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LETTER

Structural and spectroscopic studies on *mer*-dichlorotris(dimethylphenylphosphine)(thionitrosyl)technetium(I), *mer*-[Tc(NS)Cl$_2$(Me$_2$PhP)$_3$]

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The preparation of thionitrosyl complexes of technetium with phosphine ligands has been described previously [1, 2]. Recently, we reported the structure of [Tc^{II}(NS)Cl$_3$(Me$_2$PhP)(Me$_2$PhPO)] (Me$_2$PhP = dimethylphenylphosphine), a complex with the unusual coordination of a phosphine oxide ligand *trans* to the NS$^+$ group [3]. This unexpected result stimulated us to undertake a more detailed study of the technetium(I) complex [Tc(NS)Cl$_2$(Me$_2$PhP)$_3$] which is formed in a similar reaction.

Experimental

mer-[Tc(NS)Cl$_2$(Me$_2$PhP)$_3$] was prepared from TcNCl$_2$(Me$_2$PhP)$_3$ and disulfur dichloride as described previously [1, 2]. m.p. 141–143 °C. ^{1}H NMR: phenyl: 7.0–7.6m (15H); CH$_3$: 1.21d (6H), 1.75tr (6H), 1.94tr (6H) ppm. ^{13}C NMR: phenyl: 128.4–130.4m; CH$_3$: 11.22tr, 12.07tr, 14.00d. ^{31}P NMR: very broad peak without any resolution. ^{99}Tc NMR: +645 ppm (relative to TcO$_4$$^-$), $\Delta\nu_{1/2}$ = 4100 Hz.

The IR spectrum was measured using KBr discs on a UR 10 instrument. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in CDCl$_3$ on a Bruker AC 300, and the ^{99}Tc NMR spectrum was obtained using a Bruker AM 250 spectrometer. Fast atom bombardment (FAB$^+$) mass spectra were recorded on a VG ZAB-HSQ spectrometer with xenon as the primary beam gas. The ion gun was operated at 8 kV and 100 μA.

o-Nitrobenzylalcohol was used as the matrix. CID spectra were obtained using xenon as the collision gas.

The X-ray structure determination was carried out on the automated diffractometer CAD4 (Enraf-Nonius) at T = 293 K. A summary of the crystal data and structure refinement parameters is given in Table 1; see also 'Supplementary material'. Fractional and positional parameters are listed in Table 2.

Results and discussion

mer-[Tc(NS)Cl$_2$(Me$_2$PhP)$_3$], a reddish powder, is formed during the reaction of TcNCl$_2$(Me$_2$PhP)$_3$ with equimolar amounts of S$_2$Cl$_2$ in dichloromethane at room temperature. Upon recrystallization pale brown crystals are formed. This is in contrast to the reaction of the nitridotechnetium(V) complex with excess disulfur dichloride in refluxing CH$_2$Cl$_2$ which yields the red Tc(II) compound [Tc(NS)Cl$_3$(Me$_2$PhP)-(Me$_2$PhPO)], the IR spectrum of which shows the P=O stretch at 1147 cm^{-1} [3]. The IR spectrum of

TABLE 1. Crystal data for [Tc(NS)Cl$_2$(Me$_2$PhP)$_3$]

Formula	C$_{24}$H$_{33}$NSCl$_2$P$_3$Tc
Molecular weight	629.43
Space group	$P2_1/c$
a (Å)	9.4730(6)
b (Å)	18.6904(9)
c (Å)	16.1676(6)
β (°)	93.467(4)
V (Å^3)	2857.3
Z	4
D_c (g cm^{-3})	1.463
μ(Mo Kα) (cm^{-1})	9.3
λ(Mo Kα) (Å)	0.7093 (graphite monochromator)
Scan type	ω–θ
Total unique data	6780
Observed data ($I > 3\sigma(I)$)	4461
No. parameters	389
R	0.034
R_w	0.038

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TABLE 2. Positional parameters for [Tc(NS)Cl_2(Me_2PhP)$_3$]

