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LETTER

Novel TcP_3X_3 (X = S, O) cores in Tc(III) chemistry

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In recent years we devoted most of our research efforts in developing Tc chemistry with bidentate functionalized phosphines because of their ability to act both as reducing and coordinating agents [1, 2]. These functionalized phosphines contain a P(III) atom that can easily reduce the pertechnetate ion and stabilize the metal in lower oxidation states by means of its π-backbonding together with the chelation of the whole ligand. In this field encouraging results have been obtained with phosphino-carboxylic derivatives of the type $Ph_2P–R–COOH$ (R = o-C_6H_4, C_2H_4, CH_2) (abbreviated as P–COOH) [3] and more recently with the ligand (2-diphenylphosphino)benzeneamine (abbr. PNH_2) [4]. In both cases Tc(III) complexes of the type $Tc(P–X)_3$ (X = COO^-, NH^-) have been obtained, the three mono-negative bidentate ligands being coordinated around the metal in a meridional configuration.

The above mentioned 'reducing-coordinating' approach has allowed the synthesis of a class of Tc(III) complexes utilizing the tris(o-thiophenyl)phosphine, a tetradentate 'umbrella shaped' ligand. Either octahedral or trigonal bipyramidal geometries have been observed for the resulting complexes, depending on the concentration of the ancillary isonitrile ligand [5].

In this context we now report on the reaction of pertechnetate with the two bidentate functionalized phosphines, (2-diphenylphosphino)thiophenol (abbr. P–SH) and (2-diphenylphosphino)phenol (abbr. P–OH) with the aim of looking at the molecular structure of the resulting complexes and to confirm the favourable reducing and coordinating properties of such a class of ligands towards technetium. The synthesis and characterization (including X-ray structure) of the resulting $Tc^{III}(P–S)_3$ (1) and $Tc^{III}(P–O)_3$ (2) complexes are reported here.

Synthesis

Preparation of $Tc^{III}(P–S)_3$ (1)

$NH_4[TcO]_4$ (16 mg, 0.09 mmol) was suspended in 10 ml of ethanol and a five-fold molar excess of diphenylphosphino-thiophenol [6] (130 mg, 0.45 mmol) was added at room temperature. After a few minutes of stirring the ligand was completely dissolved and the solution became pale blue–green. The reaction mixture was then refluxed for 1 h yielding a deep green precipitate from a deep blue–green solution. The mixture was cooled and then filtered. The green solid collected was washed with ethanol, diethyl ether and dried under vacuum (yield 90% with respect to $[TcO_4]^-$). **1** is soluble in chlorinated solvents giving turquoise green solutions and is insoluble in other common organic solvents and water.

Preparation of $Tc^{III}(P–O)_3$ (2)

$NH_4[TcO_4]$ (20 mg, 0.11 mmol) was suspended in 10 ml of ethanol and five-fold molar excess of diphenylphosphino-phenol [7] (154 mg, 0.55 mmol) was added under stirring at room temperature. The solution became orange within a few minutes. The mixture was then refluxed for 1.5 h until a deep-red solid appeared from a purple–red solution. After cooling the solid was collected by filtration, washed with ethanol and dried under a nitrogen stream (yield 55% with respect to $[TcO_4]^-$). **2** is soluble in common organic solvents and insoluble in alcohols and water.

For both complexes elemental analyses, conductivity and magnetic susceptibility measurements, and ^1H NMR and IR spectra are consistent with the formulation $Tc(P–X)_3$ (X = S, O). *Anal.* Calc. for $C_{54}H_{42}P_3S_3Tc$ (**1**): C, 66.24; H, 4.32; S, 9.82; Tc, 10.11. Found: C, 66.91; H, 4.82; S, 9.08; Tc, 9.55%. Calc. for $C_{54}H_{42}P_3O_3Tc$ (**2**): C, 69.67; H, 4.54; Tc, 10.63. Found: C, 70.42; H, 4.60; Tc, 9.96%. Magnetic susceptibility measurements performed in dichloromethane by the Evans method yield a value of $\mu = 3.0\ \mu_B$ for **1** and $\mu = 2.7\ \mu_B$ for **2** in agreement with a d^4 system typical for Tc(III). Electronic spectra in dichloromethane/acetonitrile solution show absorption maxima at 605 (7000), 410 (3250) and 290 (10600) nm for **1** and 470 (3500) and 240 (77500 $dm^3\ mol^{-1}\ cm^{-1}$) nm for **2**.

