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TETRACHLOROBIS[1,2-BIS(DIMETHYLAMINO)ETHANE]URANIUM(IV)
$UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$

A. Zalkin, P.G. Edwards, D. Zhang, and R.A. Andersen

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Tetrachlorobis[1,2-bis(dimethylamino)ethane]uranium(IV)

$UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$

By Allan Zalkin, Peter G. Edwards, Dechun Zhang & Richard A. Andersen

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and

Department of Chemistry, University of California, Berkeley CA 94720

Abstract. M_r = 612.26, orthorhombic, $P2_12_12_1$, a = 13.094(4), b = 13.265(4), c = 12.633(4) Å, V = 2199.2 $Å^3$, Z = 4, D_x = 1.849 g cm^{-3}, λ(MoKα)=0.71073 Å, μ = 74.9 cm^{-1}, F(000) = 1168, T = 296 K, R = 0.041 for 2617 unique reflections with $F^2>2\sigma(F^2)$. The uranium atom is bonded to a distorted square of four chlorine atoms and to the four nitrogen atoms of the 1,2-bis(dimethylamino)ethane ligand with average U-Cℓ and U-N distances of 2.609 ± 0.009 Å and 2.786 ± 0.019 Å, respectively.

Introduction. The crystal structure of the phosphine complex, $U(OC_6H_5)_4 \cdot [(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$, (Edwards, Andersen & Zalkin, 1983) showed that the uranium atom is eight coordinate and the phosphorus atoms are located on the A-sites and the oxygen atoms are located on the B-sites of an idealized D_{2d}-dodecahedron (Hoard & Silverton, 1963). The nitrogen analogue of tetravalent uranium, $UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$, was prepared so that the solid state geometry and solution state stereochemistry of the eight coordinate complexes could be compared.

Experimental. The complex was prepared from UCl_4 and excess $(CH_3)_2NCH_2CH_2N(CH_3)_2$ in toluene and large green prisms were obtained by cooling the mother liquor (-20°C). Full synthesis details will be published separately. The crystal used in the X-ray study was selected from these crystals; because of its sensitivity to air it was sealed inside a quartz capillaries under argon. Crystal 0.16 x 0.22 x 0.23 mm with 8 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 25 reflections, $20° < 2\theta < 34°$; analytical absorption correction, range 2.94 to 3.72; max. $(\sin\theta)/\lambda = 0.60$ A^{-1}, h 0 to 15, k -15 to 15, ℓ 0 to 15; three standard reflections, 1% variation in intensities from average, intensities adjusted accordingly; 4232 data, 3879 unique (including 1262, $F^2 < 2\sigma$), $R_{int} = 0.035$; structure solved by Patterson and Fourier methods; refined on F, 190 parameters; 32 hydrogen atoms in calculated positions and fixed isotropic thermal parameters; anisotropic thermal parameters for non-hydrogen atoms; R = 0.10 for 3879 data, R = 0.041 for 2617 reflections for which $F^2 > 2\sigma$, wR = 0.029, S = 1.0; $w = [\sigma(F)]^{-2}$, p = 0.02 in calc. of $\sigma(F^2)$; max (shift/σ) = 0.01; empirical extinction correction, $F_{corr} = (1 + 5.0 \times 10^{-7} I)$; max. and min. of ΔF synthesis 1.3 and -1.5 e A^{-3}; atomic f for neutral U, Cl, N and C, and spherical

bonded H from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965).

Atomic parameters are listed in Table 1,* and distances and angles are listed in Table 2. Fig.1 shows the molecule and numbering scheme.

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*Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Eight coordinate molecules generally fall into three idealized geometries, the D_{2d}-dodecahedron, C_{2v}-bicapped trigonal prism, and D_{4h}-square antiprism (Hoard & Silverton, 1963; Kepert, 1978; Kepert, 1982). A convenient way to illustrate the distortion from an idealized geometry is by the shape parameters δ' and ϕ (Porai-Koshits & Aslanov, 1972; Muetterties & Guggenberger, 1974), where δ' is the angle of intersection of the triangular faces along the line connecting the AA- and BB- sites in a dodecahedron and ϕ is the dihedral angle between two triangles constructed from the BAAB-trapezoidal atoms. As shown in Table 3, $UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$ is best described as a dodecahedron with the nitrogen atoms on the A-sites and the chloride ligands on the B-sites.