Atom	x	y	z
Tc	0.52327(3)	0.10324(2)	0.20925(2)
Cl1	0.3272(1)	0.12471(6)	0.29716(7)
Cl2	0.4501(1)	−0.02345(6)	0.19014(7)
S	0.7974(1)	0.08030(9)	0.09605(8)
P1	0.6413(1)	0.06112(6)	0.34100(6)
P2	0.3508(1)	0.12352(6)	0.09136(7)
P3	0.5859(1)	0.22758(6)	0.22373(7)
N	0.6682(4)	0.0918(2)	0.1487(2)
C11	0.8173(5)	0.0237(2)	0.3319(3)
C12	0.8339(5)	−0.0254(3)	0.2690(3)
C13	0.9684(6)	−0.0541(3)	0.2568(4)
C14	1.0817(6)	−0.0331(3)	0.3084(4)
C15	1.0644(6)	0.0139(3)	0.3716(4)
C16	0.9327(5)	0.0429(3)	0.3840(4)
C17	0.6577(6)	0.1223(3)	0.4294(3)
C18	0.5474(5)	−0.0136(3)	0.3859(3)
C21	0.2630(4)	0.2096(2)	0.0767(2)
C22	0.3032(5)	0.2599(2)	0.0196(3)
C23	0.2372(5)	0.3257(3)	0.0126(3)
C24	0.1291(5)	0.3421(3)	0.0622(3)
C25	0.0861(5)	0.2925(3)	0.1182(3)
C26	0.1515(5)	0.2270(3)	0.1255(3)
C27	0.1996(6)	0.0630(3)	0.0878(4)
C28	0.4276(6)	0.1074(3)	−0.0071(3)
C31	0.7400(4)	0.2503(2)	0.2921(3)
C32	0.7402(5)	0.3053(3)	0.3493(3)
C33	0.8601(6)	0.3204(3)	0.3995(3)
C34	0.9803(5)	0.2813(3)	0.3933(3)
C35	0.9840(5)	0.2274(3)	0.3362(3)
C36	0.8642(5)	0.2117(3)	0.2859(3)
C37	0.6423(6)	0.2672(3)	0.1274(3)
C38	0.4485(5)	0.2881(3)	0.2542(4)

the title complex shows no evidence of a phosphine oxide frequency.

[Tc(NS)Cl_2(Me_2PhP)$_3$] is diamagnetic as expected for the d^6 configuration of technetium(I). The proton NMR spectrum is characterized by narrow lines and a coupling pattern which is characteristic for the meridional arrangement of the Me_2PhP ligands [4].

The methyl protons of the two equivalent phosphine ligands occur at different chemical shifts in the NMR spectrum. The signals are characterized by typical high order splittings due to ^{31}P. These splittings are identical for the downfield shifted CH_3 signals but differ from the resonance at 1.21 ppm. With the ^{31}P decoupling, all signals in the aliphatic region become sharp singlets with an intensity ratio of 1:1:1.

In contrast to the ^{1}H spectra, the ^{31}P NMR shows only one very broad peak. The expected A_2B type spectrum after ^{1}H decoupling could not be observed due to considerable broadening of the resonance. This most probably arises from coupling of the ^{31}P nuclei with the large quadrupole moment of ^{99}Tc ($Q = 0.3 \times 10^{-28}$ m^2). Similar results could be obtained with the diamagnetic Tc(V)nitrido complexes [4].

The ^{99}Tc resonance of [Tc(NS)Cl_2(Me_2PhP)$_3$] (Fig. 1) is found at +645 ppm and falls outside the range which was recently published for Tc(I) (−3600 to −1400 ppm) [5]. The chemical shift measured suggests the technetium in the title compound to be 'Tc^{3+}'. The typical region of Tc(III) compounds is −1350 to +2900 ppm with respect to a number of recently measured complexes which are not included in ref. 5 ([Tc(CO)(et_2dtc)$_3$]: +590 ppm, $\Delta\nu_{1/2}$ = 17.6 kHz (et_2dtc = diethyldithiocarbamate) [6]; [Tc(Me_2PhP)(et_2dtc)$_3$]: +455 ppm, $\Delta\nu_{1/2}$ = 18.6 kHz [6]; [Tc(Et_2PhP)(et_2dtc)$_3$]: +315 ppm, $\Delta\nu_{1/2}$ = 11.25 kHz [6]; [Tc(Ph_3P)($S_2COC_4H_9$)$_3$]: +2862 ppm, $\Delta\nu_{1/2}$ = 7.8 kHz [7]). The 'unusual' chemical shift of [Tc(NS)Cl_2(Me_2PhP)$_3$] cannot be explained in a similar way as has been done for a number of mixed-ligand complexes with isocyanide/bidentate aromatic amine ligands. Here, one of the isocyanide ligands has a bent arrangement and can be discussed as a formally 'CNR^{2-}' ligand [8]. The thionitrosyl group is coordinated with an angle of 178.8° (*vide infra*). This is close to a formulation of NS^+. To give a more satisfying explanation of the ^{99}Tc NMR chemical shift observed, some more Tc(I)thionitrosyl and nitrosyl complexes should be studied using this method.