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Crystallography

Good quality crystals were grown on cooling CH_2Cl_2/MeOH solutions of **1** and **2**, respectively. Crystallographic data are summarized in Table 1. The intensities were processed in the normal fashion (10653 independent reflections were measured, of which only 6814 were judged to be observed for **1**; 7774 independent reflections were measured, of which 5340 were observed for **2**). An empirical absorption correction, based on measurements of eight reflections at χ *c.* 270° for different azimuthal angles (Ψ-scan), was made and the transmission factor ranged from 0.69 to 1.0 for **1** and from 0.89 to 1.0 for **2**. The structures were solved by standard heavy-atom methods and refined by least-squares methods. The programs used were those of the SHELXTL PLUS package [8]. Relevant bond lengths and angles are listed in Table 2. The molecular structure of **1** is shown in Fig. 1.

Results and discussion

Reduction–substitution reactions onto $[TcO_4]^-$ operated by a five-fold molar excess of functionalized P–XH (X = S, O) phosphine ligands give rise to the corresponding phosphine oxide and to neutral *mer*-$Tc^{III}(P\text{–}X)_3$ complexes as detailed in the following equation.

$$NH_4[TcO_4] + 5P\text{–}XH \longrightarrow Tc(P\text{–}X)_3 + 2O{=}P\text{–}XH + NH_4OH + H_2O$$

TABLE 1. Crystallographic data for **1** and **2**

	1	2
Formula	$C_{54}H_{42}P_3S_3Tc$	$C_{54}H_{42}P_3O_3Tc$
Formula weight	978.9	930.7
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.428(3)	10.144(2)
b (Å)	17.313(5)	16.841(4)
c (Å)	26.077(6)	26.309(6)
β (°)	100.84(2)	102.24(2)
V (Å^3)	4624(2)	4392(2)
Z	4	4
Diffractometer	Siemens R3m/V	
T	294	
λ (Mo Kα) (Å)	0.71073	
μ (mm^{-1})	0.57	0.47
ρ_{obs} (g cm^{-3})	1.40(2)	1.40(2)
ρ_{calc} (g cm^{-3})	1.405	1.406
No. observed reflections	6814	5340
$R(F_o)$	0.050	0.039
R_w	0.063	0.051
w	$(\sigma^2(F)+0.0023F^2)^{-1}$	$(\sigma^2(F)+0.0012F^2)^{-1}$
GOF	1.02	1.16

TABLE 2. Selected bond lengths (Å) and angles (°) for **1** (X = S) and **2** (X = O) with e.s.d.s in parentheses

	1	2
Tc–P(1)	2.477(1)	2.416(1)
Tc–P(2)	2.406(1)	2.444(1)
Tc–P(3)	2.424(1)	2.454(1)
Tc–X(1)	2.489(2)	2.000(3)
Tc–X(2)	2.258(1)	1.990(3)
Tc–X(3)	2.297(1)	2.074(3)
P(1)–C(1)	1.811(5)	1.801(4)
P(1)–C(7)	1.846(5)	1.836(4)
P(1)–C(13)	1.856(5)	1.844(4)
P(2)–C(19)	1.838(5)	1.812(4)
P(2)–C(25)	1.857(4)	1.831(4)
P(2)–C(31)	1.831(6)	1.824(5)
P(3)–C(37)	1.836(4)	1.800(4)
P(3)–C(43)	1.847(5)	1.814(4)
P(3)–C(49)	1.836(5)	1.826(5)
P(1)–Tc–P(2)	96.0(1)	95.4(1)
P(1)–Tc–P(3)	96.5(1)	99.5(1)
X(1)–Tc–P(1)	78.8(1)	81.6(1)
X(2)–Tc–P(1)	87.0(1)	93.2(1)
X(3)–Tc–P(1)	158.8(1)	169.3(1)
X(1)–Tc–X(2)	166.8(1)	165.7(1)
P(2)–Tc–P(3)	166.8(1)	160.4(1)
X(1)–Tc–P(2)	96.3(1)	99.1(1)
X(2)–Tc–P(2)	84.5(1)	79.9(1)
X(3)–Tc–P(2)	85.9(1)	87.6(1)
X(1)–Tc–P(3)	90.3(1)	95.6(1)
X(2)–Tc–P(3)	91.9(1)	86.6(1)
X(3)–Tc–P(3)	84.0(1)	80.1(1)
Tc–P(1)–C(1)	109.6(2)	97.9(1)
Tc–P(1)–C(7)	116.8(2)	119.7(1)
Tc–P(1)–C(13)	119.5(1)	122.1(1)

