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Rearrangement of tetramethylthiourea to dimethyldithiocarbamate and crystal structures of $[Tc(O)(C_5H_{12}N_2S)_2((CH_3)_2NCSS)](PF_6)_2$ and $[Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$

Fernande D. Rochon*, Robert Melanson and Pi-Chang Kong
Département de Chimie, Université du Québec à Montréal, C.P. 8888, Succ. A, Montreal, Que., H3C 3P8 (Canada)

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Abstract

The reaction of $[Tc^V(O)(\text{tetramethylthiourea})_4](PF_6)_3$ with bis(diphenylphosphino)ethane (DPPE) in DMF solution produced at least two compounds, which were identified by X-ray diffraction methods as $[Tc^V(O)(\text{tetramethylthiourea})_2((CH_3)_2NCSS)](PF_6)_2$ and $[Tc^{II}(DPPE)_2((CH_3)_2NCSS)](PF_6)$. The bidentate dithiocarbamate ligand was produced from the reaction of bonded tetramethylthiourea in the reaction medium. The crystals of the Tc(V) compound, $[Tc(O)(\text{tetramethylthiourea})_2((CH_3)_2NCSS)](PF_6)_2$ are monoclinic with $P2_1/c$ space group, $a=9.388(4)$, $b=26.745(20)$, $c=11.990(3)$ Å, $\beta=101.62(3)°$ and $Z=4$. The structure was refined to $R=0.059$ and $R_w=0.069$. The geometry around the Tc atom is square pyramidal. The Tc–O bond distance is 1.661(6) Å while the Tc–S bond lengths are 2.328(2) and 2.343(2) Å for tetramethylthiourea and 2.349(2) and 2.353(2) Å for dimethyldithiocarbamate. The crystals of $[Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$ are monoclinic, $P2_1$ space group with $a=11.693(8)$, $b=19.282(7)$, $c=12.148(6)$ Å, $\beta=104.78(5)°$ and $Z=2$. The structure was refined to $R=0.074$ and $R_w=0.063$. The Tc(II) complex has a distorted octahedral geometry. The Tc–P bond distances vary from 2.413(6) to 2.473(6) Å while the Tc–S distances are 2.439(6) and 2.448(7) Å. The bidentate dimethyldithiocarbamate ligand is planar. A mechanism for the formation of the ligand is suggested.

Introduction

The chemistry of technetium has become very important recently especially in relation to the use of the isotope 99m in nuclear medicine. It has been used for several years for bone scanning and recently it has been used to study the heart, the brain, the kidneys, the liver and other organs and also tumor tissue. A good review on medical diagnostic imaging with complexes of ^{99m}Tc was published by Clarke and Podbielski in 1987 [1]. The most recent advances in this area are collected in ref. 2.

We have recently started a project on the synthesis of new technetium compounds. The main objective of our research project is to synthesize mixed-ligand Tc complexes with ligands which could have some interest in the radiopharmaceutical industry. Few mixed-ligand Tc complexes have been reported in the literature. Furthermore, the methods must be simple and adaptable to the use of kits to be useful in the radiopharmaceutical industry. One type of ligand under study in our laboratory is thiourea derivatives. These compounds react with metals in high oxidation states not only as complexing agents but also as reductants. A review on compounds of thiourea and its complexes with metal salts was published a few years ago [3]. The reaction of $NH_4Tc^{VII}O_4$ with thiourea, *N*-methylthiourea and *N,N'*-dimethylthiourea in acidic aqueous solution produces the hexacoordinated Tc(III) compound $[Tc(\text{thiourea})_6]^{3+}$ [4–6]. The crystal structures of the complexes with thiourea, *N*-methylthiourea and *N,N*-dimethylthiourea have been published [5, 6]. In the same experimental conditions, the reaction of $[TcO_4]^-$ with *N,N,N',N'*-tetramethylthiourea (TMT) produces $[Tc^V(O)(TMT)_4]^{3+}$ [4]. The ligand is too bulky to form the hexacoordinated Tc complex. In these reactions, no other reducing agent is used. Therefore, the thiourea ligand acts as reducing agent and can be oxidized. There are several examples in the literature of thiourea being oxidized by metal compounds. One well-documented example is the reaction of OsO_4 with thiourea in dilute acid solution to form $[Os(\text{thiourea})_6]^{3+}$ and formamidine disulfide [7].

The synthesis of mixed-ligand Tc compounds with thiourea derivatives has not yet been reported. In a first attempt, we have synthesized several Tc compounds with different thiourea derivatives and studied their reactions with several monodentate and bidentate phos-

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*Author to whom correspondence should be addressed.

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phines. In most cases, we obtained a mixture of non-crystalline compounds which we were unable to separate or identity. These reactions seem to be much more complicated than anticipated. One reaction gave some crystalline products which we were able to identify and the results of this study will be discussed below.

Experimental

Ammonium pertechnetate ($NH_4{}^{99}TcO_4$) was obtained from Oak Ridge National Laboratory. It was recrystallized in nitric acid (**Caution:** ammonium pertechnetate in acid medium will produce some radioactive volatile compound) and dissolved in water. A solution 0.286 M was prepared. 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). Tetramethylthiourea and DPPE were bought from Aldrich.

$[Tc(O)(TMT)_4](PF_6)_3$

This compound was synthesized according to the method published by Abrams *et al.* [4]. The IR spectrum of the compound was identical to the published one.