The fast atom bombardment mass spectrum of [Tc(NS)Cl_2(Me_2PhP)$_3$] (the high mass region of the spectrum is illustrated in Fig. 2(a)) shows the molecular ion peak (M^+) at m/z = 629 and numerous metal containing fragments. The observation of the molecular ion is in contrast to FAB^+-MS studies

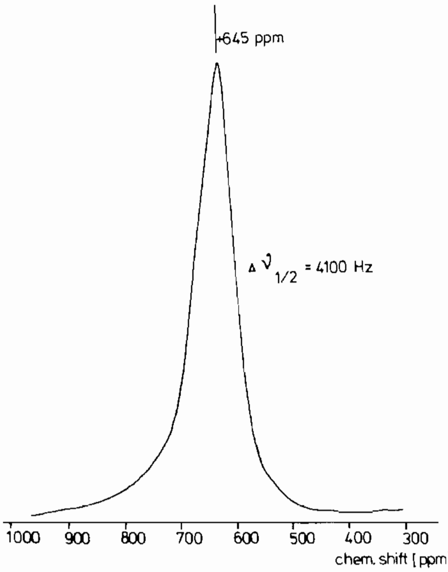


Fig. 1. ^{99}Tc NMR spectrum of *mer*-[Tc(NS)Cl_2(Me_2PhP)$_3$] in CD_2Cl_2.

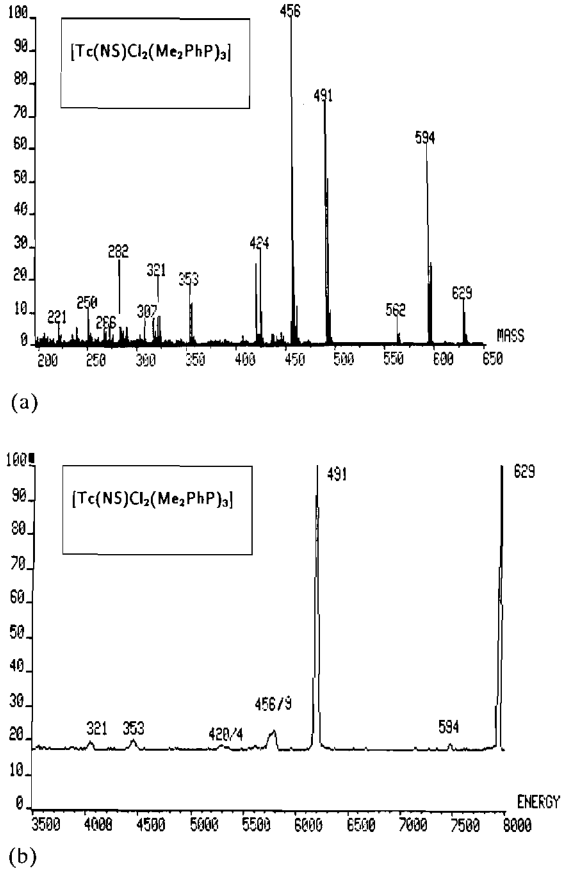
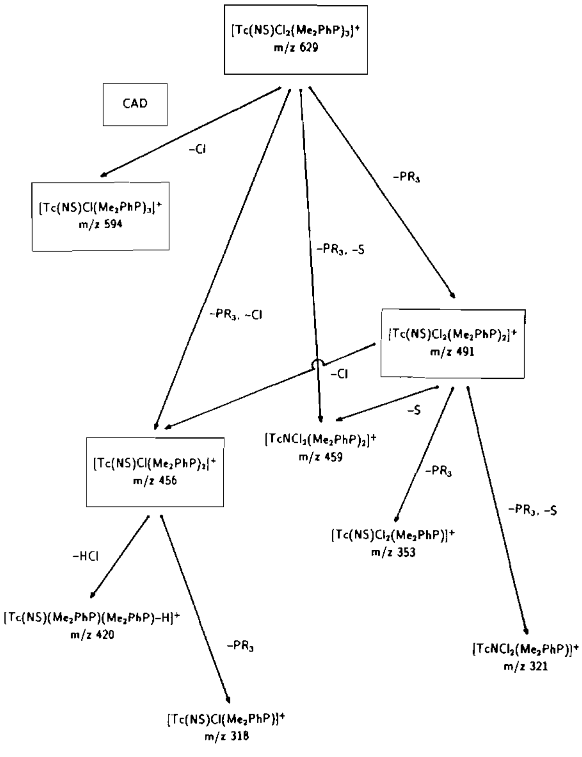


