

were performed on a MicroVAX II computer using *TEXSAN* software package (Molecular Structure Corporation, 1985). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *TEXSAN*.*

Discussion. The Ni atom in this crystal has a distorted square-pyramidal coordination with four S atoms of the two diethyldithiophosphates in the square plane and one P atom of triphenylphosphine at the apex; the Ni atom is 0.549 Å above the basal plane of the four S atoms. The lengths of the Ni—S bonds are in the range 2.391 (2) to 2.436 (2) Å, the chelate angles S—Ni—S are 82.06 (6) and 82.86 (6)°. The Ni—S distances are intermediate between four-coordinated Ni complexes (Lin *et al.*, 1987; McConnell & Kastalsky, 1967) and six-coordinated Ni complexes (You *et al.*, 1986; Liu *et al.*, 1987; Liu

et al., 1990; You *et al.*, 1990; Ooi & Fernando, 1967).

In the triphenylphosphine, the P atom is in the three phenyl ring planes; the deviations of C atoms in the same ring from the ring plane are less than 0.014 Å. The dihedral angles between the basal plane consisting of the four S atoms and each of the three phenyl rings are 129.6, 145.2 and 125.7°, respectively.

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* Lists of structure factors, anisotropic thermal parameters, full bond distances and angles not including H atoms, least-squares planes, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52970 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of *cis*- and *trans*-Dichlorodioxobis(triphenylphosphine oxide)-uranium(VI)

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Abstract. *cis*-[UO₂Cl₂(tppo)₂], [UCl₂O₂(C₁₈H₁₅OP)₂]₂, (1), *M_r* = 897.52, monoclinic, *C*2/*c*, *a* = 17.233 (3), *b* = 12.112 (2), *c* = 17.085 (4) Å, β = 105.90 (2)°, *V* = 3429.7 Å³, *Z* = 4, *D_x* = 1.737 g cm⁻³, Mo *Kα*, λ = 0.71073 Å, μ = 47.64 cm⁻¹, *F*(000) = 1736, *T* = 293 K, *R* = 0.040 for 2855 observed reflections with *I* > 3σ(*I*). *trans*-[UO₂Cl₂(tppo)₂], [UCl₂O₂(C₁₈H₁₅OP)₂]₂, (2), *M_r* = 897.52, monoclinic, *B*2₁, *a* = 10.158 (11), *b* = 18.849 (17), *c* = 19.139 (14) Å, β = 90.4 (1)°, *V* = 3664.4 Å³, *Z* = 4, *D_x* = 1.638 g cm⁻³, Mo *Kα*, λ = 0.71073 Å, μ = 44.74 cm⁻¹, *F*(000) = 1736, *T* = 293 K, *R* = 0.042 for 2603 observed

reflections with *I* > 3σ(*I*). In both forms the complex has a distorted octahedral arrangement about the U atom.

Introduction. The uranium(VI) compounds [UO₂X₂(OPR₃)₂] (*X* = Cl or Br; *R* = Me, Et or Ph) have been reported (Gans & Smith, 1964) and further studies have included the iodo compound (*X* = I) (Day & Venanzi, 1966). The compounds were expected to show a near linear arrangement of the uranyl (O—U—O) bonds with the remaining atoms or ligands in the equatorial plane. This allows for *cis* or

