Structures of the Tetramethylammonium Salts of the Bromide, Chloride and Azide Adducts of Uranyl Bis(hexafluoroacetylacetonate),*
$[UO_2\{(CF_3CO)_2CH\}_2X]^-\cdot[N(CH_3)_4]^+$†

BY L. PRASAD, E. J. GABE, B. GLAVINCEVSKI AND S. BROWNSTEIN

Chemistry Division, National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6

Abstract. (1) $X = $ Br, $M_r = 838.18$, monoclinic, $P2_1$, $a = 11.854$ (2), $b = 8.302$ (1), $c = 12.966$ (1) Å, $\beta = 98.37$ (1)°, $V = 1262.42$ Å^3, $Z = 2$, $D_x = 2.21$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, $\mu = 7.775$ mm^{-1}, $T = 296$ K. Final $R = 0.061$ for 1152 observed reflections. (2) $X = $ Cl, $M_r = 793.73$, monoclinic, $P2_1$, $a = 11.785$ (2), $b = 7.900$ (2), $c = 12.748$ (2) Å, $\beta = 99.09$ (1)°, $V = 1171.95$ Å^3, $Z = 2$, $D_x = 2.25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, $\mu = 6.801$ mm^{-1}, $T = 115$ K. Final $R = 0.051$ for 2008 observed reflections. (3) $X = $ N$_3$, $M_r = 800.29$, triclinic, $P\bar{1}$, $a = 8.438$ (3), $b = 10.749$ (3), $c = 14.586$ (5) Å, $\alpha = 108.54$ (3), $\beta = 92.01$ (3), $\gamma = 108.69$ (3)°, $V = 1174.25$ Å^3, $Z = 2$, $D_x = 2.26$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, $\mu = 6.681$ mm^{-1}, $T = 115$ K. Final $R = 0.059$ for 3532 observed reflections. The structures of the three compounds are similar. The coordination around the U atom is pentagonal bipyramidal, with the four O atoms of the hexafluoroacetylacetonate ligands and the Br(Cl,N) atom in the equatorial plane, and the uranyl O atoms in the axial positions.

Introduction. There has been some discussion of the detailed mechanism by which magnetically nonequivalent trifluoromethyl groups are interchanged in solutions of uranyl bis(hexafluoroacetylacetonate) [uranyl bis(HFAA)] adducts (Kramer, Dines, Hall, Kaldor, Jacobson & Scanlon, 1980). In those cases where exchange occurs by an intramolecular rearrangement, a detailed knowledge of the structure is necessary to decide between different exchange mechanisms. Two proposed mechanisms are by migration of the adduct around the uranyl axis above the plane defined by the U atom and the ligand O atoms, or by rotation of one of the ligands out of this plane. From the differences in the structures of these adducts, compared with activation energies for their exchange, it has been possible to suggest that ligand rotation is the preferred mechanism (Glavincevski & Brownstein, 1982).

Experimental. The tetramethylammonium bromide, chloride and azide adducts were prepared by displacement of tetrahydrofuran from uranyl bis(HFAA)-tetrahydrofuran in sulphur dioxide solvent. They were recrystallized as yellow, irregular-shaped crystals from methylene chloride.

Initially, intensity data for the bromide and chloride adducts were measured at room temperature. The crystals were highly mosaic and solution of the structures indicated very high thermal motion for the trifluoromethyl groups. Therefore, it was decided to remeasure the intensity data at low temperature. Since the quality of the crystals of the bromide adduct was very poor, intensity data for the chloride adduct only were remeasured. The intensity data for the azide adduct were measured at low temperature only. We report here the room-temperature (296 K) structure of the bromide adduct and the low-temperature (115 K) structures of the chloride and azide adducts.