Fig. 2. (a) High mass region of the FAB$^+$ mass spectrum of *mer*-[Tc(NS)Cl$_2$(Me$_2$PhP)$_3$]. (b) CAD/MIKE spectrum of mass selected molecular ions.

on [Tc(NS)Cl$_3$(Me$_2$PhP)(Me$_2$PhPO)] where only a peak due to [$M-$Cl]$^+$ could be observed [3]. Fragmentation mainly occurs by loss of complete ligands and by cleavage of the NS group. This is confirmed by the measurement of MIKE (Mass analyzed Ion Kinetic Energy) spectra of the mass selected ions of the $m/z=629$ peak.

The MIKE spectrum obtained by collision activation is shown in Fig. 2(b). The most abundant fragment ion ($m/z=491$) is formed by loss of one Me$_2$PhP ligand. Only three fragmentation products can be observed under metastable conditions: [Tc(NS)Cl$_2$(Me$_2$PhP)$_2$]$^+$, $m/z=491$; [Tc(NS)Cl(Me$_2$PhP)$_2$]$^+$, $m/z=456$ and [TcNCl$_2$(Me$_2$PhP)$_2$]$^+$, $m/z=459$. It is interesting to note that [Tc(NS)Cl(Me$_2$PhP)$_3$]$^+$ ($m/z=594$) is formed by collision activated dissociation (CAD) only. Important unimolecular fragmentation reactions of the molecular ion and some important fragment ions are summarized in Scheme 1.

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene/n-hexane solution in the form of pale brown blocks. The structure



Scheme 1. Unimolecular fragmentation reactions of [Tc(NS)Cl$_2$(Me$_2$PhP)$_3$]$^+$ and of some important fragment ions.

consists of discrete monomeric molecules. A SCHAKAL plot together with the molecular numbering scheme is given in Fig. 3. Table 3 contains selected distances and angles.

The technetium is six-coordinate, with the three phosphine ligands coordinated meridionally *cis* to the thionitrosyl group. The complex is slightly distorted from the octahedral geometry, as the three phosphine ligands are bent out of the equatorial plane away from the thionitrosyl. The N–Tc–Cl(2) angle is found to be 90.72(4)°, the Cl(2)–Tc–P(3) angle is 177.54(5)° and the P(1)–Tc–P(2) angle is 163.59(4)°. This indicates significant π-bonding in the direction of the TcN bond. The short bond length of 1.75 Å for Tc–NS confirms this suggestion. It falls in the region which is typical for thionitrosyl complexes [3, 9–11].

The resulting TcNS core is nearly linear with a bond angle of 178.8(2)° and thus, the bonding mode of the thionitrosyl group has to be discussed as NS$^+$ with extensive backbonding from the Tc(I) centre. The N=S bond length of 1.55 Å in *mer*-[Tc(NS)Cl$_2$(Me$_2$PhP)$_3$] is comparable to the averaged value of 1.53 Å which can be derived from other thionitrosyl complexes [9]. Taken together, the bonding feature of *mer*-[Tc(I)(NS)Cl$_2$(Me$_2$PhP)$_3$] comes closer to that in the comparable *mer*-

