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Reactivity of MOCl(L) (M = Tc or Re; L = *N*-(2-Oxidophenyl)salicylideneiminate or *N*-(2-Sulphidophenyl)salicylideneiminate) with Tertiary Phosphines. X-ray Molecular Structure of μ-Oxo-bis[(*N*-(2-oxidophenyl)salicylideneiminato-(2−)*NOO'*)bis(dimethylphenylphosphine)technetium(III)]

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Abstract

μ-O[Tc(L)(P)$_2$]$_2$ and ReOCl(L)(P) complexes (L = *N*-(2-oxidophenyl)salicylideneiminate (L^1) or *N*-(2-sulphidophenyl)salicylideneiminate (L^2) and P = PMe_2Ph or PPh_3) were synthesized starting from the MOCl(L) (M = Tc or Re) compounds. The characterization was performed by means of the usual physicochemical techniques and for μ-O[Tc(L^1)(PMe_2Ph)$_2$]$_2$ by means of X-ray structure determination. In the complex the coordination around each technetium atom is approximately octahedral with two phosphine ligands in the *trans* position and the remaining four equatorial sites occupied by ONO donor atom set of L^1 ligand and the bridge-oxo oxygen. Consequently the oxo oxygen is *trans* to the imino nitrogen of the L^1 ligand. The complex crystallizes in triclinic space group $P\bar{1}$ with a = 16.709(7), b = 15.255(6), c = 11.702(4) Å, α = 104.43(5), β = 86.49(6), γ = 106.91(6)°, U = 2763.6(1.8) Å^3, Z = 2. The structure has been refined to R = 0.08 for 2311 independent reflections.

Introduction

The favourable nuclear properties of the metastable isomer ^{99m}Tc has increased its use as a radiodiagnostic in nuclear medicine [1]. Consequently the knowledge of the basic chemistry of the long-lived isotope ^{99}Tc has been developed in the last few years permitting the design and preparation of new ^{99m}Tc radiopharmaceuticals [2–5].

The oxidation state of the metal seems to play, together with the ligands coordinated around it and the total charge of the resulting complex, a fundamental role in determining the biological pathway of the compound when injected in the blood pool. One of the main problems is the reduction of $Tc^{VII}O_4^-$ to lower oxidation states. An interesting series of reducing agents, less known and used by nuclear medicine practitioners than tin chloride or sodium dithionite, can be tertiary phosphines. Previous studies have established that tertiary phosphines reduce pertechnetate in acid media producing Tc(IV) and Tc(III) complexes depending on the Tc:phosphine ratio and the type of phosphine used [6]. Furthermore, tertiary phosphines can reduce oxo-Tc(V) complexes containing Schiff base ligands to the corresponding Tc(III) compounds [7, 8]. Because of the higher reduction potential [9], the oxo-Re(V) analogues do not undergo reduction reaction by tertiary phosphines. This paper deals with the synthesis of novel technetium(III) dimer complexes starting from Tc^V OCl(L) (L = *N*-(2-oxidophenyl)salicylideneiminate or *N*-(2-sulphidophenyl)salicylideneiminate) with PMe_2Ph or PPh_3. The Schiff base ligand (L) and two tertiary phosphines (P) coordinate each metal centre and an oxygen-bridge bonds two technetium atoms showing a very unusual Tc^{III}–O–Tc^{III} electronic configuration with general formulation μ-O[Tc(L)(P)$_2$]$_2$. The reactivity of ReOCl(L^2) with the same phosphines is different and, as reported in the literature for ReOCl(L^1) analogues [10], leads to ReOCl(L^2)(P) complexes, in order to reach the six-coordination, but without reduction.

The products were characterized by elemental analysis, spectroscopical measurements and X-ray structure determination for μ-O[Tc(L^1)(PMe_2Ph)$_2$]$_2$.

Experimental

Ammonium pertechnetate ($NH_4{}^{99}TcO_4$) was purchased from Radiochemical Centre, Amersham (U.K.); the starting materials for the ligand exchange

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preparations, MOCl(L) (M = Tc and Re; L = *N*-(2-oxidophenyl)salicylideneiminate or *N*-(2-sulphidophenyl)salicylideneiminate) were prepared by published methods [10–12]. PPh_3 and PMe_2Ph were obtained from Strem Chemicals, Inc. and used without further purifications.

