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Hexakis(*N*-methylthiourea)technetium(III) Hexafluorophosphate Hydrate and Hexakis(*N*,*N*′-dimethylthiourea)technetium(III) Hexafluorophosphate

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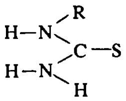
Abstract. $[Tc(C_2H_6N_2S)_6](PF_6)_3.H_2O$, $M_r = 1092{\cdot}70$, triclinic, $P\bar{1}$, $a = 6{\cdot}754\,(3)$, $b = 11{\cdot}737\,(8)$, $c = 13{\cdot}217\,(7)$ Å, $\alpha = 74{\cdot}45\,(5)$, $\beta = 86{\cdot}30\,(4)$, $\gamma = 86{\cdot}39\,(5)°$, $V = 1006\,(1)$ Å^3, $Z = 1$, $D_x = 1{\cdot}803$, $D_m = 1{\cdot}82$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·879 mm^{-1}, $F(000) = 548$, room temperature, $R = 0{\cdot}059$ for 3731 unique observed reflections. The cation is approximately octahedral and the methylthiourea ligands are S bonded. The Tc atom lies on an inversion centre with Tc—S distances = 2·419 (1), 2·451 (1) and 2·460 (1) Å. All the methylthiourea ligands have the *cis* configuration. One PF_6^- anion is also located on an inversion centre. Most of the F atoms show high thermal motion. The compound crystallizes with a disordered molecule of water. The structure is stabilized by hydrogen bonds. $[Tc(C_3H_8N_2S)_6](PF_6)_3$, $M_r = 1158{\cdot}85$, monoclinic, $P2_1/c$, $a = 13{\cdot}306\,(13)$, $b = 20{\cdot}943\,(15)$, $c = 17{\cdot}082\,(13)$ Å, $\beta = 102{\cdot}54\,(7)°$, $V = 4646\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}656$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·759 mm^{-1}, $F(000) = 2344$, room temperature, $R = 0{\cdot}079$ for 2961 unique observed reflections. The cation is approximately octahedrally coordinated by the six S atoms of the dimethylthiourea ligands. The Tc—S distances are 2·426 (3), 2·451 (3), 2·430 (3), 2·436 (3), 2·460 (3) and 2·436 (3) Å. All the dimethylthiourea ligands have the *cis-trans* configuration. The F atoms have high thermal motion. The structure is stabilized by intra- and intermolecular hydrogen bonds.

Introduction. Thiourea derivatives are ligands of interest due to the presence of three potential donor sites, the S and the two N atoms. The binding site assigned by infrared data on several metal complexes has been controversial. But all crystal structure determinations have shown that the binding site is the S atom. Furthermore, the C—N bonds of thiourea derivatives have an appreciable double bond character. Therefore *N*-alkyl derivatives of thiourea can have different configurations where the thioamide H atom and the thiocarbonyl bonds are either *cis* or *trans*. For *N*-alkylthiourea, there are two isomers, *cis* and *trans*, whereas for *N*,*N*′-dialkylthiourea, there are three isomers, *cis-cis*, *trans-trans* and *cis-trans*.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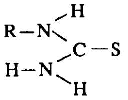
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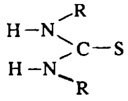
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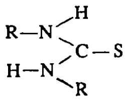
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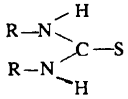
cis-cis

The infrared spectra of several such derivatives were studied in the solid state. *N*-Methylthiourea (Metu) was suggested to be the *trans* isomer, while *N*,*N*′-dimethylthiourea (Me_2tu) was reported as the *trans-trans* isomer (Lane, Yamaguchi, Guagliano, Ryan & Mizushima, 1959). The interpretation of the infrared spectra is not easy since many absorption bands result from a mixture of vibrations. But the crystal structure analyses of $Ag(Metu)_3Cl$ (Lee & Amma, 1972) and of $[Pt(N\text{-ethylthiourea})_4]Cl_2$ (Bachechi, Zambonelli & Marcotrigiano, 1976) have shown that the ligands all have the *cis* configuration while in $[Cu(Me_2tu)_3Cl]^+$ (Girling & Amma, 1971) and $[Pt(Me_2tu)_4]Cl_2$ (Bachechi, Zambonelli & Marcotrigiano, 1977) the *cis-trans* configuration was observed.

The chemistry of technetium compounds has recently become an active research field especially in relation to the development of new compounds for use in diagnostic nuclear medicine. We have recently synthesized two technetium complexes $[Tc(Metu)_6]Cl_3$ and $[Tc(Me_2tu)_6]Cl_3$ as starting material for a study on Tc mixed-ligand compounds. We decided to characterize all the complexes by X-ray diffraction. The crystal structure of $[Tc(thiourea)_6]Cl_3.4H_2O$ has already been reported (Abrams, Davison, Faggiani, Jones & Lock, 1984). The above two compounds did not produce crystals adequate for crystallography. We therefore replaced the chloride ions by the larger PF_6^- anions and we obtained beautiful red crystals adequate for diffraction methods. The preparation of

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[Tc(Me$_2$tu)$_6$](PF$_6$)$_3$ has already been reported (Abrams, Brenner, Davison & Lock, 1983). The results obtained on the crystal structure determination of [Tc(Metu)$_6$](PF$_6$)$_3$.H$_2$O and [Tc(Me$_2$tu)$_6$](PF$_6$)$_3$ are reported below.

