Synthesis and Characterization of Technetium(V) Complexes with Tridentate Schiff Base Ligands. X-Ray Crystal Structure of Chloro[N-(2-hydroxyphenyl)salicylideneiminato]oxotechnetium(V)

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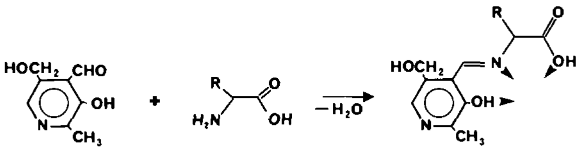
Received February 20, 1984

Five-coordinate technetium(V) complexes of the form TcO(L)Cl where L is one of the two tridentate Schiff base ligands N-(2-oxidophenyl)salicylideneiminate or N-(2-mercaptophenyl)salicylideneiminate have been synthesized and characterized. These neutral complexes precipitate from methanol upon reaction of the Schiff base ligand with $TcOCl_4^-$*. A single crystal X-ray structure determination shows that the chloro[[N-(2-oxidophenyl)salicylideneiminato](2–)-N,O,O′]oxotechnetium(V) complex,* $[TcO(C_{13}H_9NO_2)Cl]$*, formula weight 362, has a distorted square pyramidal coordination geometry with the oxo ligand in the axial position. The steric requirements of the oxo group cause the Tc atom to be displaced 0.67 Å out of the mean equatorial plane of the other four donor atoms. This complex crystallizes in the monoclinic space group* $P2_1/a$ *with* $a = 13.423(6)$ Å, $b = 12.570(5)$ Å, $c = 7.769(3)$ Å, $\beta = 106.53(5)°$, $V = 1256.7(9)$ Å^3, *and* $Z = 4$*. The structure has been refined to* $R = 0.047$ *for 1775 observed reflections.*

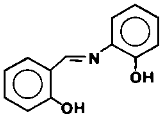
Introduction

Complexes formed from the short lived isotope ^{99m}Tc ($t_{1/2} = 6$ h) are widely used in nuclear medicine as imaging agents because of the ideal nuclear properties of this isotope [1]. Technetium-99m complexes of pyridoxylideneaminates, derived from the condensation of pyridoxyl with amino acids, have shown promise as hepatobiliary imaging agents [2].

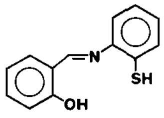


Pyridoxylideneamine

These Tc-99m radiopharmaceuticals are prepared by the reduction of pertechnetate ($^{99m}TcO_4^-$) in the presence of excess pyridoxylideneaminate ligand, however nothing is known of the structure or composition of these agents due in part to the very small amounts of product formed in radiopharmaceutical preparations. Since these pyridoxylideneaminate ligands can function as tridentate chelates (*via* the imine nitrogen atom, phenolic oxygen atom, and carboxylate oxygen atom) there are a number of possible ways in which coordination to a reduced technetium center can occur. In order to determine which of these possible coordination modes might be favored, we have investigated the interaction of the analogous tridentate Schiff base ligands N-(2-hydroxyphenyl)salicylideneimine* (hereafter referred to as H_2Ophsal, with the doubly deprotonated form being designated Ophsal) and N-(2-mercaptophenyl)salicylideneimine** (hereafter referred to as H_2Sphsal, with the doubly deprotonated from being designated Sphsal)



H_2Ophsal



H_2Sphsal

with technetium(V) using macroscopic amounts of the relatively stable isotope ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ y).

The technetium(V) complex $TcOCl_4^-$ has been recently characterized and shown to be a convenient starting material for the synthesis of a variety of

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*Current Chemical Abstracts index name is 2-[[2-hydroxyphenyl)imino]methyl]phenol.

**Current Chemical Abstracts index name is 2-[[(2-mercaptophenyl)imino]methyl]phenol.

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technetium(V) complexes [3, 4]. These synthetic reactions involve simple displacement of the relatively labile chlorides by the ligand of interest. In this paper we report on the synthesis and characterization of complexes of technetium(V) prepared by substitution of H_2Ophsal and H_2Sphsal onto $TcOCl_4^-$ and the X-ray crystal structure of the complex formed with H_2-Ophsal.