The average U-Cl bond length in $UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$ of 2.609 ± 0.009 Å is shorter than that found in other eight-coordinate structures: i.e. $UCl_4 \cdot (NCCH_3)_4$ 2.623 ± 0.002 Å (Cotton, Marler & Schwotzer, 1984); $UCl_2[(OC_6H_4)C(OH)NCH_2CH_2NC(OH)(C_6H_4O)] \cdot (OC_4H_4)_2$ 2.67 ± 0.02 Å

(Calderazzo, Floriani, Pasquali, Cesari & Perego, 1976); $[UCl_2(OS(CH_3)_2)_6]^{2+}$ 2.70 ± 0.02 A (Bombieri & Bagnall, 1975); UCl_4 2.869(3) A and 2.638(4) A (Taylor & Wilson, 1973). The average U-N distance of 2.786 ± 0.019 A is substantially longer than the equivalent distance in $UCl_4 \cdot (NCCH_3)_4$ of 2.589 ± 0.006 A (Cotton, Marler & Schwotzer, 1984) and substantially longer than expected based upon the averaged U-P distance in $U(OC_6H_5)_4 \cdot [(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$ of 3.104 ± 0.006 A (Edwards, Andersen & Zalkin, 1983) since the tetrahedral covalent radius of phosphorus is 0.40 A longer than nitrogen (Pauling, 1960). The longer than expected U-N bond distance is most reasonably ascribed to intramolecular steric repulsions between the methyl groups on the nitrogen atoms and the chloride ligands since each chloride ligand has four C···Cl contact distances of ca. 3.4 A, close to the sum of the van der Waals radii of these two atoms (Pauling, 1960). Hence a shorter U-N bond would cause substantial atom-atom repulsions and the structure is a compromise between attractive (U-N, U-Cl) and repulsive (C···Cl) forces.

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Table 1. Atomic Parameters

$$B_{eq} = \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j / 3, \quad \text{Å}^2.$$

Atom	x	y	z	B_{eq}(Å^2)
U(1)	0.21551(3)	0.26075(3)	0.26680(3)	3.418(9)
Cl(1)	0.0830(3)	0.1541(3)	0.37142(29)	6.6(1)
Cl(2)	0.3581(4)	0.14217(28)	0.3411(4)	8.2(2)
Cl(3)	0.29997(28)	0.31098(23)	0.08658(24)	5.9(1)
Cl(4)	0.12503(27)	0.43548(21)	0.2639(3)	7.0(1)
N(1)	0.0488(6)	0.2466(9)	0.1321(7)	5.1(3)
N(2)	0.2100(9)	0.0820(6)	0.1477(8)	5.2(3)
N(3)	0.3786(10)	0.3880(8)	0.3152(10)	5.9(4)
N(4)	0.2221(12)	0.3266(8)	0.4747(8)	6.7(4)
C(1)	-0.0514(9)	0.2631(13)	0.1817(10)	8.7(5)
C(2)	0.0507(13)	0.3160(11)	0.0404(12)	7.8(6)
C(3)	0.0409(14)	0.1414(14)	0.0905(14)	7.8(7)
C(4)	0.1308(16)	0.0952(14)	0.0639(15)	10.1(8)
C(5)	0.3091(12)	0.0586(10)	0.0914(13)	8.2(6)
C(6)	0.1898(12)	-0.0086(8)	0.2075(12)	9.3(6)
C(7)	0.3690(11)	0.4891(10)	0.2703(12)	8.5(5)
C(8)	0.4790(11)	0.3508(12)	0.2719(15)	9.4(6)
C(9)	0.3958(13)	0.3932(11)	0.4269(13)	7.0(6)
C(10)	0.2981(17)	0.4141(10)	0.4837(10)	7.9(6)
C(11)	0.2514(11)	0.2527(12)	0.5525(9)	9.5(6)
C(12)	0.1180(17)	0.3635(12)	0.5112(12)	9.9(8)

Table 2. Selected distances (Å) and angles(°)

