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LETTER

Mixed-ligand complexes of technetium XII. Synthesis, characterization and X-ray crystal structure of (*o*-mercaptophenolato)bis[1,2-bis(dimethylphosphino)ethane] technetium(III) tetraphenylboranate, [Tc(meph)(DMPE)$_2$](BPh$_4$)*

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Introduction

Recent developments in the coordination chemistry of technetium are strongly stimulated by the widespread use of ^{99m}Tc complexes (^{99m}Tc: γ-emitter, $E_\gamma = 140$ keV, half-life $t_{1/2} = 6$ h) in diagnostic nuclear medicine [2, 3]. Chemical studies, however, are commonly done with the long-lived isotope ^{99}Tc (weak β^--emitter, $E_{max} = 2.12 \times 10^5$ years) [4].

Synthesis, characterization and biological properties of mixed-ligand complexes of technetium with chelating phosphines and monodentate thiol ligands have been reported recently [5–9]. Here, we discuss the synthesis and structure of a mixed-ligand complex containing the bis(tertiary phosphine) 1,2-bis(dimethylphosphino)ethane (DMPE) and *o*-mercaptophenolate (meph).

Experimental

All manipulations were carried out in a low-level radiation laboratory with gloves. Normal glassware gives adequate protection against the weak β^--emission of ^{99}Tc. *o*-Mercaptophenol was a commercial product (Merck) and [Tc(DMPE)$_2$Cl$_2$]Cl was prepared by a literature method [10].

[Tc(meph)(DMPE)$_2$](BPh$_4$)

6 mg (0.01 mmol) [Tc(DMPE)$_2$Cl$_2$]Cl were dissolved in 1 ml ethanol to which 50 μl of *o*-mercaptophenol were added. The mixture was kept at 70 °C for 5 h. After evaporation of the solvent the oily residue was washed twice with diethyl ether and redissolved in 0.2 ml ethanol. 50 μl of a saturated NaBPh$_4$ solution in ethanol were then added. The resulting red, crystalline precipitate was isolated by centrifugation and dried under vacuum. Yield 6.3 mg (46% based on Tc).

Anal. Calc. for $C_{42}H_{56}OSP_4BTc$: C, 59.9; H, 6.7; Tc, 11.6. Found: C, 58.5; H, 6.5; Tc, 11.5%. UV–Vis spectrum: λ_{max} (nm) (logϵ) 514 (3.78).

Physical measurements

The optical spectrum was measured in CHCl$_3$ on a SPECORD M40; the IR spectrum was determined using KBr pellets on a UR 10 instrument. Fast atom bombardment (FAB$^+$) mass spectra were recorded on a VG ZAB-HSQ spectrometer with xenon as primary beam gas. The ion gun was operated at 8 kV and 100 μA. Glycerol was used as the matrix.

TABLE 1. Crystal data for [Tc(meph)(DMPE)$_2$](BPh$_4$)

Formula	$C_{42}H_{56}B_1O_1P_4S_1Tc$
Molecular weight	841.69
Space group	$P2_1/c$ (No. 14)
a (Å)	12.525(1)
b (Å)	9.961(1)
c (Å)	33.789(6)
β (°)	93.28(2)
V (Å^3)	4208.9
Z	4
D_c (g cm^{-3})	1.328
μ(Cu Kα) (cm^{-1})	49.70
λ(Cu Kα) (Å)	1.5406 (graphite monochromator)
Scan type	ω–θ
Total unique data	7753
Observed data ($I > 3\sigma(I)$)	4451
No. parameters	444
R	0.061
R_w	0.063
Program used	MolEN [12]
Computer used	CONVEX C220

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*For Part XI see ref. 1.

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0020-1693/91/$3.50

The technetium content of the compound was determined by bremsstrahlung measurements using a scintillation detector as described in ref. 11.

X-ray structure determination

Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile/ethanol solution. The collection of the intensities for the X-ray structure determination was carried out on the automated diffractometer CAD 4 (Fa. Enraf-Nonius, Delft, The Netherlands) at $T=223$ K. A summary of data collection and structure refinement parameters is given in Table 1. See also 'Supplementary material'. Positional parameters are given in Table 2.