$[Tc(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$

$[Tc(O)(TMT)_4](PF_6)_3$ (0.2 g) was dissolved in 10 ml DMF and 0.4 g of DPPE was added to the solution. The solution became brown. The next day, crystals suitable for X-ray diffraction methods were isolated from the dark brown solution. Yield ~30%.

$[Tc(DPPE)_2((CH_3)_2NCSS)]PF_6$

$[Tc(O)(TMT)_4](PF_6)_3$ (0.2 g) and 0.4 g of DPPE were dissolved in 10 ml of DMF. The solution was slowly concentrated to about 2 ml at room temperature. The brown crystals were washed with ether and the solution decanted. The residue was dissolved in ethanol and the solution was left at room temperature for slow evaporation. After a few days, crystals suitable for X-ray diffraction methods were isolated. Yield ~20%.

Crystallographic measurements and structure resolution

The two brown crystals $[Tc(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**) and $[Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (**2**) were selected after examination under a polarizing microscope for homogeneity. The unit cell parameters were obtained by least-squares refinement of the angles 2θ(16–25°), ω and χ for 15 well-centered reflections on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo Kα radiation. Crystal data and other information are summarized in Table 1. Scan rates and data treatment have already been described [8]. Corrections were made for Lorentz–polarization effects and the anomalous dispersion terms of Tc, P and Cl were included in the calculations [9].

TABLE 1. Experimental details of the X-ray diffraction studies of $[TcO(C_5H_{12}N_2C)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**) and $[Tc(DPPE)_2((CH_3)_2NCSS)])PF_6$ (**2**)

	1	**2**
Compound	$C_{13}H_{30}N_5OF_{12}S_4P_2Tc$	$C_{55}H_{54}NS_2P_5F_6Tc$
Formula weight	789.49	1160.94
Space group	$P2_1/c$	$P2_1$
a (Å)	9.388(4)	11.693(8)
b (Å)	26.745(20)	19.282(7)
c (Å)	11.990(3)	12.148(6)
β (°)	101.62(4)	104.78(5)
Volume (Å^3)	2949(3)	2649(2)
Z	4	2
$F(000)$	1584	1190
ρ_{calc} (Mg m^{-3})	1.774	1.455
μ(Mo Kα) (mm^{-1})	0.94	0.54
2θ max (°)	60	50
Octants	$h, k, \pm l$	$h, k, \pm l$
h, k, l	$0 \rightarrow 13, 0 \rightarrow 37, -16 \rightarrow 16$	$0 \rightarrow 13, 0 \rightarrow 22, -14 \rightarrow 13$
Scan technique	$2\theta/\theta$	$2\theta/\theta$
Standard reflections	4 0 −4, 0 7 −1, 0 0 4	0 6 0, 1 2 −2, 3 3 4
No. independent reflections	8658	4837
No. observed reflections	$4936 I_{net} > 2.5\sigma$	$2441 I_{net} > 2.5\sigma$
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_o \rvert \rvert / \Sigma \lvert F_o \rvert$	0.059	0.074
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma \lvert F_o \rvert^2]^{1/2}$	0.069	0.063
Δ/σ(max)	0.45	0.56
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_o \rvert)^2/(m-n)]^{1/2}$	1.70	1.26

The coordinates of the Tc atom were determined from the three-dimensional Patterson maps and the positions of all the other non-hydrogen atoms were found by the usual Fourier methods. The refinements of the structures were done by block-diagonal least-squares analysis minimizing $\Sigma w(|F_o| - |F_c|)^2$. Most H atoms could be located, but they were fixed at their calculated positions with $U_{eq} = 0.076$. For the methyl H atoms, at least one H was obtained from a difference Fourier map and the positions of the remaining atoms were calculated. Individual weights $w = 1/\sigma^2(F)$ were applied. The thermal factors of some of the F atoms in the PF_6^- ions were quite high, but it was not possible to resolve the disorder. Isotropic secondary-extinction corrections [10] were included in the calculations. The refinement of the scale factor, coordinates and anisotropic temperature factors of all the non-hydrogen atoms converged to $R = 0.059$ and $R_w = 0.069$ for **1**, to $R = 0.074$ and $R_w = 0.063$ for **2**. There were a few residual peaks (<0.33 (for **1**) and <0.7 (for **2**) e Å^{-3}) in the close environment of the Tc atom.

The scattering curves of Cromer and Waber [11] were used except for the hydrogen atoms [12]. The calculations were done on a Cyber 830 with programs already described [8]. See also 'Supplementary material'.