U(1) - Cl(1)	2.600(4)	U(1) - N(1)	2.774(8)
U(1) - Cl(2)	2.615(4)	U(1) - N(2)	2.810(8)
U(1) - Cl(3)	2.617(3)	U(1) - N(3)	2.791(11)
U(1) - Cl(4)	2.603(3)	U(1) - N(4)	2.769(9)
Cl(1)-U(1)-Cl(2)	88.07(14)	Cl(3)-U(1)-N(1)	79.40(21)
Cl(1)-U(1)-Cl(3)	149.63(12)	Cl(3)-U(1)-N(2)	76.11(22)
Cl(1)-U(1)-Cl(4)	100.85(13)	Cl(3)-U(1)-N(3)	73.34(27)
Cl(2)-U(1)-Cl(3)	99.43(15)	Cl(3)-U(1)-N(4)	137.02(27)
Cl(2)-U(1)-Cl(4)	149.93(12)	Cl(4)-U(1)-N(1)	72.15(25)
Cl(3)-U(1)-Cl(4)	87.32(12)	Cl(4)-U(1)-N(2)	137.06(25)
Cl(1)-U(1)-N(1)	75.52(23)	Cl(4)-U(1)-N(3)	79.21(26)
Cl(1)-U(1)-N(2)	78.21(23)	Cl(4)-U(1)-N(4)	75.34(27)
Cl(1)-U(1)-N(3)	136.77(26)	N(1) -U(1)-N(2)	66.0(3)
Cl(1)-U(1)-N(4)	73.15(28)	N(1) -U(1)-N(3)	141.1(3)
Cl(2)-U(1)-N(1)	137.82(25)	N(1) -U(1)-N(4)	128.9(4)
Cl(2)-U(1)-N(2)	72.73(26)	N(2) -U(1)-N(3)	130.4(4)
Cl(2)-U(1)-N(3)	74.87(24)	N(2) -U(1)-N(4)	140.8(3)
Cl(2)-U(1)-N(4)	80.03(29)	N(3) -U(1)-N(4)	65.0(4)

Table 3. Shape Parameters

	δ'°	φ°
$UCl_4 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$	20.4, 21.9, 38.7, 39.6	1.6
D_{2d}-dodecdahedron	29.5, 29.5, 29.5, 29.5	0.0
C_{2v}-bicapped trigonal prism	0.0, 21.8, 48.2, 48.2	14.1
D_{4h}-square antiprism	0.0, 0.0, 52.4, 52.4	24.5