(1) $0.5 \times 0.3 \times 0.2$ mm, 48 reflections in refinement of cell parameters, max. absorption correction 0.65, min. 0.23, $2\theta_{max} = 45°$, 1780 unique, 1152 observed with $I > 3\sigma(I)$, 628 unobserved, R (observed) = 0.061, R_w (observed) = 0.049, R (all) = 0.112, R_w (all) = 0.049, $F(000) = 776$; (2) $0.45 \times 0.3 \times 0.25$ mm, 56 reflections in refinement of cell parameters, max. absorption correction 0.63, min. 0.25, $2\theta_{max} = 50°$, 2237 unique, 2008 observed with $I > 2.5\sigma(I)$, 229 unobserved, R (observed) = 0.051, R_w (observed) = 0.053, R (all) = 0.061, R_w (all) = 0.054, $F(000) = 740$; (3) $0.35 \times 0.3 \times 0.2$ mm, 36 reflections in refinement of cell parameters, max. absorption correction 0.49, min. 0.34, $2\theta_{max} = 50°$, 4131 unique, 3532 observed with $I > 2.5\sigma(I)$, 599 unobserved, R (observed) = 0.059, R_w (observed) = 0.053, R (all) = 0.071, R_w (all) = 0.054, $F(000) = 748$; cell constants by least-squares refinement, intensities by $\theta/2\theta$ scan method with line-profile analysis (Grant & Gabe, 1978), Picker four-circle automatic diffractometer, graphite-monochromatized Mo $K\alpha$; data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979), Lorentz and polarization, and absorption by Gaussian approximation; for Br and azide adducts U atom

---

located in a Patterson map, other non-H by heavy-atom method, Cl adduct assumed isomorphous to Br, anisotropic parameters for U and Br (Cl) atoms and isotropic for C, N, O; H atoms not located, disorder indicated for CF_3 groups; $N(Z)$ curves for Br and Cl adducts followed the centrosymmetric curve of Hargreaves (1955), but refinement in $P2_1/m$ failed and structures were refined in $P2_1$ by block-diagonal least squares on $\sum w(F_o-F_c)^2$ with $w = 1/\sigma^2(F)$, including anomalous dispersion for U and Br (Cl) (*International Tables for X-ray Crystallography*, 1974); calculations performed using NRC PDP8-e system of programs (Larson & Gabe, 1978).

Discussion. Atomic positional and equivalent isotropic temperature factors are listed in Table 1.*

The structure of the azide adduct with the atom names is shown in Fig. 1. The tetramethylammonium counterion is not shown. Bond lengths and angles for these structures are given in Table 2.

---

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles in the CF_3 groups have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38165 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

E.s.d.'s refer to the last digit printed. B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