Elemental analysis were performed on a Carlo Erba 1106 elemental analyser; technetium quantitative determinations were carried out on a Rackbeta II (model 1215) instrument, with Insta-gel, a ready-for-use xylene-based liquid scintillation cocktail (Packard Instrument Int., Zurich). Infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer spectrometer as KBr pellets or Nujol mulls between CsI pellets. ^1H NMR spectra were obtained on a Varian FT80 instrument using chloroform as solvent and $SiMe_4$ as internal reference. Conductivity measurements were made in dimethylformamide or acetonitrile solutions at 25 °C using a Metrohm Herison E518 conductometer. All the complexes were found to be non-conductive. UV–Vis spectra were recorded in dichloromethane using a Cary 17D spectrophotometer.

^{99}Tc is a weak β-emitter ($E_{\beta max} = 292$ keV with $t_{1/2} = 2.12 \times 10^5$ years). All handling of this material was carried out in laboratories approved for low-level radioactivity using glove-boxes under moderate vacuum for the synthesis and recovery operations.

Synthesis of μ-O[Tc(L)(P$_2$)]$_2$

A typical preparation is given for μ-O[Tc(L^1)-(PMe_2Ph)$_2$]$_2$. TcOCl(L^1) (51 mg, 0.14 mmol) was dissolved in EtOH (20 ml). The resulting red solution was treated with a tenfold molar excess of PMe_2Ph (0.2 ml) in EtOH solution and left stirring at room temperature for 12 h. The solution became deep red–brown and a solid was collected by filtration, washed with EtOH and several times with Et_2O to eliminate the oily unreacted phosphine. The red–brown product is soluble in CH_2Cl_2, slightly soluble in MeCN, MeOH, EtOH, insoluble in Me_2CO and Et_2O. The yields for the four μ-O[Tc(L)(P)$_2$]$_2$ complexes ranged from 50 to 70%.

Synthesis of ReOCl(L^2)(P)

ReOCl(L^2) (144 mg, 0.32 mmol) was dissolved in MeOH (30 ml) and treated with phosphine (PPh_3: 106 mg or PMe_2Ph: 0.09 ml) (0.64 mmol) at room temperature for 3 h. The starting red solution became brown–violet and a dark red–brown solid appeared. The product was filtered off, washed with EtOH and Et_2O and air dried. It is soluble in CH_2Cl_2, Me_2CO, DMF and MeCN and slightly soluble in Et_2O and alcohols. (Yield: 90–95%.)

Crystal Data

Transparent, red and irregularly shaped crystals of μ-O[Tc(L^1)(PMe_2Ph)$_2$]$_2$ were obtained by slow evaporation of a solution in CH_2Cl_2/EtOH (4/1 *v/v*).

$C_{58}H_{62}N_2O_5P_4Tc_2$, $M = 1189.0$, triclinic, $a = 16.709(7)$, $b = 15.255(6)$, $c = 11.702(4)$ Å, $\alpha = 104.43(5)$, $\beta = 86.49(6)$, $\gamma = 106.91(6)°$, $U = 2763.6(1.8)$ Å^3, $Z = 2$, $D_c = 1.428$ g cm^{-3}, $F(000) = 1220$, μ(Mo Kα) = 5.8 cm^{-1}, space group $P\bar{1}$.

Data Collection and Structure Determination

An unique data set was collected at 20 °C on a Philips PW1100 diffractometer by using a ω–2θ scan mode for all reflections for which $3 \leqslant 2\theta \leqslant 48°$, a scan range of 1.2°, a scan rate of 0.04° s^{-1} and a total background time of 16 s. The intensities of 7669 independent reflections were measured, of which only 2311 (*ca.* 30% of the total) obeyed the condition $I > 3\sigma(I)$ and were used in subsequent calculations. The data were corrected for Lorentz and polarization effects, but not for extinction or absorption. A three-dimensional Patterson map revealed the position of the Tc atoms and least-squares refinements based on Tc(1) and Tc(2) gave $R = 0.34$. A number of cycles of least-squares refinement (on treating the phenyl rings as 'rigid bodies' and assigning $w = 1$ to each reflection), followed by difference syntheses, enabled location of all non-hydrogen atoms and yielded $R = 0.13$. At this stage, all the 71 atoms of the complex exhibited rather high values of thermal motion and a Fourier difference map showed relevant electron-density peaks in the neighbourhood of both –CH=N– bridges, suggesting a positional disorder resembling that found in other similar compounds [13]. The bridge atoms were assigned two orientations corresponding to the peaks in the difference map, with a tentative population of *ca.* 1:1 and further refinement (Tc and P atoms anisotropically refined) showed that thermal motions for the 'disordered' N(1), C(1), N(1)′, C(1)′, N(2), C(30), N(2)′, C(30)′ atoms were no greater than those observed in the inner core of the compound, the model was chemically acceptable and finally the difference map in the vicinity of both bridges showed no spurious peaks. No additional refinement was carried out, owing to the low no. of parameters (2311)/no. of variables (283) ratio, even if the R value was high ($R = 0.08$).