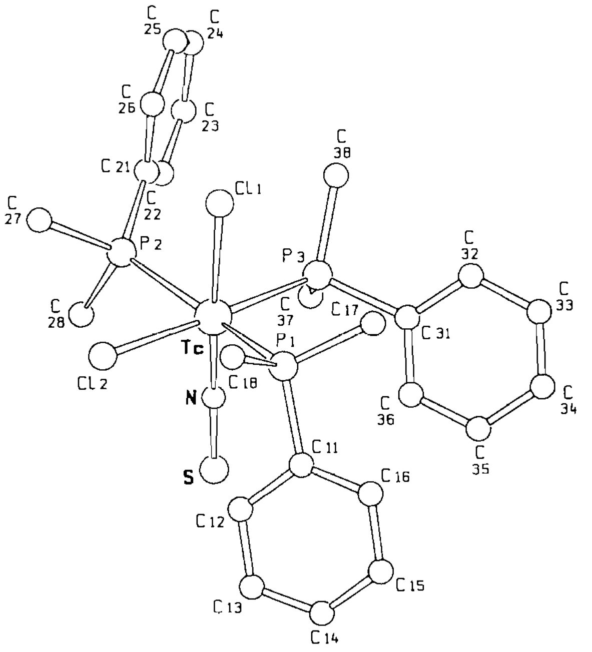


Fig. 3. Structure of *mer*-[Tc(NS)Cl_2(Me_2PhP)$_3$] along with the atomic numbering scheme.

[Tc(I)(NS)Cl_2(pic)$_3$] (pic = 4-methylpyridine), the structure of which has been published recently by Lu and Clarke [11], as opposed to [Tc(NS)Cl_3(Me_2PhP)(Me_2PhPO)] [3].

The thionitrosyl ligand in the title compound shows only a negligible structural *trans*-effect. The Tc–Cl(1) bond length of 2.44 Å is 0.04 Å shorter than that *trans* to the phosphine and is close to the values found for the Tc–Cl bonds in *mer*-[Tc(NS)Cl_2(pic)$_3$] (2.43 and 2.44 Å). This behaviour is in strong contrast to the bonding situation in nitrosyltechnetium(I) complexes where the bonds *trans* to NO^+ are lengthened by 0.05–0.1 Å [12, 13]. A significant *trans*-labilization effect in *mer*-[Tc(NS)Cl_2(Me_2PhP)$_3$] can be observed for the phosphines. The Tc–Cl as well as the Tc–P bonds *trans* to Me_2PhP are longer by 0.04 and 0.06 Å, respectively.

Supplementary materials

Further details of the crystal structure determination have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, as Supplementary Publication No. 54963.

TABLE 3. Bond distances (Å) and angles (°)

Tc–Cl1	2.439(1)
Tc–Cl2	2.481(1)
Tc–P1	2.474(2)
Tc–P2	2.464(1)
Tc–P3	2.407(1)
Tc–N	1.747(3)
S–N	1.548(4)
P1–C11	1.823(4)
P1–C17	1.830(5)
P1–C18	1.829(6)
P2–C21	1.819(4)
P2–C27	1.822(6)
P2–C28	1.816(5)
P3–C31	1.826(5)
P3–C37	1.833(5)
P3–C38	1.815(5)
Cl1–Tc–Cl2	90.72(4)
Cl1–Tc–P1	82.60(4)
Cl1–Tc–P2	86.14(4)
Cl1–Tc–P3	88.65(4)
Cl1–Tc–N	177.0(1)
Cl2–Tc–P1	84.95(4)
Cl2–Tc–P2	83.29(4)
Cl2–Tc–P3	177.54(5)
Cl2–Tc–N	92.2(1)
P1–Tc–P2	163.59(4)
P1–Tc–P3	97.33(4)
P1–Tc–N	96.5(1)
P2–Tc–P3	94.30(4)
P2–Tc–N	95.3(1)
P3–Tc–N	88.6(1)
Tc–N–S	178.8(2)
C11–P1–C17	105.6(2)
C11–P1–C18	102.0(2)
C17–P1–C18	100.8(2)
C21–P2–C27	101.1(2)
C21–P2–C28	103.7(2)
C27–P2–C28	103.0(3)
C31–P3–C37	99.1(2)
C31–P3–C38	104.5(2)
C37–P3–C38	103.3(2)

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