Results and discussion

The starting material Tc(V) compound $[Tc(O)(TMT)_4](PF_6)_3$ was synthesized according to the published method [4], from the reaction of TcO_4^- with tetramethylthiourea in acidic aqueous solution. Its reaction with bidentate bis(diphenylphosphino)ethane (DPPE) was studied in DMF in slightly different conditions. In two of these reactions, a brown crystalline product was obtained. The two types of crystals, which had different shapes, were analyzed by X-ray diffraction methods. They were identified as $[Tc^V(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**) and $[Tc^{II}(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (**2**). The first compound **1** is probably an intermediate in the formation of compound **2**. These two complexes contain a bidentate dimethyldithiocarbamate ligand produced from the reaction of bonded tetramethylthiourea. To our knowledge, no such rearrangement of thiourea derivatives has been reported in the literature. Thiourea is known to oxidize to formamidine disulfide in the presence of dilute acid. We do not think at the moment that formamidine disulfide is an intermediate in the conversion of the thiourea derivative to the dithiocarbamate ion. Dithiocarbamate can be activated to thiourea derivatives in certain conditions (for example by 2-halothiazolium salts [13]), but we have not found examples of the reversed reaction. A reaction mechanism is suggested (Fig. 1) for the rearrangement of tetramethylthiourea to the dimethyldithiocarbamate ligand. For this reaction, the presence of water (from the solvent) would be necessary. The solvent (DMF) was not dried for this reaction. Dithiocarbamate Tc complexes have been reported, but they were synthesized with the sodium salt of dialkyldithiocarbamate in the presence of a reducing agent [14–19]. The crystal structures of $Tc^V(N)(diethyldithiocarbamato)_2$ [14], $Tc^{III}(CO)(diethyldithiocarbamato)_3$ [15] and $Tc^{III}(NS)(diethyldithiocarbamato)_2Cl_2$ [17] have been published. These structures are often disordered. For example the first crystal of $Tc^{III}(NS)(diethyldithiocarbamato)_2Cl_2$ [17] was disordered by about 20%, while in the second crystal, the disorder was lower (≈5%). A Tc(IV) complex, $[Tc(PMe_2Ph)(diethyldithiocarbamato)_3(PF_6)$, has been reported, synthesized from $TcCl_3(PMe_2Ph)_3$, but the crystal structure was not determined [20].

The crystal structures of the two dimethyldithiocarbamate Tc compounds which we have studied, are described below.

$[Tc(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$

The refined atomic parameters of the structure are listed in Table 2. A labelled diagram of the molecule is shown in Fig. 2. The bond distances and angles are shown in Table 3. The geometry around the Tc atom is square pyramidal with the O atom located in the apical position. The O–Tc–S angles vary from 107.7(2) to 111.6(2)°, The *cis* S–Tc–S angles range from 83.0(1)–89.8(1)° except for the chelate angle which is 74.0(1)°, while the *trans* angles are 137.5(1) and 141.9(1)°. These values are similar to those observed in the structure of $Tc^V(N)(diethyldithiocarbamate)_2$ [14]. The Tc–O distance is 1.661(6) Å.

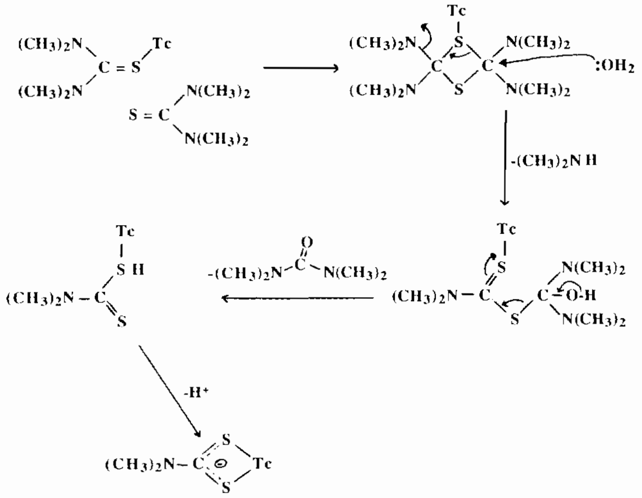

Fig. 1. Suggested reaction mechanism for the formation of dimethyldithiocarbamate.

TABLE 2. Positional parameters (×10^4) with their e.s.d.s and temperature factors (10^4)

