Neutral Oxo and Nitrido Complexes of Technetium(V) and Rhenium(V) with an Unsaturated Tetradentate (N_2S_2) Ligand. Crystal Structure of [*N,N'*-Ethylenebis(thioacetylacetonylideneiminato)(2−)-*S,S',N,N'*]nitridotechnetium(V)†

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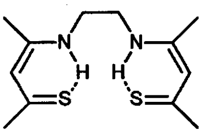
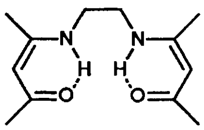
Ligand-exchange reactions of the tetradentate unsaturated N_2S_2 Schiff-base ligand *N,N'*-ethylenebis(thioacetylacetonylideneimine) (H_2L) with labile monooxo-technetium(V) and -rhenium(V) compounds ($[NBu_4][TcOCl_4]$; $[NBu_4][ReOCl_4]$ or $[ReOCl_3(PPh_3)_2]$) gave two types of neutral six-co-ordinated species [MO(L)Cl] and $[\{MO(L)\}_2O]$ (M = Tc or Re). The monooxo monomeric complexes rearrange to the μ-oxo dimeric species *via* a charged labile intermediate in wet organic solvents or when solutions are kept in contact with air. Reaction of H_2L with $[NBu_4][Tc^{VI}NCl_4]$ follows a reduction–substitution route to give another neutral, but five-co-ordinated species, [TcN(L)] which contains the $[Tc^{V}{\equiv}N]^{2+}$ nitrido core. All complexes have been characterized by means of standard spectroscopic techniques. The influence of the metal on ligand ^1H NMR chemical shifts is discussed. The technetium centre shifts all the ligand protons more downfield than does rhenium. This behaviour is in general agreement with the stronger acidity of the $[TcO]^{3+}$ core with respect to $[ReO]^{3+}$. The five-co-ordination of the nitrido complex [TcN(L)] is confirmed by its X-ray structure determination: monoclinic, space group $P2_1/n$, $a = 14.654(7)$, $b = 12.62(5)$, $c = 7.819(4)$ Å, $\beta = 92.60(3)°$ and $Z = 4$. The co-ordination sphere around the Tc centre is nearly square pyramidal with an apical multiply bonded nitrogen atom [Tc≡N 1.621(8) Å].

During the past decade, the application of the principles and techniques of inorganic chemistry has enhanced the knowledge of many clinically used ^{99m}Tc radiopharmaceuticals.[1] Because of the pre-eminence of this isotope in diagnostic nuclear medicine, this new approach has created a growing interest in the inorganic chemistry of the long-lived isotope ^{99}Tc (weak β-emitter, $E_{\beta max} = 292$ keV; $t_{\frac{1}{2}} = 2.12 \times 10^5$ years). Driven by the aims of nuclear medicine, several new technetium compounds have been proposed and evaluated as useful ^{99m}Tc organ-imaging agents.[2] A specific goal of this work has been the design and synthesis of a class of neutral oxotechnetium(V) complexes containing bis(aminethiol) N_2S_2 ligands.[3–10] The ability of such compounds to cross the blood brain barrier has been demonstrated and, in order to improve both the uptake and/or the retention in the brain tissue, many structural modifications on the ligand skeleton have been attempted. Up to now, only saturated bis(aminethiol) ligands have been studied extensively and all the resulting technetium complexes involve co-ordination around the $[TcO]^{3+}$ core. In this preliminary work, we have studied co-ordination of the unsaturated N_2S_2-type ligand, *N,N'*-ethylenebis(thioacetylacetonylideneimine) (H_2L) to the well known $[MO]^{3+}$ (M = Tc or Re) core and we have extended this investigation to the relatively less well known $[TcN]^{2+}$ core. Neutral complexes of the general formulae [MO(L)Cl], $[\{MO(L)\}_2O]$ (M = Tc or Re) and [TcN(L)] have been synthetized and characterized. The ligand H_2L shows a great versatility in that it allows stabilization of Tc^V and Re^V within different cores. Moreover, H_2L as well as bis(aminethiol) ligands offers wide possibilities for structural modification without alteration of the N_2S_2 donor-atom set.



H_2L



H_2L'

Another interesting feature is the comparison of the reactivity of H_2L with that of the oxo analogue *N,N'*-ethylenebis(acetylacetonylideneimine)(H_2L'). Wilkinson and co-workers[11,12] have developed the rhenium(V) chemistry of this ligand while Deutsch and co-workers[13,14] have studied the Tc^V and Tc^{III} chemistries with particular emphasis on complexes of type $[Tc^{III}(L')(PR_3)_2]^+$ (PR_3 = tertiary phosphine). These reduced cationic species are the prototypes for a series of new potential ^{99m}Tc heart imaging agents.[15,16]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Crystal and data collection parameters for [TcN(L)]

Formula	$C_{12}H_{18}N_3S_2Tc$
M	367.3
Crystal size/mm (lath)	$r = 0.1, l = 0.4$
System	Monoclinic
Space group	$P2_1/n$
Unit cell parameters	
a/Å	14.654(7)
b/Å	12.621(5)
c/Å	7.819(4)
β/°	92.60(3)
U/Å³	1444.6(1.2)
Z	4
F(000)	744
μ(Mo-Kα) cm⁻¹	11.5
D(calc.), *D*(obs.)/g cm⁻³	1.688, 1.70 (by flotation in $CCl_4/CHCl_3$)
Diffractometer	Philips PW 1100
Radiation	Mo-Kα (λ = 0.7107 Å)
Scan mode/°	θ–2θ
Scan range/°	1.3
Scan rate/° min⁻¹	1.8
Background time	10 s at each end
Max 2θ/°	54
No. independent reflections	3145
No. reflections [$I > 3\sigma(I)$] in refinement	1653
No. variables	163
Function minimized	$\Sigma(F_o - F_c)^2$
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.049
Final shift/error max. (av.)	0.08 (0.03)
Final difference-map highest peak/e Å⁻³	0.7