Results and discussion

The reaction of $[Tc(DMPE)_2Cl_2]Cl$ with excess *o*-mercaptophenol leads to the formation of the mixed-ligand cation $[Tc(meph)(DMPE)_2]^+$ in reasonable yields. The product can be isolated as a tetraphenylboranate salt in the form of red crystals which are easily soluble in dichloromethane, acetone and acetonitrile and only slightly soluble in ethanol. The IR spectrum of the compound reflects the expected pattern and shows no evidence of a Tc–O stretch.

The fast atom bombardment mass spectrum of the compound shows the molecular ion (M^+) of the complex cation ($m/z=523$). Fragmentation takes place by the loss of complete ligands ($m/z=399$; M^+-meph and with less abundance $m/z=373$; M^+-DMPE) as well as by bond cleavages in the organic ligands. Typical fragments are $m/z=461$; $[M-2CH_3, -S]^+$, $m/z=431$; $[M-C_6H_4O]^+$, $m/z=415$; $[M-C_6H_4S]^+$ and $m/z=369$; $[M-\text{meph}, -2CH_3]^+$. Besides the molecular ion and the fragments discussed, ions could be observed which occur at higher m/z and the intensity of which increases with time. These ions are due to products of reactions and ligand rearrangements in the FAB matrix. Ions observed at $m/z=539$ and 555 can be assigned to cations with one or two 1,2-bis(dimethylphosphino)ethane monoxide ligands. Similar reactions have recently been observed during mass spectrometric studies on $[Tc(DMPE)_2X_2]^+$ [13] ($X=Cl$, Br) and $[Tc(DMPE)_2(EtS)_2]^+$ cations [14].

TABLE 2. Positional parameters for $[Tc(meph)(DMPE)_2](BPh_4)$

Atom	x	y	z
Tc	0.25965(5)	0.51309(6)	0.40596(2)
S	0.1530(2)	0.5954(3)	0.45560(9)
P1	0.1373(2)	0.6133(3)	0.35744(7)
P2	0.3608(2)	0.4972(2)	0.34783(6)
P3	0.3787(2)	0.3516(3)	0.43406(8)
P4	0.1460(3)	0.3245(3)	0.40410(8)
O	0.3633(3)	0.6671(4)	0.4257(1)
C1	0.1752(7)	0.583(1)	0.3074(2)
C2	0.2961(7)	0.5921(9)	0.3066(3)
C3	0.327(1)	0.183(1)	0.4262(4)
C4	0.210(1)	0.183(1)	0.4320(4)
C5	0.2300(7)	0.7230(9)	0.4709(3)
C6	0.3290(6)	0.7454(8)	0.4579(2)
C7	0.3960(9)	0.848(1)	0.4725(3)
C8	0.362(1)	0.928(1)	0.5002(3)
C9	0.263(1)	0.913(1)	0.5156(3)
C10	0.1935(9)	0.811(1)	0.5015(3)
C11	0.1518(7)	0.794(1)	0.3641(3)
C12	−0.0067(6)	0.595(1)	0.3553(3)
C21	0.386(1)	0.3372(9)	0.3243(3)
C22	0.4917(7)	0.578(1)	0.3504(4)
C31	0.5207(8)	0.340(1)	0.4263(3)
C32	0.3768(8)	0.375(1)	0.4873(3)
C41	0.023(1)	0.335(2)	0.4279(4)
C42	0.103(1)	0.243(1)	0.3578(4)
C51	0.2402(6)	0.6343(8)	0.1610(2)
C52	0.2334(7)	0.7072(8)	0.1958(3)
C53	0.2323(7)	0.8469(9)	0.1968(3)
C54	0.2393(6)	0.9181(9)	0.1628(3)
C55	0.2449(7)	0.8506(9)	0.1274(3)
C56	0.2457(6)	0.7106(8)	0.1267(3)
C61	0.3868(6)	0.4542(7)	0.1695(3)
C62	0.4353(7)	0.456(1)	0.2072(3)
C63	0.5449(7)	0.459(1)	0.2151(3)
C64	0.6122(7)	0.4587(9)	0.1844(4)
C65	0.5683(6)	0.4547(8)	0.1465(3)
C66	0.4575(6)	0.4547(8)	0.1389(3)
C71	0.2113(6)	0.3977(8)	0.1204(2)
C72	0.1171(6)	0.4402(9)	0.0995(3)
C73	0.0719(7)	0.372(1)	0.0670(3)
C74	0.1200(8)	0.259(1)	0.0529(3)
C75	0.2116(8)	0.2115(9)	0.0732(3)
C76	0.2559(7)	0.2802(8)	0.1058(2)
C81	0.1896(6)	0.3980(8)	0.1960(2)
C82	0.2231(7)	0.2794(9)	0.2153(3)
C83	0.1603(8)	0.2126(9)	0.2416(3)
C84	0.0614(7)	0.2616(9)	0.2499(3)
C85	0.0247(7)	0.3775(9)	0.2316(3)
C86	0.0875(6)	0.4432(8)	0.2050(2)
B	0.2564(6)	0.4700(9)	0.1615(3)

