The reaction of $TcCl_3(Me_2PhP)_3$ with dithio ligands. Synthesis, characterization and X-ray crystal structures of $[TcCl_2(Me_2PhP)_2(Me_2dtp)]$ and $[Tc(Me_2PhP)(Etxan)_3]$ (Me_2PhP = dimethylphenylphosphine, Me_2dtp^- = *O,O'*-dimethyldithiophosphate, $Etxan^-$ = ethylxanthate)

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Abstract

Trichlorotris(dimethylphenylphosphine)technetium(III), $[TcCl_3(Me_2PhP)_3]$, reacts with dithio ligands to form chelate complexes of different compositions and coordination geometries. The reaction with ethylxanthate ($Etxan^-$) yields the diamagnetic seven-coordinate $[Tc(Me_2PhP)(Etxan)_3]$, which crystallizes monoclinic in the space group $P2_1/c$ with $Z=4$ ($a=18.44(5)$, $b=9.2(1)$, $c=15.36(6)$ Å, $\beta=104.3(2)°$). The final R value is 0.029. The metal has a pentagonal-bipyramidal environment. With ammonium dimethyldithiophosphate, $(NH_4)Me_2dtp$, $[TcCl_3(Me_2PhP)_3]$ forms the paramagnetic $[TcCl_2(Me_2PhP)_2(Me_2dtp)]$ in which the technetium atom has a distorted octahedral coordination sphere. The compound crystallizes orthorhombic, space group *Pbcn*, with $Z=4$ ($a=16.207(1)$, $b=10.445(1)$, $c=14.878(1)$). The final R value is 0.031. The chloro ligands are in *trans* arrangement.

Introduction

The widespread use of the metastable ^{99m}Tc (γ-emitter with $E_\gamma=140$ keV, half-lifetime $t_{1/2}=6$ h) in diagnostic nuclear medicine [1, 2] also encourages the development of the basic coordination chemistry of this artifical element [3, 4]. Most chemical studies are done with the long-lived β-emitting isotope ^{99}Tc ($E_{max}=0.29$ MeV, $t_{1/2}=2.12\times10^5$ years) which is available in macroscopic amounts from fission products.

Recently, Nicholson *et al.* [5] reported the synthesis of $[Tc(Ph_3P)(Buxan)_3]$ ($Buxan^-$ = n-butylxanthate) from $TcOCl_4^-$, Ph_3P and excess K(Buxan). This seven-coordinate compound has a capped-octahedral structure which is in contrast to the pentagonal-bipyramidal environment of technetium in $[Tc(Me_3PhP)(Et_2dtc)_3]$ (Et_2dtc^- = diethyldithiocarbamate) [6, 7].

Here, we describe the synthesis, characterization and X-ray crystal structures of the products which result from ligand exchange reactions of $[TcCl_3(Me_2PhP)_3]$ with potassium ethylxanthate and ammonium dimethyldithiophosphate.

Experimental

Health precautions

All work involving ^{99}Tc was done in laboratories approved for the use of low levels of radioactive materials. Use of milligramm quantities of ^{99}Tc does not present a health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem with small quantities due to the low energy of the beta particle emission, but normal radiation safety procedures must be used at all times to prevent contamination.

Synthesis

$[TcCl_3(Me_2PhP)_3]$ was prepared following a literature procedure [8]. All manipulations were carried out in an atmosphere of dry nitrogen.

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TABLE 1. Crystal data collection and structure refinement parameters

	[Tc(Me_2PhP)(Etxan)$_3$]	[TcCl_2(Me_2PhP)$_2$(Me_2dtp)]
Crystal dimensions (mm)	03.×0.2×0.2	0.25×0.3×0.3
Formula	$C_{17}H_{26}O_3PS_6Tc$	$C_{18}H_{28}Cl_2O_2P_3S_2Tc$
Molecular weight	599.75	588.27
Space group	monoclinic $P2_1/c$	orthorhombic *Pbcn*
Lattice dimensions		
a (Å)	18.44(5)	16.207(1)
b (Å)	9.2(1)	10.445(1)
c (Å)	15.36(6)	14.878(1)
α (°)	90	90
β (°)	104.3(2)	90
γ (°)	90	90
V (Å^3)	2522.5	2518.4
D_c (g cm^{-3})	1.420	1.551
Radiation used (λ)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Scan type	ω/θ	ω/θ
Total unique data	6210	6580
Observed data ($I>3\sigma(I)$)	4467	2046
No. parameters	254	174
R	0.029	0.030
R_w	0.029	0.035
Programs used	SDP [9]	SDP [9]

