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Mixed-Ligand Complexes of Technetium. XIV. Structure of *trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$]

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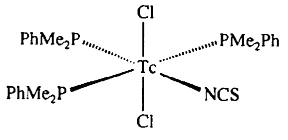
Abstract

mer-[TcCl$_3$(Me$_2$PhP)$_3$] reacts with potassium thiocyanate with the replacement of only one Cl$^-$ ligand by NCS$^-$ and forms selectively (*OC*-6-12)-dichlorotris(dimethylphenylphosphine)(thiocyanato-κN)-technetium(III) {*mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$]}. No evidence could be found for the formation of the *cis* analogue. The title compound crystallizes in monomeric units. The Tc atom is coordinated in a distorted octahedral manner with the two Cl ligands in *trans* positions to each other. The NCS$^-$ ligand is N-bonded with a Tc—N bond length of 2.104 (3) Å.

Comment

Coordination compounds of technetium with the metastable γ-emitting ^{99m}Tc (E_γ = 140 keV, half-life $t_{1/2}$ = 6 h) are frequently used in diagnostic nuclear medicine (Clarke & Podbielski, 1987). This has also encouraged the development of the basic coordination chemistry of the artificial element (Baldas, 1994). Most chemical studies are carried out with the long-lived β-emitting isotope ^{99}Tc ($E_{\max}$ = 0.29 MeV, $t_{1/2}$ = 2.12 × 10^5 years) which is available from fission products in macroscopic amounts.

In the course of our systematic studies on mixed-ligand complexes of technetium, we studied the ligand-exchange behaviour of trichlorotris(dimethylphenylphosphine)technetium(III). *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$], (I), is formed by refluxing *mer*-[TcCl$_3$(Me$_2$PhP)$_3$] with an excess of KSCN in methanol. No products with larger NCS$^-$ contents could be isolated in crystalline form (even using a larger excess of KSCN). Significantly longer refluxing periods result in the decomposition of the technetium(III) complex and the formation of dark oily products that could not be structurally characterized.



(I)

The title compound is readily soluble in organic solvents such as CH$_2$Cl$_2$ or CHCl$_3$ and moderately soluble in alcohols. It is indefinitely stable in air as a solid and in solution. The IR spectrum of the compound shows an intense band for the ν(NCS) vibration at 2076 cm^{-1}. This is in good agreement with the spectrum of the rhenium analogue *mer,trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] which has recently been structurally characterized (Hübener, Ortner, Strähle& Abram, 1995). Interestingly, the rhenium compound undergoes an isomerization to the *cis* isomer when refluxed in CH$_2$Cl$_2$/methanol for a longer period. This could not be observed for *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$].

Crystals of *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$] were obtained from a CH$_2$Cl$_2$/methanol solution. The structure consists of neutral monomeric technetium(III) complexes with N-bonded NCS$^-$ ligands. The reorientation matrix $\bar{1}00/\bar{1}0\bar{2}/0\bar{1}0$ gives a metrically *C*-centred orthorhombic cell with a = 14.997, b = 35.263, c = 10.840 Å, but the $R_{\rm int}$ value (0.59) for this Laue symmetry is too high. Fig. 1 shows a representation of the structure of the molecule together with the atom-numbering scheme.

The Tc atom is octahedrally coordinated with the phosphine ligands in meridional positions, but distortions from the idealized octahedral geometry are evident. Angles P1—Tc—P2 and P2—Tc—P3 of 94.79 (4) and 99.14 (4)°, respectively, are much larger than the N1—Tc—P1 [82.09 (9)°] and N1—Tc—P3 [84.14 (9)°] angles. The geometry of *mer,trans*-[TcCl$_2$(NCS)(Me$_2$PhP)$_3$] is thus similar to that of the analogous rhenium complex *mer,trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] (Hübener *et al.*, 1995) and that of [TcNCl$_2$(Me$_2$PhP)$_3$] (Batsanov, Struchkov, Lorentz & Olk, 1988). The linear NCS$^-$ ligand [N—C—S 179.1 (4)°] is coordinated in the *trans* position to Me$_2$PhP. In accordance with all other struc-

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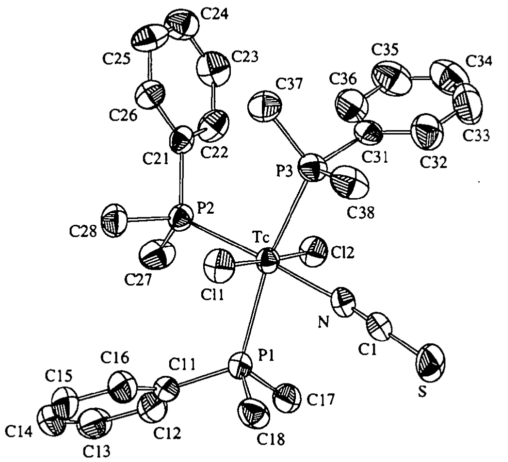