Experimental. NH$_4$^{99}TcO$_4$ was bought from Oak Ridge National Laboratories. All manipulations were made in a laboratory approved for low-level radioactive material (^{99}Tc is a β-emitter with a particle energy of 0·292 MeV and a half-life of 2·13 × 10^5 years).

The method used to synthesize the two compounds is a slight modification of the method reported by Abrams *et al.* (1984). 1·5 g of the thiourea derivative was dissolved in 25 mL of water. If the solution was not clear, it was filtered through charcoal. Then 6 mL of HCl (12 *M*) was added to the thiourea solution. An aqueous solution of NH$_4$TcO$_4$ (0·472 mmol in 2 mL H$_2$O) was added dropwise with stirring to the acid solution. The next day the deep-red solution was filtered and 1 g of NH$_4$PF$_6$ (dissolved in 10 mL of water) was added to the filtrate. The red precipitate was filtered and washed with cold water. The product was recrystallized in a mixture of acetone and HCl solution (2 *M*). Yield: 80% for Me$_2$tu and 60% for Metu. [Tc(Me$_2$tu)$_6$](PF$_6$)$_3$ (II) has already been characterized (Abrams *et al.*, 1983). [Tc(Metu)$_6$](PF$_6$)$_3$.H$_2$O (I): m.p. 446–455 K (dec.); IR (KBr): 3645*m*, 3573*w*, 3320–3470(broad), 1634*s*, 1582*s*, 1502*m*, 1460*w*, 1422*m*, 1365*w*, 1295*m*, 1172*m*, 1158*m*, 850*s*(broad), 755*m*, 679*m*, 609*m*, 560*m* and 479*m* cm^{-1}; optical spectrum (acetonitrile): 488 (ε = 4070 L mol^{-1} cm^{-1}), 430 (ε = 5300 L mol^{-1} cm^{-1}) and 244 nm (ε = 35300 L mol^{-1} cm^{-1}); magnetic moment: μ = 2·9 BM (1 BM ≃ 9·274 × 10^{-24} JT^{-1}) (295 K).

The two crystals were selected after examination under a polarizing microscope, for homogeneity. The unit-cell parameters were obtained by least-squares refinement of the angles 2θ, ω and χ for 15 well-centred reflections on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Crystal data and other information are summarized in Table 1. Scan rates and data treatment have already been described (Melanson & Rochon, 1975). Corrections were made for absorption and Lorentz–polarization effects. The anomalous-dispersion terms of Tc, S and P were included in the calculations (Cromer, 1965).

The coordinates of the Tc atoms were determined from the three-dimensional Patterson map. The position of Tc in the Metu compound was found to lie on an inversion centre. The positions of all the other non-H atoms were found by structure factor and difference Fourier-map calculations. One P atom in compound (I) was located on a centre of symmetry.

Table 1. *Experimental details of the X-ray studies of* [Tc(*Metu*)$_6$](PF$_6$)$_3$.H$_2$O (I) *and* [Tc(*Me$_2$tu*)$_6$](PF$_6$)$_3$ (II)

	(I)	(II)
Compound	$C_{12}H_{38}F_{18}N_{12}OP_3S_6Tc$	$C_{18}H_{48}F_{18}N_{12}P_3S_6Tc$
Crystal faces and dimensions (mm)	(001)–(00$\bar{1}$)(0·096) (010)–(0$\bar{1}$0)(0·076) (112)–($\bar{1}\bar{1}\bar{2}$)(0·384)	(100)–($\bar{1}$00)(0·038) (010)–(0$\bar{1}$0)(0·250) (001)–(00$\bar{1}$)(0·654)
Transmission factor range	0·913–0·942	0·836–0·970
$2\theta_{\max}$ (°)	60	50
Quadrants	h, $\pm k$, $\pm l$	h, k, $\pm l$
h, k, l	0→9, −16→16, −18→18	0→15, 0→24, −20→19
Scan technique	$2\theta/\theta$	$2\theta/\theta$
Standard reflections	20$\bar{1}$, 0$\bar{4}$0, 013	330, 052, 20$\bar{4}$
Temperature (K)	295	295
No. of independent reflections	5929	8230
No. of observed reflections [$I > 2\cdot5\sigma(I)$]	3731	2961
R	0·059	0·079
wR	0·066	0·065
Standard deviation (unit weight)	1·9	1·40