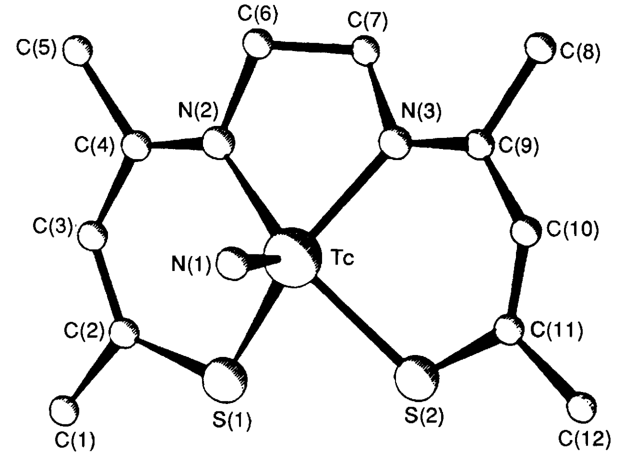


Fig. 1 ORTEP diagram of [TcN(L)]

Table 2 Atomic positional parameters (× 10⁴) for [TcN(L)]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Tc	2013.4(6)	710.8(7)	358.5(10)
S(1)	3559(2)	421(2)	1139(4)
S(2)	2530(2)	2453(2)	−71(4)
N(1)	1480(5)	758(8)	2127(10)
N(2)	1845(5)	−879(7)	−405(10)
N(3)	1028(5)	912(6)	−1685(10)
C(1)	4703(8)	−1182(10)	2194(17)
C(2)	3774(7)	−904(9)	1394(12)
C(3)	3178(8)	−1711(9)	995(14)
C(4)	2284(8)	−1718(8)	141(14)
C(5)	1893(9)	−2829(9)	−150(16)
C(6)	956(7)	−1015(8)	−1349(16)
C(7)	805(8)	−104(8)	−2544(14)
C(8)	−129(8)	1713(11)	−3690(17)
C(9)	628(6)	1781(8)	−2259(14)
C(10)	879(7)	2831(8)	−1739(14)
C(11)	1646(7)	3199(8)	−921(13)
C(12)	1792(8)	4394(9)	−782(14)

Experimental

Materials.—Unless otherwise stated, all chemicals were of reagent grade. The complex $[ReOCl_3(PPh_3)_2]$ was prepared from potassium perrhenate (Aldrich) using the method of Chatt *et al*.;[17] $[NBu_4][ReOCl_4]$ was obtained by the methods described in the literature.[18] Technetium as $[NH_4][^{99}TcO_4]$ was purchased from the Radio Chemical Centre, Amersham; $[NBu_4][TcOCl_4]$ and $[NBu_4][TcNCl_4]$ were synthesized by published procedures.[19,20] All solvents were stored over molecular sieves, except for toluene which was dried over sodium wire.

Physical Measurements.—Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser. Determinations of technetium were carried out on a Rackbeta II (model 1215) instrument, with Instagel, a ready-for-use xylene-based liquid scintillation cocktail (Packard Instrument, Zürich). Infrared spectra were recorded in the range 4000–300 cm⁻¹ on a Perkin-Elmer 984 spectrometer using KBr pellets or Nujol mulls between CsI discs. NMR spectra were run on a Bruker WH 90, WH 200 or WH 250 instrument using $SiMe_4$ (¹H spectra) or $CDCl_3$ (¹³C spectra) as internal reference. Magnetic measurements on powdered samples were carried out with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. UV/VIS spectra were recorded in different solvents using a Cary 17D spectrophotometer. Conductivity measurements were made at 25 °C using a Metrohm Herison E518 conductometer. Fast-atom bombardment (FAB) mass spectra in the positive mode were recorded by using a glycerol matrix on a VG 30-250 spectrometer (VG Instrument) at the probe temperature. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV and 100 μA. Data were collected over the mass range 100–1000 at 0.7 s per scan. Technetium-99 is a weak β emitter ($E_{\beta max} = 292$ keV, $t_{\frac{1}{2}} = 2.12 \times 10^5$ years). 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.

Crystal Structure Determination of [TcN(L)].[21]—Crystal data and other information related to the data collection and structure determination are summarized in Table 1. The technetium atom was found from a three-dimensional Patterson synthesis. Two cycles of full-matrix least-squares refinements and electron density difference syntheses revealed all non-hydrogen atoms. The choice of unit weighting scheme in the refinement procedure, with anisotropic thermal parameters for all atoms was justified by the successful refinement of the structure. An experimental absorption correction based on γ scans was applied following the published method.[22] The molecular structure of [TcN(L)] with the associated atom numbering scheme is depicted in Fig. 1. Final atomic positional parameters are listed in Table 2, while interatomic distances and bond angles are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Synthesis of the Ligands.—The ligand *N*,*N*′-ethylenebis(thioacetylacetonylideneimine) (H_2L) was obtained by successive treatment of the parent ligand *N*,*N*′-ethylenebis(acetylacetonylideneimine) (H_2L') with Et_2OBF_4 and NaSH, according to the procedure described by Cummings and co-workers.[23]