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of *mer,trans*-[$TcCl_2(NCS)(Me_2PhP)_3$] showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

turally characterized NCS^- complexes of technetium (Baldas, 1994), the pseudohalide ligand is bonded *via* the N-donor atom. The Tc—N bond length of 2.104 (3) Å is somewhat longer than observed for [$Tc^{II}(NCS)_2(dppe)_2$] [dppe = bis(diphenylphosphino)ethane] (mean value 2.041 Å; Bandoli *et al.*, 1984), the [$Tc^{III}(NCS)_6$]$^{3-}$ anion (2.045 Å; Trop *et al.*, 1980), the technetium(IV) anion [$Tc(NCS)_6$]$^{2-}$ (mean value 2.005 Å; Williams, Bonnyman & Baldas, 1987) and *trans,trans*-[$Tc^VN(NCS)_2(Ph_3P)_2(CH_3CN)$] (mean value 2.057 Å; Baldas, Bonnyman & Williams, 1984). This can be interpreted in terms of a structural *trans* influence of the Me_2PhP ligand, which labilizes the Tc—N bond in *mer,trans*-[$TcCl_2(NCS)(Me_2PhP)_3$]. A longer Tc—NCS bond distance has been reported for the anion [$Tc^VO(CN)_4(NCS)$]$^{2-}$ (2.162 Å; Rood, Leipoldt, Deutsch & Sullivan, 1992) where the isothiocyanate is positioned *trans* to O^{2-}, a multi-bonded ligand that exerts a strong *trans* labilizing influence.

The bond lengths within the isothiocyanate ligand together with the Tc—N1—C1 angle of 171.3 (3)° suggest the preference of the mesomeric form Tc—N═C—S. This is in line with the bonding situation in the other structurally characterized isothiocyanato complexes of technetium (Baldas, 1994).

Experimental

62 mg of *mer*-[$TcCl_3(Me_2PhP)_3$] was dissolved in 20 ml of CH_2Cl_2 and a fivefold excess of KSCN in 20 ml of methanol was added. The mixture was refluxed for 1 h and the precipitated KCl was removed by filtration. Upon standing overnight, orange–red crystals of *trans*-[$TcCl_2(NCS)(Me_2PhP)_3$] were formed, which were filtered off and washed with water and methanol. Yield: 45 mg (70% based on Tc). All synthetic operations were carried out in a fume cupboard using gloves to avoid contamination. The weak β emission of ^{99}Tc is stopped by the glass of the reaction vessels. Secondary X-rays (*bremsstrahlung*) only become important if handling larger amounts of ^{99}Tc.

Crystal data

[$TcCl_2(NCS)(C_8H_{11}P)_3$]
M_r = 641.39 (based on ^{99}Tc)
Monoclinic
$P2_1/n$
a = 14.997 (7) Å
b = 10.840 (2) Å
c = 19.160 (8) Å
β = 113.04 (2)°
V = 2866 (2) Å^3
Z = 4
D_x = 1.486 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.79–13.58°
μ = 0.944 mm^{-1}
T = 213 (2) K
Plate
0.25 × 0.2 × 0.1 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (Frenz, 1983)
T_{min} = 0.976, T_{max} = 1.000
8402 measured reflections
7582 independent reflections
4918 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0351
θ_{max} = 28.93°
$h = -1 \rightarrow 20$
$k = 0 \rightarrow 14$
$l = -26 \rightarrow 24$
3 standard reflections monitored every 200 reflections
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0491
$wR(F^2)$ = 0.0891
S = 1.155
7578 reflections
430 parameters
H atoms refined freely
$w = 1/[\sigma^2(F_o^2) + (0.0044P)^2 + 3.102P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.002
$\Delta\rho_{max}$ = 0.531 e Å^{-3}
$\Delta\rho_{min}$ = −0.658 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Tc	0.31846 (2)	0.18675 (3)	0.05073 (2)	0.02523 (8)
Cl1	0.18397 (8)	0.31718 (11)	0.02170 (6)	0.0392 (2)
Cl2	0.44655 (7)	0.04947 (9)	0.07820 (6)	0.0348 (2)
P1	0.35880 (8)	0.28942 (9)	−0.04878 (6)	0.0280 (2)
P2	0.21690 (8)	0.02802 (10)	−0.03369 (6)	0.0282 (2)
P3	0.29081 (8)	0.13616 (11)	0.16703 (6)	0.0329 (3)
N	0.4114 (2)	0.3234 (3)	0.1193 (2)	0.0324 (8)
S	0.51189 (10)	0.52736 (11)	0.19781 (7)	0.0531 (4)
C1	0.4524 (3)	0.4077 (4)	0.1520 (2)	0.0318 (9)
C11	0.2924 (3)	0.2648 (4)	−0.1499 (2)	0.0321 (9)
C12	0.3308 (4)	0.1978 (5)	−0.1935 (3)	0.0457 (12)
C13	0.2753 (5)	0.1810 (6)	−0.2700 (3)	0.060 (2)
C14	0.1843 (5)	0.2268 (6)	−0.3025 (3)	0.067 (2)
C15	0.1462 (4)	0.2933 (6)	−0.2607 (3)	0.062 (2)
C16	0.1998 (3)	0.3122 (5)	−0.1838 (3)	0.0435 (11)
C17	0.4839 (3)	0.2633 (5)	−0.0336 (3)	0.0396 (11)
C18	0.3524 (4)	0.4564 (4)	−0.0430 (3)	0.0414 (12)