Table 2. *Positional parameters with e.s.d.'s in parentheses and temperature factors* (× 10^4)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
[Tc(Metu)$_6$](PF$_6$)$_3$.H$_2$O				
Tc	0	0	0	243
S(1)	−1979 (2)	1406 (1)	773 (1)	328
S(2)	−3006 (2)	49 (1)	−915 (1)	342
S(3)	1706 (2)	1519 (1)	−1373 (1)	361
P(1)	5000	5000	0	460
P(2)	4763 (3)	2557 (2)	4534 (2)	643
N(1)	1171 (7)	2718 (4)	707 (4)	521
N(2)	−1350 (7)	2879 (4)	1891 (3)	416
N(3)	−4133 (8)	−211 (7)	−2681 (4)	897
N(4)	−865 (6)	92 (4)	−2709 (3)	394
N(5)	864 (8)	3093 (5)	−3134 (4)	676
N(6)	−1661 (7)	2860 (4)	−1876 (3)	476
C(1)	−582 (8)	2415 (4)	1150 (4)	341
C(2)	−2597 (8)	−28 (5)	−2204 (4)	392
C(3)	123 (8)	2589 (5)	−2173 (4)	392
C(4)	−448 (11)	3845 (6)	2201 (5)	619
C(5)	−399 (9)	6 (6)	−3776 (4)	565
C(6)	−3086 (11)	3672 (7)	−2561 (6)	716
F(1)	7189 (6)	4546 (4)	−228 (3)	837
F(2)	4726 (6)	3967 (4)	1048 (3)	812
F(3)	4152 (7)	4212 (5)	−645 (4)	1032
F(4)	2532 (9)	2625 (9)	4446 (6)	1927
F(5)	4605 (11)	2349 (8)	5706 (4)	1895
F(6)	4909 (12)	2726 (9)	3374 (4)	1978
F(7)	6988 (9)	2433 (7)	4652 (6)	1876
F(8)	4742 (16)	1246 (6)	4734 (7)	2271
F(9)	4774 (17)	3816 (6)	4403 (9)	2793
O(1)	−725 (25)	4659 (11)	4855 (10)	1379
[Tc(Me$_2$tu)$_6$](PF$_6$)$_3$				
Tc	7413·0 (6)	2237·1 (5)	6048·8 (5)	376
S(1)	6143 (2)	2727 (2)	4984 (2)	535
S(2)	6701 (2)	2571 (1)	7193 (2)	577
S(3)	8097 (2)	1904 (1)	4905 (2)	479
S(4)	8442 (2)	3194 (1)	6436 (2)	469
S(5)	6378 (2)	1264 (1)	5700 (2)	563
S(6)	8714 (2)	1746 (2)	7101 (2)	528
P(1)	2279 (3)	3201 (2)	8321 (2)	804
P(2)	2889 (3)	4679 (2)	1598 (2)	929
P(3)	2196 (3)	4408 (2)	5237 (3)	1105
N(1)	8515 (6)	3451 (4)	4897 (5)	600
N(2)	9448 (8)	4090 (4)	5867 (5)	733
N(3)	6090 (7)	3796 (4)	5856 (5)	674
N(4)	4775 (7)	3646 (5)	4679 (6)	819
N(5)	9804 (6)	1794 (4)	4387 (5)	615
N(6)	10031 (6)	2192 (4)	5667 (4)	522
N(7)	4787 (6)	2323 (5)	6361 (5)	639
N(8)	4937 (6)	2994 (4)	7478 (5)	667
N(9)	8887 (6)	707 (4)	6188 (5)	692

Table 2 (*cont.*)

	x	y	z	U_{eq}(Å^2)
N(10)	10292 (7)	964 (5)	7193 (5)	694
N(11)	6269 (8)	126 (5)	6360 (7)	952
N(12)	6375 (7)	984 (5)	7215 (6)	814
C(1)	5651 (7)	3439 (5)	5209 (6)	532
C(2)	5351 (7)	2623 (5)	6978 (6)	559
C(3)	9382 (7)	1973 (4)	4998 (5)	376
C(4)	8821 (7)	3599 (4)	5665 (6)	442
C(5)	6360 (8)	751 (6)	6497 (7)	708
C(6)	9320 (7)	1082 (5)	6792 (6)	476
C(7)	9384 (9)	166 (6)	5880 (8)	968
C(8)	9204 (9)	1566 (6)	3608 (6)	931
C(9)	9818 (10)	4353 (6)	6665 (7)	893
C(10)	8896 (9)	3723 (6)	4199 (6)	718
C(11)	5515 (8)	3393 (6)	8157 (7)	750
C(12)	3626 (7)	2343 (6)	6138 (7)	750
C(13)	6222 (12)	−201 (7)	5583 (10)	1279
C(14)	10899 (8)	1368 (6)	7854 (7)	886
C(15)	4191 (10)	3298 (6)	3983 (8)	1147
C(16)	11168 (7)	2269 (6)	5788 (6)	629
C(17)	6321 (13)	584 (8)	7930 (9)	1373
C(18)	5772 (9)	4427 (6)	6055 (8)	849
F(1)	2800 (5)	2691 (4)	7892 (4)	1371
F(2)	3292 (5)	3243 (4)	8991 (4)	1343
F(3)	1821 (7)	2688 (4)	8810 (5)	1440
F(4)	1268 (6)	3141 (5)	7641 (5)	1778
F(5)	2752 (7)	3740 (5)	7861 (6)	1677
F(6)	1746 (6)	3723 (4)	8748 (6)	1873
F(7)	3675 (7)	4360 (5)	1147 (6)	1673
F(8)	2075 (7)	4964 (4)	2013 (6)	1613
F(9)	2686 (8)	5229 (5)	996 (7)	1918
F(10)	3738 (8)	5079 (6)	2022 (7)	2588
F(11)	3030 (10)	4143 (6)	2177 (7)	2310
F(12)	2022 (8)	4319 (6)	1071 (7)	2400
F(13)	1106 (6)	4610 (4)	4835 (6)	1557
F(14)	2550 (7)	5122 (5)	5237 (7)	1986
F(15)	1820 (9)	3744 (4)	5238 (9)	2537
F(16)	2563 (8)	4333 (6)	4472 (6)	2446
F(17)	1887 (8)	4563 (7)	6025 (6)	2419
F(18)	3276 (7)	4234 (7)	5724 (7)	2694