Table 1. Data collection and structure refinement parameters

	<i>cis</i>	<i>trans</i>
Crystal size (mm)	0.09 × 0.12 × 0.16	0.06 × 0.38 × 0.42
Diffractometer used	CAD-4, Enraf-Nonius	Stoe STADI-2
No. and θ range (°) of reflections for lattice parameters	25; 8-9	141; 3.5-15
Scan type	ω -2 θ	ω
Scan angle	0.8 + 0.3tan θ	1.2 + 0.7sin μ /tan (UPS)
Monochromator		Graphite
Range for data collection		
θ (°)		3.5/27
<i>h</i>	-21/21	-24/24*
<i>k</i>	0/15	-12/12
<i>l</i>	0/21	0/21
Max scan time (s)	30	48
Background	0.25 of scan time at each of scan limits	
Scan rate (° min ⁻¹)	2.75-5.49	1.5-12.3
Reference reflections	3 every 2 h	every 50 reflections
Orientation reflections	3 every 600	—
Intensity decrease (%)	2.8	—
Measured reflections	7865	7126
Averaged reflections	3680	3353
Observed reflections	2855	2603
$I > 3\sigma(I)$		
Programs used	SHELX76†, GX‡	SHELX76†, SHELXS§
Scattering factors ¶		Neutral atoms
R_w **	0.040, 0.049	0.042, 0.039
Weighting parameter (g)††	0.0036	0.006
No. of parameters	169	333
Ratio of observed to parameters	16.9	7.8
Max. shift/e.s.d.	0.18	0.46
Residual electron density (e Å ⁻³)	-2.76 to 3.95	-1.15 to 1.72,
	0.93 Å from U	1.0 Å from U

* Referred to the unit cell used for data collection.

† Sheldrick (1976).

‡ Mallinson & Muir (1985).

§ Sheldrick (1986).

¶ *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 99).** The quantity minimized in the least-squares procedure is $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.†† Weighting $w = 1/[\sigma^2(F) + g(F)^2]$.

trans arrangement of the phosphine oxide ligands. An earlier structural study of the title compound (Bombieri, Forsellini, Day & Azeez, 1978) revealed a *trans* form of the compound in a triclinic space group [now designated α -*trans* UO₂Cl₂(tppo)₂], and the authors anticipated the existence of the *cis*-UO₂Cl₂(tppo)₂. We report in this paper the crystal structures of the anticipated *cis* form and a new *trans* form in a monoclinic space group, in which the molecular units are in an alternative packing arrangement. The latter is designated β -*trans* UO₂Cl₂(tppo)₂.

Experimental. The crystals of *cis*- and *trans*-UO₂Cl₂(tppo)₂ were isolated separately as by-products from the reactions of Me₃SiCl with the products from the interaction of UF₅ with tppo in acetonitrile. Pale-green irregular crystals of the *cis* form were isolated from an Me₃SiCl/UF₅/tppo (5:1:2), acetonitrile solution after standing in a glass