Selected interatomic distances and angles are listed in Table 1. See also 'Supplementary Material'. The atom numbering scheme is shown in Fig. 1. The major calculations were made with the SHELX 76 program package [14].

Results and Discussion

The chemistry of transition metal ions is full of oxo-bridged binuclear complexes, that usually form spontaneously in a symmetric fashion [15]. Despite

TABLE 1. Bond Distances (Å) and Angles (°) for the 'Inner Core' of μ-O[Tc(L^1)(PMeP$_2$Ph)$_2$]$_2$[a]

Tc(1)–O(1)	1.81(2)	Tc(2)–O(1)	1.87(2)
Tc(1)–P(1)	2.45(1)	Tc(2)–P(3)	2.43(1)
Tc(1)–P(2)	2.40(1)	Tc(2)–P(4)	2.46(1)
Tc(1)–O(2)	2.02(2)	Tc(2)–O(4)	2.08(3)
Tc(1)–O(3)	2.04(3)	Tc(2)–O(5)	2.01(3)
Tc(1)–N(1)	2.14(4)	Tc(2)–N(2)	2.09(4)
Tc(1)–N(1)'	2.09(4)	Tc(2)–N(2)'	2.07(5)
	Tc(1)–O(1)–Tc(2)	176.1(1.4)	
O(1)–Tc(1)–P(1)	91.7(0.8)	O(1)–Tc(2)–P(3)	92.9(0.7)
O(1)–Tc(1)–P(2)	93.3(0.8)	O(1)–Tc(2)–P(4)	91.3(0.7)
O(1)–Tc(1)–O(2)	98.5(1.0)	O(1)–Tc(2)–O(4)	96.1(1.0)
O(1)–Tc(1)–O(3)	94.4(1.0)	O(1)–Tc(2)–O(5)	95.3(1.1)
O(1)–Tc(1)–N(1)	164.6(1.5)	O(1)–Tc(2)–N(2)	165.0(1.7)
O(1)–Tc(1)–N(1)'	169.2(1.6)	O(1)–Tc(2)–N(2)'	165.8(1.6)
P(1)–Tc(1)–P(2)	174.9(0.4)	P(3)–Tc(2)–P(4)	175.6(0.4)
O(2)–Tc(1)–O(3)	167.1(1.1)	O(4)–Tc(2)–O(5)	168.3(1.1)
O(2)–Tc(1)–N(1)'	70.7(1.5)	O(4)–Tc(2)–N(2)'	69.7(1.6)
O(3)–Tc(1)–N(1)	70.6(1.4)	O(5)–Tc(2)–N(2)	69.9(1.7)

[a]e.s.d.s given in parentheses.