(1) Bromide adduct

	x	y	z	$B_{eq}(\text{Å}^2)$
U	0.15168 (12)	1/4	0.31224 (11)	4.37 (13)
Br	0.3845 (3)	0.258 (3)	0.4007 (3)	6.6 (3)
O(1)	0.1542 (22)	0.469 (3)	0.3069 (20)	5.3 (6)
O(2)	0.1474 (21)	0.065 (3)	0.3104 (19)	4.5 (6)
O(3)	0.1380 (15)	0.268 (9)	0.4956 (14)	5.1 (6)
O(4)	−0.0487 (15)	0.228 (5)	0.3381 (18)	3.9 (6)
O(5)	0.0219 (16)	0.250 (12)	0.1509 (14)	5.8 (6)
O(6)	0.2496 (15)	0.214 (3)	0.1641 (14)	3.7 (6)
N	0.5486 (20)	0.268 (11)	0.7233 (18)	6.2 (8)
C(1)	0.0675 (22)	0.254 (17)	0.5582 (20)	4.2 (8)
C(2)	−0.045 (3)	0.242 (14)	0.5178 (25)	7.0 (12)
C(3)	−0.0965 (24)	0.276 (11)	0.4115 (22)	5.3 (10)
C(4)	0.1106 (23)	0.300 (6)	0.6720 (21)	4.1 (10)
C(5)	−0.240 (3)	0.228 (8)	0.3830 (24)	6.0 (12)
C(6)	0.031 (3)	0.263 (19)	0.0602 (23)	6.7 (10)
C(7)	0.125 (3)	0.285 (9)	0.0021 (23)	6.0 (11)
C(8)	0.2186 (24)	0.267 (15)	0.0749 (22)	5.5 (9)
C(9)	−0.114 (3)	0.252 (20)	−0.003 (3)	7.8 (11)
C(10)	0.326 (3)	0.245 (19)	0.012 (3)	9.5 (14)
C(11)	0.6181 (24)	0.216 (6)	0.6361 (22)	4.5 (11)
C(12)	0.485 (4)	0.111 (7)	0.716 (4)	10.5 (17)
C(13)	0.619 (3)	0.196 (6)	0.818 (3)	8.8 (16)
C(14)	0.470 (4)	0.388 (7)	0.712 (3)	10.0 (16)
F(41)	0.2013 (18)	0.166 (3)	0.6935 (17)	8.0 (7)
F(42)	0.1393 (19)	0.414 (4)	0.6988 (18)	9.3 (8)
F(43)	0.0311 (15)	0.303 (4)	0.7260 (14)	7.6 (7)
F(51)	−0.2679 (20)	0.122 (4)	0.4310 (19)	9.5 (8)
F(52)	−0.2718 (19)	0.380 (4)	0.4327 (18)	9.5 (8)
F(53)	−0.2595 (14)	0.205 (3)	0.2921 (13)	5.9 (6)
F(91)	−0.1137 (20)	0.369 (3)	−0.0528 (19)	10.4 (9)
F(92)	−0.0775 (22)	0.158 (3)	−0.1060 (20)	11.2 (9)
F(93)	−0.1693 (18)	0.147 (3)	0.0290 (16)	7.3 (7)
F(101)	0.3099 (19)	0.329 (3)	−0.0838 (18)	10.5 (9)
F(102)	0.3815 (22)	0.108 (4)	0.0167 (20)	10.8 (9)
F(103)	0.4116 (21)	0.341 (4)	0.0547 (20)	13.3 (11)

Table 1 (*cont.*)