Preparations.—*Oxotechnetium*(V) *complexes*. (*a*) [TcO(L)Cl]. To a solution of $[NBu_4][TcOCl_4]$ (67 mg, 0.13 mmol) in acetonitrile (7 cm³) was added H_2L (34 mg, 0.13 mmol) with

Table 3 Interatomic distances (Å) and angles (°) for [TcN(L)]

Tc–S(1)	2.347(3)	Tc–S(2)	2.354(3)
Tc–N(2)	2.105(8)	Tc–N(3)	2.119(8)
Tc–N(1)	1.621(8)	C(6)–C(7)	1.49(2)
S(1)–C(2)	1.71(1)	S(2)–C(11)	1.71(1)
C(2)–C(1)	1.51(2)	C(11)–C(12)	1.53(2)
C(2)–C(3)	1.37(1)	C(11)–C(10)	1.35(1)
C(3)–C(4)	1.44(1)	C(10)–C(9)	1.43(1)
C(4)–C(5)	1.53(1)	C(9)–C(8)	1.54(2)
C(4)–N(2)	1.30(1)	C(9)–N(3)	1.31(1)
N(2)–C(6)	1.48(1)	N(3)–C(7)	1.48(1)

N(1)–Tc–N(2)	102.8(4)	N(1)–Tc–N(3)	107.5(3)
N(1)–Tc–S(1)	106.3(3)	N(1)–Tc–S(2)	105.0(3)
N(2)–Tc–N(3)	80.4(3)	S(1)–Tc–S(2)	82.5(1)
S(1)–Tc–N(2)	91.4(2)	S(2)–Tc–N(3)	89.6(2)
Tc–N(2)–C(4)	129.3(7)	Tc–N(3)–C(9)	118.9(8)
Tc–N(2)–C(6)	110.0(6)	Tc–N(3)–C(7)	111.6(6)
Tc–S(1)–C(2)	110.7(4)	Tc–S(2)–C(11)	109.1(4)
S(1)–C(2)–C(3)	126.0(9)	S(2)–C(11)–C(10)	126.5(8)
S(1)–C(2)–C(1)	115.6(8)	S(2)–C(11)–C(12)	114.5(8)
C(1)–C(2)–C(3)	118.3(01)	C(12)–C(11)–C(10)	118.9(10)
C(2)–C(3)–C(4)	131.7(10)	C(11)–C(10)–C(9)	130.6(10)
C(3)–C(4)–N(2)	124.9(10)	C(10)–C(9)–N(3)	124.9(9)
C(3)–C(4)–C(5)	113.6(10)	C(10)–C(9)–C(8)	115.2(9)
C(5)–C(4)–N(2)	121.4(10)	C(8)–C(9)–N(2)	119.8(10)
N(2)–C(6)–C(7)	109.0(9)	N(3)–C(7)–C(6)	111.2(9)

stirring at room temperature in an inert atmosphere. The solution became intense dark green and deposited a green solid within a few seconds. The mixture was stirred further for 5 min. The solid was then removed by filtration and washed with a few drops of MeCN and Et_2O (Found: C, 35.8; H, 4.3; Cl, 7.6; N, 6.4; S, 14.9; Tc, 23.1. $C_{12}H_{18}ClN_2OS_2Tc$ requires C, 35.6; H, 4.5; Cl, 8.7; N, 6.9; S, 15.8; Tc, 24.4%).

(*b*) [{TcO(L)}$_2$O]. The complex [NBu_4][$TcOCl_4$] (92 mg, 0.18 mmol) was dissolved in methanol (15 cm^3) and the ligand H_2L (47 mg, 0.18 mmol) added under stirring at room temperature. The solution rapidly turned red-brown. It was stirred for 10 min and refluxed for 30 min and subsequently allowed to cool. The volume was reduced slowly by allowing the reaction mixture to stand in contact with air. After 3 h a solid appeared which was removed by filtration and washed with a few drops of ethanol (Found: C, 39.1; H, 5.0; N, 7.3; S, 16.2; Tc, 25.2. $C_{24}H_{36}N_4O_3S_4Tc_2$ requires C, 38.2; H, 4.8; N, 7.4; S, 17.0; Tc, 26.3%).

Oxorhenium(V) *complexes*. (*a*) [ReO(L)Cl]. To a solution of [NBu_4][$ReOCl_4$] (76 mg, 0.13 mmol) in dry methanol (50 cm^3) was added H_2L (60 mg, 0.23 mmol) at room temperature under an inert atmosphere. The solution immediately turned from pale green to brown and was refluxed for 20 h, maintaining its initial brown colour. No precipitate was observed. After cooling, the solvent was evaporated slowly under an argon stream. The product was recovered as a reddish brown material which deposited on the inner surface of the flask (Found: C, 29.3; H, 3.6; Cl, 6.2; N, 5.6; Re, 37.0; S, 13.0. $C_{12}H_{18}ClN_2OReS_2$ requires C, 29.3; H, 3.7; Cl, 7.2; N, 5.7; Re, 37.8; S, 12.6%).

(*b*) [{ReO(L)}$_2$O]. To a deaerated toluene solution (50 cm^3) of H_2L (0.15 g, 0.6 mmol) and triethylamine (0.12 g, 1.2 mmol) was added powdered [$ReOCl_3(PPh_3)_2$] (0.5 g, 0.6 mmol). The mixture was stirred and warmed at reflux for 1 h in an inert atmosphere. Then the red-brown solution was filtered and evaporated to a small volume (5 cm^3). Light petroleum (b.p. 40–60 °C) was added to yield a reddish brown solid which was removed by filtration and washed with methanol and diethyl ether (Found: C, 30.8; H, 4.0; N, 5.9; Re, 39.7; S, 13.7. $C_{24}H_{36}N_4O_3Re_2S_4$ requires C, 31.0; H, 3.9; N, 6.0; Re, 40.1; S, 13.8%).

