 23(7) |
| N6 | 45(7) | 70(9) | 87(10) | 24(7) | 13(7) | 16(7) |
| C11 | 160(18) | 94(14) | 93(13) | −38(11) | −31(13) | 86(14) |
| C12 | 103(16) | 81(14) | 161(20) | 28(14) | −13(14) | 35(12) |
| C21 | 103(13) | 117(15) | 73(11) | −30(10) | −15(10) | 77(12) |
| C22 | 157(18) | 122(16) | 52(11) | 5(10) | −24(11) | 77(14) |
| C31 | 120(17) | 136(18) | 115(17) | 50(14) | 58(13) | 65(14) |
| C32 | 58(12) | 154(19) | 134(17) | 2(14) | 10(12) | 52(12) |
| C41 | 139(17) | 82(13) | 113(15) | −5(11) | −13(12) | 81(13) |
| C42 | 229(30) | 104(17) | 238(28) | 48(18) | 165(25) | 98(19) |
| C51 | 83(13) | 144(18) | 107(15) | −6(13) | −22(11) | 59(14) |
| C52 | 180(22) | 117(17) | 105(16) | −30(14) | −46(16) | 84(17) |
| C61 | 109(14) | 100(14) | 70(12) | 20(10) | 16(11) | 48(12) |
| C62 | 73(13) | 102(15) | 151(19) | 48(14) | 16(12) | 13(12) |

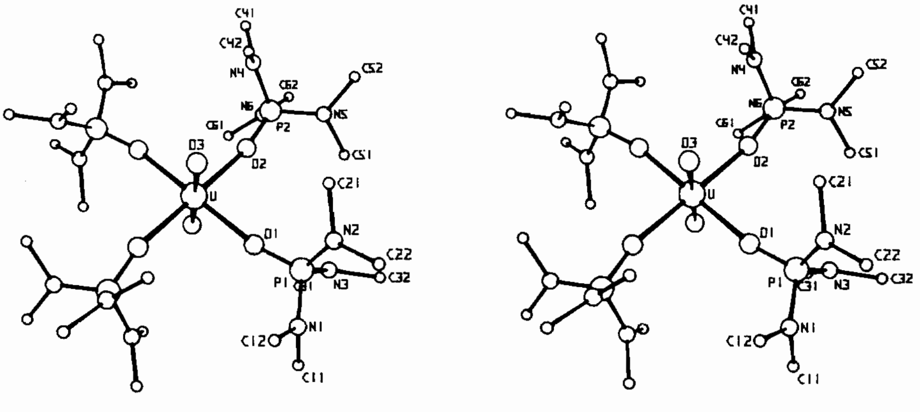

Fig. 1. Stereoscopic view illustrating the configuration of the complex cation $UO_2(tdpo)_4^{2+}$.

of the P atoms from the equatorial plane which are larger in magnitude and which alternate in sense (+0.74, −0.57, +0.48, −0.76 Å, calculated from data in ref. 15).

Bond lengths and angles omitted from Table I lie in the following ranges: N–C 1.43(1)–1.50(2) Å, N–P–N 105.5(6)–111.5(7)°, P–N–C 118(1)–126(1), C–N–C 113(1)–116(1).

The tri-iodide ions are discrete and symmetrical with I–I distances at the lower end of the range reported for a series of tri-iodide salts [12]. The shortest non-bonded I···C distance is 3.95 Å.

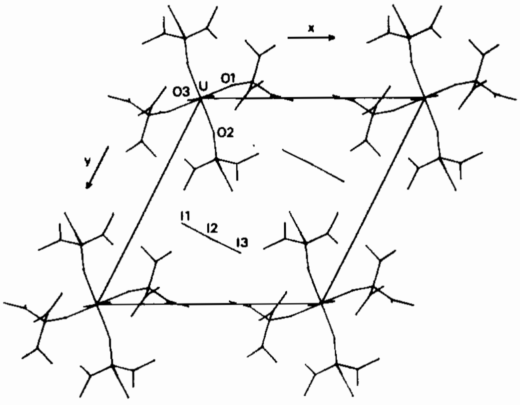

Fig. 2. Projection along [001].

Figure 1 shows that the shape of the cation resembles a disc with the uranyl group as its axis. The tilt of the cations, measured by the angle between the equational plane of the cation and the cell *ab* face is 32°. The crystal thus consists of layers of cations on the *ab*-planes, interleaved by tri-iodide ions whose centres of gravity lie close to $Z = 0.5$. From the projection along [001] in Fig. 2, it can be inferred that each cation has six identical nearest-neighbour cations arranged in an approximately hexagonal array ($a \approx b$, $\gamma = 117.02^\circ$).

The iodide analysis was ultimately performed by dissolving the compound in a small amount of N,N-dimethylformamide acidified by dilute sulphuric acid and reduced to iodide through a zinc column followed by an argentometric titration. Iodide found; 43.4%, calculated for title compound; 43.55%. The shift in the P=O stretch frequency was found to be 147 $\text{cm}^{-1}$. A thermogravimetric analysis indicated no mass loss up to 120 °C. Some significant degradation occurs over 200 °C. The stability of tri-iodides is a function of the size of the cation *e.g.* $KI_3$ decomposes at ~70 °C and CsI at ~250 °C. The tri-iodide therefore acts as a large counter anion similar to the perchlorate.

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