(2) Chloride adduct

	x	y	z	B_{eq} (Å^2)
U	0.15393 (7)	1/4	0.31377 (5)	1.24 (4)
Cl	0.3763 (4)	0.255 (3)	0.4008 (3)	2.4 (3)
N	0.5431 (12)	0.270 (5)	0.7108 (9)	1.6 (3)
O(1)	0.1454 (17)	0.4756 (23)	0.3202 (13)	3.8 (4)
O(2)	0.1578 (16)	0.0471 (21)	0.3067 (12)	2.8 (3)
O(3)	0.1457 (11)	0.2185 (18)	0.5006 (8)	1.3 (3)
O(4)	−0.0388 (10)	0.2174 (18)	0.3436 (8)	1.1 (3)
O(5)	0.0199 (10)	0.236 (3)	0.1481 (8)	1.4 (3)
O(6)	0.2547 (12)	0.2110 (18)	0.1649 (9)	1.8 (3)
C(1)	0.0677 (14)	0.234 (4)	0.5552 (11)	0.7 (4)
C(2)	−0.0471 (16)	0.228 (4)	0.5232 (12)	1.4 (4)
C(3)	−0.0943 (15)	0.272 (6)	0.4169 (12)	1.7 (4)
C(4)	0.1178 (15)	0.279 (4)	0.6784 (11)	1.2 (4)
C(5)	−0.2255 (15)	0.280 (4)	0.3920 (11)	1.3 (4)
C(6)	0.0204 (15)	0.238 (5)	0.0516 (11)	1.3 (4)
C(7)	0.1201 (17)	0.216 (3)	0.0038 (13)	1.3 (4)
C(8)	0.2276 (19)	0.212 (3)	0.0615 (15)	2.0 (5)
C(9)	−0.0951 (17)	0.268 (7)	−0.0161 (13)	2.3 (4)
C(10)	0.3346 (20)	0.203 (3)	0.0034 (15)	2.4 (5)
C(11)	0.6219 (20)	0.209 (3)	0.8158 (16)	2.7 (6)
C(12)	0.476 (3)	0.104 (4)	0.7056 (21)	4.8 (7)
C(13)	0.465 (3)	0.408 (4)	0.6948 (20)	4.0 (6)
C(14)	0.6158 (15)	0.261 (8)	0.6217 (12)	1.9 (3)
F(41)	0.2110 (11)	0.3485 (17)	0.7001 (8)	2.3 (3)
F(42)	0.1437 (12)	0.0968 (19)	0.7061 (9)	2.8 (3)
F(43)	0.0391 (10)	0.2047 (14)	0.7342 (7)	1.52 (25)
F(51)	−0.2692 (12)	0.3845 (18)	0.4336 (9)	2.7 (3)
F(52)	−0.2639 (9)	0.2276 (20)	0.2907 (7)	1.53 (25)
F(53)	−0.2682 (11)	0.1150 (17)	0.4369 (8)	1.84 (24)
F(91)	−0.1792 (11)	0.2022 (15)	0.0279 (8)	2.4 (3)
F(92)	−0.1170 (14)	0.4133 (22)	−0.0437 (11)	4.6 (4)
F(93)	−0.0982 (11)	0.1616 (16)	−0.1092 (8)	2.0 (3)
F(101)	0.3079 (12)	0.1832 (17)	−0.0955 (10)	3.2 (3)
F(102)	0.3966 (14)	0.0810 (21)	0.0400 (10)	4.1 (4)
F(103)	0.3952 (15)	0.3290 (23)	0.0311 (12)	6.3 (5)

(3) Azide adduct

	x	y	z	B_{eq} (Å^2)
U	0.06015 (8)	0.44742 (6)	0.23334 (5)	1.847 (23)
N(1)	−0.0933 (14)	0.2143 (11)	0.1268 (8)	2.32 (25)
N(2)	−0.1963 (15)	0.1243 (11)	0.1385 (9)	2.8 (3)
N(3)	−0.3047 (18)	0.0284 (14)	0.1448 (11)	5.5 (4)
N(4)	0.1474 (14)	0.8934 (11)	0.1547 (9)	2.4 (3)
O(1)	−0.0019 (11)	0.5157 (9)	0.1509 (7)	2.42 (20)
O(2)	0.1208 (12)	0.3897 (9)	0.3187 (7)	2.57 (21)
O(3)	−0.2138 (11)	0.3887 (9)	0.2839 (7)	2.10 (19)
O(4)	0.0345 (11)	0.6441 (9)	0.3615 (7)	2.55 (21)
O(5)	0.3260 (12)	0.6431 (9)	0.2828 (7)	2.65 (21)
O(6)	0.2720 (11)	0.3910 (9)	0.1376 (7)	2.49 (20)
C(1)	−0.2633 (16)	0.4276 (13)	0.3651 (10)	1.8 (3)
C(2)	−0.1843 (17)	0.5554 (13)	0.4449 (10)	2.1 (3)
C(3)	−0.0459 (17)	0.6523 (13)	0.4328 (10)	1.9 (3)
C(4)	−0.4327 (18)	0.3338 (14)	0.3751 (11)	2.8 (3)
C(5)	0.0305 (19)	0.8008 (15)	0.5150 (12)	3.1 (3)
C(6)	0.4772 (17)	0.6603 (13)	0.2704 (10)	2.1 (3)
C(7)	0.5440 (17)	0.5712 (13)	0.2052 (10)	2.1 (3)
C(8)	0.4284 (17)	0.4449 (13)	0.1420 (10)	2.1 (3)
C(9)	0.6048 (19)	0.8085 (15)	0.3376 (12)	3.1 (3)
C(10)	0.5020 (18)	0.3526 (14)	0.0600 (11)	2.7 (3)
C(11)	0.2589 (19)	0.8137 (15)	0.1054 (11)	3.1 (3)
C(12)	0.1668 (18)	0.9157 (14)	0.2593 (11)	2.8 (3)
C(13)	−0.0358 (18)	0.8073 (14)	0.1083 (11)	2.9 (3)
C(14)	0.2003 (20)	1.0292 (16)	0.1356 (13)	4.1 (4)
F(41)	−0.4492 (11)	0.3364 (7)	0.3364 (7)	3.79 (20)
F(42)	−0.5562 (12)	0.3463 (10)	0.3290 (8)	5.7 (3)
F(43)	−0.4581 (13)	0.3535 (10)	0.4643 (8)	5.9 (3)
F(51)	0.1454 (11)	0.7969 (9)	0.5746 (7)	4.40 (22)
F(52)	0.0948 (10)	0.8991 (8)	0.4794 (6)	3.72 (20)
F(53)	−0.0889 (11)	0.8287 (8)	0.5659 (7)	3.85 (20)
F(91)	0.5974 (13)	0.8228 (10)	0.4276 (8)	6.3 (3)
F(92)	0.5683 (13)	0.9034 (10)	0.3186 (8)	5.8 (3)
F(93)	0.7615 (12)	0.8223 (9)	0.3241 (7)	5.19 (24)
F(101)	0.4027 (11)	0.3017 (9)	−0.0247 (7)	4.32 (22)
F(102)	0.6516 (11)	0.4245 (9)	0.0487 (7)	4.36 (22)
F(103)	0.5114 (12)	0.2468 (9)	0.0837 (7)	5.03 (24)

