geometry of the acetonitrile molecule (Barrow, 1981; Karakida, Fukuyama & Kuchitsu, 1974).

The difference between the mean U—Cl and U—N bond lengths is 0·20 Å lower than the difference between the appropriate bond radii of Cl and N (Pauling, 1960), again providing evidence that in the dodecahedron *M—A* type bonds tend to be the weaker.

The stacking in the crystal is through van der Waals contacts with possible C—H···Cl hydrogen bonds (details deposited).

The main differences between the two crystal structure determinations [*A* = Cotton *et al.* (1984), *B* = this work] are in the diffractometer measurements. In the cell-parameter determination 15 reflections in the range $15 \leq 2\theta \leq 28°$ are used in *A* and 25 reflections in the range $13 \leq 2\theta \leq 35°$ in *B*. This fact, the different sample size, the centring of the crystal and the specimen temperature (278 and 295 K respectively) lead to cell parameters *a* = 14·709 (4), *b* = 8·459 (3), *c* = 13·938 (4) Å, *β* = 91·79 (2)° for *A* and *a* = 14·677 (4), *b* = 8·452 (2), *c* = 13·959 (3) Å, *β* = 91·77 (2)° for *B*, showing the typical underestimation of standard deviations in cell parameters. The ranges of intensity data collected are the same, $4 \leq 2\theta \leq 50°$, but *h*0/17, *k*0/11, *l*—17/17 for *A* and *h*—18/18, *k*0/11, *l* 0/16 for *B*, and the number of independent reflections used in the refinements are 1051 and 1224 respectively. The ratios of number of reflections/number of parameters are 12·98 and 15·11. The final *R* and *wR* values are 0·040, 0·049 for *A* and 0·052, 0·031 for *B*. A half-normal probability-plot comparison (Abrahams & Keve, 1971) of non-hydrogen parameters shows that only one, the *y* coordinate of the U atom, deviates by $>2{\cdot}5\ (\sigma_1^2 + \sigma_2^2)^{1/2}$, $\sigma_i$ being the e.s.d. in the coordinates for each structure; slope 1·8 (1) and intercept −0·1 (1) (the large slope, however, indicating that the standard deviations are significantly underestimated). A $\chi^2$ test shows that the two structure determinations are in good agreement if the *y* coordinate of the U atom is neglected; indeed $\chi^2 = \sum(\Delta/\sigma)^2 = 44{\cdot}27$ and $\chi^2(25)_{0.995} = 46{\cdot}93$ (Coppens *et al.* 1984; Hamilton, 1964). A half-normal probability plot of the differences in 72 non-hydrogen interatomic lengths gives a straight line with a slope of 1·22 (1) [intercept 0·09 (1)] (De Camp, 1973). Only the distance Cl(1)···Cl(2′) 3·878 (6) Å [*A*], 3·858 (2) Å [*B*] deviates by greater than $3 \times (\sigma_1^2 + \sigma_2^2)^{1/2}$.

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# Bis[1,2-bis(dimethylamino)ethane]tetrachlorouranium(IV)

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**Abstract.** $[UCl_4\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2]$, $M_r$ = 612·26, orthorhombic, $P2_12_12_1$, *a* = 13·094 (4), *b* = 13·265 (4), *c* = 12·633 (4) Å, *V* = 2194 Å$^3$, *Z* = 4, $D_x$ = 1·853 g cm$^{-3}$, $\lambda$(Mo *Kα*) = 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

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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 (9) and 2·79 (2) Å, respectively.

**Introduction.** The crystal structure of the phosphine complex, $[U(OC_6H_5)_4\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2]$ (I) (Edwards, Andersen & Zalkin, 1983), showed that the U atom is eight-coordinate and that the P atoms are located on the *A* sites and the O atoms on the *B* sites of an idealized $D_{2d}$ dodecahedron (Hoard & Silverton, 1963). A nitrogen analogue of tetravalent uranium, $[UCl_4\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2]$, 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; large green prisms were obtained by cooling the mother liquor (253 K). 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 capillary under argon. Crystal 0·16 × 0·22 × 0·23 mm with eight faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 25 reflections, $20 < 2\theta < 34°$; analytical absorption correction, range 2·94–3·72; maximum $(\sin\theta)/\lambda = 0{\cdot}60\ \text{Å}^{-1}$, $h$ 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, $F^2 < 2\sigma$), $R_{\text{int}} = 0{\cdot}035$; structure solved by Patterson and Fourier methods; refined on $F$, 190 parameters; 32 H atoms in calculated positions and fixed isotropic thermal parameters; anisotropic thermal parameters for non-H atoms; $R = 0{\cdot}10$ for 3879 data, $R = 0{\cdot}041$ for 2617 reflections for which $F^2 > 2\sigma$, $wR = 0{\cdot}029$, $S = 1{\cdot}0$; $w = [\sigma(F)]^{-2}$, $p = 0{\cdot}02$ in calculation of $\sigma(F^2)$; maximum (shift/σ) = 0·01; empirical extinction correction, $F_{\text{corr}} = (1 + 5{\cdot}0 \times 10^{-7}I)$; max. and min. of $\Delta F$ synthesis 1·3 and $-1{\cdot}5\ \text{e Å}^{-3}$; atomic $f$ for neutral U, Cl, N and C, and spherical bonded H from *International Tables for X-ray Crystallography* (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.