[TcN(L)]. To a solution of [NBu_4][$TcNCl_4$] (42 mg, 0.08 mmol) in dichloromethane (5 cm^3) was added H_2L (21 mg, 0.08 mmol) dissolved in ethanol (3 cm^3) under stirring at room temperature. The solution rapidly turned red-brown and yielded a precipitate. The mixture was stirred further for 30 min and the solid was filtered off and washed with EtOH and Et_2O. The resulting red powder was dissolved in a dilute solution of dimethylformamide (dmf)–MeOH (1:1) and charged onto a chromatography column filled with Sephadex LH 20 substrate. The desired orange product was found in the first fraction eluted with MeOH (yield < 5%). Crystals suitable for X-ray analysis were grown from MeOH–MeCN after slow evaporation at room temperature (Found: C, 38.7; H, 5.1; N, 10.8; S, 16.9; Tc, 28.5. $C_{12}H_{18}N_3S_2Tc$ requires C, 39.2; H, 4.95; N, 11.4; S, 17.4; Tc, 27.0%).

Results

Syntheses.—Monooxo-technetium(V) and -rhenium(V) complexes [MO(L)Cl] can be prepared by reaction of the corresponding M^V complexes, [$MOCl_4$]$^-$, in a 1:1 ligand-metal molar ratio, under anaerobic conditions. Addition of H_2L to a pale green solution of [$TcOCl_4$]$^-$ in dry acetonitrile at room temperature yields a dark green precipitate characterized as the neutral species [TcO(L)Cl]. When dissolved in CH_2Cl_2, $CHCl_3$ or acetonitrile this complex gives a bright emerald green solution, but with time the colour turns red-brown. Similar red-brown solutions are observed when the green powder is dissolved in alcohols. The red-brown species is attributed to the charged complexes [TcO(L)(ROH)]Cl (R = H, Me or Et) although these could not be isolated from the reaction mixtures. Upon addition of a 1:1 stoichiometric amount of the ligand to a methanolic solution of [$ReOCl_4$]$^-$, the analogous complex [ReO(L)Cl] can be obtained after refluxing the reaction mixture for 1 h. A reddish brown powder is recovered after slow solvent evaporation under an argon stream. No rearrangements to charged species are observed.

The μ-oxo dimer [{TcO(L)}$_2$O] is prepared by reaction of [$TcOCl_4$]$^-$ with H_2L in a 1:1 molar ratio in refluxing methanol while the corresponding reaction for the Re complex [{ReO(L)}$_2$O] requires a higher temperature (refluxing toluene), a deprotonating agent (NEt_3) and a different class of starting material [$ReOCl_3(PPh_3)_2$]. Both μ-oxo species are red-brown and are poorly soluble in common organic solvents.

The nitridotechnetium(V) complex, [TcN(L)] is prepared by reduction–substitution reaction of [$Tc^{VI}NCl_4$]$^-$ with a 1:1 ligand molar ratio in CH_2Cl_2–EtOH at room temperature. The reaction yields an orange-red powder consisting of a mixture of several species. These are separated using column chromatography and the desired orange species is the first fraction eluted with MeOH from a Sephadex LH-20 substrate.

Crystal Structure of [TcN(L)].—It can be seen from Fig. 1 that [TcN(L)] has the gross geometry of a rectangular pyramid with the 'nitrido' nitrogen atom at the apex and the co-ordinated atoms of the tetradentate Schiff base ligand composing the basal plane. The structure is similar to those found for the nitrido [MNX_4]$^-$ complexes (M = Mo, Re, Ru or Os; X = F, Cl, Br, I or N_3), in which the metal atom is located *ca.* 0.55 Å above the pyramid base[24] and for three five-co-ordinate [Tc^VN]$^{2+}$ complexes (mean value of 0.65 Å) described recently.[25–31] The displacement of Tc from the base of the pyramid enlarges the N–Tc≡N angles to 102.8 and 107.5° and S–Tc≡N to 106.3 and 105.0°. The ligand around the [TcN]$^{2+}$ moiety is planar to a high degree and none of the 12 non-hydrogen atoms in the inner core [except for C(7)] deviates by more than 0.13 Å from the mean plane. Consequently, the pertinent torsion angles approach 0°, apart from N(2)–C(6)–C(7)–N(3) (−45.5°). The only intermolecular contact shorter than 3.5 Å is N(1)$\cdots$C(7) (at $-x$, $-y$, $-z$) [3.48 Å, with N(1)$\cdots$H(7) at 2.55 Å] and this interaction would justify the major displacement (−0.58 Å) of the C(7) atom from the N_2S_2 plane. Bond lengths and angles are in agreement with literature data[32,33] and are essentially the same as

Table 4 Relevant IR data (cm^{-1})

H_2L	[ReO(L)Cl]	[{ReO(L)}$_2$O]	[TcO(L)Cl]	[TcN(L)]	[{TcO(L)}$_2$O]	Assignment
3420w						N–H ··· S stretch
2480–2880w	2460–2920w	2460–2420w				C–H stretch (CH_2,CH_3)
1610s	1600s	1580s	1570s	1575s	1560s	C=S stretch
1587s	1520s	1510s	1510s	1500s	1500s	C=N stretch
1528s						C=C stretch
				1075m		Tc≡N
1278s						S–H deformation
	960s	900–925vw	938m		910w	M=O stretch
		705–780s			680s	M–O–M stretch
	376m		372m			M–Cl asym. stretch

