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Bis(2-methylimidazolium) Tetrachlorodioxouranate(VI), $2C_4H_7N_2^+.UCl_4O_2^{2-}$

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Abstract. $M_r = 578{\cdot}07$, monoclinic, $P2_1/c$, $a = 7{\cdot}177\,(2)$, $b = 18{\cdot}526\,(4)$, $c = 12{\cdot}600\,(3)$ Å, $\beta = 94{\cdot}08\,(2)°$, $U = 1671{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}30$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 98·6 cm^{-1}, $F(000) = 1000{\cdot}3$, $T = 296$ K, $R = 0{\cdot}035$ for 1501 observed reflections where $F^2 > \sigma(F^2)$. The structure consists of the packing of columns of $UO_2Cl_4^{2-}$ anions and columns of $CH_3C_3N_2H_4^+$ cations parallel to the a axis. The distances and angles of the $UO_2Cl_4^{2-}$ anion are in good agreement with values reported previously.

Introduction. Uranyl complexes exhibit a highly characteristic luminescence spectrum in both solution and solid state. This luminescence will often display considerable vibrational structure, and the spectral details are quite dependent on the overall structure of the complex and the nature of the coordination sphere about the central uranyl ion (Brittain & Perry, 1980, 1981; Perry, 1982). The luminescence properties of the title compound are significantly different from those of the unsubstituted imidazolium tetrachlorodioxouranium(VI) complex (Perry, Freyberg & Zalkin, 1980).

Experimental. Material made by combining 2-methylimidazole (2 mmol) and uranyl chloride trihydrate (1 mmol) in water, adjusting the pH to 2 with HCl and evaporating to dryness; crystals by recrystallization from water. Crystal *ca* 0·09 × 0·05 × 0·20 mm, mounted with epoxy glue to a glass fiber, modified FACS-I Picker diffractometer, ~40 reflections with $20 < 2\theta < 35°$ used to determine cell dimensions and their standard deviations, systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$, analytical absorption correction applied (Templeton & Templeton, 1973) (corrections ranged from 1·52 to 2·68), $2\theta_{\max} = 45°$, $-7 \le h \le 7$, $0 \le k \le 19$, $-13 \le l \le 13$, 3 standard reflections (202, 111, 040) every 200th measurement, accuracy better than 1·5%; standards showed isotropic decay of ~25%, data adjusted accordingly. 2733 intensities measured, 2183 unique, 550 reflections measured twice, $R_{\rm int} = 0{\cdot}028$, 603 unobserved reflections with $I < \sigma(I)$. Atomic positions of uranium and chlorine derived from three-dimensional Patterson map. Electron density map, calculated from observed structure factors and phases based on heavy atoms, revealed positions of carbon, nitrogen and oxygen atoms. Full-matrix least-squares refinement on F, calculated non-methyl hydrogen positional parameters included in least squares but not refined. Because of some large discrepancies in the low-angle data, all 79 data where $\sin\theta/\lambda < 0{\cdot}18$ Å^{-1} were assigned zero weights in final refinements; anisotropic thermal parameters for non-hydrogen atoms, $R = 0{\cdot}035$, $R_w = 0{\cdot}027$ for 1501 data $[F^2 > \sigma(F^2)]$, $S = 1{\cdot}06$, $w = [\sigma(F)]^{-1}$, derived from $\sigma(F^2) = [C + (pF^2)^2]^{1/2}$; C is variance due to counting statistics and $p = 0{\cdot}02$. After final refinement, largest shift/error < 0·0004, max. and min. heights in final difference Fourier were 1·23 and −1·20 e Å^{-3}, respectively; empirical correction of the form $F_{\rm corr} = F_{\rm obs}(1+kI)$, $k = 3{\cdot}5 \times 10^{-6}$, applied to the data to adjust for extinction and other systematic errors not identified in the present description of the work; scattering factors for U, Cl, O, N, and C from *International Tables for X-ray Crystallography* (1974), hydrogen scattering factors from Stewart, Davidson & Simpson (1965), anomalous scattering factors from Cromer & Liberman (1970); f'' values used for U, Cl, O, N and C were 9·654, 0·159, 0·006, 0·003 and 0·002, respectively. With the exception of *ORTEP* (Johnson, 1965), all computer programs used in this structure determination were written by the authors for a CDC 7600 computer.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
U	0·23303 (6)	0·12987 (2)	0·27456 (3)	2·82
Cl(1)	−0·0720 (4)	0·12993 (16)	0·38428 (20)	4·10
Cl(2)	0·0723 (4)	0·03771 (13)	0·13287 (12)	3·94
Cl(3)	0·5416 (4)	0·12628 (15)	0·16763 (21)	4·03
Cl(4)	0·3920 (4)	0·22788 (14)	0·40844 (21)	4·15
O(1)	0·1412 (11)	0·2032 (3)	0·1970 (5)	3·96
O(2)	0·3214 (11)	0·0564 (3)	0·3504 (6)	4·11
N(1)	0·2030 (14)	0·8919 (5)	0·2446 (9)	4·08
N(2)	0·2430 (14)	0·7783 (5)	0·2461 (7)	3·81
N(3)	0·7208 (13)	0·8607 (4)	0·2567 (6)	3·09
N(4)	0·7125 (14)	0·9750 (4)	0·2847 (8)	3·49
C(1)	0·2767 (17)	0·8768 (8)	0·3438 (10)	4·73
C(2)	0·2989 (19)	0·8036 (7)	0·3460 (11)	4·53
C(3)	0·1836 (17)	0·8336 (7)	0·1848 (10)	3·51
C(4)	0·1158 (21)	0·8277 (6)	0·0711 (10)	5·29
C(5)	0·7784 (16)	0·8711 (7)	0·3599 (9)	3·65
C(6)	0·7767 (17)	0·9419 (7)	0·3804 (9)	3·96
C(7)	0·6817 (16)	0·9249 (6)	0·2111 (9)	3·45
C(8)	0·6167 (18)	0·9370 (6)	0·0961 (9)	4·50