Table 2. The final atom coordinates and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
<i>cis</i> -UO ₂ Cl ₂ ZTTPPO				
U	0.50000	0.33654 (3)	0.25000	0.028
P	0.34936 (9)	0.56053 (13)	0.21415 (9)	0.030
Cl	0.39426 (13)	0.18939 (15)	0.17087 (14)	0.058
O	0.4592 (3)	0.3386 (4)	0.3345 (3)	0.032
Op	0.40974 (24)	0.4793 (3)	0.19598 (24)	0.047
C(1)	0.24883 (19)	0.5173 (3)	0.16478 (25)	0.033
C(2)	0.18323 (19)	0.5856 (3)	0.16316 (25)	0.044
C(3)	0.10526 (19)	0.5516 (3)	0.12249 (25)	0.054
C(4)	0.09287 (19)	0.4493 (3)	0.08348 (25)	0.057
C(5)	0.15847 (19)	0.3811 (3)	0.08512 (25)	0.056
C(6)	0.23647 (19)	0.4150 (3)	0.12576 (25)	0.043
C(11)	0.36205 (29)	0.69323 (28)	0.17302 (25)	0.034
C(12)	0.35193 (29)	0.69831 (28)	0.08924 (25)	0.056
C(13)	0.36192 (29)	0.79844 (28)	0.05281 (25)	0.068
C(14)	0.38205 (29)	0.89346 (28)	0.10018 (25)	0.059
C(15)	0.39217 (29)	0.88838 (28)	0.18395 (25)	0.062
C(16)	0.38217 (29)	0.78826 (28)	0.22037 (25)	0.051
C(21)	0.36109 (24)	0.5744 (4)	0.32083 (17)	0.034
C(22)	0.43680 (24)	0.6039 (4)	0.37069 (17)	0.042
C(23)	0.44899 (24)	0.6129 (4)	0.45461 (17)	0.046
C(24)	0.38551 (24)	0.5923 (4)	0.48865 (17)	0.052
C(25)	0.30981 (24)	0.5628 (4)	0.43878 (17)	0.058
C(26)	0.29760 (24)	0.5539 (4)	0.35487 (17)	0.049
β - <i>trans</i> -UO ₂ Cl ₂ ZTTPPO				
U(1)	0.23198 (5)	0.24902 (0)	0.38354 (2)	0.0358
Cl(1)	0.1916 (6)	0.2049 (3)	0.25239 (24)	0.0705
Cl(2)	0.2826 (5)	0.2859 (4)	0.51504 (24)	0.0847
O(1)	0.3625 (12)	0.3021 (7)	0.3549 (6)	0.0608
O(2)	0.0986 (12)	0.1957 (7)	0.4104 (7)	0.0539
P(1)	-0.0467 (4)	0.37781 (24)	0.38371 (20)	0.0414
O(3)	0.0886 (12)	0.3434 (6)	0.3732 (5)	0.0467
C(1)	-0.1420 (11)	0.3356 (7)	0.4505 (5)	0.0504
C(2)	-0.0839 (11)	0.3230 (7)	0.5156 (5)	0.0604
C(3)	-0.1569 (11)	0.2916 (7)	0.5687 (5)	0.0742
C(4)	-0.2880 (11)	0.2728 (7)	0.5567 (5)	0.0892
C(5)	-0.3461 (11)	0.2855 (7)	0.4916 (5)	0.0980
C(6)	-0.2730 (11)	0.3169 (7)	0.4386 (5)	0.0954
C(11)	-0.0252 (12)	0.4692 (5)	0.4089 (6)	0.0429
C(12)	-0.1212 (12)	0.5056 (5)	0.4465 (6)	0.0594
C(13)	-0.1053 (12)	0.5776 (5)	0.4609 (6)	0.0918
C(14)	0.0066 (12)	0.6133 (5)	0.4379 (6)	0.0813
C(15)	0.1026 (12)	0.5768 (5)	0.4004 (6)	0.0903
C(16)	0.0866 (12)	0.5049 (5)	0.3859 (6)	0.0741
C(21)	-0.1409 (13)	0.3766 (7)	0.3047 (5)	0.0450
C(22)	-0.2174 (13)	0.4342 (7)	0.2832 (5)	0.0631
C(23)	-0.2841 (13)	0.4319 (7)	0.2193 (5)	0.0755
C(24)	-0.2742 (13)	0.3720 (7)	0.1768 (5)	0.0915
C(25)	-0.1976 (13)	0.3145 (7)	0.1982 (5)	0.1045
C(26)	-0.1309 (13)	0.3168 (7)	0.2622 (5)	0.0841
P(2)	0.4429 (4)	0.08413 (25)	0.40170 (23)	0.0412
O(4)	0.3717 (12)	0.1524 (7)	0.4036 (6)	0.0553
C(31)	0.5997 (11)	0.0970 (8)	0.3593 (6)	0.0511
C(32)	0.7190 (11)	0.0988 (8)	0.3959 (6)	0.0832
C(33)	0.8355 (11)	0.1138 (8)	0.3609 (6)	0.1063
C(34)	0.8329 (11)	0.1273 (8)	0.2892 (6)	0.1337
C(35)	0.7137 (11)	0.1257 (8)	0.2526 (6)	0.1126
C(36)	0.5971 (11)	0.1107 (8)	0.2876 (6)	0.0792
C(41)	0.3502 (11)	0.0179 (6)	0.3571 (6)	0.0453
C(42)	0.4079 (11)	-0.0410 (6)	0.3256 (6)	0.0782
C(43)	0.3290 (11)	-0.0929 (6)	0.2945 (6)	0.0867
C(44)	0.1923 (11)	-0.0858 (6)	0.2948 (6)	0.1018
C(45)	0.1345 (11)	-0.0269 (6)	0.3263 (6)	0.0875
C(46)	0.2135 (11)	0.0250 (6)	0.3575 (6)	0.0550
C(51)	0.4775 (17)	0.0553 (6)	0.4890 (5)	0.0561
C(52)	0.4758 (17)	0.1061 (6)	0.5420 (5)	0.0657
C(53)	0.5052 (17)	0.0865 (6)	0.6107 (5)	0.0978
C(54)	0.5363 (17)	0.0161 (6)	0.6263 (5)	0.1234
C(55)	0.5380 (17)	-0.0346 (6)	0.5733 (5)	0.1214
C(56)	0.5086 (17)	-0.0151 (6)	0.5046 (5)	0.0850