The refinement of the structure containing Metu was done by using full-matrix least squares minimizing $\sum w(F_o - F_c)^2$. Compound (I) was found to contain a disordered molecule of water. Half occupancy was postulated, because full occupancy would require two symmetry equivalent oxygens to be only 1·4 Å apart. Even then the thermal factors of O were fairly large ($U_{eq} = 0{\cdot}138$ Å^2). Several H atoms were located, others were calculated. The refinement of compound (II) was done using block-diagonal matrices. The H atoms of the methyl groups in (II) were found to be disordered and therefore were neglected. Isotropic secondary-extinction corrections (Coppens & Hamilton, 1970) were included in the calculations. Individual weights $w = 1/\sigma^2(F)$ were applied. The refinement of the scale factor, coordinates and anisotropic temperature factors of all atoms converged to $R = 0{\cdot}059$ and $wR = 0{\cdot}066$ for (I) and to $R = 0{\cdot}079$ and $wR = 0{\cdot}065$ for (II). The H atoms were not refined and their thermal factors were fixed at $U = 0{\cdot}076$ Å^2. There were a few residual peaks [$<0{\cdot}5$ e Å^{-3} for (I) and $<0{\cdot}3$ e Å^{-3} (II)] in the close environment of the Tc atom. The high R value of compound (II) is caused by disorder of the F atoms in the PF_6^- anions. Attempts to resolve the disorder were not successful.

The scattering curves of Cromer & Waber (1965) and of Stewart, Davidson & Simpson (1965) for H were used. The calculations were performed on a Cyber 830 with programs already described (Melanson & Rochon, 1975).

Discussion. The refined atomic parameters of the two structures are listed in Table 2. Labelled diagrams of the molecules are shown in Figs. 1 and 2. The bond distances and angles are reported in Table 3.*

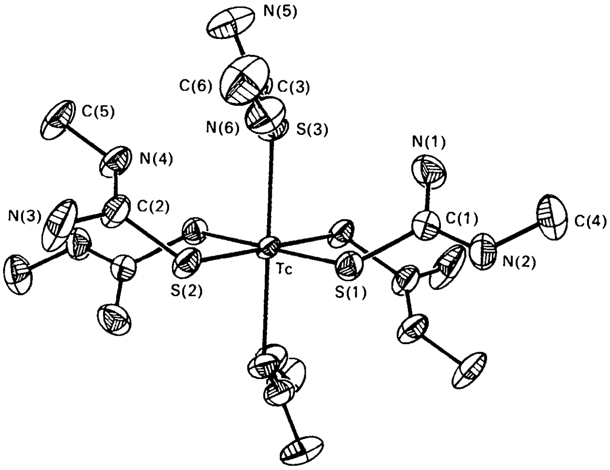

Fig. 1. Labelled diagram of $[Tc(Metu)_6]^{3+}$.

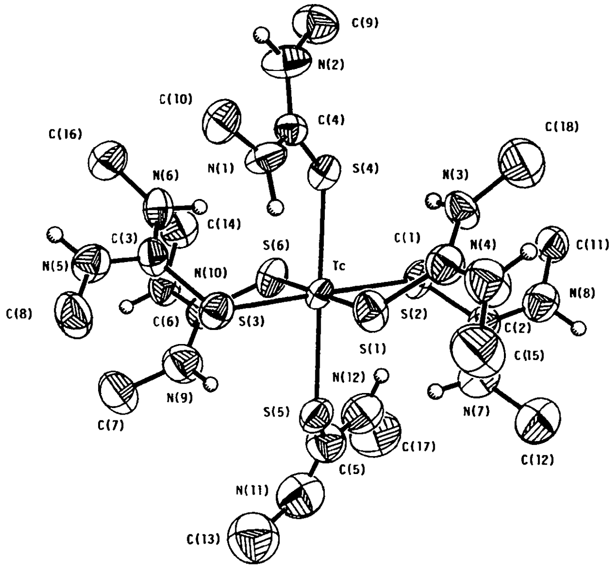

Fig. 2. Labelled diagram of $[Tc(Me_2tu)_6]^{3+}$ (the smaller circles correspond to the thioamide H atoms).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, weighted best planes data and distances and angles in the PF_6^- anions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52415 (63 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°)