Experimental

General

Technetium-99 emits a low energy (0.292 MeV) beta particle with a half-life of 2.12×10^5 years. When this material is handled in milligram amounts, it does not present a serious health hazard since common laboratory materials provide adequate shielding. *Bremsstralung* is not a significant problem due to the low energy of the beta particle emission, but normal radiation safety procedures must be used at all times to prevent contamination.

All chemicals were of reagent grade. Infrared spectra were obtained from KBr pellets using a Perkin-Elmer 599 spectrometer. UV-Vis spectra were recorded in ethanol solutions using a Cary 210 spectrophotometer.

*Preparation of TcO(Ophsal)Cl and TcO(Sphasal)Cl****

H_2Ophsal was prepared by condensation of salicylaldehyde with 2-aminophenol in ethanol. H_2Sphsal was prepared similarly using 2-aminothiophenol. $[Bu_4N]TcOCl_4$ (where Bu = n-C_4H_9) was prepared as reported [3]. TcO(Ophsal)Cl was prepared by dissolving 0.150 g (0.301 mmol) of $[Bu_4N]TcOCl_4$ in 10 mL of methanol and adding a solution of 0.147 g (0.689 mmol) of H_2Ophsal in 5 mL of methanol. The resulting green-brown colored solution was stirred for 15 min and placed in the freezer overnight. A dark purple precipitate was recovered by filtration, washed with methanol and ether and dried *in vacuo* over P_2O_5. The yield of TcO(Ophsal)-Cl was 94%. *Anal.* Calcd. for TcO(Ophsal)Cl: C, 43.16; H, 2.51; N, 3.87; Cl, 9.81. Found: C, 42.39; H, 3.34; N, 3.53; Cl, 9.89. TcO(Sphsal)Cl was similarly prepared in 70% yield. *Anal.* Calcd. for TcO(Sphsal)Cl: C, 41.39; H, 2.40; N, 3.71; S, 8.48; Cl, 9.41. Found: C, 42.66; H, 2.68; N, 4.11; S, 9.86; Cl, 9.62.

Crystal Structure Determination of TcO(Ophsal)Cl

Single crystals of the complex were obtained from a dichloromethane-tetrachloroethylene solution by slow evaporation. Crystal data and other information related to data collection are summarized in Table I. The technetium atom was found from a three-dimensional Patterson synthesis. A series of full matrix least-squares refinements and electron density difference syntheses revealed all atoms. At this stage the temperature factors of the technetium and chlorine atoms were made anisotropic, while the isotropic factor *U* for the hydrogen atoms was fixed to 0.06 Å^2. The choice of unit weighting scheme was justified by the successful refinement of the structure. The scattering curves and anomalous dispersion corrections were taken from the literature [5]. All calculations were carried out on a CDC CYBER70/model 76 computer system [6].

Results

Synthesis and Characterization

The utility of $TcOCl_4^-$ as starting material for the preparation of Tc(V) complexes has been demonstrated previously [7–11]. In this work, solid products were readily obtained from methanol by simple displacement of three of the chloride ligands of $TcOCl_4^-$ by either of the Schiff base ligands N-(2-oxidophenyl)salicylideneiminate (Ophsal) or N-(2-mercaptophenyl)salicylideneiminate (Sphsal). While relatively insoluble in methanol, these products are much more soluble in nonpolar organic solvents such as chloroform and dichloromethane.

Table II lists the UV-Vis and IR spectral parameters of the two complexes. The UV-Vis spectra are similar with respect to the bands at approximately 335 nm and 220 nm, while the band that appears as a shoulder at 445 nm for the Ophsal complex is shifted to 406 nm for the Sphsal species. More dramatically, there is a band at 271 nm for the Sphsal complex which does not appear in the spectrum of the Ophsal analog.

The salient IR parameter for these complexes is the strong absorption at 980 cm^{-1} for the Ophsal complex and at 970 cm^{-1} for the Sphsal complex assignable to the Tc=O stretch of the TcO^{3+} core. Strong absorptions in this region are almost always observed for complexes containing the technetium-(V) TcO^{3+} core [1].