Atom	x	y	z	u_{eq}[a]
$[Tc(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**)				
Tc	3000.0(5)	5660.7(2)	5533.4(4)	322
S(1)	4270(2)	6391(1)	6146(1)	380
S(2)	929(2)	6162(1)	4986(1)	410
S(3)	4353(2)	5233(1)	7107(1)	408
S(4)	1352(2)	5124(1)	6179(1)	416
P(1)	8163(2)	873(1)	5045(2)	524
P(2)	3000(3)	2054(1)	2502(2)	639
O(1)	3470(5)	5433(2)	4371(4)	545
F(1)	6956(5)	1271(2)	4506(5)	912
F(2)	9342(5)	1174(2)	4522(5)	945
F(3)	9407(6)	491(2)	5576(5)	1063
F(4)	6981(6)	582(2)	5560(5)	1046
F(5)	7788(7)	549(3)	3939(5)	1345
F(6)	8576(6)	1216(2)	6142(5)	1149
F(7)	2882(9)	1851(3)	3680(5)	1299
F(8)	4668(8)	2141(4)	2899(9)	2044
F(9)	1343(8)	2001(4)	2102(7)	1946
F(10)	3178(10)	2236(3)	1284(6)	1591
F(11)	2790(10)	2600(3)	2890(7)	1533
F(12)	3303(11)	1512(3)	2147(6)	1701
N(1)	2678(6)	4593(2)	8010(5)	443
N(2)	6233(5)	6366(2)	8092(4)	369
N(3)	6914(5)	5956(2)	6559(5)	473
N(4)	868(6)	7122(2)	5514(5)	473
N(5)	2201(6)	6941(2)	4135(5)	492
C(1)	2790(7)	4906(2)	7230(5)	400
C(2)	1270(8)	4383(3)	8120(7)	637
C(3)	3943(9)	4442(3)	8882(7)	633
C(4)	5962(6)	6215(2)	7021(5)	337
C(5)	5110(8)	6553(3)	8658(6)	633
C(6)	7739(7)	6446(3)	8742(6)	572
C(7)	6859(8)	5956(4)	5320(7)	753
C(8)	7960(8)	5611(3)	7220(7)	672
C(9)	1403(6)	6799(2)	4867(5)	367
C(10)	2397(10)	6634(4)	3158(7)	744
C(11)	3164(9)	7370(3)	4320(9)	747
C(12)	518(10)	7635(3)	5153(8)	721
C(13)	360(10)	6980(3)	6529(7)	708
$Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (**2**) (coordinates ×10^4 for Tc, S and P, ×10^3 C, N, and F)				
Tc	375(1)	3000	1779(1)	236
S(1)	1508(6)	2433(4)	3520(6)	630
S(2)	2473(5)	3238(3)	2021(5)	454
P(1)	737(5)	1967(3)	710(5)	332
P(2)	−1519(5)	2409(3)	1579(5)	312
P(3)	−503(5)	3816(3)	300(5)	312
P(4)	336(5)	4007(3)	2985(5)	343
P(5)	5006(10)	5936(5)	2226(8)	1168
N	377(2)	267(1)	394(2)	596
C(1)	−46(2)	134(1)	71(2)	404
C(2)	−165(2)	171(1)	51(2)	390
C(3)	−98(2)	459(1)	99(2)	244
C(4)	0(2)	482(1)	207(2)	433
C(5)	268(2)	277(1)	324(2)	342
C(6)	397(2)	223(2)	498(2)	835
C(7)	480(2)	295(2)	368(2)	787
C(11)	207(2)	147(1)	130(2)	368
C(12)	220(2)	103(1)	224(2)	548
C(13)	325(2)	69(1)	275(2)	654
C(14)	418(2)	75(1)	223(2)	466
C(15)	414(2)	112(2)	131(3)	812
C(16)	302(2)	151(1)	82(2)	759
C(21)	81(2)	211(1)	−78(2)	385
C(22)	146(2)	265(1)	−103(2)	556
C(23)	161(2)	274(1)	−211(2)	557
C(24)	101(2)	233(2)	−297(2)	969
C(25)	34(3)	180(1)	−279(2)	931
C(26)	20(2)	168(1)	−165(2)	476
C(31)	−169(2)	190(1)	282(2)	455
C(32)	−280(2)	182(2)	313(2)	808
C(33)	−288(2)	140(1)	403(2)	773
C(34)	−193(2)	104(1)	462(2)	502
C(35)	−91(2)	108(1)	435(2)	496
C(36)	−71(2)	151(1)	350(2)	676
C(41)	−296(2)	284(1)	113(2)	357
C(42)	−388(2)	255(1)	31(2)	468
C(43)	−496(2)	289(1)	−1(2)	566
C(44)	−516(2)	350(1)	52(2)	492
C(45)	−423(2)	379(1)	139(2)	526
C(46)	−315(2)	345(1)	168(2)	391
C(51)	−187(2)	361(1)	−83(2)	398
C(52)	−287(2)	404(1)	−97(2)	507
C(53)	−394(2)	382(1)	−184(2)	521
C(54)	−390(2)	325(1)	−249(2)	668
C(55)	−286(2)	285(1)	−239(2)	501
C(56)	−183(2)	304(1)	−150(2)	557
C(61)	42(2)	424(1)	−59(2)	341
C(62)	−4(2)	434(1)	−176(2)	451
C(63)	67(2)	468(1)	−233(2)	495
C(64)	186(2)	488(1)	−181(2)	537
C(65)	224(2)	481(1)	−67(2)	511
C(66)	159(2)	446(1)	0(2)	401
C(71)	−71(1)	404(1)	392(2)	389
C(72)	−140(2)	463(1)	397(2)	481
C(73)	−222(2)	461(1)	465(2)	543
C(74)	−234(2)	402(1)	524(2)	685
C(75)	−163(2)	341(1)	522(2)	542
C(76)	−85(2)	342(1)	449(2)	409
C(81)	177(2)	423(1)	406(2)	499
C(82)	266(2)	458(1)	371(2)	493
C(83)	374(2)	470(1)	448(2)	610
C(84)	395(2)	445(1)	561(2)	684
C(85)	307(2)	408(1)	593(2)	611
C(86)	192(2)	398(1)	519(2)	449
F(1)	553(3)	587(1)	350(2)	2551
F(2)	546(3)	668(1)	230(2)	2226
F(3)	456(2)	596(1)	101(2)	1750
F(4)	453(2)	517(1)	227(2)	1520
F(5)	620(2)	569(1)	212(3)	2491
F(6)	395(3)	624(1)	259(4)	3192

[a] $U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

The bond distances Tc–S (TMT) are 2.328(2) and 2.343(2) Å, significantly shorter than the values observed in the three Tc(III) compounds $[Tc(tu)_6]^{3+}$ (tu = thiourea (2.412(1)–2.440(1) Å [5]), *N*-methylthio-