Table 5 Proton NMR spectral data (in $CDCl_3$) for the free ligands H_2L, H_2L' and for technetium and rhenium complexes. Values in parentheses refer to Δδ from the free-ligand value

	δ			
Compound	N–H (2 H)	C–H (2 H)	CH_2 (4 H)	CH_3 (6 H)
H_2L	14.30(s)	6.15(s)	3.70(s + d)	2.51(s), 2.08(s)
[TcO(L)Cl]		6.93(s) (+0.78)	4.50(m) (+0.80)	2.90(s), 2.67(s)
[TcO(L)(H_2O)]Cl		6.43(s) (+0.28)	4.24(m) (+0.54)	2.58(s), 2.48(s)
[{TcO(L)}$_2$O]		6.65(s) (+0.50)	4.47(m) (+0.77)	2.65(s), 2.62(s)
[TcN(L)]*		7.97(s) (+1.82)	4.89(m) (+1.19)	2.99(s), 2.86(s)
[ReO(L)Cl]		6.42(s) (+0.27)	4.20(m) (+0.50)	2.59(s), 2.43(s)
[{ReO(L)}$_2$O]		6.12(s) (−0.03)	3.90(m) (+0.20)	2.44(s), 2.31(s)
H_2L'	11.4	4.98(s)	3.47 (s + d)	1.90(s), 1.84(s)
[TcO(L′)(H_2O)]Cl		5.57(s) (+0.59)	4.23(m) (+0.75)	2.43(s), 2.34(s)

* In CD_3OD.

Table 6 UV/VIS bands for the ligands H_2L, H_2L' and their technetium complexes

Compound	Solvent	λ/nm
H_2L'	CH_2Cl_2	315, 300(sh)
H_2L	CH_2Cl_2	384, 366(sh)
[TcO(L)Cl]	CH_2Cl_2	655, 430, 402(sh), 305(sh), 287
[TcO(L)(H_2O)]Cl	CH_2Cl_2	472, 305(sh), 288
[TcN(L)]	MeOH	362, 238
[TcO(L′)(H_2O)]Cl	CH_2Cl_2	463, 302(sh)

those found in corresponding nitridotechnetium complexes.[20,25–31,34–36]

Characterization.—In addition to the single-crystal X-ray determination for [TcN(L)], the complexes have been characterized by elemental analysis, IR spectroscopy (Table 4) and proton NMR spectroscopy (Table 5). Where possible, other techniques have been used to characterize the compounds further. Conductivity measurements have been performed for selected complexes and, for the rhenium species, their diamagnetism in the solid state has been confirmed. UV/VIS data are also reported for the monooxotechnetium(v) complexes (Table 6). All the complexes show intense and characteristic stretching vibration bands consistent with the exhibited core. Monooxo species show ν(M=O) in the region 960–938 cm^{-1}, ν(M–Cl) in the range 380–373 cm^{-1}. The μ-oxo complexes show a very weak absorption around 910 cm^{-1} attributable to the ν(M–O) stretching vibration and a strong band around 700 cm^{-1} assigned to ν_{asym}(M–O–M), as reported previously for similar $[M_2O_3]^{4+}$ species.[37] In addition, the ν(S ··· H–N) and ν(S–H) absorptions, which appear in the spectrum of the free ligand at 3420 and 1278 cm^{-1} respectively, are no longer observed in the spectra of the complexes. Rhenium complexes were found to be diamagnetic in the solid state, in agreement with the data reported previously for Re^V d^2 species containing the $[ReO]^{3+}$ and $[Re_2O_3]^{4+}$ cores in a distorted octahedral or in a square pyramidal environment.[38]

Positive-ion FAB MS of [TcO(L)Cl] does not show the molecular ion but only a fragment at *m/z* 370 assignable to $[TcO(L)]^+$.

Table 5 reports all the proton chemical shifts of the free ligand H_2L and those of related technetium and rhenium complexes. The free ligand shows five distinguishable signals, two of which are characteristic resonances: (*i*) a multiplet arising from the ethylene chain is a sum of a doublet (coupling with N–H) and a singlet centred at δ 3.70 (the thiol–amino equilibrium is responsible for this behaviour)[23] and (*ii*) a broad singlet describing the –S ··· H ··· N– intramolecular hydrogen bond at δ 14.30. Homonuclear decoupling at the latter value results in a sharp singlet for the ethylene bridging chain.

When the ligand is co-ordinated to the metal, the –S ··· H ··· N– signal disappears and the methylene protons show a typical A_2B_2 system multiplet (Fig. 2). In the complex, these protons are no longer equivalent, in agreement with previous structural studies of some Schiff-base complexes which indicate a *gauche* conformation for the system.[39,40] Three further singlets are observed for the free ligand and which are shifted in all the complexes. The most downfield of the three signals arises from the methyne protons and it can be assigned straightforwardly while for the remaining two non-equivalent methyl singlets the attribution is quite difficult especially when the ligand is co-ordinated. Concentrated solutions of the free ligand allow two-dimensional nuclear Overhäuser effect experiments to be conducted and from the resulting map the through-space coupling between the methylene and the N-close methyl protons becomes clear. Consequently, the S-close methyl signal is assigned at δ 2.51 and the N-close one at δ 2.08.

Due to both the poor solubility (especially μ-oxo species) and instability (monomer) of the complexes, such two-dimensional NMR experiments cannot be conducted when the ligand is co-ordinated and therefore it is not possible to distinguish one methyl group from the other.