The S and O atoms occupy disordered positions each refined with population 0.72(S)/0.28(O) and 0.72(O)/0.28(S), respectively.

The substitution of the chloro ligands in $[Tc(DMPE)_2Cl_2]Cl$ by an *o*-mercaptophenolate is quite uncommon. Usually, reactions with thiols [15] or other reducing agents such as cyanide, azide or thiocyanate [10] do not lead to ligand substitution but result in the reduction of Tc(III) to Tc(II) without modification of the $[Tc(DMPE)_2Cl_2]^{0,+}$ core. Mixed thiol/phosphine complexes of Tc could only be obtained by starting from halide-free precursors. The rearrangement of the DMPE ligands to give a *cis* arrangement, however, has been observed with the reaction of $[TcO(OH)(DMPE)_2]^+$ and *o*-chlorobenzenethiol which yields a mixture of *trans*- and *cis*-$[Tc(II)(DMPE)_2(SC_6H_4\text{-}p\text{-}Cl)_2]^0$ with a greater tendency towards the *cis* isomer [9].

$[Tc(meph)(DMPE)_2](BPh_4)$ crystallizes in discrete complex cations and tetraphenylboranate anions. Figure 1 shows a plot of the technetium(III) cation with the atomic numbering scheme. Selected bond lengths and angles are summarized in Tables 3 and 4. The coordination sphere of the technetium atom can be described as a distorted octahedron with the atoms S, O, P2, P4 in the basal plane. Apical positions are occupied by the atoms P1 and P3 with an angle P1–Tc–P3 of 157.7(1)°. The distortion of the octahedral geometry is expressed furthermore by the dihedral angle of 18.1(3)° between the planes (Tc, S, O) and (Tc, P2, P4). The structure exhibits disorder for the donor atoms of the *o*-mercaptophenolate ligand. Thus, the distances Tc–O (2.095(4) Å) and Tc–S (235.2(3) Å) are not significant for further interpretation. The Tc–P distances (2.356(3)–2.403(2) Å) are shorter than those observed in the comparable Tc(III) DMPE complexes $[Tc^{III}(DMPE)_2Cl_2]^+$ (2.43, 2.66 Å) [17] and $[Tc^{III}(DMPE)_2(SCH_3)_2]$ (2.42–2.453 Å) [6] but are similar to the Tc–P bond length of 2.40(2) Å found in $[Tc^{I}(DMPE)_3]^+$ which was determined by EXAFS analysis. They are also similar to the related mixed-ligand technetium(II) complexes *cis*- and *trans*-$[Tc(DMPE)_2(SC_6H_4\text{-}p\text{-}Cl)_2]^0$ [9].

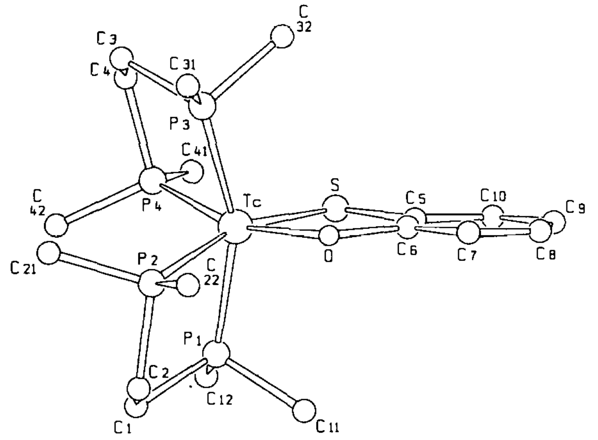

Fig. 1. Plot [16] of the cation in $[Tc(meph)(DMPE)_2](BPh_4)$. H atoms are omitted for clarity.