TABLE 2. Fractional positional parameters for [Tc(Me_2PhP)(Etxan)$_3$]

Atom	x	y	z
Tc	0.27540(1)	0.11132(3)	0.12350(2)
P	0.20670(5)	0.0819(1)	0.23268(6)
S1	0.34405(4)	0.1181(1)	0.00449(5)
S2	0.25008(4)	−0.1113(1)	0.03512(5)
S3	0.36113(5)	−0.0711(1)	0.20948(6)
S4	0.38263(5)	0.2276(1)	0.23044(6)
S5	0.24716(4)	0.3757(1)	0.10558(6)
S6	0.15416(5)	0.1551(1)	0.01697(7)
O12	0.3169(1)	−0.1263(3)	−0.0954(1)
O22	0.4745(1)	0.0309(3)	0.3308(2)
O32	0.1158(1)	0.4271(3)	−0.0127(2)
C11	0.3071(2)	−0.0453(4)	−0.0275(2)
C13	0.3619(2)	−0.0681(5)	−0.1535(2)
C14	0.4414(2)	−0.1118(7)	−0.1201(3)
C21	0.4142(2)	0.0625(4)	0.2662(2)
C23	0.5183(2)	0.1499(5)	0.3788(3)
C24	0.5843(3)	0.0846(6)	0.4431(4)
C31	0.1664(2)	0.3353(4)	0.0328(2)
C33	0.1303(2)	0.5831(4)	0.0013(2)
C34	0.0643(2)	0.6604(4)	−0.0565(3)
C41	0.1489(2)	−0.0819(4)	0.2219(2)
C42	0.1772(2)	−0.2083(4)	0.2645(3)
C43	0.1348(3)	−0.3333(5)	0.2572(3)
C44	0.0630(2)	−0.3344(5)	0.2071(3)
C45	0.0339(2)	−0.2121(7)	0.1634(3)
C46	0.0758(2)	−0.0851(6)	0.1698(3)
C47	0.1404(3)	0.2254(5)	0.2421(3)
C48	0.2593(2)	0.0712(5)	0.3502(2)

TABLE 3. Fractional positional parameters for [TcCl_2(Me_2PhP)$_2$(Me_2dtp)]

Atom	x	y	z
Tc1	0.000	0.33228(4)	0.250
Cl1	−0.14412(6)	0.3186(1)	0.26169(7)
S1	−0.00500(9)	0.51363(9)	0.14311(7)
P1	0.000	0.6282(1)	0.250
P2	0.00198(8)	0.17978(9)	0.12790(6)
O1	−0.0718(2)	0.7301(3)	0.2529(3)
C1	−0.1561(3)	0.6882(6)	0.2513(5)
C2	0.0587(3)	0.0309(4)	0.1432(3)
C3	0.0539(3)	0.2439(5)	0.0295(3)
C11	−0.0984(3)	0.1302(4)	0.0852(3)
C12	−0.1384(3)	0.2045(4)	0.0207(3)
C13	−0.2149(3)	0.1686(6)	−0.0125(4)
C14	−0.2520(3)	0.0579(6)	0.0188(4)
C15	−0.2146(3)	−0.0139(5)	0.0831(4)
C16	−0.1374(3)	0.0206(5)	0.1163(3)

Parameters of the symmetry-related atoms can be generated by the symmetry operation $-x$, y, $0.5-z$.

[Tc(Me_2PhP)(Etxan)$_3$]

320 mg (2 mmol) KEtxan were dissolved in 30 ml tetrahydrofuran and 310 mg (0.5 mmol) solid [TcCl_3(Me_2PhP)$_3$] were added. The mixture was stirred under reflux for 1 h and the solvent was reduced to about 2 ml. 10 ml of n-hexane were added. Upon standing overnight large, dark red crystals result which were collected, washed with a small amount of dry n-hexane and dried in vacuum. Yield 150 mg (50% based on Tc). Melting point 80 °C. *Anal.* Found: C, 34.7; Tc, 15.9. Calc. for $C_{17}H_{26}O_3PS_6Tc$: C, 34.0; Tc, 16.5%. IR: C=S 1185 cm^{-1}. UV–Vis (λ_{max} (lg ϵ)): 253 (4.41); 445 (3.46); 505 sh (3.27). ^{1}H NMR: 7.72–7.21 m (5H, phenyl); 4.52 qu (6H, CH_2); 1.48 d (6H, PCH_3), J(P–H)=7.8 Hz; 1.39 tr (9H, CH_3) ppm.