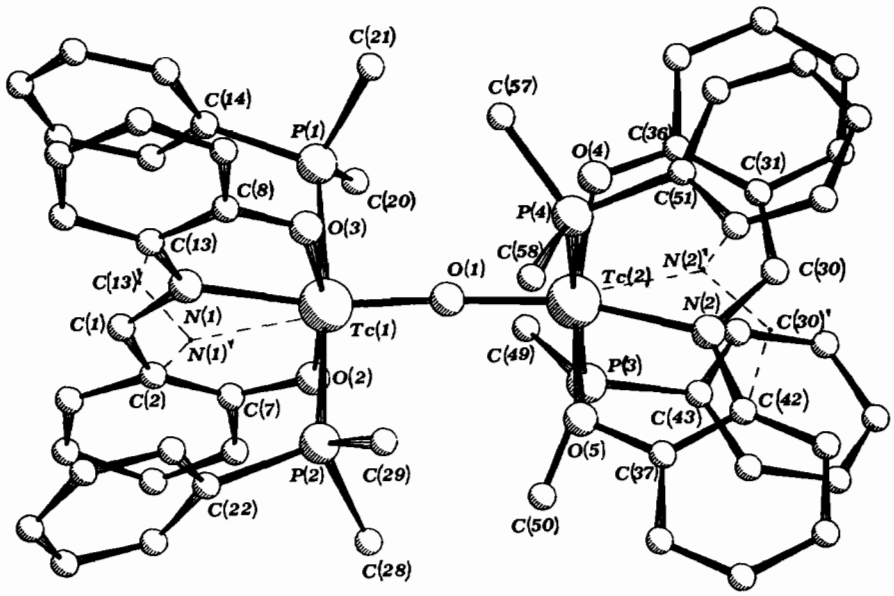

Fig. 1. Perspective view of the molecular structure of μ-O[Tc(L^1)(PMe$_2$Ph)$_2$]$_2$ together with the atom-labelling scheme. Dashed lines indicate the second orientation.

this fact the synthesis of technetium oxo-bridged binuclear complexes is quite unknown even though some examples have already been reported in the literature [16]. Of these μ-O[TcO(sal$_2$pn)]$_2$ (sal$_2$pn = *N,N'*-ethylenebis(salicylideneiminate)) was the first structurally characterized compound containing an oxo bridge between two Tc^V=O groups [17]. Only recently Clarke *et al.* reported a second structure containing the core Tc–O–Tc in the asymmetric complex [Cl(Pic$_4$Tc–O–TcCl$_4$Pic)·H$_2$O] (Pic = picoline) [18]. ESCA studies suggests that the best formulation of the oxidation states for this complex is as Tc(III)–Tc(IV) [19]. The compounds μ-O[Tc(L)(P)$_2$]$_2$ here reported represent an other example of 'thermodynamic sinks' with the metal in the unusual Tc^{III}–O–Tc^{III} electronic configuration.

The behaviour of phosphine ligands with Tc(V) and Re(V) complexes has already been investigated with octahedral starting complexes. The disubstituted Schiff base oxocomplexes Tc^{V}OCl(L')$_2$ (L' =

TABLE 2. General Properties and Elemental Analysis for the Complexes

Complex	Colour	Yield (%)	Analysis: found (calc.) (%)				
			C	H	N	P	Tc
$[Tc(L^1)(PPh_3)_2]_2O$	violet	70	69.4(69.8)	4.3(4.7)	1.8(1.7)	7.2(7.3)	11.2(11.7)
$[Tc(L^1)(PMe_2Ph)_2]_2O$	red	56	59.2(58.6)	4.9(5.2)	2.3(2.4)	10.1(10.4)	16.3(16.0)
$[Tc(L^2)(PPh_3)_2]_2O$	violet	60	68.3(68.5)	4.8(4.6)	1.5(1.6)	7.0(7.2)	11.2(10.8)
$[Tc(L^2)(PMe_2Ph)_2]_2O$	red	51	56.4(57.0)	5.0(5.2)	2.5(2.3)	9.8(10.1)	15.8(15.2)
$ReOCl(L^2)(PPh_3)$[a]	brown	95	51.5(51.2)	3.5(3.3)	1.7(1.9)	4.0(4.2)	
$ReOCl(L^2)(PMe_2Ph)$[b]	brown	91	41.9(41.8)	3.3(3.3)	2.3(2.3)	5.0(5.1)	

[a]Cl 4.8(4.9)%. [b]Cl 5.7(5.9)%.

TABLE 3. Some Important IR and UV–Vis Bands for the Complexes

Complex	ν(C=N)	ν(Re=O)	ν(Re–Cl)	Others[a]	λ_{max} (nm)[b] (ϵ ($dm^3\ mol^{-1}\ cm^{-1}$))
$[Tc(L^1)(PPh_3)_2]_2O$	1596			1095	255(7700) 410(sh) 605(sh)
$[Tc(L^1)(PMe_2Ph)_2]_2O$	1597				265(5200) 420(sh) 580(sh)
$[Tc(L^2)(PPh_3)_2]_2O$	1601			1093	265(8000) 410(sh) 575(sh)
$[Tc(L^2)(PMe_2Ph)_2]_2O$	1603				260(5300) 415(sh) 570(sh)
$ReOCl(L^2)(PPh_3)$	1608	960	324	1096	260(5000) 340(sh) 570(sh)
$ReOCl(L^2)(PMe_2Ph)$	1608	964	329		240(4600) 350(sh) 565(sh)