Crystal Structure of TcO(Ophsal)Cl

The molecular structure of the title complex, with the associated atom numbering scheme, is depicted in Fig. 1. Final atomic positional parameters are listed in Table III. Selected interatomic distances and bond angles are listed in Table IV. Information concerning selected molecular planes, dihedral angles, torsion angles and intramolecular contacts is given in Table V. Temperature factors (Table A), positional parameters for hydrogen atoms (Table B) and observed and calculated structure factors (Table C) have

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***Current Chemical Abstracts index names are chloro[[2-[[(2-hydroxyphenyl)imino]methyl]phenolato](2–)-N,O,O′]-oxotechnetium and chloro[[2-[[(2-mercaptophenyl)imino]-methyl]phenolato](2–)-1-N,O,S]oxotechnetium.

TABLE I. Crystal and Data Collection Parameters for TcO(Ophsal)Cl.

Formula weight	361.70
Crystal size, mm (cylinder)	$r = 0.08$, $l = 0.32$
System	monoclinic
Space group	$P2_1/a$
Unit cell parameters	$a = 13.423(6)$, $b = 12.570(5)$, $c = 7.769(3)$ Å, $\beta = 106.53(5)$
V; Z; $F(000)$	1256.7(9) Å^3; 4; 648
ρ(calc), ρ^a(obs), g/cm^3	1.74, 1.73(1)
Linear abs. coeff., cm$^{-1\,b}$	13.1
Diffractometer, radiation	Philips PW1100, Mo-K$_\alpha$ (λ = 0.7107 Å)
Scan mode	$\theta - 2\theta$
Scan range	1.3°
Scan rate	1.8° min^{-1}
Background time	10 sec at each end
Max 2θ; octant	56°; $\pm h, k, l$
Standard reflection (est, %)	002(2.4), $\bar{2}$22(1.8), 600(1.4)
No. independent reflections	3033
No. reflections in refinement	1775
No. variables (last cycle)	114
Function minimized; w	$\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2$; 1
$R_1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.047
Final shift/error max (av) non-hydrogen atoms	0.15(0.04)
Final difference map highest peak, e/Å^3; location	0.7; 0.56; 0.29; 0.01 and 0.7; 0.49; 0.34; −0.14

[a] By flotation in $CCl_4/CHCl_3$. [b] An experimental absorption correction, based on ψ scans, was applied following the method of A. C. T. North, D. C. Philipps and F. S. Mathews, *Acta Cryst., Sect. A, 24*, 351 (1968).

TABLE II. UV-Vis and IR Spectral Parameters for TcO(Ophsal)Cl and TcO(Sphsal)Cl[a, b].

Complex	$\lambda_{max}(\epsilon)^c$	$\nu_{Tc=O}$
TcO(Ophsal)Cl	223(22,000) 333(12,000) 445(sh)(4,000)	980
TcO(Sphsal)Cl	215(27,000) 271(15,000) 335(11,000) 406(sh)(4,000)	970

[a] λ_{max} in nm, ϵ in M^{-1} cm^{-1}, ν in cm^{-1}. [b] Ligand acronyms defined in Introduction. [c] Ethanol solutions.

been deposited with the editors of this journal as supplementary material.

Discussion

Synthesis and Characterization

The complexes TcO(Ophsal)Cl and TcO(Sphsal)Cl are the first reported members of a new class of technetium(V) complexes, i.e. those containing a tridentate Schiff base ligand. They extend the range of known Tc(V) Schiff base complexes, derivatives of bidentate [10] and tetradentate [7] Schiff base ligands having been very recently reported. These newer complexes are characterized by elemental analyses which give results in agreement with the

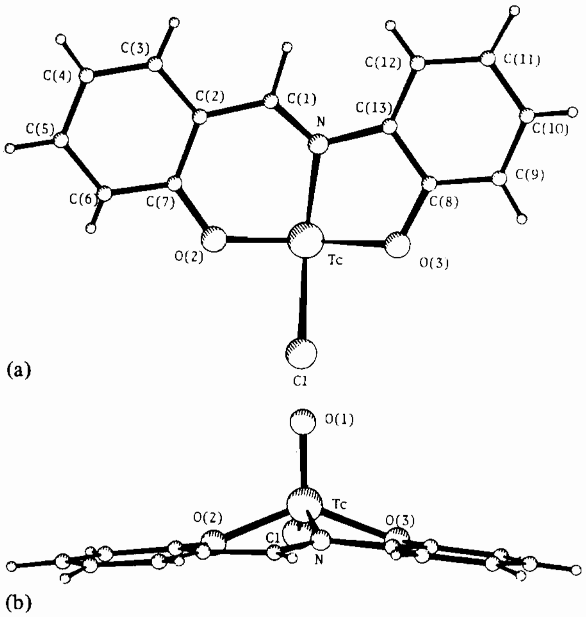


Fig. 1. (a) Perspective view of TcO(Ophsal)Cl viewed down the Tc–O(1) axis. (b) Perspective view of the coordination around the technetium atom in TcO(Ophsal)Cl.