Discussion

The monooxo species [M^VO(L)Cl] (M = Tc or Re) are prepared by direct replacement of the chloride ligands in

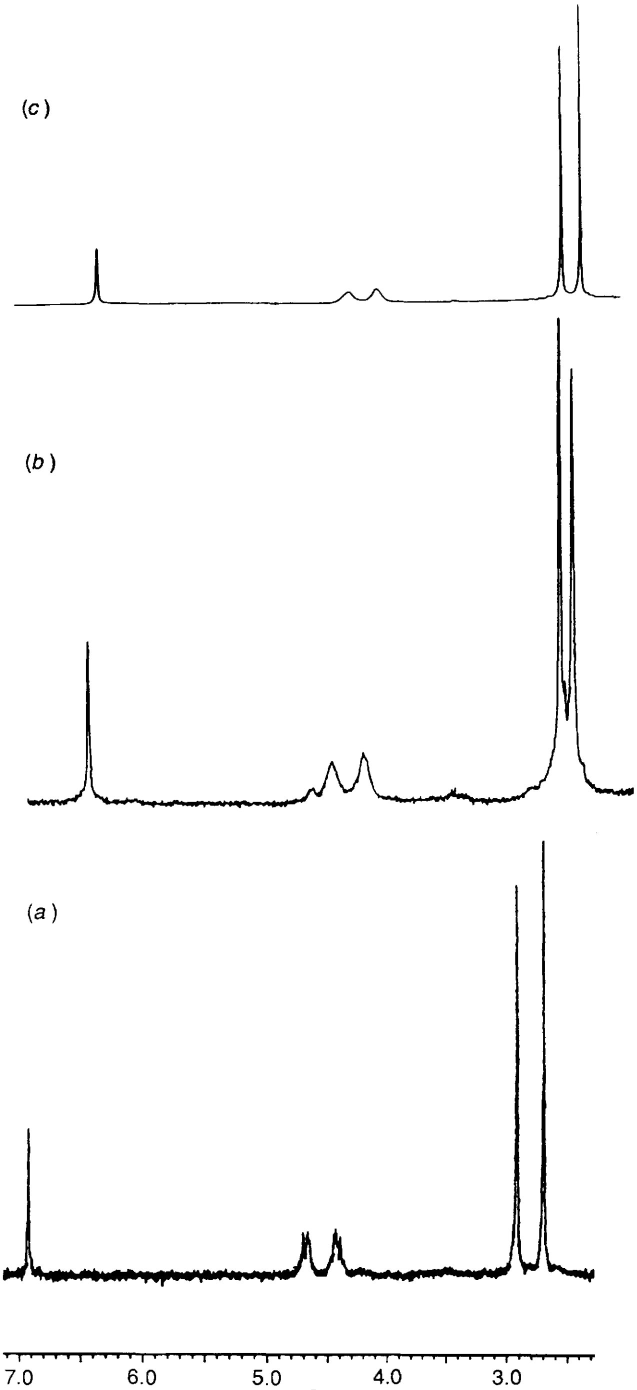
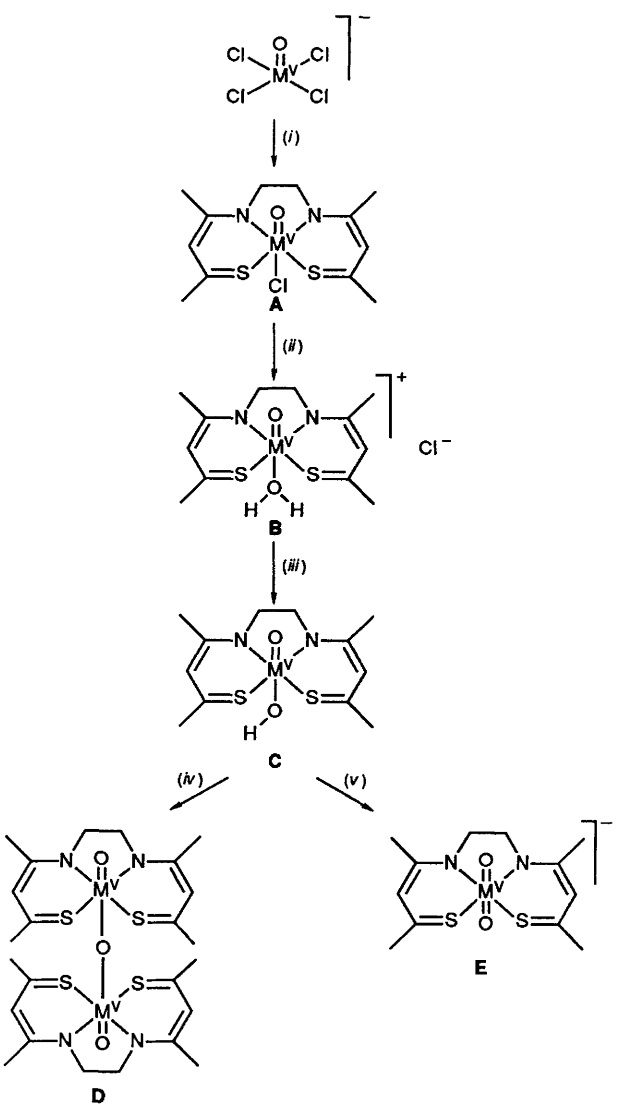


Fig. 2 250 MHz Proton NMR spectra in $CDCl_3$ at ambient temperature. (*a*) [TcO(L)Cl] *t* = 30 min, (*b*) [TcO(L)Cl] *t* = 1 week; and (*c*) [ReO(L)Cl]