Equivalent isotropic temperature factor *U* defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

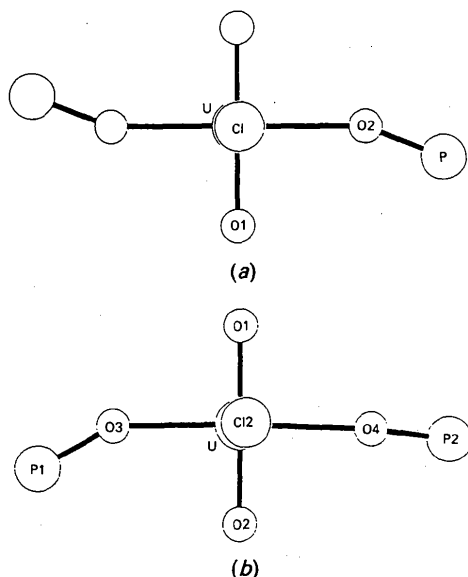


Fig. 3. Projections of (a) the α -trans-UO₂Cl₂(tppo)₂ form and (b) the β -trans-UO₂Cl₂(tppo)₂ form along the Cl—U—Cl bonds.

Selected bond lengths and angles (Table 3) show that the distances about the U atom are equivalent within e.s.d.'s for the *cis* and β -*trans* structures. The distances are also in agreement with the α -*trans* structure (Bombieri, Forsellini, Day & Azeez, 1978) and a search of the Cambridge Structural Database (Table 3).

The angle at the bridging O atom of the triphenyl phosphine oxide ligand is found to be lowest for the *cis* form, 144.5°, compared with values from 154 to 167° observed in the data search and is probably due to steric hindrance between the adjacent bulky ligands. The values observed in the β -*trans* structure of 151.7 and 166.2° are assumed to be different only because of packing constraints.

In the paper by Bombieri *et al.* (1978) on the α -*trans*-UO₂Cl₂(tppo)₂ structure the probability of the *cis* form being determined was anticipated. The determination of the new β -*trans*-UO₂Cl₂(tppo)₂ structure suggests that there may be more structure forms dependent only upon conditions of crystallization.

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Structure of Tetraphenylarsonium Bis(1,2-dithiooxalato-*S,S'*)palladate(II)

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Abstract. [As(C₆H₅)₄]₂[Pd(C₂O₂S₂)₂], *M_r* = 1113.37, triclinic, *P* $\bar{1}$, *a* = 11.101 (7), *b* = 13.316 (5), *c* = 18.485 (8) Å, α = 110.90 (5), β = 77.74 (8), γ = 106.28 (8)°, *V* = 2431 (2) Å³, *Z* = 2, *D_m* = 1.53 (1), *D_x* = 1.52 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ =

19.317 cm⁻¹, *T* = 296 K, *F*(000) = 1120, *R* = 0.041, *wR* = 0.045 for 5034 observed reflections with *I* > 3 σ (*I*). The asymmetric unit of the title compound contains one discrete complex [Pd(C₂S₂O₂)₂]²⁻ anion and two [As(C₆H₅)₄]⁺ cations linked through electrostatic interactions and hydrogen contacts of type C—H...O.

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