TABLE III. Atomic Positional Parameters (×10^4) for TcO(Ophsal)Cl*.

Atom	x	y	z
Tc	3385(0)	2767(1)	−2418(1)
Cl	1654(2)	3100(2)	−2750(3)
O1	3434(4)	2092(5)	−4190(8)
O2	3445(4)	4293(4)	−2818(1)
O3	3285(4)	1839(5)	−465(8)
N1	4872(5)	2851(6)	−732(8)
C1	5553(6)	3569(7)	−751(11)
C2	5337(6)	4507(6)	−1840(10)
C3	6170(7)	5172(7)	−1818(12)
C4	6011(7)	6109(8)	−2754(13)
C5	5022(6)	6439(7)	−3683(11)
C6	4178(7)	5816(7)	−3688(12)
C7	4312(6)	4840(6)	−2785(10)
C8	4218(6)	1456(6)	590(10)
C9	4272(7)	610(7)	1754(12)
C10	5228(8)	289(8)	2787(13)
C11	6128(7)	779(8)	2714(13)
C12	6084(7)	1638(8)	1567(12)
C13	5118(6)	1960(6)	512(11)

*Ligand acronym defined in Introduction.

TABLE IV. Interatomic Distances (Å) and Angles (Deg) for TcO(Ophsal)Cl*.

Tc–Cl	2.302(3)	C(6)–C(7)	1.40(1)
Tc–O(1)	1.634(7)	C(7)–C(2)	1.42(1)
Tc–O(2)	1.948(5)	C(7)–O(2)	1.35(1)
Tc–O(3)	1.948(6)	O(3)–C(8)	1.37(1)
Tc–N	2.055(6)	C(8)–C(13)	1.38(1)
N–C(1)	1.29(1)	C(8)–C(9)	1.38(1)
C(1)–C(2)	1.43(1)	C(9)–C(10)	1.37(1)
C(2)–C(3)	1.39(1)	C(10)–C(11)	1.37(1)
C(3)–C(4)	1.37(1)	C(11)–C(12)	1.39(1)
C(4)–C(5)	1.38(1)	C(12)–C(13)	1.38(1)
C(5)–C(6)	1.38(1)	C(13)–N	1.45(1)
O(1)–Tc–Cl	106.3(2)	N–C(1)–C(2)	124.0(8)
O(1)–Tc–O(2)	111.3(3)	C(1)–C(2)–C(7)	123.3(7)
O(1)–Tc–O(3)	111.9(3)	C(2)–C(7)–O(2)	124.2(7)
O(1)–Tc–N	107.4(3)	C(7)–O(2)–Tc	125.1(5)
Cl–Tc–O(2)	83.6(2)	Tc–O(3)–C(8)	114.9(5)
Cl–Tc–O(3)	84.6(2)	O(3)–C(8)–C(13)	118.3(7)
Cl–Tc–N	145.9(2)	C(8)–C(13)–N	110.3(7)
O(2)–Tc–N	88.5(3)	C(1)–C(2)–C(3)	117.4(8)
O(2)–Tc–O(3)	136.8(2)	C(6)–C(7)–O(2)	116.8(8)
N–Tc–O(3)	78.7(3)	O(3)–C(8)–C(9)	121.9(8)
Tc–N–C(1)	126.3(6)	N–C(13)–C(12)	128.1(8)
Tc–N–C(13)	112.3(5)	$C_{ph}-C_{ph}-C_{ph}$ mean	120.0(5)
C(1)–N–C(13)	121.3(7)		

*Ligand acronym defined in Introduction.