C21	0.1948 (3)	−0.1174 (4)	0.0055 (2)	0.0287 (9)
C22	0.2689 (3)	−0.2034 (5)	0.0335 (3)	0.0402 (11)
C23	0.2545 (4)	−0.3162 (5)	0.0611 (3)	0.0456 (12)
C24	0.1655 (4)	−0.3455 (4)	0.0607 (3)	0.0434 (12)
C25	0.0913 (4)	−0.2625 (5)	0.0332 (3)	0.0455 (12)
C26	0.1056 (3)	−0.1497 (4)	0.0059 (2)	0.0342 (10)
C27	0.2621 (5)	−0.0326 (5)	−0.1020 (3)	0.0458 (13)
C28	0.0957 (4)	0.0790 (5)	−0.0943 (3)	0.0411 (11)
C31	0.3806 (3)	0.0369 (4)	0.2358 (2)	0.0325 (10)
C32	0.4451 (4)	0.0785 (5)	0.3054 (3)	0.0521 (14)
C33	0.5116 (4)	−0.0019 (6)	0.3558 (3)	0.061 (2)
C34	0.5142 (4)	−0.1222 (6)	0.3361 (3)	0.060 (2)
C35	0.4521 (5)	−0.1652 (5)	0.2672 (3)	0.0579 (15)
C36	0.3854 (4)	−0.0860 (5)	0.2176 (3)	0.0475 (13)
C37	0.1760 (4)	0.0676 (6)	0.1578 (3)	0.0483 (13)
C38	0.2914 (5)	0.2751 (5)	0.2199 (3)	0.0502 (14)

Table 2. *Selected geometric parameters (Å, °)*

Tc—N	2.104 (3)	Tc—P1	2.4784 (13)
Tc—Cl2	2.3216 (13)	Tc—P3	2.4823 (14)
Tc—Cl1	2.3449 (13)	N—C1	1.142 (5)
Tc—P2	2.4430 (12)	S—C1	1.624 (4)
N—Tc—Cl2	91.29 (10)	P2—Tc—P1	94.79 (4)
N—Tc—Cl1	91.25 (10)	N—Tc—P3	84.14 (9)
Cl2—Tc—Cl1	177.21 (4)	Cl2—Tc—P3	93.96 (4)
N—Tc—P2	176.32 (9)	Cl1—Tc—P3	85.16 (4)
Cl2—Tc—P2	86.84 (5)	P2—Tc—P3	99.14 (4)
Cl1—Tc—P2	90.69 (5)	P1—Tc—P3	165.16 (4)
N—Tc—P1	82.09 (9)	C1—N—Tc	171.3 (3)
Cl2—Tc—P1	91.88 (4)	N—C1—S	179.1 (4)
Cl1—Tc—P1	89.61 (4)		

Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*, *SDP* (Frenz, 1983), *HKL* (Kretschmar, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trimethyl(1-methyl-4-phenylpiperazine-N^1)aluminium

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Abstract

The X-ray single-crystal structure determination of the title compound, $[Al(CH_3)_3(C_{11}H_{16}N_2)]$, reveals that the Al atom is four-coordinate in a distorted tetrahedral environment and is bonded to the N atom of the piperazine molecule carrying the methyl group, with an Al—N bond length of 2.050 (2) Å. The piperazine ring adopts a chair conformation.

Comment

Alkylaluminium compounds have been used extensively as one of the major precursors in the preparation of semiconductor compounds by metal–organic chemical vapour deposition (MOCVD). Recently, there has been increasing interest in the preparation of alkylaluminium complexes with N or P donor ligands, which are either used directly as MOCVD precursors or applied in