Synthesis and Characterization of Technetium(v) and Rhenium(v) Oxo-complexes with Schiff-base Ligands containing the ONN Donor-atom Set. Molecular Structure of *trans*-Dichloro-oxo[1-(8′-quinolyliminomethyl)-2-naphtholato-*NN′O*]technetium(v)†

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Six-co-ordinate complexes of technetium(v) and rhenium(v) containing the MO^{3+} (M = Tc or Re) core were synthesized from $[MOCl_4]^-$ *via* ligand-exchange reactions using tridentate Schiff-base ligands containing the ONN donor-atom set. The complexes of general formula $[MOCl_2L^n]$ [n = 1—4; L^1 = 1-(8′-quinolyliminomethyl)-2-naphtholate, L^2 = *N*-(8′-quinolyl)salicylideneiminate, L^3 = 3-methoxy-*N*-(8′-quinolyl)salicylideneiminate, L^4 = *N*-(2′-dimethylaminoethyl)salicylideneiminate] were characterized by means of physico-chemical measurements and $[TcOCl_2L^1]$ also by *X*-ray diffraction analysis. The technetium co-ordination environment in the last complex is a distorted octahedron with the N_2O ligand-atom set and the oxo-oxygen occupying the equatorial plane and the two chlorine atoms, respectively *trans*, in axial positions. The complex crystallizes in monoclinic space group $P2_1/a$ with a = 23.262(8), b = 7.301(4), c = 11.444(5)Å, β = 98.98(5)°, and Z = 4. The structure has been refined to R = 0.048 for 2 693 observed reflections.

The inorganic chemistry of technetium(v) and rhenium(v) centres mainly on the behaviour of the $M=O^{3+}$ core [1,2] which strongly affects the co-ordination of the remaining ligands. The principal effect of the M=O group is the labilization of the bond *trans* to the oxo-oxygen so that square-pyramidal configurations are frequently observed.[3,4] Even in six-co-ordinated complexes, mainly with technetium, this labilization occurs producing weak bonds between the metal and the co-ordinated atom *trans* to Tc=O.[5,6]

Schiff-base ligands co-ordinate around the MO^{3+} core in different ways depending on the number and type of their donor groups. Focusing on the site *trans* to the M=O linkage, bidentate ligands containing ON donor atoms always give complexes with a phenolate oxygen *trans* to M=O.[7,8] In contrast, quasi-rigid tridentate ligands with an ONX (X = O or S) donor-atom set lie on the equatorial plane and the resulting complexes have a chlorine atom or small oxygenated molecule (H_2O, MeOH) *trans* to Re=O or with the position *trans* to the Tc=O group vacant, at least in the solid state.[3,4,9] In a similar way tetradentate ligands containing the donor set XNNX (X = O or S) co-ordinate on the equatorial plane and the complexes have a molecule of water or alcohol or an halogenide ion *trans* to M=O [6,10] or an oxygen bridge between two metal centres, giving the $M_2O_3^{4+}$ core.[11,12] Finally, pentadentate Schiff-base ligands of type ON_3O resemble the bidentate ones and the complexes have a phenolate oxygen *trans* to the M=O linkage.[13]

With the aim of attaining other stable configurations around the MO^{3+} core, Schiff-base ligands HL^n (n = 1—4) containing the ONN donor atom set have been used as chelating agents. The behaviour of these ligands is unusual, leading to products in which the imino nitrogen is *trans* to the M=O group.

Experimental

Materials.—Technetium as $[NH_4][TcO_4]$ was purchased from Radiochemical Centre, Amersham; $[NBu_4][TcOCl_4]$ and $[NBu_4][ReOCl_4]$ were prepared by literature methods.[14,15] All other materials were reagent-grade chemicals.

Apparatus.—Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser; quantitative determination of technetium were carried out on a Rackbeta II instrument, model 1215, with Instagel, a ready-for-use xylene-based liquid-scintillation cocktail (Packard Instrument Int., Zurich). Infrared spectra were recorded in the range 4 000—250 cm^{-1} on a Perkin-Elmer PE580B spectrometer using Nujol mulls between CsI or KBr pellets, proton n.m.r. spectra on a Bruker AC200 instrument using $SiMe_4$ as internal reference (where not differently specified, J means ^3J). Mass spectrometric measurements were carried out on a ZABZF instrument operating in electron-inpact mode [70 eV (*ca.* 1.12 × 10^{-17} J), 200 A]. Conductivity measurements were made in acetonitrile and acetonitrile–methanol solutions at 25 °C using a Metrohm Herison E518 conductometer. U.v.–visible spectra were recorded in different solvents using a Cary 17D spectrometer. Cyclic voltammetric measurements were performed on a BAS (Bioanalytical System Inc.) CV-IB cyclic voltammograph. The working electrode was a stationary-disk platinum electrode and the auxiliary electrode was a platinum wire. Controlled-potential coulometries were performed with an AMEL model 721 integrator and the following electrodes: platinum-spiral wire working electrode (area about 3.3 cm^2), platinum-auxiliary foil electrode isolated inside a salt bridge by a medium-glass frit, and calomel reference electrode. The measurements were done in dry and degassed dimethylformamide (dmf) (Aldrich gold label solvent) with 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. Potentials were recorded *versus* the saturated calomel electrode