The observed structures are similar to those of the tetrahydrofuran (Kramer *et al.*, 1980) and trimethylphosphate (Levy & Waugh, 1977*a*,*b*,*c*) adducts. The

uranium coordination is pentagonal bipyramidal, with the four O atoms of the HFAA ligands and the anion (Br, Cl, N_3) in the equatorial plane and the two uranyl O atoms in axial positions.

The bond lengths and angles in the three structures are in general comparable to one another and to those in the related structures of the tetrahydrofuran (Kramer et al., 1980) and trimethylphosphate (Levy & Waugh, 1977b,c) adducts. The effect of high thermal motion (probably due to positional disorder of F atoms) is seen in the rather large e.s.d.'s in the bond lengths and angles for the CF_3 groups, especially in the bromide adduct. The high thermal motion is evident even at low temperatures in the case of the Cl adduct, while the azide adduct is reasonably stabilized.

One significant difference is the asymmetry of the uranium—uranyl oxygen bond lengths in the bromide and chloride adducts. The only other such case found in the literature is for bis(tetra-N-propylammonium)uranyl tetrachloride (DiSipio, Tondello, Pelizzi, Ingletto & Montenero, 1974), where no rationalization is presented. The average values for this bond length in the bromide and chloride adducts are within the range normally observed for such a bond. Ideally one should obtain for a hepta-coordinate uranyl species equal-length uranium—uranyl oxygen bonds and a regular arrangement of the other five ligands in the equatorial plane. For bulky ligands relief of steric compression could destroy the equatorial planarity and simultaneously lengthen the uranium—oxygen bond on the concave side of the ligands and reduce it on the convex side. The distortion from an equatorial plane for the bromide, chloride and azide adducts is listed in Table 3.