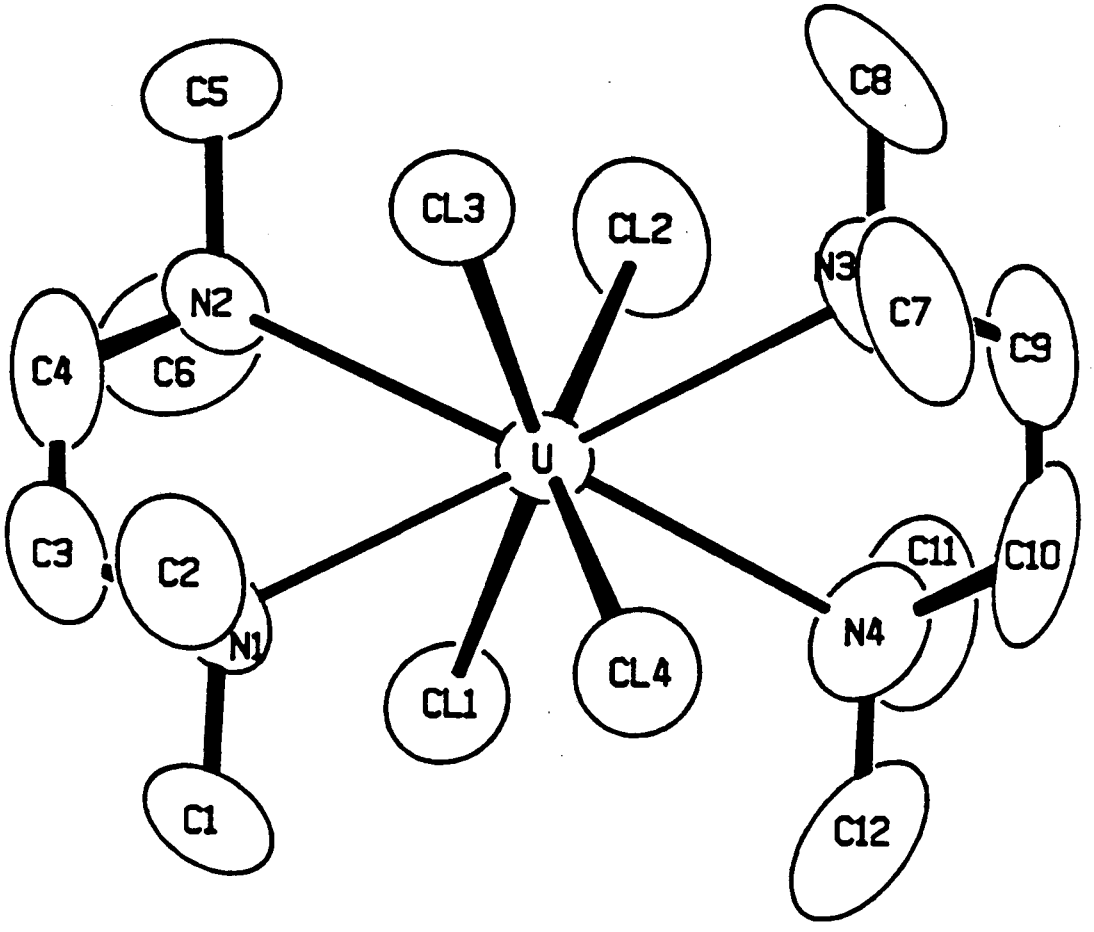

Fig. 1. ORTEP (Johnson, 1965) of the molecule showing the atomic numbering scheme.

Supplemental Material for

Tetrachlorobis[1,2-bis(dimethylamino)ethane)uranium(IV)

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Abstract. M_r = 612.26, orthorhombic, $P2_12_12_1$, a = 13.094(4), b = 13.265(4), c = 12.633(4) A, V = 2199.2 A^3, Z = 4, D_x = 1.849 g cm^{-3}, λ(MoKα)=0.71073 A, μ = 74.9 cm^{-1}, F(000) = 1168, T = 296 K, R = 0.041 for 2617 unique reflections with $F^2 > 2\sigma(F^2)$. The uranium atom is bonded to a distorted square of four chlorine atoms and to the four nitrogen atoms of the 1,2-bis(dimethylamino)ethane ligand with average U-Cℓ and U-N distances of 2.609 ± 0.009 A and 2.786 ± 0.019 A, respectively.

Table S1. Anisotropic Thermal Parameters (A^2)[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	3.306(15)	3.081(15)	3.867(16)	0.073(22)	0.043(20)	0.255(19)
Cl(1)	7.02(26)	7.43(23)	5.31(19)	-2.40(20)	2.20(18)	-0.22(17)
Cl(2)	7.96(29)	5.32(19)	11.2(3)	1.86(19)	-3.54(26)	0.21(20)
Cl(3)	5.67(21)	6.63(17)	5.31(16)	-1.38(16)	1.39(17)	0.46(13)
Cl(4)	6.44(20)	4.78(15)	9.73(25)	1.80(14)	-1.14(23)	-1.65(19)
N(1)	3.9(5)	4.6(5)	6.9(5)	-0.1(6)	-1.5(4)	-0.4(6)
N(2)	3.5(5)	3.8(4)	8.3(6)	-0.9(5)	0.1(7)	-1.3(4)
N(3)	5.6(8)	5.7(6)	6.4(8)	-1.2(5)	-1.7(6)	1.8(5)
N(4)	9.1(8)	6.5(6)	4.6(6)	-0.4(8)	0.5(7)	-0.3(5)
C(1)	3.1(6)	12.5(11)	10.5(9)	1.1(10)	-1.4(6)	-3.0(11)
C(2)	7.5(11)	8.1(10)	7.6(11)	0.3(8)	-3.0(9)	1.0(8)
C(3)	5.9(10)	10.2(12)	7.4(12)	-1.1(9)	-2.4(9)	-1.9(9)
C(4)	8.7(14)	10.0(13)	11.6(14)	-1.4(11)	-2.9(13)	-5.8(11)
C(5)	6.0(11)	5.6(7)	12.9(12)	-0.6(7)	3.4(9)	-4.1(8)
C(6)	11.3(13)	2.6(5)	14.1(12)	-1.7(6)	4.0(11)	-0.3(7)
C(7)	9.6(11)	7.6(8)	8.2(9)	-5.5(8)	-3.3(9)	3.1(8)
C(8)	4.1(7)	13.0(11)	11.2(12)	-4.0(8)	-1.5(9)	1.5(11)
C(9)	8.0(12)	6.1(8)	6.8(10)	-0.8(8)	-4.3(9)	-0.4(8)
C(10)	14.1(15)	5.2(7)	4.5(7)	-3.1(10)	-1.9(10)	-1.4(6)
C(11)	14.9(15)	8.7(8)	4.9(6)	-2.6(12)	-2.4(7)	1.3(8)
C(12)	14.6(17)	8.6(11)	6.4(10)	-2.8(11)	3.7(11)	-2.9(8)