Scheme 1 M = Tc or Re; (*i*) H_2L, reflux, N_2; (*ii*) moisture; (*iii*) −HCl; (*iv*) +[MO(L)Cl], −HCl; (*v*) $-H^+$

$[M^VOCl_4]^-$ by the Schiff-base ligand H_2L. This route has already been followed for the synthesis of analogous Tc^V and Re^V complexes containing the tetradentate parent ligand H_2L'.[11,13,14] The latter ligand is similar to H_2L but the sulphur atoms are replaced by oxygen atoms, resulting in a change of the donor atom set from N_2S_2 to N_2O_2. Reaction of $[TcOCl_4]^-$ with H_2L' in ethanol produces the red-brown charged species $[TcO(L')(H_2O)]^+$ while the same reaction using the similar N_2O_2 ligand *N,N'*-ethylenebis(salicylideneimine) (H_2L'') gives the neutral product [TcO(L″)Cl].[13] These examples demonstrate that Tc^V chemistry is dominated by the oxo group. Many reported complexes contain either the $[Tc{=}O]^{3+}$ or *trans*-$[O{=}Tc{=}O]^+$ core, but the factors determining which of these cores a Tc^V complex will contain are not completely understood. π-Donor ligands such as Schiff-base ligands co-ordinated in the equatorial plane orthogonal to the Tc=O linkage seem to favour the $[TcO]^{3+}$ core while π-acceptor and saturated tetraamine ligands[41–44] stabilize the *trans*-dioxo moiety.[2c] The arrangement shown by $[TcO(L)(H_2O)]^+$ {with a $[O{=}Tc{-}(OH_2)]^{3+}$ core} can be considered as intermediate between the $[O{=}Tc{=}O]^+$ and $[Tc{=}O]^{3+}$ cores as can other reported Tc^V complexes containing the $[O{=}Tc{-}OR]^{2+}$ core.[42] μ-Oxo species containing the $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ moiety[37,45] can be considered as an extension of the latter core. Oxorhenium(v) chemistry with tetradentate ligands exhibits no dramatic differences except for a greater tendency to form dimer species.[46–48] For instance, reactions of $[Re^VOCl_3(PPh_3)_2]$ with H_2L' give various products, depending on the nature and purity of the solvent, reaction temperature and/or reaction time. Among these products, we find [ReO(L′)Cl] ($[Re{=}O]^{3+}$ core) and $[\{ReO(L')\}_2O]$ (μ-oxo core).[11] It is clear, therefore, that Tc^V and Re^V chemistries with N_2O_2-tetradentate Schiff-base ligands are similar in that the same cores are observed.

Our studies with the N_2S_2-ligand H_2L lead to similar results. We have synthesized [MO(L)Cl] and $[\{MO(L)\}_2O]$ (M = Tc or Re) and furthermore obtained some evidence for charged $[TcO(L)(H_2O)]^+$ species in solution (see below). Considering

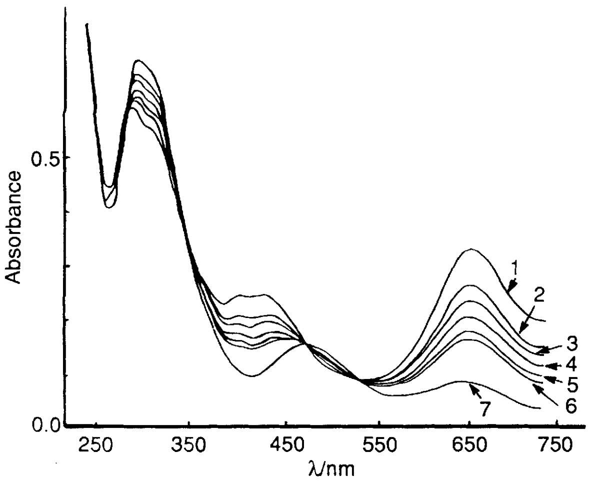


Fig. 3 Sequential scans of the UV/VIS spectra of [TcO(L)Cl] (5×10^5 mol dm^3 in CH_2Cl_2). 1, *t* = 0; 2, 15; 3, 30; 4, 60; 5, 100; 6, 150; and 7, 1200 min. The final spectrum contains $[TcO(L)(H_2O)]^+$

previous results[49] together with the present study, the reaction mechanism in Scheme 1 may be suggested.

Species $[M^VOCl_4]^-$ (M = Tc or Re) react with the N_2S_2-tetradentate Schiff-base ligand in dry solvents, under anaerobic conditions to give the complexes [MO(L)Cl] which are unstable in solution mainly due to the high lability of the sixth-site chlorine ligand *trans* to the M=O core. Traces of moisture in the solvent or prolonged contact with air of such solutions leads to rearrangement into the charged aqua species $[MO(L)(H_2O)]Cl$ **B**. The technetium complex clearly shows this transformation [^1H NMR spectra (Fig. 2): UV/VIS spectra (Fig. 3)]. Neutral [TcO(L)Cl] ($\Lambda_{eq} = 47$ Ω^{-1} cm^2 mol^{-1} in MeCN), a green powder, gives bright emerald green solutions when dissolved in chlorinated solvents, acetonitrile or dmf. On standing in air, these solutions turn red-brown, no longer neutral and show a 1:1 electrolyte ratio ($\Lambda_{eq} = 89$ Ω^{-1} cm^2 mol^{-1} in dmf). The UV/VIS pattern of the charged species $[TcO(L)(H_2O)]^+$ in dichloromethane is very similar (with a small red shift) to that for the cationic species $[TcO(L')(H_2O)]^+$. Their proton NMR spectra in chloroform show the same general behaviour with different chemical shifts for all the ligand protons (see Table 5). Attempts to obtain pure $[TcO(L)(H_2O)]Cl$ failed, a mixture of several products always being obtained. By comparison with the well characterized complex $[TcO(L')(H_2O)]$ and consistent with our spectroscopic data, we ascribe the red-brown solution produced from the green powder {[TcO(L)Cl]} to $[TcO(L)(H_2O)]^+$. This species then rearranges to the μ-oxo complex $[\{TcO(L)\}_2O]$ through another intermediate [TcO(L)(OH)] which could not be detected in our system. It is interesting to note that the last transformation is favoured in basic media, *i.e.* the conditions used to prepare $[\{ReO(L)\}_2O]$. The use of NEt_3 helps deprotonation of the ligand during the first step and drives the reaction to give finally the μ-oxo complex **D**. The hydroxy species **C** may react *via* two possible pathways both involving proton loss and the same media.