Other differences between the three adducts are the deviations of the U atom from the equatorial pentagonal plane, the tilting of the HFAA ligands with respect to the equatorial plane and the deviations from planarity of the HFAA ligands (Table 3).
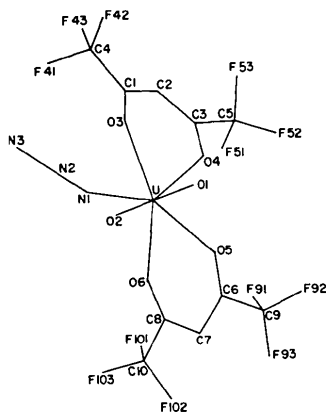
Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Adduct Br	Cl	N_3
U–O(1)	1·82 (3)	1·79 (2)	1·73 (1)
U–O(2)	1·54 (2)	1·61 (2)	1·69 (1)
U–O(3)	2·41 (2)	2·41 (1)	2·40 (1)
U–O(4)	2·45 (2)	2·38 (1)	2·41 (1)
U–O(5)	2·41 (2)	2·43 (1)	2·42 (1)
U–O(6)	2·40 (2)	2·41 (1)	2·42 (1)
U–Br[Cl, N(1)]	2·831 (4)	2·679 (5)	2·38 (1)
O(3)–C(1)	1·25 (3)	1·24 (2)	1·26 (2)
C(1)–C(2)	1·37 (4)	1·35 (2)	1·42 (2)
C(2)–C(3)	1·45 (5)	1·42 (3)	1·35 (2)
C(3)–O(4)	1·24 (5)	1·29 (2)	1·26 (2)
C(1)–C(4)	1·54 (5)	1·63 (2)	1·51 (2)
C(3)–C(5)	1·73 (5)	1·53 (2)	1·57 (2)
O(5)–C(6)	1·20 (4)	1·23 (2)	1·26 (2)
C(6)–C(7)	1·44 (5)	1·42 (3)	1·39 (2)
C(7)–C(8)	1·36 (4)	1·36 (3)	1·39 (2)
C(8)–O(6)	1·24 (6)	1·31 (2)	1·25 (2)
C(6)–C(9)	1·80 (5)	1·51 (3)	1·58 (2)
C(8)–C(10)	1·62 (5)	1·56 (3)	1·58 (2)
N(1)–N(2)	—	—	1·14 (2)
N(2)–N(3)	—	—	1·17 (2)
O(1)–U–O(2)	177 (1)	178·4 (9)	176·8 (4)
O(1)–U–Br(Cl,N)	88·3 (9)	91·4 (8)	91·4 (4)
O(1)–U–O(3)	89 (2)	92·7 (6)	93·7 (4)
O(1)–U–O(4)	96 (1)	92·2 (7)	87·4 (4)
O(1)–U–O(5)	89 (2)	92·9 (8)	88·4 (4)
O(1)–U–O(6)	95 (1)	101·6 (6)	90·2 (4)
O(2)–U–Br(Cl,N)	93 (1)	90·3 (8)	91·7 (4)
O(2)–U–O(3)	94 (2)	87·6 (6)	86·4 (4)
O(2)–U–O(4)	84 (1)	86·4 (7)	89·7 (4)
O(2)–U–O(5)	88 (2)	85·8 (8)	89·4 (4)
O(2)–U–O(6)	83 (1)	78·8 (7)	91·1 (4)
Br(Cl,N)–U–O(3)	78·5 (4)	77·4 (3)	74·9 (3)
Br(Cl,N)–U–O(6)	76·8 (4)	75·9 (3)	78·2 (3)
O(3)–U–O(4)	70·4 (6)	69·0 (4)	68·7 (3)
O(4)–U–O(5)	67·1 (6)	68·1 (4)	69·4 (3)
O(5)–U–O(6)	68·1 (7)	69·2 (4)	69·0 (3)
U–O(3)–C(1)	141 (2)	134 (1)	132·7 (8)
O(3)–C(1)–C(2)	118 (2)	128 (1)	127 (1)
O(3)–C(1)–C(4)	116 (4)	112 (1)	116 (1)
C(2)–C(1)–C(4)	124 (3)	120 (1)	117 (1)
C(1)–C(2)–C(3)	127 (4)	120 (2)	118 (1)
C(2)–C(3)–O(4)	119 (5)	116 (2)	129 (1)
C(2)–C(3)–C(5)	115 (4)	116 (1)	119 (1)
O(4)–C(3)–C(5)	108 (4)	118 (2)	111 (1)
C(3)–O(4)–U	130 (2)	133 (1)	132·4 (8)
U–O(5)–C(6)	135 (2)	140 (1)	135·9 (8)
O(5)–C(6)–C(7)	135 (3)	124 (2)	130 (1)
O(5)–C(6)–C(9)	103 (3)	115 (2)	113 (1)
C(7)–C(6)–C(9)	122 (3)	120 (1)	117 (1)
C(6)–C(7)–C(8)	104 (3)	122 (2)	117 (1)
C(7)–C(8)–O(6)	142 (5)	127 (2)	131 (1)
C(7)–C(8)–C(10)	106 (2)	120 (2)	116 (1)
O(6)–C(8)–C(10)	106 (4)	113 (2)	113 (1)
C(8)–O(6)–U	126 (3)	136 (1)	136·0 (8)
U–N(1)–N(2)	—	—	132 (1)
N(1)–N(2)–N(3)	—	—	176 (2)