$[Tc(Metu)_6](PF_6)_3.H_2O$			
Tc—S(1)	2·451 (1)	C(2)—N(4)	1·306 (7)
S(1)—C(1)	1·748 (5)	N(4)—C(5)	1·453 (7)
C(1)—N(1)	1·313 (7)	Tc—S(3)	2·460 (1)
C(1)—N(2)	1·309 (7)	S(3)—C(3)	1·761 (5)
N(2)—C(4)	1·480 (8)	C(3)—N(5)	1·329 (7)
Tc—S(2)	2·419 (1)	C(3)—N(6)	1·290 (7)
S(2)—C(2)	1·734 (5)	N(6)—C(6)	1·479 (9)
C(2)—N(3)	1·306 (8)		
S(1)—Tc—S(2)	82·17 (4)	S(1)—Tc—S(3)	95·36 (4)
S(1)—Tc—S(2′)	97·83 (4)	S(1)—Tc—S(3′)	84·64 (4)
S(2)—Tc—S(3)	97·00 (4)	S(2)—Tc—S(3′)	83·00 (4)
Tc—S(1)—C(1)	114·3 (2)	Tc—S(2)—C(2)	114·1 (2)
Tc—S(3)—C(3)	114·9 (2)	S(1)—C(1)—N(1)	122·2 (4)
S(1)—C(1)—N(2)	117·7 (4)	S(2)—C(2)—N(3)	116·9 (5)
S(2)—C(2)—N(4)	123·7 (4)	S(3)—C(3)—N(5)	115·5 (4)
S(3)—C(3)—N(6)	123·5 (4)	N(1)—C(1)—N(2)	120·1 (5)
N(3)—C(2)—N(4)	119·4 (5)	N(5)—C(3)—N(6)	121·0 (5)
C(1)—N(2)—C(4)	123·5 (5)	C(2)—N(4)—C(5)	126·8 (5)
C(3)—N(6)—C(6)	124·7 (5)		
$[Tc(Me_2tu)_6](PF_6)_3$			
Tc—S(1)	2·426 (3)	C(4)—N(2)	1·32 (1)
Tc—S(4)	2·436 (3)	C(6)—N(9)	1·32 (1)
S(1)—C(1)	1·71 (1)	N(2)—C(9)	1·45 (1)
S(4)—C(4)	1·73 (1)	N(5)—C(8)	1·47 (1)
C(1)—N(3)	1·36 (1)	N(8)—C(11)	1·50 (1)
C(2)—N(8)	1·36 (1)	N(11)—C(13)	1·48 (2)
C(4)—N(1)	1·32 (1)	Tc—S(3)	2·430 (3)
C(5)—N(12)	1·32 (1)	Tc—S(6)	2·436 (3)
N(1)—C(10)	1·51 (1)	S(3)—C(3)	1·69 (1)
N(4)—C(15)	1·47 (1)	S(6)—C(6)	1·75 (1)
N(7)—C(12)	1·51 (1)	C(2)—N(7)	1·31 (1)
N(10)—C(14)	1·50 (1)	C(3)—N(6)	1·35 (1)
Tc—S(2)	2·451 (3)	C(5)—N(11)	1·33 (1)
Tc—S(5)	2·460 (3)	C(6)—N(10)	1·35 (1)
S(2)—C(2)	1·76 (1)	N(3)—C(18)	1·45 (1)
S(5)—C(5)	1·74 (1)	N(6)—C(16)	1·49 (1)
C(1)—N(4)	1·38 (1)	N(9)—C(7)	1·47 (1)
C(3)—N(5)	1·34 (1)	N(12)—C(17)	1·50 (2)
S(1)—Tc—S(2)	98·7 (1)	S(1)—Tc—S(3)	80·8 (1)
S(1)—Tc—S(4)	96·6 (1)	S(1)—Tc—S(5)	84·6 (1)
S(1)—Tc—S(6)	178·8 (1)	S(2)—Tc—S(3)	179·3 (1)
S(2)—Tc—S(4)	80·9 (1)	S(2)—Tc—S(5)	97·8 (1)
S(2)—Tc—S(6)	82·4 (1)	S(3)—Tc—S(4)	99·6 (1)
S(3)—Tc—S(5)	81·7 (1)	S(3)—Tc—S(6)	98·2 (1)
S(4)—Tc—S(5)	178·3 (1)	S(4)—Tc—S(6)	83·1 (1)
S(5)—Tc—S(6)	95·7 (1)	Tc—S(1)—C(1)	116·1 (4)
Tc—S(2)—C(2)	113·9 (4)	Tc—S(3)—C(3)	116·6 (4)
Tc—S(4)—C(4)	115·9 (4)	Tc—S(5)—C(5)	115·1 (4)
Tc—S(6)—C(6)	114·5 (4)	S(1)—C(1)—N(3)	123 (1)
S(1)—C(1)—N(4)	116 (1)	S(2)—C(2)—N(7)	121 (1)
S(2)—C(2)—N(8)	116 (1)	S(3)—C(3)—N(5)	119 (1)
S(3)—C(3)—N(6)	124 (1)	S(4)—C(4)—N(1)	124 (1)
S(4)—C(4)—N(2)	117 (1)	S(5)—C(5)—N(11)	119 (1)
S(5)—C(5)—N(12)	120 (1)	S(6)—C(6)—N(9)	124 (1)
S(6)—C(6)—N(10)	117 (1)	N(3)—C(1)—N(4)	121 (1)
N(7)—C(2)—N(8)	123 (1)	N(5)—C(3)—N(6)	117 (1)
N(1)—C(4)—N(2)	119 (1)	N(11)—C(5)—N(12)	121 (1)
N(9)—C(6)—N(10)	120 (1)	C(1)—N(3)—C(18)	127 (1)
C(1)—N(4)—C(15)	127 (1)	C(2)—N(7)—C(12)	124 (1)
C(2)—N(8)—C(11)	127 (1)	C(3)—N(5)—C(8)	124 (1)
C(3)—N(6)—C(16)	127 (1)	C(4)—N(1)—C(10)	128 (1)
C(4)—N(2)—C(9)	127 (1)	C(5)—N(11)—C(13)	127 (1)
C(5)—N(12)—C(17)	124 (1)	C(6)—N(9)—C(7)	127 (1)
C(6)—N(10)—C(14)	125 (1)		