Table 2. *Distances* (Å) *and angles* (°)

U–Cl(1)	2·671 (3)	N(1)–C(1)	1·35 (2)	N(3)–C(5)	1·35 (2)
U–Cl(2)	2·672 (3)	C(1)–C(2)	1·37 (2)	C(5)–C(6)	1·34 (2)
U–Cl(3)	2·674 (3)	C(2)–N(2)	1·38 (2)	C(6)–N(4)	1·40 (3)
U–Cl(4)	2·678 (3)	N(2)–C(3)	1·33 (2)	N(4)–C(7)	1·32 (2)
U–O(1)	1·773 (6)	C(3)–N(1)	1·32 (2)	C(7)–N(3)	1·34 (2)
U–O(2)	1·756 (7)	C(3)–C(4)	1·48 (2)	C(7)–C(8)	1·51 (2)

Cl(1)–U–Cl(2)	90·9 (1)	C(3)–N(1)–C(1)	112 (1)
Cl(1)–U–Cl(3)	178·3 (1)	N(1)–C(1)–C(2)	105 (1)
Cl(1)–U–Cl(4)	90·1 (1)	C(1)–C(2)–N(2)	107 (1)
Cl(1)–U–O(1)	89·9 (3)	C(2)–N(2)–C(3)	109 (1)
Cl(1)–U–O(2)	89·8 (3)	N(2)–C(3)–N(1)	106 (1)
Cl(2)–U–Cl(3)	88·9 (1)	N(2)–C(3)–C(4)	125 (1)
Cl(2)–U–Cl(4)	176·9 (1)	N(1)–C(3)–C(4)	129 (1)
Cl(2)–U–O(1)	89·8 (3)	C(7)–N(4)–C(6)	109 (1)
Cl(2)–U–O(2)	89·4 (2)	N(4)–C(6)–C(5)	106 (1)
Cl(3)–U–Cl(4)	90·2 (1)	C(6)–C(5)–N(3)	109 (1)
Cl(3)–U–O(1)	91·7 (3)	C(5)–N(3)–C(7)	109 (1)
Cl(3)–U–O(2)	88·6 (3)	N(3)–C(7)–N(4)	108 (1)
Cl(4)–U–O(1)	87·3 (2)	N(3)–C(7)–C(8)	126 (1)
Cl(4)–U–O(2)	93·6 (2)	N(4)–C(7)–C(8)	127 (1)
O(1)–U–O(2)	179·1 (3)		

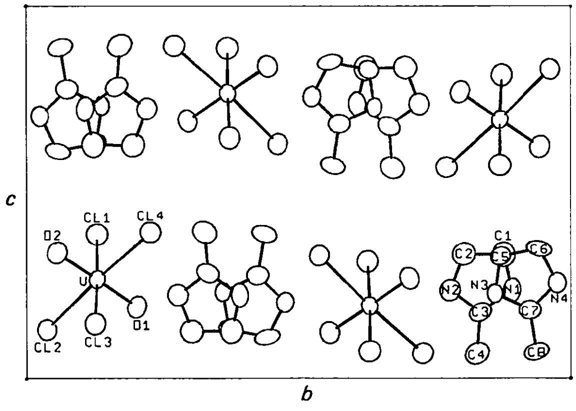

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the contents of one unit cell as viewed down the *a* axis. The origin is at the lower left corner.

Discussion. The atomic coordinates are given in Table 1 with the numbering scheme as shown in Fig. 1; a list of distances and angles is given in Table 2.* The structure consists of the packing of columns of $UO_2Cl_4^{2-}$ anions and columns of $CH_3C_3N_2H_4^+$ cations parallel to the *a* axis. Fig. 1 shows the view down the *a* axis of one formula unit.

The $UO_2Cl_4^{2-}$ anion is a flattened octahedron with the oxygen atoms occupying the apices and the chlorine atoms the equatorial positions. The anion has been well characterized by other structure determinations, and the distances and angles reported here are in good agreement with those previously determined (Perry, Freyberg & Zalkin, 1980).