Fig. 1. The structure of the azide adduct of uranyl bis(hexafluoroacetylacetonate).

Table 3. *Structural differences between the adducts*

		Br	Cl	N_3
Deviations from	U	0·08 (5)	−0·26 (3)	0·04 (2)
equatorial plane (Å)	Br[Cl,N(1)]	0·13 (6)	−0·40 (4)	0·15 (2)
[O(3), O(4), O(5), O(6)]*	O(3)	0·09 (6)	−0·04 (5)	−0·03 (3)
	O(4)	−0·16 (6)	0·06 (5)	0·05 (3)
	O(5)	0·17 (6)	−0·07 (5)	−0·05 (3)
	O(6)	−0·10 (6)	0·04 (5)	0·03 (3)
Dihedral angles between equatorial plane and HFAA ligands (°)		2 (1·5)	8 (1)	25 (1)
		17 (1·5)	6 (1)	11 (1)
Max. deviation (Å) from the plane of HFAA ligand		0·26 (6) [C(2)]	0·35 (3) [C(3)]	0·04 (2) [C(2) and C(7)]
		[O(3),O(4), C(1),C(3)]*	[O(3),O(4), C(1),C(2)]*	[O(3),O(4), C(1),C(3) and O(5),O(6), C(6),C(8)]*

* Atoms defining the plane.

There appears to be a direct correlation between the activation energies for the exchange of non-equivalent trifluoromethyl groups and the deviations from planarity of the HFAA ligands, but no correlation with the deviation of the U atom from the equatorial plane. On this basis ligand rotation has been proposed as the mechanism for the intramolecular exchange reaction in these compounds (Glavincevski & Brownstein, 1982).

References

DiSipio, L., Tondello, E., Pelizzi, G., Ingletto, G. & Montenero, A. (1974). *Cryst. Struct. Commun.* **3**, 731–734.

Glavincevski, B. & Brownstein, S. (1982). *Inorg. Chem.* In the press.

Grant, D. F. & Gabe, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.

Hargreaves, A. (1955). *Acta Cryst.* **8**, 12–14.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kramer, G. M., Dines, M. B., Hall, R. B., Kaldor, A., Jacobson, A. J. & Scanlon, J. C. (1980). *Inorg. Chem.* **19**, 1340–1347.

Larson, A. C. & Gabe, E. J. (1978). *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, p. 81. Delft Univ. Press.

Le Page, Y., Gabe, E. J. & Calvert, L. D. (1979). *J. Appl. Cryst.* **12**, 25–26.