[a]P sensitive stretching vibration. [b]Dichloromethane solutions.

bidentate Schiff bases: *N*-methylsalicylideneiminate, *N*-phenylsalicylideneiminate, 8-quinolinolate) are reduced by PMe_2Ph to give the corresponding Tc(III) disubstituted complexes $TcCl(L')_2(PMe_2Ph)$ [7]; the disubstituted 'mixed' Schiff base oxocomplexes $TcO(L')(L^1)$, treated with PEt_2Ph produced the corresponding Tc(III) disubstituted complexes $Tc(L')(L^1)(PEt_2Ph)$ [8]. On the contrary, the analogous rhenium(V) oxocomplexes $ReOCl(L')_2$ and $ReO(L')(L)$ are completely inert to such a reduction reaction under the same conditions [7, 8].

The reduction reactions of five-coordinate complexes MOCl(L) (M = Tc, Re) with tertiary phosphine such as PPh_3 and PMe_2Ph behave differently. $ReOCl(L^2)$ reacts with phosphine ligand and gives the resulting $ReOCl(L^2)(P)$ complexes, maintaining the initial 5+ oxidation state of the metal in agreement with the previous reported $Re^VOCl(L^1)$ compounds [10], the phosphine acting as neutral ligand. Under the same reduction conditions TcOCl(L) are converted to the unusual corresponding Tc(III) dimer complexes μ-$O[Tc(L)(P)_2]_2$.

Elemental analysis for the complexes is given in Table 2; IR and UV–Vis data are given in Table 3.

The complexes μ-$O[Tc(L)(P)_2]_2$ were prepared by treating TcOCl(L) with an excess of phosphine at room temperature. The resulting red–violet products do not show in the infrared spectra any absorption in the typical region 900–1000 cm^{-1} attributable to Tc=O stretching vibration, but present the ν(C=N)

stretching frequency around 1600 cm^{-1}, characteristic of the Schiff base aldimine nitrogen coordinated to the metal. Furthermore the PPh_3 derivatives show a P sensitive absorption at 1093–1095 cm^{-1}. All Tc(III) complexes exhibit an absorption around 625 cm^{-1} which could be tentatively attributed to Tc–O–Tc stretching vibrations. UV–Vis spectra show an intense absorbance at *ca.* 260 nm (ϵ = 5000–8000 M^{-1} cm^{-1}), with two shoulders tailing into the visible region (410 and 580 nm) resulting in a red to violet colour. Conductivity measurements show the products non-conducting in dimethylformamide revealing no free charge in the complex.

The $ReOCl(L^2)(P)$ complexes were produced from the reaction of $ReOCl(L^2)$ with an excess of tertiary phosphines at room temperature. These six-coordinated compounds are particular inert to reduction reaction and maintain their structure unchanged even in boiling toluene. IR spectra of both the complexes exhibit an intense vibration at 1608 cm^{-1} (Schiff base aldimine group bonded to the metal). $ReOCl(L^2)PPh_3$ presents ν(Re=O) at 960, ν(Re–Cl) at 324 cm^{-1} and P sensitive stretching at 1096 cm^{-1}. The PMe_2Ph analogue shows ν(Re=O) at 964, and ν(Re–Cl) at 329 cm^{-1}. UV–Vis spectra of the two complexes in dichloromethane present an intense absorbance at *ca.* 250 nm and two shoulders at 345 and 570 nm. ^1H NMR in $CHCl_3$ evidentiate the presence of aldiminic proton at δ = 8.78 and 8.88 ppm for PPh_3 and PMe_2Ph derivatives, respectively. Aromatic protons fall in the region δ = 8.01–6.79 ppm while a doublet of methyl protons of $ReOCl(L^2)(PMe_2Ph)$ centred at δ = 2.34 ppm is evidentiated. Rhenium complexes are also neutral being non-conducting in acetonitrile solutions.

Spectroscopic data and elemental analysis confirm the ReOCl(L)(P) formulation. The more probable configuration around the ReO^{3+} core provides the four coordinating sites on the plane perpendicular to Re=O occupied by the tridentate ligand coordinating atoms (ONS) and the phosphorous of the phosphine ligand. The sixth site *trans* to the Re=O group should be occupied by a chlorine atom. Such a configuration has already been found and crystallographically confirmed for the analogue $ReOCl(L^1)(PMe_2Ph)$ [10].