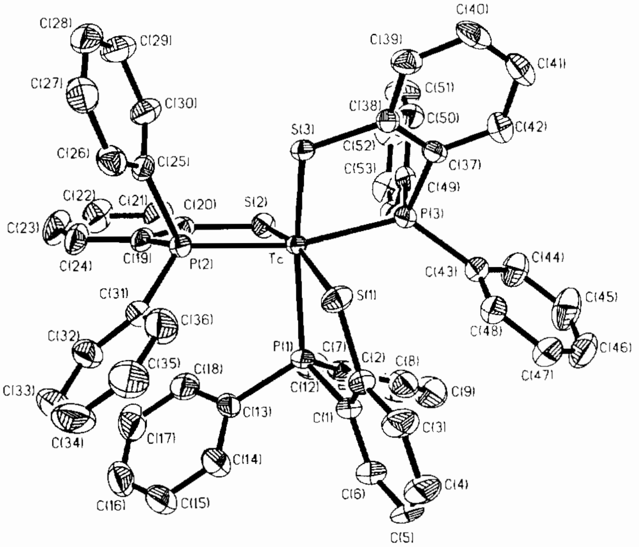

Fig. 1. ORTEP drawing of complex **1**. The atom numbering scheme and the thermal ellipsoids at the 50% probability level are shown. The same scheme holds for **2**, with O atoms instead of S ones.

Both structures consist of discrete, well separated molecules of $Tc(P\text{–}X)_3$ with no interatomic contacts shorter than the sum of van der Waals radii. The coordination environments are best described as distorted octahedrons with some severe distortions from the ideal Tc-centered octahedral configurations: (i) the Tc atom lies out of the mean equatorial plane by only 0.02 Å in **1**, but 0.10 Å in **2**; (ii) a non-linear X(1)–Tc–X(3) axis, of 158.8° in **1** and 169.3° in **2**, is accomplished by P(2)–Tc–P(3) and X(1)–Tc–X(2) angles of 166.8 and 165.7°, respectively in **1**, with the corresponding values of 160.4 and 174.6° in **2**; (iii) the P(1)--P(2), P(1)--P(3) and P(2)--S(1) edge distances are much longer than the others with the mean P–Tc–X bite angle (82.4° in **1** and 80.5° in **2**) departing from ideal 90°. Large portions of both structures are virtually superimposable (Fig. 2) with a weighted r.m.s. deviation of only 0.19 Å when the fitting is performed throughout the $Tc(P\text{–}C_3)_3$ moieties [9]. As far as we are aware, the TcP_3S_3 and TcP_3O_3 inner cores have not been observed elsewhere. The values for Tc–O(1) and Tc–O(2) in **2** (2.000(3) and 1.990(3) Å) parallel those already found in other complexes having a Tc(III)–O(phenolato) bond (mean *c.* 2.00 Å) [10], but they are shorter than the Tc–O(3) bond (2.075(3) Å), where O(3) is *trans* to P(1).