proposed formulations, by a single crystal X-ray structure determination of TcO(Ophsal)Cl (*vide infra*), and by the analogous UV-Vis and IR spectral parameters of the two complexes (Table II). The magnitude of the extinction coefficients in the UV-Vis spectra indicates that the absorptions are due to charge transfer transitions. In particular, the band at 271 nm in the Sphsal complex does not appear in the Ophsal analog. From this evidence the 271 nm band may be assigned as arising from a sulfur-to-metal charge transfer transition. Such transitions are often observed when thiols are coordinated to potentially oxidizing metal centers [12]. The individual spectra of other technetium(V) complexes containing coordinated sulfur exhibit absorption bands at widely varying energies [13–17] and therefore the energy of sulfur-to-Tc(V) charge transfer band appears to be very dependent on the nature of the sulfur-containing ligand.

Crystal Structure of TcO(Ophsal)Cl

Figure 1 illustrates the geometry and the atom numbering scheme for the title complex. The Ophsal moiety acts as a tridentate O, N, O ligand to the Tc atom which resides in an approximately square pyramidal coordination environment. The Ophsal ligand occupies three of the four coordination sites of the

TABLE V. Selected Geometrical Features for TcO(Ophsal)Cl*.

(a) Least squares planes

Plane	Atoms defining plane	Dev. of atoms from the plane (Å)
1	Cl, O(2), N, O(3)	Cl 0.01; O(2) –0.04; N 0.01; O(3) –0.06; Tc 0.67; C(7) –0.09; C(2) –0.10; C(1) –0.13; C(13) –0.08; C(8) –0.15; O(1) 2.30
2	C(2), C(3), C(4), C(5), C(6), C(7)	C(2) 0.01; C(3) –0.02; C(4) 0.01; C(5) 0.01; C(6) –0.01; C(7) 0.00; O(2) –0.05; O(1) –0.09; N 0.00
3	C(8), C(9), C(10), C(11), C(12), C(13)	C(8)–(13) 0.00; O(3) –0.03; N –0.05

(b) Dihedral angles between planes and between line Tc–O(1)(L) and normal to planes

1–2	4.4°	1–L	0.3°
1–3	8.0°	2–L	4.6°
2–3	11.5°	3–L	8.1°

(c) Torsion angles

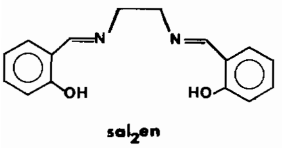
Tc–O(2)–C(7)–C(2)	–24.3°	C(1)–N–C(13)–C(8)	165.2°
O(2)–C(7)–C(2)–C(1)	–2.8°	N–C(13)–C(8)–O(3)	0.6°
C(7)–C(2)–C(1)–N	11.2°	C(13)–C(8)–O(3)–Tc	17.2°
C(2)–C(1)–N–C(13)	–174.9°		

(d) Some intramolecular contacts (Å)

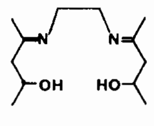
Tc- - -C(1)	3.00	Tc- - -C(8)	2.82
Tc- - -C(13)	2.93	O(2)- - -N	2.80
Tc- - -C(7)	2.94	O(3)- - -N	2.54
Tc- - -C(2)	3.34		

*Ligand acronym defined in Introduction.

basal plane of this pyramid. This is but one of the anticipated ways in which a tridentate Schiff base ligand could coordinate to a technetium(V) center. It is known that upon reaction with $TcOCl_4^-$, tetradentate Schiff base ligands such as sal$_2$en and acac$_2$en

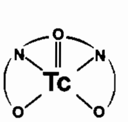


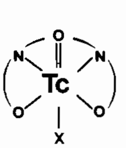
sal$_2$en



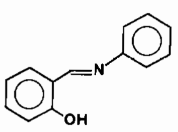
acac$_2$en

form five- or six-coordinate technetium(V) complexes of the general formula *tr*-TcO(L)X, where X is a monodentate ligand or a vacant coordination site [7]. In these complexes, the tetradentate Schiff base ligand occupies the four planar coordination sites of a square pyramid (about TcO^{3+}) or an octahedron (about *tr*-$TcO(X)^{n+}$).