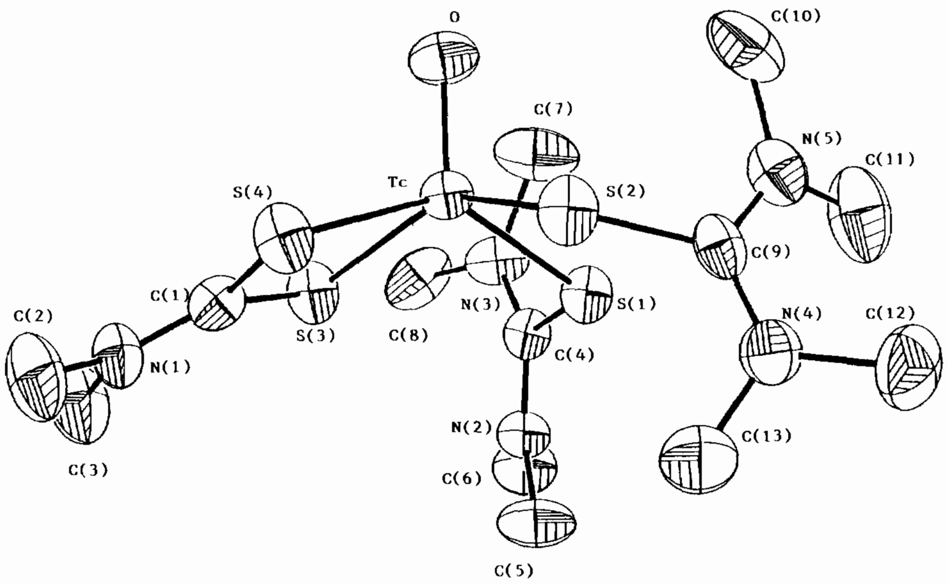

Fig. 2. Labelled diagram of $[Tc(O)(TMT)_2((CH_3)_2NCSS)]^{2+}$ (**1**).

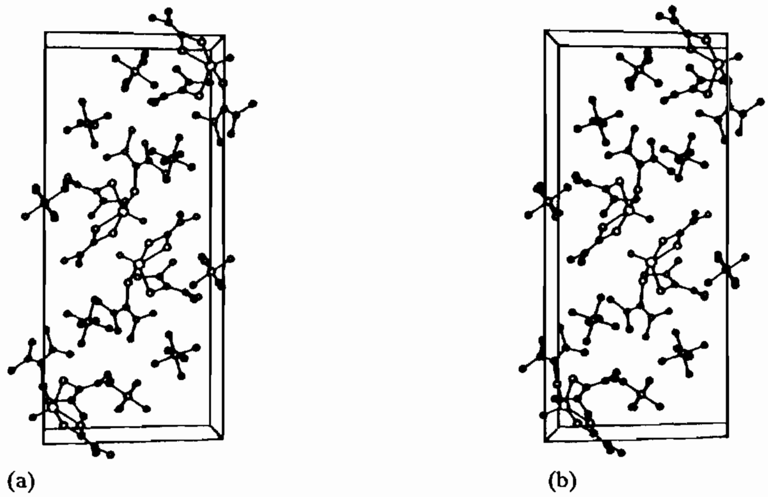

Fig. 3. Stereoscopic view of the unit cell in the crystal $[Tc(O)(TMT)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**) (*b* axis vertical, *c* axis horizontal).

urea (2.419(1)–2.460(1) Å [6]) and *N*,*N*′-dimethylthiourea (2.426(3)–2.460(3) Å [6]). The shorter distances were ascribed to the smaller size of the Tc(V) atom. This crystal structure analysis is the first example of a Tc(V)–thiourea compound. The Tc–S (dimethyldithiocarbamate) bonds are 2.349(2) and 2.353(2) Å, much shorter than the values (2.440(3)–(2.520(3) Å observed in the seven-coordinated Tc(III) compounds Tc(CO)(diethyldithiocarbamate)$_3$ [15] and Tc(NS)(diethyldithiocarbamate)$_2$Cl$_2$ [17]. For the neutral Tc(V) compound, Tc(N)(diethyldithiocarbamate)$_2$ [14], the Tc–S bonds vary from 2.392(2) to 2.405(2) Å, still slightly longer than our values.

The bond distances and angles in the tetramethylthiourea ligands agree well with those found in the three reported complexes [Tc(thiourea derivative)$_6$]$^{3+}$ [5, 6], but there are a few differences. 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 close to the plane (deviation: 0.298(8) to 0.645(9) Å), while the Tc atom is out of the plane by −1.9577(5) and −1.8757(5) Å. The angle between the two planes is 92.1°. The Tc–S–C angles are 107.7(3) and 111.4(3)°, which is slightly smaller than the values observed in the three Tc–thiourea published structures where these values are between 113.9 and 117.7 Å [3, 4]. The N–C–N angles are 123.1(7) and 122.4(8)°, slightly larger than the values (117–121°) observed in the three published structures [5, 6]. These differences are probably caused by steric factors due to the presence of

TABLE 3. Selected bond distances (Å) and angles (°)