[$TcCl_2(Me_2PhP)_2(Me_2dtp)$]

350 mg (2 mmol) $(NH_4)Me_2dtp$ were dissolved in 30 ml acetone and 310 mg (0.5 mmol) solid $[TcCl_3(Me_2PhP)_3]$ were added. The mixture was refluxed for 1 h, filtered and the solvent was reduced to about 5 ml. Upon addition of 10 ml ethanol and standing overnight in a refrigerator, orange–red crystals deposited, which were collected, washed with EtOH and dried in vacuum. Yield 200 mg (66% based on Tc). Melting point 180 °C (with decomposition). *Anal.* Found: C, 35.6; Tc, 16.4. Calc. for $C_{18}H_{28}Cl_2O_2P_3S_2Tc$: C, 35.8; Tc, 16.4%. IR: P=S 770 cm^{-1}. UV–Vis (γ_{max} (lg ϵ)): 254 (4.40); 372 (3.38); 421 (3.43). ^1H NMR: 14.60 s (broad), 13.48 s, 5.79 s (10H, phenyl); 1.97 s (broad) (6H, OCH_3); −28.06 s (broad) (12H, PCH_3) ppm.

Physical measurements

Routine IR spectra were recorded as KBr discs on a SPECORD 75 IR. ^1H NMR spectra were obtained in CD_2Cl_2 solutions on a BRUKER AM-250 spectrometer and the UV–Vis spectra were measured on a SPECORD M 40.

The technetium contents of the samples were determined by liquid scintillation measurements.

X-ray diffraction

X-ray data were collected on an Enraf-Nonius CAD 4 diffractometer. The structure was solved by the Patterson method. All non-hydrogen atoms were located from successive Fourier maps. The hydrogen atoms were placed at calculated positions and included in the structure-factor calculations. Crystal data and details of the refinements are summarized in Table 1. See also ‘Supplementary material’. Positional parameters are given in Tables 2 and 3.

Results and discussion

The reactions of *mer*-$[TcCl_3(Me_2PhP)_3]$ [8] with different bidentate dithioligands result in the formation of chelate complexes of various compositions and coordination geometries. With diethyldithiocarbamate a diamagnetic seven-coordinate complex is formed in which the technetium has a distorted pentagonal-bipyramidal environment [7]. The same coordination feature can be achieved with ethylxanthate. The complex $[Tc(Me_2PhP)(Etxan)_3]$ can be prepared in good yields and isolated as large, deep red crystals, which are easily soluble in $CHCl_3$ or benzene. The seven-coordinate d^4 complex is diamagnetic. This is not unexpected with respect to the general behaviour of seven-coordinate d^4 complexes [10]. Principally, three possibilities of coordination geometries are given for seven-coordinate complexes: (i) a pentagonal bipyramide, (ii) a capped octahedron, (iii) a capped trigonal prism. All three basic coordination geometries have well-separated energy levels which enable spin pairing. In the pentagonal bipyramid the low-lying e_1'' (xz, yz) which does not mix in any ligand character is markedly separated from the two metal–ligand σ-antibonding combinations e_2' (xy, x^2-y^2) and a_1' (z^2). Similar situations can be derived for a capped octahedron and a capped trigonal prism [10]. Consequently, the ^1H NMR spectrum consists of narrow lines; its pattern is in good accordance with the stated structure. The three xanthate ligands are magnetically equivalent. The observed IR frequency at 1185 cm^{-1} can be assigned to the C=S stretch and is in accordance with other xanthate complexes [5].

A pentagonal-bipyramidal coordination sphere was found for $[Tc(Me_2PhP)(Etxan)_3]$ by X-ray analysis. Figure 1 shows a plot of the structure. Typical bond lengths and angles are given in Table 4. The ‘axial’ angle P–Tc–S1 is 174.5° and comes much closer to the ideal value of 180° than the comparable angle in $[Tc(Me_2PhP)(Et_2dtc)_3]$ which is 168.9°. The equatorial S–Tc–S angles vary between 68.6 and 76.3° and differ only by 2–4° from the value in an ideal pentagonal pyramide (72°). Atoms S3–S6 are coplanar with 0.0051(1) Å. The sulfur atom S2 deviates from this plane by 0.946(1) Å. This result, however, can easily be explained by the restricting bite angle of the xanthate ligand.