Tc–P bond lengths in both complexes are within the range so far observed for Tc(III) P-coordinated complexes [7, 10, 11], with the exception of the Tc–P(1) distance in **1** (*vide infra*). The Tc(III)–S bond length in **1** ranges from 2.258 to 2.249 Å, the two values arising from the relative *trans* sulfur atoms. Such bond distances lie on the border line of the range shown by the structurally characterized complexes containing a Tc(III)–S bond [7, 12]. In **1** the sulfur showing the longest Tc–S bond distance belongs to the ligand that also exhibits a rather long Tc–P bond distance (2.477(1) Å in comparison with 2.406(1) and 2.424(1) Å) and a narrow P–Tc–S bite angle (78.8° compared with 84.0 and 84.5° for the two other ligands). These values might suggest the coordination of a ligand as phosphinothiol giving a complex of the type $[Tc(P\text{–}S)_2(P\text{–}SH)]^{0/+}$. However, in solution, the magnetic moment of **1** is consistent with two unpaired electrons supporting the metal in a d^4 configuration and the conductivity measurements are in agreement with the complex being neutral. Consequently, all three ligands must be deprotonated. P–XH (X = S, O) molecules, formally derived from triphenylphosphine, are bulky ligands having three phenyl rings bonded to a P(III) atom. When this inherent characteristic is accompanied by a rather encumbered functional group, as the thiophenolato system, the Tc(III) ion does not easily accommodate three ligands. On the other hand, the formation of a five-membered ring upon ligand coordination allows a good delocalization of the negative charge by conjugation through the aromatic ring between the P and X ligating atoms, and makes consequently possible the tris-coordination. When such conjugation is removed by joining the coordination atoms of the ligand with an aliphatic chain, trigonal bipyramidal configurations are observed [13]. Moreover in the molecular structure of **1** (Fig. 1) each coordinated ligand experiences, through the metal, a different situation: 'P(1)–S(1)' ligand in fact, faces two sulfur atoms, 'P(3)–S(3)' faces two phosphorous atoms and 'P(2)–S(2)' faces a phosphorous and a sulfur, respectively. So the lengthening of the Tc–P(1) and Tc–S(1) bond distances may also be the result of the *trans* labilization operated by the S(2) and S(3) atoms since they belong to the tightly bonded ligands that possess a *trans* stabilization dictated by the P(2) and P(3) atoms. In addition a formal lone pair (presumably one from S(2)) might contribute to complete the 18 valence shell of the metal, further weakening its *trans* Tc–S(1) bond length. On the contrary in the inner core of **2**, as a consequence of the *trans* stabilizing effect of the O(1) and O(2) atoms, the 'P(3)–O(3)' chelate shows the longest metal–donor bond distances.

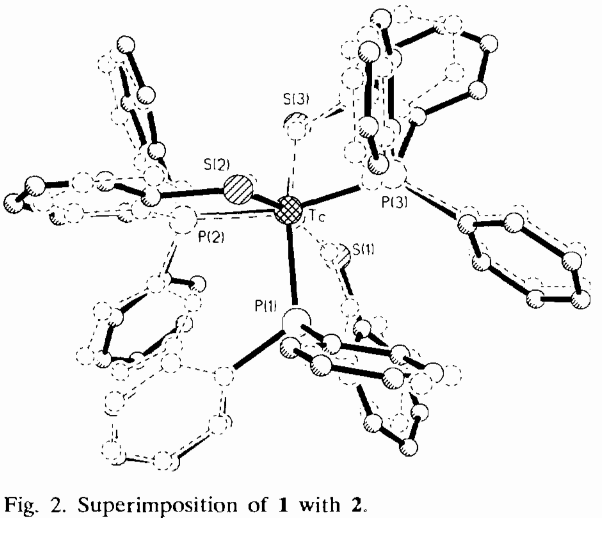

Fig. 2. Superimposition of **1** with **2**.

Supplementary material

Full presentation of data collection parameters and refinement information, fractional atomic coordinates, bond distances and angles, least-squares planes, deviations of the relevant atoms, dihedral angles, torsion angles, hydrogen atom coordinates, anisotropic displacement coefficients, observed and calculated structure factors for both compounds are available from author G.B. upon request.

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