

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, $C2/c$, $a = 17.233$ (3), $b = 12.112$ (2), $c = 17.085$ (4) Å, $\beta = 105.90$ (2)°, $V = 3429.7$ Å³, $Z = 4$, $D_x = 1.737$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 47.64$ cm⁻¹, $F(000) = 1736$, $T = 293$ K, $R = 0.040$ for 2855 observed reflections with $I > 3\sigma(I)$. *trans*-[UO₂Cl₂(tppo)₂], [UCl₂O₂(C₁₈H₁₅OP)₂]₂, (2), $M_r = 897.52$, monoclinic, $B2_1$, $a = 10.158$ (11), $b = 18.849$ (17), $c = 19.139$ (14) Å, $\beta = 90.4$ (1)°, $V = 3664.4$ Å³, $Z = 4$, $D_x = 1.638$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 44.74$ cm⁻¹, $F(000) = 1736$, $T = 293$ K, $R = 0.042$ for 2603 observed

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

Introduction. The uranium(VI) compounds [UO₂X₂(OPR₃)₂] ($X = \text{Cl or Br}$; $R = \text{Me, Et or Ph}$) have been reported (Gans & Smith, 1964) and further studies have included the iodo compound ($X = \text{I}$) (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
<i>R</i> , ** <i>wR</i>	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.

Table 3. Selected bond distances (Å) and angles (°) of the *cis* form, the α - and β -*trans* forms and database values (Cambridge Structural Database)

	<i>cis</i> form	β - <i>trans</i> form	α - <i>trans</i> form	Database	
				Obs	Av
U—Cl	2.641 (2)	2.673 (4), 2.657 (4)	2.645 (5)	158	2.63 (5)
U=O	1.771 (4)	1.753 (12), 1.767 (12)	1.764 (9)	285	1.76 (3)
U—O(P)	2.340 (4)	2.306 (12), 2.339 (12)	2.300 (8)	8	2.30 (6)
P—O(P)	1.524 (4)	1.535 (3), 1.477 (12)	1.518 (8)	8	1.51 (2)
U—O—P	144.5 (2)	151.7 (8), 166.2 (8)	158.7 (6)	8	162 (5)
Cl—U—Cl	95.1 (1)	176.3 (2)			
O=U=O	178.4 (2)	178.6 (6)			
(P)O—U—O(P)	84.7 (1)	175.3 (4)			

apparatus for several weeks. The pale green rhomboid crystals of the *trans* form were produced in a similar manner from an Me₃SiCl/UF₅/tppo (2:1:2) solution. The crystals for structure determination were sealed in preseasoned (F₂) Pyrex glass capillaries.

The unit-cell parameters of the *cis* form were determined by a least-squares fit of setting angles of 25 reflections. The intensity data for the β -*trans* form were collected from a crystal mounted about the *b* axis. Four quadrants of data were collected as preliminary photographs did not conclusively support monoclinic symmetry. The cell parameters of the β -*trans* form were determined from the optimized counter angles for zero and upper layer reflections. The standard *P*2₁ setting was rejected in favour of the nearly orthogonal *B*2₁ cell. The merge of 7126 reflections to 3353 unique reflections after absorption correction gave *R*_{int} of 0.0271, which was taken as conclusive support of the monoclinic symmetry.

For both structures the position of the uranium atom was located by Patterson methods and the remaining atoms were located by Fourier techniques. Details of the procedures used for data collection and refinement are given in Table 1. H atoms were included in calculated positions (C—H = 1.08 Å) for the final cycles of refinement, with a common fixed isotropic thermal parameter. An absorption correction was applied to the data set for the *trans* form with the maximum and minimum transmission factors 0.764 and 0.274 respectively.