$[Tc(O)(C_5H_{12}N_2C)_2((CH_3)_2NCSS)](PF_6)_2$ (**1**)					
Tc–S(1)	2.328(2)	Tc–S(2)	2.343(2)	Tc–S(3)	2.349(2)
Tc–S(4)	2.353(2)	Tc–O	1.661(6)	S(1)–C(4)	1.784(8)
S(2)–C(9)	1.776(9)	S(3)–C(1)	1.740(9)	S(4)–C(1)	1.751(9)
C(1)–N(1)	1.278(11)	N(1)–C(2)	1.47(1)	N(1)–C(3)	1.48(1)
C(4)–N(2)	1.32(1)	C(4)–N(3)	1.34(1)	C(9)–N(4)	1.33(1)
C(9)–N(5)	1.32(1)	N(2)–C(5)	1.46(1)	N(2)–C(6)	1.49(1)
N(3)–C(7)	1.48(1)	N(3)–C(8)	1.46(1)	N(4)–C(12)	1.46(1)
N(4)–C(13)	1.45(1)	N(5)–C(10)	1.48(1)	N(5)–C(11)	1.45(1)
P(1)–F(av.)	1.58(1)	P(2)–F(av.)	1.56(1)		
S(1)–Tc–S(2)	87.2(1)	S(1)–Tc–S(3)	89.8(1)	S(1)–Tc–S(4)	137.5(1)
S(1)–Tc–O	111.6(2)	S(2)–Tc–S(3)	141.9(1)	S(2)–Tc–S(4)	83.0(1)
S(2)–Tc–O	108.6(2)	S(3)–Tc–S(4)	74.0(1)	S3)–Tc–O	107.7(2)
S(4)–Tc–O	110.8(2)	Tc–S(1)–C(4)	107.7(3)	Tc–S(2)–C(9)	111.4(3)
Tc–S(3)–C(1)	89.1(3)	Tc–S(4)–C(1)	88.7(3)	S(3)–C(1)–S(4)	108.2(5)
S(3)–C(1)–N(1)	126.0(7)	S(4)–C(1)–N(1)	125.5(7)	C(1)–N(1)–C(2)	121.7(8)
C(1)–N(1)–C(3)	121.7(8)	C(2)–N(1)–C(3)	116.5(8)	S(1)–C(4)–N(2)	117.8(6)
S(1)–C(4)–N(3)	119.0(6)	S(2)–C(9)–N(4)	116.6(6)	S(2)–C(9)–N(5)	121.0(6)
N(2)–C(4)–N(3)	123.1(7)	N(4)–C(9)–N(5)	122.4(8)	C(4)–N(2)–C(5)	123.1(7)
C(4)–N(2)–C(6)	122.0(7)	C(4)–N(3)–C(7)	121.2(8)	C(4)–N(3)–C(8)	122.3(8)
C(9)–N(4)–C(12)	121.8(8)	C(9)–N(4)–C(13)	123.3(8)	C(9)–N(5)–C(10)	123.2(8)
C(9)–N(5)–C(11)	122.9(8)	C(5)–N(2)–C(6)	114.0(7)	C(7)–N(3)–C(8)	115.5(8)
C(12)–N(4)–C(13)	114.1(8)	C(10)–N(5)–C(11)	113.1(8)		
$[Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (**2**)					
Tc–S(1)	2.448(7)	Tc–S(2)	2.439(6)	Tc–P(1)	2.473(6)
Tc–P(2)	2.447(6)	Tc–P(3)	2.413(6)	Tc–P(4)	2.441(6)
S(1)–C(5)	1.64(2)	S(2)–C(5)	1.69(2)	C(5)–N	1.36(2)
N–C(6)	1.48(3)	N–C(7)	1.43(3)	P(1)–C(1)	1.85(2)
P(1)–C(11)	1.81(2)	P(1)–C(21)	1.85(2)	P(2)–C(2)	1.85(2)
P(2)–C(31)	1.86(2)	P(2)–C(41)	1.83(2)	P(3)–C(3)	1.86(2)
P(3)–C(51)	1.86(2)	P(3)–C(61)	1.89(2)	P(4)–C(4)	1.90(2)
P(4)–C(71)	1.87(2)	P(4)–C(81)	1.89(2)	C(1)–C(2)	1.53(3)
C(3)–C(4)	1.58(3)	P(5)–F(av.)	1.52(3)	C–C(av.)	1.40(3)
P(1)–Tc–P(2)	81.1(2)	P(1)–Tc–P(3)	103.4(2)	P(1)–Tc–P(4)	171.3(2)
P(1)–Tc–S(1)	88.1(2)	P(1)–Tc–S(2)	85.0(2)	P(2)–Tc–P(3)	91.6(2)
P(2)–Tc–P(4)	105.9(2)	P(2)–Tc–S(1)	98.9(2)	P(2)–Tc–S(2)	163.1(2)
P(3)–Tc–P(4)	81.8(2)	P(3)–Tc–S(1)	165.6(2)	P(3)–Tc–S(2)	101.0(2)
P(4)–Tc–S(1)	85.7(2)	P(4)–Tc–S(2)	87.2(2)	S(1)–Tc–S(2)	71.0(2)
Tc–S(1)–C(5)	86.4(7)	Tc–S(2)–C(5)	85.5(7)	Tc–P(1)–C(1)	107.5(7)
Tc–P(1)–C(11)	117.6(7)	Tc–P(1)–C(21)	116.4(7)	Tc–P(2)–C(2)	108.7(7)
Tc–P(2)–C(31)	116.6(7)	Tc–P(2)–C(41)	123.6(7)	Tc–P(3)–C(3)	107.9(6)
Tc–P(3)–C(51)	122.2(7)	Tc–P(3)–C(61)	120.6(7)	Tc–P(4)–C(4)	109.7(7)
Tc–P(4)–C(71)	120.3(7)	Tc–P(4)–C(81)	116.7(7)	S(1)–C(5)–S(2)	117(1)
P(1)–C(1)–C(2)	111(1)	P(2)–C(2)–C(1)	108.9(8)	P(3)–C(3)–C(4)	111(1)
P(4)–C(4)–C(3)	105(1)	S(1)–C(5)–N	121(1)	S(2)–C(5)–N	122(1)
C(5)–N–C(6)	123(2)	C(5)–N–C(7)	121(2)	C(6)–N–C(7)	117(2)
C(1)–P(1)–C(11)	103(1)	C(1)–P(1)–C(21)	109(1)	C(11)–P(1)–C(21)	103(1)
C(2)–P(2)–C(31)	100(1)	C(2)–P(2)–C(41)	103(1)	C(31)–P(2)–C(41)	102(1)
C(3)–P(3)–C(51)	102(1)	C(3)–P(3)–C(61)	101(1)	C(51)–P(3)–C(61)	100(1)
C(4)–P(4)–C(71)	105(1)	C(4)–P(4)–C(81)	103(1)	C(71)–P(4)–C(81)	100(1)

two methyl groups on each N atom in the TMT complex. The terminal C–N–C angles vary from 113.1(8) to 115.5(8)° while the non-terminal values are 121.8(8)–123,1(7)°.