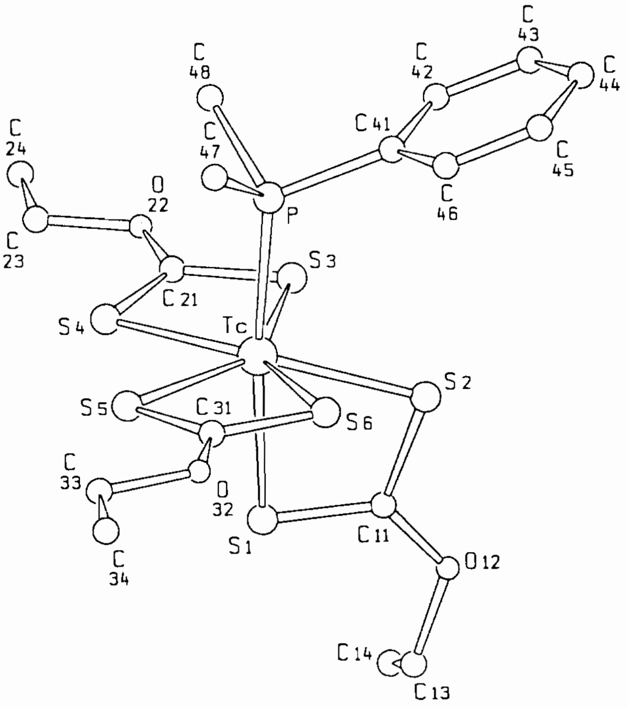

Fig. 1. SCHAKAL [11] plot of $[Tc(Me_2PhP)(Etxan)_3]$ along with the atomic numbering scheme.

TABLE 4. Selected bond lengths and angles in [Tc(Me_2PhP)(Etxan)$_3$] with e.s.d.s in parentheses

Bond lengths (Å)					
Tc–S1	2.467(1)	Tc–S6	2.456(1)	S3–C21	1.675(3)
Tc–S2	2.436(1)	Tc–P	2.353(1)	S4–C21	1.669(3)
Tc–S3	2.455(1)	S1–C11	1.672(3)	S5–C31	1.668(3)
Tc–S4	2.479(1)	S2–C11	1.702(3)	S6–C31	1.682(3)
Tc–S5	2.488(1)				

Bond angles (°)			
S1–Tc–S2	70.82(3)	S3–Tc–S4	68.63(3)
S1–Tc–S3	92.05(3)	S3–Tc–S5	144.78(3)
S1–Tc–S4	90.51(3)	S3–Tc–S6	146.09(3)
S1–Tc–S5	91.43(4)	S3–Tc–P	85.79(3)
S1–Tc–S6	92.95(4)	S4–Tc–S5	76.29(3)
S1–Tc–P	174.53(3)	S4–Tc–S6	144.76(3)
S2–Tc–S3	74.65(3)	S4–Tc–P	93.39(4)
S2–Tc–S4	138.00(3)	S5–Tc–S6	68.58(3)
S2–Tc–S5	138.87(3)	S5–Tc–P	93.23(3)
S2–Tc–S6	75.44(3)	S6–Tc–P	86.10(3)
S2–Tc–P	103.74(3)		

The pentagonal-bipyramidal geometry of [Tc(Me_2PhP)(Etxan)$_3$] is in contrast to the structure of its analogue [Tc(Ph_3P)(Buxan)$_3$] [5]. In the latter complex the angles P–Tc–S1 and P–Tc– 'equatorial'S are lowered to 127° and mean 78°, respectively, to meet the requirements of a capped-octahedral coordination sphere. The main reason for the observed differences between the two [Tc(PR_3)(Rxan)$_3$] complexes may be attributed to the steric requirement of the bulky triphenylphosphine ligand. Significant differences in bond lengths could not be found. The magnitude of the C–S bonds suggests a widespread delocalization of electron density throughout the chelate rings.