$[Tc(Metu)_6](PF_6)_3.H_2O$: As expected the six methylthiourea ligands are S bonded to the Tc atom. The Tc atom lies on an inversion centre. The coordination is octahedral but there are important distortions. All the S—Tc—S angles differ considerably from the ideal 90° [range 82·17 (4)–97·83 (4)°]. Two Tc—S(2) bonds [2·419 (1) Å] are significantly shorter than the other four [2·451 (1)–2·460 (1) Å]. A similar distortion has been observed in the structure of $[Tc(thiourea)_6]Cl_3.4H_2O$ (Abrams *et al.*, 1984). The authors assigned the deformation to a marked Jahn–Teller distortion. They have observed both tetragonal and trigonal distortions. We have also observed similar distortions. Tc^{III} has a d^4 configuration and is spin-paired as shown by the magnetic moment μ of 2·9 BM. The tetragonal distortion is shown by the shorter Tc—S(2) bonds. The trigonal distortion can be illustrated by comparing the S···S non-bonding distances in the following triangular faces S(1)···S(2) = 3·200 (2), S(1)···S(3) = 3·631 (2), S(2)···S(3) = 3·655 (2) Å *vs* S(1)···S(2′) = 3·670 (2), S(1)···S(3′) = 3·306 (2) and S(2′)···S(3′) = 3·655 (2) Å. The corresponding S—Tc—S angles are also quite different (Table 3).

The six methylthiourea ligands have the *cis* configuration, the methyl groups being oriented away from the Tc atom in order to minimize repulsion. This configuration is similar to the one observed in $Ag(Metu)_3Cl$ (Lee & Amma, 1972) and in [Pt(*N*-ethylthiourea)$_4$]Cl$_2$ (Bachechi, Zambonelli & Marcotrigiano, 1976). Because of the multiple nature of the C—N bonds, the four atoms S, C, N and N are planar. The C atoms from the methyl groups are almost in the plane [deviation: C(4) 0·158 (7), C(5) −0·039 (7) and C(6) 0·110 (8) Å] while the Tc atom is slightly out of the plane by −0·952, −0·445 and 0·974 Å respectively. The angles between the three planes (each containing S, C and 2N) are 33·4 [between S(1) and S(2) planes], 94·2 [between S(1) and S(3) planes] and 127·3° [between S(2) and S(3) planes]. The Tc—S—C angles are slightly greater than the tetrahedral value, 114·1 (2) to 114·9 (2)°. The S—C distances are 1·748 (5), 1·734 (5) and 1·761 (5) Å while the C—N bonds vary from 1·290 (7) to 1·329 (7) Å. Similar values were observed in the structure of $[Tc(thiourea)_6]Cl_3.4H_2O$ (Abrams *et al.*, 1984). The S—C—N angles range from 115·5 (4) to 123·7 (4)° while the C—N—CH_3 angles are slightly greater than 120° [123·5 (5) to 126·8 (5)°] as expected, the —CH_3 group being larger than H.

P(1) is located on an inversion centre while P(2) is on a general position. Most of the F atoms show

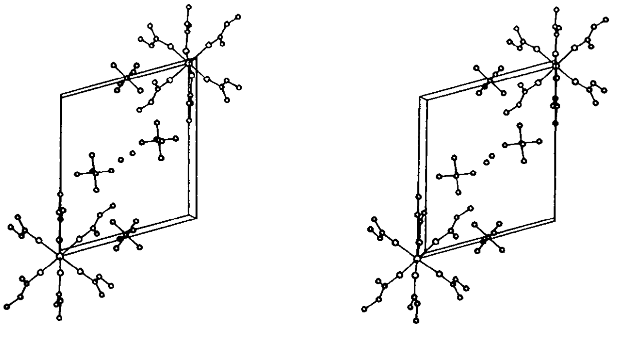

Fig. 3. Stereoscopic view of the unit cell in the crystal $[Tc(Metu)_6](PF_6)_3.H_2O$ (*c* axis vertical, down *a** axis).

Table 4. *Distances* (Å) *and angles* (°) *between atoms probably involved in hydrogen bonds*

[Tc(Metu)$_6$](PF$_6$)$_3$.H$_2$O

N(1)···F(2)	3·009 (7)	C(1)—N(1)···F(2)	139·9 (4)
N(1)···S(2^{i})	3·349 (5)	C(1)—N(1)···S(2)	95·8 (3)
N(2)···F(6^{ii})	3·080 (8)	C(1)—N(2)···F(6)	139·5 (4)
		C(4)—N(2)···F(6)	96·3 (4)
N(4)···S(3)	3·359 (5)	C(2)—N(4)···S(3)	103·9 (3)
		C(5)—N(4)···S(3)	126·8 (5)
N(4)···S(1^{i})	3·335 (4)	C(2)—N(4)···S(1)	99·3 (3)
		C(5)—N(4)···S(1)	119·7 (3)
N(5)···F(5^{iii})	3·073 (9)	C(3)—N(5)···F(5)	128·8 (4)
N(5)···O^{iii}	3·02 (2)	C(3)—N(5)···O	136·4 (5)
N(5)···O^{iv}	2·99 (1)	C(3)—N(5)···O	142·7 (5)
N(6)···S(2)	3·363 (5)	C(3)—N(6)···S(2)	95·5 (3)
		C(6)—N(6)···S(2)	115·9 (4)

Symmetry code: (i) $-x, -y, -z$; (ii) $x-1, y, z$; (iii) $x, y, z-1$; (iv) $-x, 1-y, -z$.