The geometry of the dimethyldithiocarbamate ligand is similar to the one observed in $Tc^V(N)(diethyldithiocarbamato)_2$ [14], $Tc^{III}(CO)(diethyldithiocarbamato)_3$ [15] and $Tc^{III}(NS)(diethyldithiocarbamato)_2\ Cl_2$ [17]. The Tc–S–C angles are 89.1(3) and 88.7(3)° while the S–C–S angle is 108.2(5)°. The S–C bond distances (1.740(9)–1.751(9) Å) are slightly shorter than those observed in the thiourea ligands. The C(1)–N(1) distance is also shorter (1.278(11) Å) than a normal single bond confirming the multiple nature of the bonds around the C(1) atom. Similar values were observed in the Tc–diethyldithiocarbamate compounds [14, 15, 17].

The thermal factors of the F atoms in the PF_6^- anions are very high. The disorder could not be resolved. This is quite usual for these types of anions. We can see the packing of the ions in the crystal (Fig. 3). No hydrogen bond is expected in this compound. The different ions are held together only by van der Waals forces.

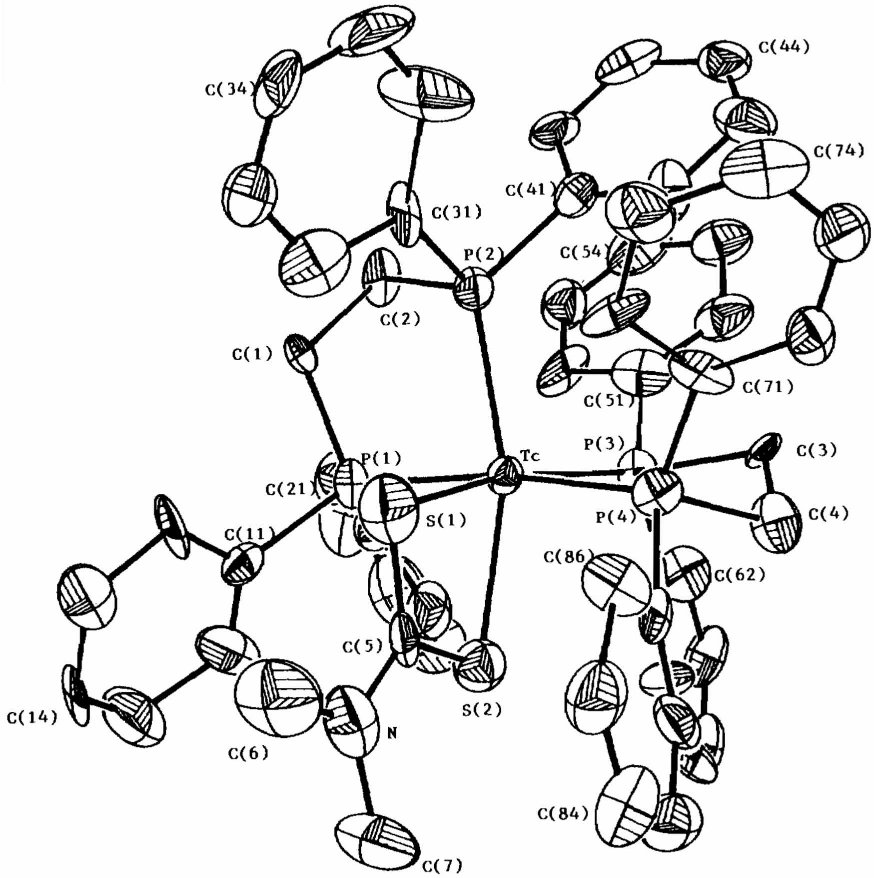

Fig. 4. Labelled diagram of $[Tc(DPPE)_2((CH_3)_2NCSS)]^+$ (2).

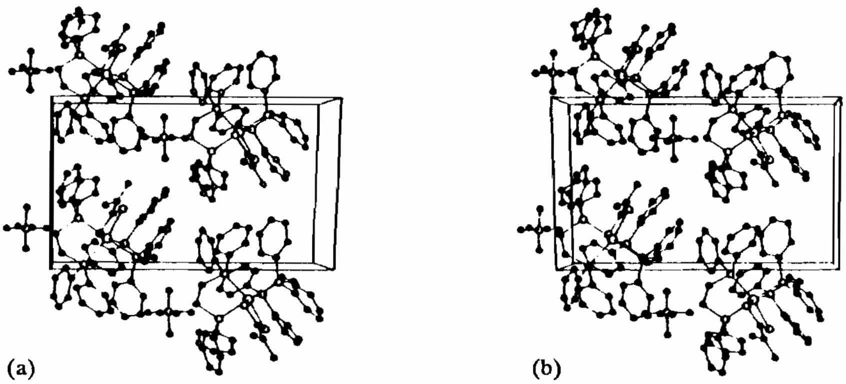
(a) (b)

Fig. 5. Stereoscopic view of the packing in the unit cell for the crystal $[Tc(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (2) (*c* axis vertical, *b* axis horizontal).