[a] The anisotropic temperature factor has the form:

$$\exp[-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \cdots].$$

Table S2. Estimated Hydrogen Positional and Isotropic Thermal Parameters (A^2)[a]

Atom	x	y	z	B
H(1) C1	-0.1055	0.2474	0.1308	10.000
H(2) C1	-0.0572	0.3337	0.2039	10.000
H(3) C1	-0.0582	0.2192	0.2438	10.000
H(4) C2	0.0429	0.3855	0.0653	10.000
H(5) C2	-0.0055	0.2993	-0.0078	10.000
H(6) C2	0.1159	0.3090	0.0030	10.000
H(7) C3	-0.0019	0.1435	0.0267	10.000
H(8) C3	0.0073	0.1003	0.1446	10.000
H(9) C4	0.1134	0.0275	0.0378	10.000
H(10)C4	0.1618	0.1343	0.0068	10.000
H(11)C5	0.3268	0.1145	0.0439	10.000
H(12)C5	0.3013	-0.0034	0.0497	10.000
H(13)C5	0.3637	0.0494	0.1435	10.000
H(14)C6	0.1911	-0.0670	0.1599	10.000
H(15)C6	0.1224	-0.0035	0.2408	10.000
H(16)C6	0.2421	-0.0167	0.2622	10.000
H(17)C7	0.3691	0.4849	0.1930	10.000
H(18)C7	0.4268	0.5306	0.2938	10.000
H(19)C7	0.3050	0.5198	0.2944	10.000
H(20)C8	0.5340	0.3960	0.2954	10.000
H(21)C8	0.4764	0.3502	0.1945	10.000
H(22)C8	0.4922	0.2826	0.2982	10.000
H(23)C9	0.4445	0.4474	0.4418	10.000
H(24)C9	0.4238	0.3289	0.4513	10.000
H(25)C10	0.3131	0.4255	0.5588	10.000
H(26)C10	0.2667	0.4747	0.4537	10.000
H(27)C11	0.2485	0.2832	0.6232	10.000
H(28)C11	0.3212	0.2299	0.5382	10.000
H(29)C11	0.2046	0.1953	0.5493	10.000
H(30)C12	0.0960	0.4197	0.4664	10.000
H(31)C12	0.1226	0.3861	0.5849	10.000
H(32)C12	0.0684	0.3084	0.5059	10.000

[a] The isotropic temperature factor has the form $\exp[-B(\sin\theta/\lambda)^2]$.

Table S3. Additional Distances and Angles

Atoms	Dist (A)	Atoms	Dist (A)
N(1) - C(1)	1.471(13)	N(3) - C(8)	1.507(19)
N(1) - C(2)	1.480(16)	N(3) - C(9)	1.430(16)
N(1) - C(3)	1.494(18)	N(4) - C(10)	1.534(17)
N(2) - C(4)	1.492(19)	N(4) - C(11)	1.440(15)
N(2) - C(5)	1.512(16)	N(4) - C(12)	1.520(20)
N(2) - C(6)	1.443(14)	C(3) - C(4)	1.369(23)
N(3) - C(7)	1.461(15)	C(9) - C(10)	1.493(21)

Atoms	Angle(°)	Atoms	Angle(°)
C(1) -N(1) -C(2)	104.8(11)	C(8) -N(3) -C(9)	103.7(13)
C(1) -N(1) -C(3)	103.1(12)	C(10)-N(4) -C(11)	106.9(12)
C(2) -N(1) -C(3)	107.8(11)	C(10)-N(4) -C(12)	108.4(12)
C(4) -N(2) -C(5)	106.7(12)	C(11)-N(4) -C(12)	104.5(11)
C(4) -N(2) -C(6)	110.0(12)	N(1) -C(3) -C(4)	116.5(15)
C(5) -N(2) -C(6)	103.5(11)	N(2) -C(4) -C(3)	118.4(16)
C(7) -N(3) -C(8)	103.6(12)	N(3) -C(9) -C(10)	110.4(13)
C(7) -N(3) -C(9)	110.7(12)	N(4) -C(10)-C(9)	112.3(12)

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720