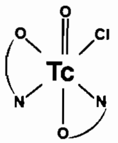


It is also known that upon reaction with $TcOCl_4^-$ the bidentate Schiff base ligand Hphsal forms the

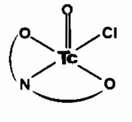


Hphsal

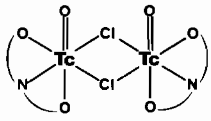
six-coordinate bis(chelate) complex $TcO(L)_2Cl$ in which one Schiff base ligand occupies two equatorial coordination sites, and the other Schiff base ligand bridges equatorial and apical coordination sites [10].



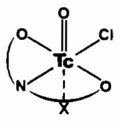
From these observations, and the tendency of technetium(V) to accept a variety of ligand configurations about TcO^{3+} and *tr*-TcO_2^+ cores [1, 18], tridentate Schiff base ligands such as H_2Ophsal could be anticipated to satisfy the coordination requirements of technetium(V) in a variety of fashions, *e.g.*



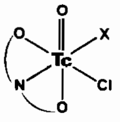
(A) five-coordinate



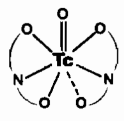
(B) six-coordinate



(C) six-coordinate



(D) six-coordinate



(E) seven-coordinate

The observation that the reaction of H_2Ophsal with $TcOCl_4^-$ in methanol leads to the five coordinate square pyramid complex (A) presumably results from the steric requirements of the tridentate ligand (*vide infra*).

Table VI lists some structural parameters for other five-coordinate Tc(V) complexes as well as for six coordinate Tc(V) Schiff base complexes. In the TcO(Ophsal)Cl complex, the bond from Tc to the 'yl' oxygen atom is 1.634(7) Å long (Table IV); this length is typical for complexes where only one Tc=O linkage is present (1.65 Å average) [18] and indicates multiple bond character in the $Tc=O^{3+}$ linkage. This tightly bonded $Tc=O^{3+}$ core dominates the chemistry of Tc(V) complexes [1, 18]. The steric requirements of the 'yl' oxygen atom severely distort the geometry of the complex and result in non-orthogonal angles at technetium (Table IV). As a result, the Tc atom is displaced 0.67 Å out of the mean equatorial plane towards the 'yl' oxygen atom (O(1)). This displacement is within the range of 0.65 to 0.80 Å reported for comparable five-coordinate Tc(V) complexes [18]. However, this 0.67 Å displacement is smaller than observed for most of the other five-coordinate species because of the steric requirements of the pi structure of the Ophsal ligand, while it is greater than observed in the six-coordinate complexes because of the steric requirements of the *trans* ligand in these species. Table VI also shows that the basal Tc–O lengths of 1.948 Å are similar to basal Tc–O lengths observed in other five-coordinate complexes, but are generally shorter than those observed for the more crowded six-coordinate species.

The Tc–Cl bond length of 2.302(3) Å is similar to that in $TcOCl_4^-$ (2.31 Å) [18], the only other five-coordinate *cis*-Tc(O)Cl species reported, and, as expected, is shorter than the Tc–Cl lengths in six-coordinate species (Table VI). The Tc–N length falls within the range reported for other imine nitrogen atoms in six-coordinate species.

The structure of $TcO(phsal)_2Cl$ has been reported [10], where phsal is the N-(phenyl)salicylideneiminate ligand described previously. This bidentate O, N donor ligand differs from the tridentate H_2-Ophsal only by the lack of a coordinating phenolato oxygen atom. Table VII lists selected angles within the TcO(Ophsal)Cl structure along with the corresponding angles associated with the equatorial phsal ligand in $TcO(phsal)_2Cl$. (The other phsal ligand bridges axial and equatorial coordination sites). Table VIIa shows angles for the six membered ring

TABLE VI. Bond Parameters (Å) for Complexes Containing the TcO^{3+} Core. (a) Five-coordinate, Square Planar, Tc(V) Complexes. (b) Six-coordinate, Octahedral, Tc(V) Schiff Base Complexes.