$Tc^{II}(DPPE)_2((CH_3)_2NCSS)](PF_6)$ (2)

A labelled diagram of the Tc(II) compound is shown in Fig. 4. The geometry around the Tc atom is a distorted octahedron. The Tc–S bond distances are longer (2.439(6) and 2.448(7) Å) than in the above Tc(V) compound which is probably normal for a Tc(II) compound. Very few Tc(II) complexes have been reported. The chelate angle S(1)–Tc–S(2) is small (71.0(2)°) as expected in a four-membered ring chelate. The Tc–S–C angles are 85.5(7) and 86.4(7)° while the S–C–S angle is 117(1)°. The latter is larger than in the above compound (108.2(5)°) probably because of the smaller strain inside the four-membered ring, caused by the longer Tc–S bond distances. The dimethyldithiocarbamate ligand is planar with S–C(5) distances of 1.64(2) and 1.69(2) Å and the C(5)–N bond is 1.36(2) Å.

The Tc–P bond distances vary from 2.413(6) to 2.473(6) Å. These distances are quite short for a Tc(II) compound. Tc(II) can be considered as a soft metal and phosphines are capable of back-acceptance of electrons from metal atoms in low oxidation states. Therefore the order of the Tc–P bond might be greater for Tc in the lower oxidation states. Another factor for the short Tc–P bond might be the d^5 configuration of Tc(II) which contains 5 electrons in the lower energy orbitals (t_{2g} in an octahedral field) with only one unpaired electron. The chelate P–Tc–P angles are 81.0(2) and 81.8(2)° while the other *cis* angles are larger than 90°. The average P–C distance is 1.86(2) Å. The angles around the P atom are close to the tetrahedral value for the Tc–P–C(ethane) angles (av. 108.5(7)°, but are larger for the Tc–P–C(phenyl) angles (av. 119.3(7)°) due to the bulkiness of the phenyl groups. The average C–C bond distance in the phenyl groups is 1.40(3) Å, with an average C–C–C angle of 120(2)°.

The PF_6^- anions show again very high thermal motion. The average P(5)–F bond distance is 1.52(2) Å. The packing of the ions inside the unit cell is shown in Fig. 5. No hydrogen bonding is expected in this compound. The packing consists of alternate layers of complexed ions and PF_6^- anions, parallel to the *ac* plane. The different layers are held together only by van der Waals forces.

Supplementary material

Lists of anisotropic temperature factors (Table S1), hydrogen coordinates (Table S2), bond distances and angles (Table S3), weighted best least-squares planes (Table S4) and observed and calculated structure amplitude (Table S5) can be obtained from the authors.

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References

1 M. J. Clarke and L. Podbielski. Coord. Chem. Rev., 78 (1987) 253.

2 M. Nicolini, G. Bandoli and U. Mazzi (eds.), *Technetium and Rhenium in Chemistry and Nuclear Medicine,* Raven Press, New York, 1990.

3 N. V. Vorob'ev-Desyatovskii, Yu. N. Kukushkin and V. V. Sibirskaya, *Sov. J. Coord. Chem.,* (1986) 741.

4 M. J. Abrams, D. Brenner, A. Davison and A. G. Jones, *Inorg. Chim. Acta, 77* (1983) L127.

5 M. J. Abrams, A. Davison, R. Faggiani, A. G. Jones and C. J. L. Lock, *Inorg. Chem., 23* (1984) 3284.

6 F. D. Rochon, R. Melanson and P. C. Kong, *Acta Crystallogr., Sect. C, 46* (1990) 571.

7 R. D. Sauerbrunn and E. B. Sandell, *J. Am. Chem. Soc., 75* (1953) 3554.

8 R. Melanson and F. D. Rochon, *Can. J. Chem., 53* (1975) 2371.

9 D. T. Cromer, *Acta Crystallogr., 18* (1965) 17.

10 P. Coppens and W. Hamilton, *Acta Crystallogr., Sect. A, 26* (1970) 71.

11 W. T. Cromer and J. T. Waber, *Acta Crystallogr., 18* (1965) 104.

12 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42* (1965) 3175.

13 H. Sugimoto, I. Makino and K. Hirai, *J. Org. Chem., 53* (1988) 2263.

14 J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams and M. F. Mackay, *J. Chem. Soc., Dalton Trans.,* (1981) 1798.

15 J. Baldas, J. Bonnyman, P. M. Pojer, G. A. Williams and M. F. Mackay, *Chem. Soc., Dalton Trans.,* (1982) 451.

16 U. Abrams and H. Spies, *Inorg. Chim. Acta, 94* (1984) L3.

17 J. Baldas, J. Bonnyman, M. F. Mackay and G. A. Williams, *Aust. J. Chem., 37* (1984) 751.

18 J. Baldas and P. M. Pojer, *Int. J. Nucl. Med. Biol., 11* (1984) 1159.

19 P. M. Pojer and J. Baldas, *Int. J. Nucl. Med. Biol., 8* (1981) 112.

20 M. Findeisen, N. Lorenz and B. Olk, *Z. Chem., 27* (1987) 447.