Discussion. Table 2 lists the final positional and isotropic thermal parameters for the *cis* and β -*trans* forms of UO₂Cl₂(tppo)₂. * Table 3 gives selected comparative bond distances and angles. Both structures show that the U atom is surrounded by two uranyl O atoms, two Cl atoms and two O atoms of the tppo

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53319 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

groups. Figs. 1 and 2 show the approximately octahedral arrangement about the U atoms of the *cis*- and β -*trans*-UO₂Cl₂(tppo)₂ molecules respectively. In both, the uranyl O atoms form an almost linear group with an O=U=O angle of 178.4 for the *cis* form and 178.6° for the *trans* form. As would be expected, the distortion from octahedral symmetry of the equatorial atoms is greater in the asymmetric *cis* form with the Cl atoms repelling each other and giving a Cl—U—Cl angle of 95.1 and a (P)O—U—O(P) angle of 84.7°, the mean deviation from octahedral for all angles is 3.4°. The angles about the U atom in the β -*trans* structure show a maximum deviation from octahedral with a O(3)—U—Cl(1) angle of 93.9° (mean deviation 1.7°).

The arrangement of the β -*trans* form found in the monoclinic space group is a less closely packed structure than the α -*trans*-UO₂Cl₂(tppo)₂ (Bombieri, Forsellini, Day & Azeez, 1978) with the respective unit-cell volumes per molecule of 908 and 872 Å³. The packing of the molecules is such that the P atoms in the β -*trans*-UO₂Cl(tppo)₂ are on the same side of the plane containing the Cl and the O atoms of the tppo groups whilst in the α -*trans*-UO₂Cl₂(tppo)₂ structure the P atoms are on the opposite sides of the plane (Fig. 3).

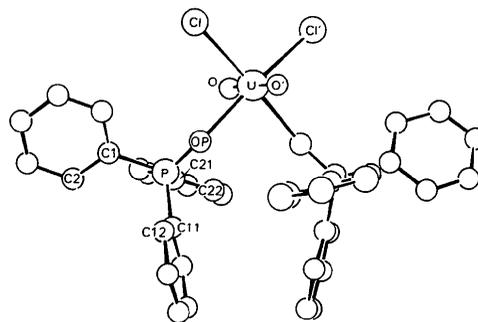


Fig. 1. ORTEPII (Johnson, 1976) view of the *cis*-UO₂Cl₂(tppo)₂ molecule.

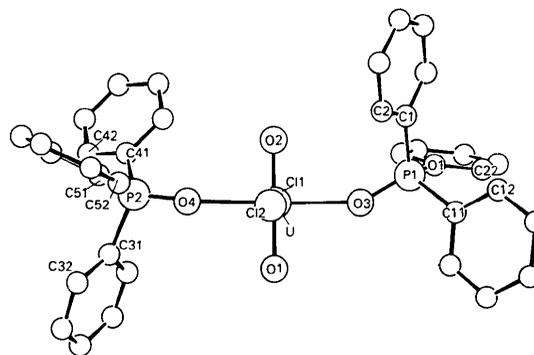


Fig. 2. View of the β -*trans*-UO₂Cl₂(tppo)₂ molecule.

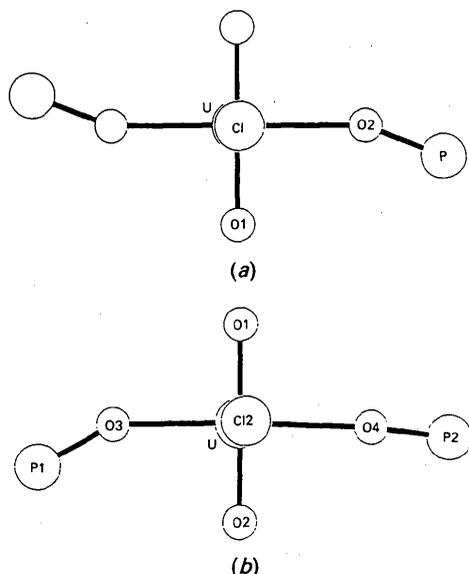


Fig. 3. Projections of (a) the α -trans-UO₂Cl₂(tppo)₂ form and (b) the β -trans-UO₂Cl₂(tppo)₂ form along the Cl—U—Cl bonds.

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, λ (Mo *K* α) = 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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