In contrast to the reactions with dithiocarbamates and xanthates, [$TcCl_3(Me_2PhP)_3$] does not yield a seven-coordinate, diamagnetic compound when reacted with dimethyldithiophosphate. An orange–red, paramagnetic, crystalline compound can be obtained which is easily soluble in $CHCl_3$, CH_2Cl_2 or benzene. The ^{1}H NMR spectrum of the complex shows the signals broadened and shifted in the range from +14.6 (phenyl protons) to −28.1 (methyl protons of the phosphine ligand) ppm. Very narrow and well separated ^{1}H NMR signals as have been discussed extensively for octahedral Tc(III) complexes with monothiodibenzoylmethanato ligands [12] could not be observed for the dithiophosphato complex under study. The measured NMR results, however, agree well with those from elemental analysis and spectroscopic studies which suggest a composition of [$TcCl_2(Me_2PhP)_2(Me_2dtp)$].

The compound exhibits a distorted octahedral coordination sphere with the two chloro ligands in *trans* position. A plot of the structure is given in Fig. 2. Table 5 contains selected bond lengths and angles of *trans*-[$TcCl_2(Me_2PhP)_2(Me_2dtp)$]. The obtained bond distances are in the expected ranges [4]. Significant deviations (e.g. due to a structural *trans*-effect of the phosphine ligands) could not be observed. The two P–S bond lengths are identical indicating an equivalency of the sulfur donors in the chelate ring.

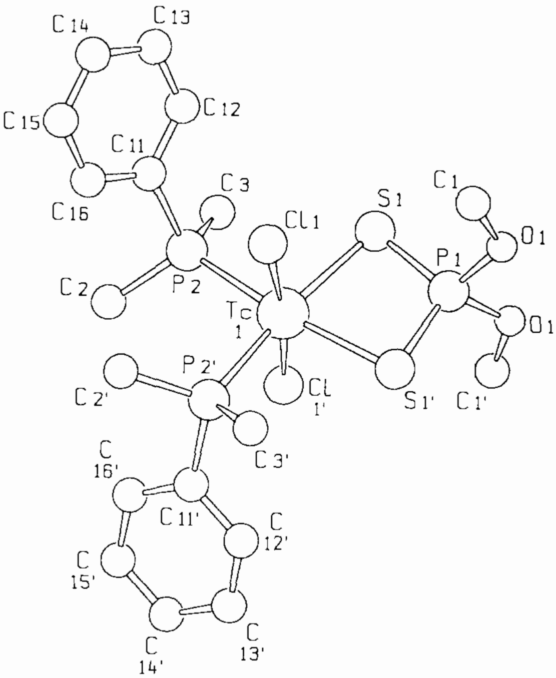

Fig. 2. SCHAKAL [11] plot of [$TcCl_2(Me_2PhP)_2(Me_2dtp)$] along with the atomic numbering scheme.

TABLE 5. Selected bond lengths and angles in [$TcCl_2(Me_2PhP)_2(Me_2dtp)$] with e.s.d.s in parentheses

Bond lengths (Å)					
Tc–Cl	2.347(1)	Tc–P2	2.416(1)	P1–O	1.578(3)
Tc–S	2.475(2)	S–P1	1.992(1)		

Bond angles (°)			
Cl–Tc–S	93.52(4)	S–Tc–S1′	80.10(3)
Cl–Tc–S′	91.80(4)	S–Tc–P2′	170.87(3)
Cl–Tc–P2	91.66(4)	P2–Tc–P2′	97.52(3)
Cl–Tc–P2′	83.74(4)	S–P1–S′	106.15(7)
Cl–Tc–Cl′	173.04(4)	Tc–S–P1	86.87(5)
S–Tc–P2	91.25(3)	S–P1–O	114.4(2)
		S–P1–O′	113.4(1)

Under the experimental conditions used, [$TcCl_2(Me_2PhP)_2(Me_2dtp)$] could be isolated as the only product. There was no evidence for the formation of six-coordinate complexes which contain more dithiophosphate ligands or a seven-coordinate compound as could be obtained from the reaction of [$TcCl_3(Me_2PhP)_3$] with dithiocarbamates and xanthates. In further work the influence of the reaction conditions and the behaviour of other 1,1- and 1,2-dithio ligands will be studied.

Supplementary material

Further details of the crystal structure determinations (F_o and F_c lists, full lists of bond lengths and angles and isotropic thermal parameters) have been deposited with the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, as Supplementary Publication No. CSD 56775 ([$TcCl_2(Me_2PhP)_2(Me_2dtp)$]).

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