Levy, J. H. & Waugh, A. B. (1977a). *J. Chem. Soc. Dalton Trans.* pp. 1628–1629.

Levy, J. H. & Waugh, A. B. (1977b). *J. Chem. Soc. Dalton Trans.* pp. 1630–1636.

Levy, J. H. & Waugh, A. B. (1977c). *J. Chem. Soc. Dalton Trans.* pp. 1636–1640.

Structure of 1,2-Ethanedithiolatobis(triphenylphosphine)platinum(II), C38H34P2PtS2

By Samuel A. Bryan and D. Max Roundhill

Department of Chemistry, Washington State University, Pullman, WA 99164, USA

Abstract. $M_r = 811.86$, triclinic, $P\bar{1}$, $a = 19.086$ (9), $b = 9.876$ (3), $c = 9.706$ (4) Å, $\alpha = 77.69$ (3), $\beta = 80.85$ (3), $\gamma = 67.98$ (3)°, $Z = 2$, $V = 1651$ (2) Å³, $D_m = 1.7$ (1), $D_x = 1.633$ (1) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 4.714$ mm⁻¹, $T = 295$ K. Final $R = 0.048$ for 3160 observed reflections. The distances Pt–S(1) and Pt–S(2) are 2.328 (4) and 2.313 (4) Å, and Pt–P(1) and Pt–P(2) are 2.296 (3) and 2.281 (4) Å. The distances S(1)–C(1), S(2)–C(2) and C(1)–C(2) are 1.82 (2), 1.83 (1) and 1.45 (2) Å, respectively.

Introduction. Organosulfur derivatives of the transition metals are of significant interest due to the novel structures and properties of the complexes formed. Metal thiolates represent the most common type of this class of compound, platinum thiolates having been reported as early as last century (Hofmann & Rabe, 1897). More recent research has focused on controlling substitution–polymerization reactions to synthesize monomeric thiolate complexes (Hayter & Humiec, 1964; Rauchfuss & Roundhill, 1975; Rauchfuss, Shu & Roundhill, 1976). Of current interest to us are the monomeric complexes of the type $Pt(SR)_2L_2$. It has been suggested that the *cis* isomers are uncommon and that the monomeric thiolate complexes are unstable to polymerization (Lai & Shaver, 1981).

Recently the complexes *cis*-$Pt(SH)_2(PPh_3)_2$ (Schmidt & Hoffman, 1980) and $Pt(SCH_2CH_2S)(PPh_3)_2$ (Rauchfuss & Roundhill, 1975) have been prepared and *cis*-$Pt(SH)_2(PPh_3)_2$ characterized by single-crystal X-ray analysis (Briant, Hughes, Minshall & Mingos, 1980). The structure of $Pt(SCH_2CH_2S)(PPh_3)_2$ has been solved to determine that the compound is monomeric and to elucidate the coordination geometry about platinum.

Experimental. Yellow crystals from a chloroform-diethyl ether solution, D_m measured by flotation in 1,1,2,2-tetrachloroethane/1,2-dibromoethane, 0.062 × 0.141 × 0.183 mm, {100}, {$\bar{1}$00}, {010} and {$0\bar{1}0$} faces developed, mounted on a glass fiber with *c* and spindle axes collinear; crystal belonged to a triclinic space group because no symmetry or systematic absences on oscillation or on zero, first, or second-level Weissenberg photographs, data collected for that crystal class, final lattice constants from least-squares refinement of reciprocal-lattice coordinates of 12 accurately centered reflections; automated Picker full-circle diffractometer, Zr filter, θ–2θ step scan of 2.4° in 2θ, 20 steps deg⁻¹, 2.0 s step⁻¹, background of 20s before and after each scan, $\sigma^2(I_o) = \sigma^2_{\text{stat}} + C^2I_o^2$, $\sigma^2(I_o)$ the estimated variance in intensity, $C = 0.03$, I_o the intensity of the reflection, σ_{stat} the error from the