Complex	Tc=O	Tc–O_{eq} [a]	Tc displacement towards Tc=O from equatorial plane	Tc–N_{eq} [b]	Tc–Cl	Ref.
(a) TcO(Ophsal)Cl[c]	1.634(7)	1.948(5)	0.67	2.055(6)	2.302(3)	d
$TcO(SCH_2CH_2S)_2^-$	1.64(1)	–	0.76	–	–	19
$TcO(SCH_2C(O)S)_2^-$	1.672(8)	–	0.79	–	–	13
$TcO(SCH_2CH_2O)_2^-$	1.662(5)	1.950(6) av	0.72	–	–	14
$TcO(O_2C_6H_4)_2^-$	1.648(5)	1.957(3) av	0.70	–	–	20
$TcO(ema)^-$ [e]	1.679(5)	–	0.77	f	–	21
(b) $TcO(sal_2en)Cl$[g]	1.626(7)	1.990(9) av	0.28	2.045(11) av	–	7
$TcO(oxMe)_2Cl$[h]	1.649(3)	1.947(3)	0.22	2.197(3) av	2.360(1)	11
$TcO(acac_2en)(H_2O)^+$ [g]	1.648(5)	2.080(2) av	0.37	2.002(2) av	–	7
$TcO(phsal)_2Cl$	1.67(1)	1.99(1)	0.19	2.12(1)	2.38(1)	18

[a] O_{eq} refers to oxygen atoms in the equatorial plane. [b] N_{eq} refers to nitrogen atoms in the equatorial plane. [c] Acronym defined in Introduction. [d] This study. [e] ema = $[SCH_2C(O)NHCH_2CH_2NHC(O)CH_2S]^{2-}$. [f] Not reported. [g] Acronym defined in Discussion. [h] oxMe = 2-methyl-8-quinolinate.

TABLE VII. Selected Angles for TcO(Ophsal)Cl[a] and $TcO(phsal)_2Cl$[b].

	TcO(Ophsal)Cl[c]	$TcO(phsal)_2Cl$[d]
a) N–Tc–O(2)	88.5(3)	90.5(5)
Tc–N–C(1)	126.3(6)	123.3(1.1)
N–C(1)–C(2)	124.0(8)	125.5(1.5)
C(1)–C(2)–C(7)	123.3(7)	124.6(1.6)
C(2)–C(7)–O(2)	124.2(7)	126.6(1.6)
C(7)–O(2)–Tc	125.1(5)	125.9(1.1)
b) Tc–N–C(13)	112.3(5)	121.0(1.0)
C(1)–N–C(13)	121.3(7)	115.4(1.3)
c) N–Tc–O(1)	107.4(3)	87.4(5)
O(1)–Tc–O(2)	111.3(3)	101.9(5)
O(1)–Tc–O(3)	111.9(3)	
O(1)–Tc–Cl	106.3(2)	101.4(4)

[a] Ligand acronym defined in Introduction. [b] Ligand acronym defined in Discussion. [c] This study. [d] Reference 10.

involving Tc and the salicylideneimine portion of the ligands. The angles are very similar, varying by at most 3° at the N atom (see also Fig. 1a). Table VIIb shows the effect of coordination of the phenolato oxygen atom (resulting in a five membered chelate ring) on the angles about the imine N. The Tc–N–C(13) angle in the ring is approximately 8° smaller than in the phsal complex, while the outer C(1)–N–C(13) angle is correspondingly larger by about 6°. (There is also a 3° difference in the C(1)–N–Tc angle.) This additional chelation effect probably contributes to the Tc–N bond of the Ophsal complex being shorter than that of the phsal complex (2.055(6) Å *vs.* 2.12(1) Å). It should also be noted that the dihedral angles between the two phenylic rings are 11.5° in TcO(Ophsal)Cl and 59.6° in $TcO(phsal)_2Cl$. The more coplanar rings in the Ophsal complex generate more steric crowding which contributes to the angular distortions about the N atom. Table VIIc shows that the angles between Tc=O and the basal coordinating atoms in TcO(Ophsal)Cl are larger than the corresponding angles in $TcO(phsal)_2Cl$, presumably because of the constraints imposed by tridenticity and the lack of a ligand *trans* to the oxo group in TcO(Ophsal)Cl.

Acknowledgements

Financial support by the National Institutes of Health through Grant number HL-21276, (to E.D.) and a Bilateral Project Grant between the CNR (Italy) and the University of Cincinnati (U.S.A.), is gratefully acknowledged.

Supplementary Material

Tables of temperature parameters (Table A), positional parameters for hydrogen atoms (Table B) and observed and calculated structure factors (Table C) have been deposited with the editors of this journal.

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