Table 1. *Atomic parameters* (*e.s.d.'s in parentheses*)

$$B_{\text{eq}} = \textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j/3.$$

| | $x$ | $y$ | $z$ | $B_{\text{eq}}$(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 bond 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) |

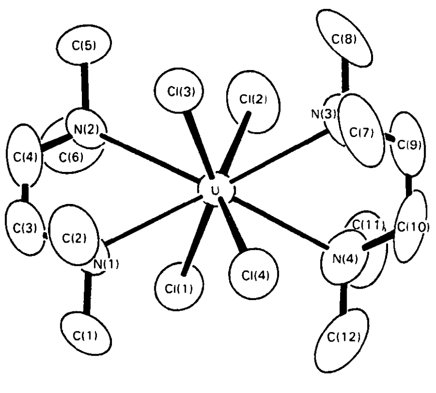

Fig. 1. *ORTEP* plot (Johnson, 1965) of the molecule showing the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43134 (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, 1982). A convenient way to illustrate the distortion from an idealized geometry is by the shape parameters $\delta'$ and $\varphi$ (Porai-Koshits & Aslanov, 1972; Muetterties & Guggenberger, 1974), where $\delta'$ is the angle of intersection of the triangular faces along the line connecting the *AA* and *BB* sites in a dodecahedron and $\varphi$ is the dihedral angle between two triangles constructed from the *BAAB* trapezoidal atoms. As shown in Table 3, the title compound 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 of 2·609 (9) Å is shorter than that found in other eight-coordinate structures: *e.g.* $[UCl_4(NCCH_3)_4]$ 2·623 (2) Å (Cotton, Marler & Schwotzer, 1984);* $[UCl_2\{(OC_6H_4)C(OH)NCH_2CH_2NC(OH)(C_6H_4O)\}(OC_4H_4)_2]$ 2·67 (2) Å (Calderazzo, Floriani, Pasquali, Cesari & Perego, 1976); $[UCl_2\{OS(CH_3)_2\}_6]^{2+}$ 2·70 (2) Å (Bombieri & Bagnall, 1975); $UCl_4$ 2·869 (3) and 2·638 (4) Å (Taylor & Wilson, 1973). The average U—N distance of 2·79 (2) Å is substantially longer than the equivalent distance in $[UCl_4(NCCH_3)_4]$ of 2·589 (6) Å (Cotton, Marler & Schwotzer, 1984) and substantially longer than expected based upon the averaged U—P distance in (I) of 3·104 (6) Å (Edwards, Andersen & Zalkin, 1983) since the tetrahedral covalent radius of phosphorus is 0·40 Å 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 Å, 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.

Table 3. *Shape parameters*

| | $\delta'$ (°) | $\varphi$ (°) |
|---|---|---|
| $[UCl_4\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2]$ | 20·4, 21·9, 38·7, 39·6 | 1·6 |
| $D_{2d}$ dodecahedron | 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 |

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* *Note added in proof:* see also preceding paper.

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# Structure of Sodium (*o*-Phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)cuprate(II)

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**Abstract.** $Na_2[Cu(C_{14}H_{12}N_2O_8)].4H_2O$, $M_r = 517·84$, monoclinic, $P2_1/n$, $a = 24·493$ (5), $b = 8·222$ (1), $c = 9·805$ (1) Å, $\beta = 90·43$ (1)°, $V = 1974·5$ (5) Å$^3$, $Z = 4$, $D_m = 1·75$, $D_x = 1·74$ g cm$^{-3}$, $\lambda(Cu\ K\alpha) = 1·5417$ Å, $\mu = 24·3$ cm$^{-1}$, $F(000) = 1060$, $T = 293$ K. Final $R = 0·033$ for 3143 observed reflections. The ligand is hexadentate. The coordination geometry is largely distorted from $O_h$ and twisted towards that of a trigonal prism, owing to the planarity of the phenylenediamine chelate ring. Two Cu—N bond

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