[Tc(Me$_2$tu)$_6$](PF$_6$)$_3$

N(1)···S(3)	3·29 (9)	C(4)—N(1)···S(3)	104·1 (6)
		C(10)—N(1)···S(3)	117·6 (6)
N(2)···F(13^{i})	3·00 (1)	C(4)—N(2)···F(13)	121·0 (7)
		C(9)—N(2)···F(13)	92·0 (7)
N(3)···S(4)	3·32 (1)	C(1)—N(3)···S(4)	104·2 (6)
		C(18)—N(3)···S(4)	125·5 (7)
N(7)···S(1)	3·38 (1)	C(2)—N(7)···S(1)	98·1 (6)
		C(12)—N(7)···S(1)	119·4 (6)
N(8)···F(1)	3·14 (1)	C(2)—N(8)···F(1)	122·5 (7)
		C(11)—N(8)···F(1)	106·1 (6)
N(9)···S(3)	3·35 (1)	C(6)—N(9)···S(3)	95·0 (6)
		C(7)—N(9)···S(3)	116·5 (7)
N(10)···F(8^{ii})	3·13 (1)	C(6)—N(10)···F(8)	136·6 (7)
		C(14)—N(10)—F(8)	97·4 (6)
N(12)···S(2)	3·35 (1)	C(5)—N(12)···S(2)	109·5 (7)
		C(17)—N(12)···S(2)	126·4 (8)

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $1+x, 0·5-y, 0·5+z$.

very high thermal motion especially those around P(2) (Table 2). The P—F distances vary from 1·441 (8) to 1·587 (4) Å with *cis* F—P—F angles ranging from 85·3 (4) to 95·6 (4)°.*

The packing of the ions in the unit cell is shown in Fig. 3. The structure is stabilized by extensive hydrogen bonding (Table 4). There are a few intramolecular hydrogen bonds with distances N(4)···S(3) = 3·359 (5) and N(6)···S(2) = 3·363 (5) Å with angles C(2)—N(4)···S(3) = 103·9 (3), C(5)—N(4)···S(3) = 126·8 (5), C(3)—N(6)···S(2) = 95·5 (3) and C(6)—N(6)···S(2) = 115·9 (4)°. There are a few other intermolecular N···S hydrogen bonds and several between the amines and the F atoms with N···F distances 3·009 (7) to 3·080 (8) Å. The water molecule is also involved in the hydrogen-bonding system *via* N(5) with distances N(5)···O = 2·99 (1) and 3·02 (2) Å.

[Tc(Me$_2$tu)$_6$](PF$_6$)$_3$: The coordination around the Tc atom is octahedral with six independent S-bonded dimethylthiourea ligands. Important distortions are observed in this structure. The *cis* S—Tc—S angles vary from 80·9 (1) to 99·6 (1)° while the *trans* angles are 178·3 (1)–179·3 (1)° (Table 3). Two *cis* Tc—S bonds [2·451 (3) and 2·460 (3) Å] seem longer than the other four [2·426 (3), 2·430 (3), 2·436 (3) and 2·436 (3) Å] but the differences might not be significant. There is no obvious evidence for a tetragonal distortion as observed in the structures of [Tc(thiourea)$_6$]Cl$_3$.4H$_2$O (Abrams *et al.*, 1984) and [Tc(Metu)$_6$](PF$_6$)$_3$.H$_2$O described above. Steric hindrance is quite important in this structure and packing energy might be an even greater factor.

All six dimethylthiourea ligands have the *cis-trans* configuration, with one methyl group oriented away from the Tc atom (the thiocarbonyl bond and the thioamide H atom are *cis*). The second methyl group is located far from the Tc atom (see Fig. 2). This configuration corresponds to minimum repulsion, since a *cis-cis* configuration would lead to a large methyl–methyl interaction and a *trans-trans* configuration would produce repulsion between one methyl group and the Tc atom. The *cis-trans* configuration was also observed in [Cu(Me$_2$tu)$_3$Cl]$^+$ (Girling & Amma, 1971) and in [Pt(Me$_2$tu)$_4$Cl$_2$ (Bachechi *et al.*, 1977). The four atoms S, C, N and N of each ligand are planar. The C atoms from the methyl groups are also almost in the plane with an average deviation of 0·06 (1) Å.* The Tc atom is also not far from these planes with an average deviation of 0·631 (1) Å. The angles between the different planes vary from 13·6 [planes S(1) and S(6)] to 122·6° [planes S(1) and S(5)]. The bond distances and angles in the ligands are shown in Table 3. The average S—C bond distance is 1·73 (1) Å and the C—N bonds are 1·31 (1)–1·38 (1) Å. The N—CH$_3$ bonds vary from 1·45 (1) to 1·51 (1) Å. The C—N—CH$_3$ angles are from 124 to 127° as observed in [Tc(Metu)$_6$]$^{3+}$ described above.