Generally the reduction of monooxorhenium(V) species proceeds directly to mononuclear Re(III) ones with removal of oxo-oxygen, and no Re(IV) intermediates accumulate in detectable concentrations. This provides the usual synthetic route to octahedral complexes of Re(III) [20]. In fact *trans*-$Re^{V}OCl_3(PPh_3)_2$ is reduced almost quantitatively in boiling acetonitrile and in the presence of PPh_3 to the corresponding *trans*-$Re^{III}Cl_3(MeCN)(PPh_3)_2$. Moreover reduction to the same product occurs in lower yield even in the absence of free PPh_3, but the reducing agent is still PPh_3 displaced from $Re^{V}OCl_3(PPh_3)_2$ by acetonitrile [21]. Similarly PPh_3 reduces $Re^{V}OCl_2(Et_2dtc)(PPh_3)$ to $ReCl_2(Et_2dtc)(PPh_3)_2$ (Et_2dtc = diethyldithiocarbamate) [22] and PR_2Ph (R = Me, Et, n-Pr and n-Bu) reduce *trans*-$Re^{V}OCl_3(PPh_3)_2$ to *mer*-$Re^{III}Cl_3(PR_2Ph)_3$ [23]. On the contrary it is interesting to notice that the presence of Schiff base ligand(s) stabilizes the Re(V) oxocomplexes with respect to further reduction reaction. In fact Re(V) oxocomplexes were recovered unchanged when $ReOCl(L')_2$ or $ReO(L')(L)$ were treated with tertiary phosphines even in drastic conditions (refluxing in ethanol or toluene for a long time [7, 8]). The tertiary phosphines are able to replace only the more labile group of the starting $[Re^{V}O(L^1)Cl_2]^-$ or $Re^{V}OCl(L^1)$ complexes to give the compound of type ReOCl(L)(P) without reduction of the central metal. So a tridentate Schiff base ligand with a ONO or ONS coordinating atom set, as well as two bidentate ones (ON, ON), coordinated around the ReO^{3+} core strongly stabilizes this configuration and no further reduction reactions occur. It seems necessary that at least three of the four coordinating sites on the perpendicular plane to Re=O should be occupied by Schiff base coordinating atoms. In fact, when only one bidentate Schiff base ligand (ON) as in $ReOCl_2(L')P$ or $[ReOCl_3(L')]^-$ is coordinated around the metal a further reduction reaction occurs (when the phosphine ligand is used in excess) giving the $Re^{III}Cl_2L(PMe_2Ph)_2$ and $Re^{III}Cl_3(PMe_2Ph)_3$ complexes [24].

Figure 1 illustrates the molecular geometry of μ-$O[Tc(L^1)(PMe_2Ph)_2]_2$. There are no unduly short intermolecular contacts in the cell. Two technetium atoms (Tc(1)– –Tc(2) separation of 3.68 Å) are bonded through the bridging O(1) atom. Moreover, each Tc atom is bound to the L^1 ligand O_2N donor atoms and to the two PMe_2Ph phosphorus donors to form a distorted octahedron, in which the nitrogen atom is *trans* to the bridging oxygen and thus the equatorial plane of the octahedron is formed by the O_2P_2 donor set. The Tc(1)–O(1)–Tc(2) bond angle is 176.1(1.4)° and thus the arrangement is substantially linear. Because of the positional disorder about the –CH=N– bridge (see 'Experimental'), only gross structural features of the complex, containing the uncommon core Tc_2O^{4+}, have been taken into account. Bond lengths and angles in the two coordination spheres (Table 1) are comparable to those in other Tc complexes and also the corresponding bond lengths and angles of L^1 and PMe_2Ph ligands themselves are almost in agreement, even if the estimated standard deviations are very high.

The Tc(1)–O(1) and Tc(2)–O(1) bond lengths are 1.81(2) and 1.87(2) Å respectively, in agreement with those just reported for $[Cl(Pic)_4Tc–O–TcCl_4(Pic)\cdot H_2O]$ (average 1.82 Å) [18] and $Tc_2O_3(sal_2pn)$ (1.90(1) Å) [17].

Supplementary Material

Atomic positional and thermal parameters (Table A) and observed and calculated structure factors (Table B) are available from the authors on request.

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