TABLE 3. Selected bond distances (Å)

Tc–S	2.352(3)
Tc–P1	2.397(2)
Tc–P2	2.403(2)
Tc–P3	2.356(3)
Tc–P4	2.356(3)
Tc–O	2.095(4)
S–C5	1.660(9)
P1–C1	1.808(9)
P1–C11	1.82(1)
P1–C12	1.810(8)
P2–C2	1.834(9)
P2–C21	1.82(1)
P2–C22	1.82(1)
P3–C3	1.82(1)
P3–C31	1.82(2)
P3–C32	1.81(1)
P4–C4	1.85(1)
P4–C41	1.78(1)
P4–C42	1.81(1)
O–C6	1.426(9)
C1–C2	1.52(1)
C3–C4	1.49(2)
C51–B	1.65(1)
C61–B	1.65(2)
C71–B	1.64(1)
C81–B	1.64(1)

TABLE 4. Selected bond angles (°).

S–Tc–P1	88.6(1)	C2–P2–C21	101.6(5)
S–Tc–P2	162.5(1)	C2–P2–C22	99.7(5)
S–Tc–P3	108.8(2)	C21–P2–C22	103.1(5)
S–Tc–P4	86.0(2)	Tc–P3–C3	111.1(6)
S–Tc–O	83.4(1)	Tc–P3–C31	126.0(4)
P1–Tc–P2	79.3(1)	Tc–P3–C32	105.7(4)
P1–Tc–P3	157.7(1)	C3–P3–C31	105.4(7)
P1–Tc–P4	87.3(1)	C3–P3–C32	103.7(6)
P1–Tc–O	105.9(1)	C31–P3–C32	102.7(5)
P2–Tc–P3	86.2(1)	Tc–P4–C4	110.6(5)
P2–Tc–P4	105.8(1)	Tc–P4–C41	118.6(6)
P2–Tc–O	87.8(1)	Tc–P4–C42	121.8(4)
P3–Tc–P4	80.4(2)	C4–P4–C41	99.9(7)
P3–Tc–O	90.4(1)	C4–P4–C42	101.4(6)
P4–Tc–O	162.8(1)	C41–P4–C42	101.3(6)
Tc–S–C5	98.4(3)	Tc–O–C6	115.8(5)
Tc–P1–C1	112.3(4)	P1–C1–C2	108.7(6)
Tc–P1–C11	105.8(3)	P2–C2–C1	110.7(6)
Tc–P1–C12	125.6(4)	P3–C3–C4	108.8(9)
C1–P1–C11	104.5(5)	P4–C4–C3	109.6(9)
C1–P1–C12	105.0(4)	S–C5–C6	123.5(7)
C11–P1–C12	101.3(6)	S–C5–C10	119.1(7)
Tc–P2–C2	110.9(4)		
Tc–P2–C21	121.9(4)	O–C6–C5	118.5(7)
Tc–P2–C22	116.6(4)	O–C6–C7	118.1(7)
C51–B–C61	102.5(6)	C61–B–C71	112.9(7)
C51–B–C71	113.0(6)	C61–B–C81	112.6(6)
C51–B–C81	112.1(6)	C71–B–C81	104.3(6)

The observed octahedral geometry of the title compound is in contrast to the tris-complexes of Tc with bidentate ligands. They exhibit in most cases trigonal-prismatic structures, e.g. the tris-complexes of Tc with *o*-aminothiophenolate, abt^{2-} ($[Tc^{VI}(abt)_3]^0$, and 1,2-benzenedithiolate, bdt^{2-} ($[Tc^{V}(bdt)_3]^-$) [18, 19]). For the technetium(II) tris-complex with DMPE, $[Tc(DMPE)_3]^{2+}$, such an array of the P atoms is strongly suggested by EPR spectroscopy [14], too.

Supplementary material

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. CSD-55084.

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