The thermal factors of the F atoms in the PF$_6^-$ anions are very high (Table 2) indicating some disorder that could not be resolved. The P—F distances vary from 1·47 (1) to 1·58 (1) Å with *cis* F—P—F angles ranging from 85·8 (6) to 97·5 (7)°.*

The packing of the molecules in the crystal is shown in Fig. 4. The crystal structure is stabilized by an extensive hydrogen-bonding system. There are several intramolecular hydrogen bonds N—H···S

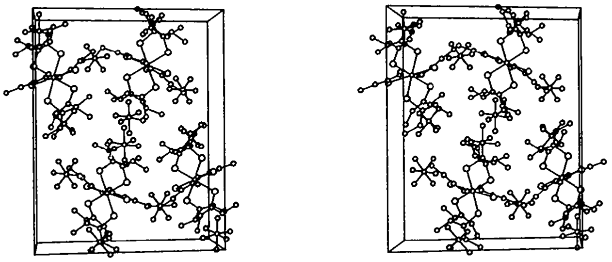

Fig. 4. Stereoscopic view of the molecules in the crystal [Tc(Me$_2$tu)$_6$](PF$_6$)$_3$ (*b* axis vertical, down *a** axis).

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* See deposition footnote.

* See deposition footnote.

with N···S distances from 3·29 (9) to 3·38 (1) Å and favourable C—N···S angles (Table 4). There are also a few hydrogen bonds with the PF_6^- ions with N···F distances from 3·00 (1) to 3·14 (1) Å.

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1,2;2,3;3,1-Tri-μ-carbonyl-1,2,2,3,3,4,4,4-octacarbonyl-1-(triisopropylphosphine)-*tetrahedro*-tetrarhodium(0)

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Abstract. $[Rh_4(CO)_{11}\{P(C_3H_7)_3\}]$, $M_r = 879·9$, monoclinic, $P2_1/c$, $a = 11·057\ (4)$, $b = 15·660\ (17)$, $c = 17·248\ (6)$ Å, $\beta = 74·44\ (1)°$, $V = 2877·1$ Å^3, $Z = 4$, $D_x = 2·031$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 22·8$ cm^{-1}, $F(000) = 1696$, $T = 293$ K, $R = 0·068$ for 2978 observed reflections with $F > 4\sigma(F)$. The Rh atoms form a nearly regular tetrahedron, with Rh—Rh bond lengths in the range 2·692–2·795 (2) Å. The carbonyls retain the C_{3v} arrangement displayed by the parent $[Rh_4(CO)_{12}]$ cluster, with three occupying bridging positions about the basal plane of the metal-atom tetrahedron. The phosphine ligand is coordinated in a basal axial position.

Introduction. The crystal structures of phosphine-substituted tetrahedral tetrarhodium clusters have been reported previously; for example, those of $[Rh_4(CO)_{10}(PPh_3)_2]$ and $[Rh_4(CO)_9\{P(OPh)_3\}_3]$ (Heaton, Longhetti, Mingos, Briant, Minshall, Theobald, Garlaschelli & Sartorelli, 1981), and $[Rh_4(CO)_8\{P(OPh)_3\}_4]$ (Ciani, Garlaschelli, Manassero, Sartorelli & Albano, 1977). However, no examples of phosphine mono-substituted tetrarhodium clusters have been described, so the X-ray crystal structure determination of $[Rh_4(CO)_{11}\{P(C_3H_7)_3\}]$ was undertaken.

Experimental. Dark red tabular air-stable crystals of the compound were prepared from dichloromethane/heptane (Iggo & Jackson, 1988); crystal size 0·35 × 0·30 × 0·15 mm. Approximate cell dimensions and space-group determination by preliminary Weissenberg photography. Intensity data recorded on a Stoe Stadi-2 2-circle diffractometer. 20 $h0l$ reflections, $5 < 2\theta < 30°$, used to determine exact cell parameters, except for b, which was determined by the positions of higher $0k0$ reflections. Crystal mounted along unique b axis, data collected in 17 layers. $2\theta_{\min} = 4°$, $2\theta_{\max} = 40°$, $0 \leq h \leq 12$, $0 \leq k \leq 16$, $-19 \leq l \leq 19$, 4305 reflection intensities measured, ω-scan mode, merging to 3755 unique. One standard reflection on each layer, measured after every 25th reflection; maximum variation in intensity 3%. Empirical absorption correction applied, transmission factors 1·0–0·65. Data reduction performed by program *STOE* (Gould & Taylor, 1986), Rh-atom positions found by automatic Patterson search procedure of *SHELX*86 (Sheldrick, 1986) and used to phase subsequent Fourier syntheses using *SHELX*76 (Sheldrick, 1976), revealing all other non-H-atom positions. Least-squares refinement with *SHELX*76 converged at $R = 0·068$ for 2978 reflections with $F > 4\sigma(F)$, $wR = 0·070$, $w = 1/[\sigma^2(F) + 0·001436F^2]$. All non-H atoms allowed anisotropic vibration param-

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