The 2-methylimidazolium cation is a planar entity and, with the exception of the methyl group, has the same geometry and dimensions as the unsubstituted imidazolium ion (Perry, Freyberg & Zalkin, 1980). The planes of the two independent 2-methylimidazolium ions (Fig. 1) are within 4° of being parallel to each other.

The shortest interatomic distances to the nitrogen atoms are: N(1)–Cl(2), 3·16 (1); N(2)–O(1), 3·21 (1), N(3)–O(1), 3·12 (1); and N(4)–O(2), 3·34 (1) Å. These distances are comparable with those in imidazolium tetrachlorodioxuranate(VI) (Perry, Freyberg & Zalkin, 1980), in which weak hydrogen bonding was suggested.

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* Lists of structure factors, anisotropic thermal parameters, and calculated hydrogen positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38610 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Dimeric Dichlorotetramethyldistannoxane,* $(C_4H_{12}Cl_2OSn_2)_2$

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Abstract. $M_r = 768{\cdot}6$, monoclinic, $P2_1/c$, $a = 7{\cdot}32$ (1), $b = 18{\cdot}56$ (2), $c = 8{\cdot}73$ (1) Å, $\beta = 110{\cdot}00$ (5)°, $V = 1115$ (1) Å^3, D_m(flotation) $= 2{\cdot}30$, $D_x = 2{\cdot}29$ Mg m^{-3} for $Z = 2$ (the molecule is dimeric and there are four asymmetric units in the cell), Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 52{\cdot}4$ cm^{-1}, $F(000) = 712$, room temperature. The structure was solved by standard methods from diffractometer data and refined to a conventional R of 6·1% for 1798 observed reflections. The centrosymmetric dimer consists of a central Sn_2O_2 ring with two additional adjacent Sn_2OCl four-membered rings. The Sn, O, and Cl atoms are approximately coplanar. The Sn atoms are pentacoordinate, approximately trigonal bipyramidal.

Introduction. Several structural studies of dialkyltin derivatives have been prompted in view of the biological activity displayed by some of these compounds and we recently reported the crystal structure of dichlorodimethylbis(3,5-dimethylpyrazole-N^2)tin(IV), $SnMe_2Cl_2(dmp)_2$ (Graziani, Casellato, Ettorre & Plazzogna, 1982).

Experimental. Very stable colourless crystals of the title compound were obtained as a hydrolysis product during the preparation of the above complex. Crystal $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}2$ mm, Philips PW 1100 four-circle diffractometer; lattice parameters by least-squares refinement of 25 medium-angle settings. Integrated intensities up to $\theta = 25°$, $h_{max} = \pm 8$, $k_{max} = 22$, $l_{max} = 10$, $\theta/2\theta$ scan mode, graphite-monochromated Mo $K\alpha$ radiation; standard reflections: no variation. 2005 unique reflections measured, 1798 with $I > 3\sigma(I)$ used; intensities corrected for Lorentz and polarization factors, and for absorption (North, Phillips & Mathews, 1968), $0{\cdot}26 < \mu R < 0{\cdot}54$. The diffraction effects are dominated by the heavy-atom contributions and the structure was solved by Patterson and Fourier methods. Full-matrix least-squares anisotropic refinement converged to $R = 6{\cdot}1\%$; $\sum w(k|F_o| - |F_c|)^2$ minimized, $w = 1$; no H atoms introduced; maximum shift-to-error ratio 0·2; maximum and minimum heights in final difference Fourier map 0·7 and −0·7 e Å^{-3}; no correction for secondary extinction. Scattering factors for the Sn atom from Cromer & Waber (1965), with corrections for anomalous dispersion (Cromer, 1965), and those for the other non-hydrogen atoms from Cromer & Mann (1968). Calculations performed using XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
Sn(1)	0·4880 (2)	0·0369 (1)	0·1685 (1)	0·051 (1)
Sn(2)	0·4436 (2)	0·1629 (1)	−0·1574 (2)	0·056 (1)
Cl(1)	0·4182 (13)	0·1796 (3)	0·1523 (8)	0·089 (5)
Cl(2)	0·4678 (12)	0·1110 (4)	−0·4068 (8)	0·092 (5)
O	0·4659 (22)	0·0612 (7)	−0·0727 (16)	0·056 (8)
C(1)	0·7746 (34)	0·0522 (16)	0·3390 (29)	0·082 (17)
C(2)	0·2077 (31)	0·0160 (16)	0·1854 (29)	0·081 (16)
C(3)	0·7210 (35)	0·2138 (15)	−0·0574 (35)	0·082 (17)
C(4)	0·1432 (39)	0·1895 (18)	−0·2527 (38)	0·103 (22)

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* IUPAC name: 1,2;3,4-di-μ-chloro-1,4-dichloro-1,1,2,2,3,3,4,4-octamethyl-1,2,3;2,3,4-di-μ_3-oxo-tetratin(IV).

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