The properties of the Schiff-base ligand (mainly its capability to donate or to accept negative charge through π orbitals) together with the acidity of the metal core determines the final product **D** or **E** or stabilizes species **A**, **B** or **C**. Redox potential values for the Cu^{II}–Cu^I couple in the square-planar system [CuL′] (−1.50 V) and [CuL] (−1.07 V)[50] show that the N_2S_2 donor atom set of L better stabilizes copper in its lower oxidation state than does L′ since [CuL] is easier to reduce than [CuL′]. Thiosulphur atoms allow better delocalization of negative charge than do oxygen atoms, allowing the thiolato complex to be more easily reduced. This generalization can explain in part why some complexes are more stable than others. For instance, the poor delocalization through oxygen p orbitals disfavours further negative charge from the sixth site *trans* to the Tc=O moiety in [TcO(L′)Cl] and replacement of Cl^- by H_2O is favoured. Replacing H_2L' with the similar N_2O_2-ligand H_2L'' however allows delocalization of negative charge within the salicylaldehyde aromatic ring and so the complex [TcO(L″)Cl] is more stable. In the same way, the N_2S_2 ligand H_2L tends to stabilize species of type **A** and **D** containing a sixth negative ligand such as Cl^- or OR. However to explain more completely which of the complexes listed in the reaction scheme will be the more stable it is necessary to consider other important factors such as the relative solubility of the different species and the kinetics of every reaction step.

The lability of the site *trans* to the Tc=O linkage in mono-oxotechnetium species of type [TcO(L)Cl] prompted us to prepare the Tc^V nitrido derivative. Due to the double positive charge of the Tc≡N core (in contrast to the triple charge of the Tc=O core), a neutral compound may be obtained by co-ordination of the ligand dianion L^{2-} in the equatorial plane orthogonal to the Tc≡N moiety. Reductive-substitution on $[Tc^{VI}NCl_4]^-$ by H_2L leads to the neutral orange complex [TcN(L)]. The yield of the reaction was very low (< 5%) and column chromatography was necessary for purification. We did not isolate or characterize any other pure complex, but this does not preclude the possible presence of intermediate species. The complex [TcN(L)] is insoluble in most organic solvents and only its slight solubility in methanol allowed its characterization in solution. The spectroscopic data (Tables 4 and 5) for [TcN(L)] are in agreement with those reported in the literature for analogous Tc^V nitrido species.[28–31,35,51,52] As reported in Table 5, the ligand proton resonances for all the complexes are shifted compared to those of the free ligand, owing to the presence of the metal and two general features can be noted: (*i*) both technetium and rhenium shift all proton signals downfield and (*ii*) technetium has a greater effect on all proton chemical shifts than does rhenium. Thus, when co-ordinated to the metal the ligand transfers electron density to the core or, in other words, the metals stabilize the complexes by accepting negative charge from the ligand therefore causing ligand protons to be deshielded. This tendency is greater for Tc^V in accordance with its stronger acid character compared to Re^V.

Comparison of homologous technetium and rhenium complexes reveals that $\delta_{Tc} - \delta_{Re}$ of methyne and methylene protons of the co-ordinated ligand range from 0.30 to 0.57 ppm (we have not considered the effect on methyl protons since their attribution is not clear: see above). A similar trend has been observed recently for other Tc^V oxo-complexes.[53] At present there are only a few data available to establish that the reported behaviour is characteristic of Tc^V and Re^V complexes however it will be interesting to analyse in detail this behaviour when characterizing new Tc^V and Re^V analogues. In fact, the redox properties of the two metals in the +5 oxidation state present behaviour that may be correlated with the proton deshielding effect. Electrochemical studies on Tc^V and Re^V oxo species containing NO-bidentate and/or NO_2-tridentate Schiff-base ligands have established that Tc^V complexes are consistently easier to reduce than are their Re^V analogues. The $E^{\circ\prime}$ potential difference for the couples Tc^V–Tc^{IV} and Re^V–Re^{IV} ranges from 0.46 to 0.57 V.[53] Since it is the stronger oxidizing power of $[TcO]^{3+}$ species with respect to those of $[ReO]^{3+}$ that leads to more ligand proton deshielding and greater ease of reduction, it would be useful to obtain information on the relative ligand proton deshielding for both metal centres. This information will be especially useful when data on redox potentials are not available due to the irreversibility of the relevant couple.

Further studies are required to understand better the chemical shift dependence as a function of the metal and to correlate such shifts with the redox properties of the complexes.

Finally, attempts to label $[^{99m}TcO_4]^-$ with the ligand H_2L seem more promising upon incorporation into nitrido species $[Tc{\equiv}N]^{2+}$.[54]

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