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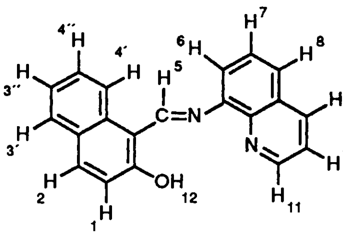
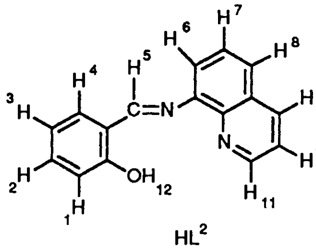
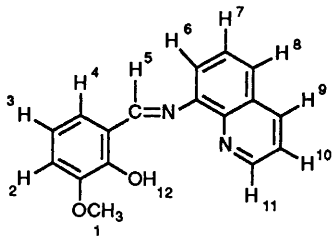
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.
Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.



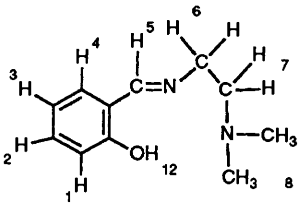
HL^1



HL^2



HL^3



HL^4

(s.c.e.). Potentials were calculated at the midpoint between the anodic and cathodic peaks of the cyclic voltammetric waveform scanned at 0.2 V s^{-1} and referred to the value of the ferrocenium–ferrocene couple used as internal standard.[16] Low-temperature measurements were made in liquid-nitrogen slurries.

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

Crystal Structure Determination of [TcOCl$_2$L^1] (1).—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of a Me$_2$CO–MeCN (1:1 v/v) solution of [TcOCl$_2$L^1] (1) at room temperature.

Crystal data. $C_{20}H_{13}Cl_2N_2O_2Tc$, M = 483.1, monoclinic, space group $P2_1/a$, a = 23.262(8), b = 7.301(4), c = 11.444(5) Å, β = 98.98(5)°, U = 1 919.8(1.5) Å^3, D_m = 1.68 (by flotation in hexane–1,2-dibromoethane), Z = 4, D_c = 1.672 g cm^{-3}, $F(000)$ = 960, μ(Mo-K_α) = 10.3 cm^{-1}.

A crystal was aligned with the c needle axis (length 0.30 mm) approximately parallel to the φ axis of a Philips PW1100 automatic diffractometer with Mo-K_α radiation (λ = 0.7107 Å). A total of 3 757 different reflections in one quadrant was measured (scan speed 2.4° min^{-1} scan width 1.2°) within the limit $\theta < 26°$. Of these, 2 693 were considered observed [$I > 3\sigma(I)$] and used for the structure analysis. The integrated intensities were corrected for Lorentz and polarization and also for absorption, using an empirical method based on ψ scans of three reflections near χ = 90°. The position of the technetium atom was derived from a three-dimensional Patterson map, and subsequent Fourier difference syntheses revealed the position of all 26 non-hydrogen atoms of the complex. All hydrogen atoms were identified from a difference map at R = 0.061; they were given a common isotopic thermal parameter U of 0.07 Å^2 and included as fixed contributions in the last cycles of refinement. Full-matrix least-squares refinement with anisotropic thermal parameters assigned to all non-hydrogen atoms converged (244 variables) with a reliability index $R = \Sigma\Delta F/\Sigma F_o$ of 0.048. The function minimized was $\Sigma w(\Delta F)^2$, where w = 1, and the maximum shift/error in the final cycle was 0.1. Final atomic positional co-ordinates, with estimated standard deviations (e.s.d.s) in parentheses, are listed in Table 1, while selected bond distances and angles are given in Table 2.

Structure determination and refinement were performed with the SHELX 76 program package.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Syntheses of the Ligands.—All the HL^n ligands were synthesized by the procedure detailed below for HL^1.

1-(8'-*Quinolyliminomethyl*)-2-*naphthol*, HL^1. By mixing 2-hydroxynaphthaldehyde (550 mg, 3.19 mmol) and 8-aminoquinoline (460 mg, 3.19 mmol) in ethanol (30 cm^3) at room temperature the solution immediately became yellow-orange and after 5 min an orange precipitate appeared. It was filtered off and washed with a few drops of EtOH and then with Et$_2$O. No recrystallization was necessary to obtain an analytically pure sample. The powder is soluble in chlorinated solvents, MeCN, Me$_2$CO, slightly soluble in alcohols, and insoluble in Et$_2$O (Found: C, 81.10; H, 4.90; N, 9.30. Calc. for $C_{20}H_{15}N_2O$: C, 80.50; H, 4.75; N, 9.40%). I.r. (KBr): 1 628, 1 541, 1 357, 1 305, 1 211, 790, and 749 cm^{-1}. Electronic spectrum (MeOH): $\lambda_{\text{max.}}$ 475 (ε 5 400), 450 (5 200), 348 (sh), 322 (1 700), 275 (sh), and 228 nm (10 000 dm^3 mol^{-1} cm^{-1}). ^{1}H N.m.r. spectrum (CDCl$_3$): δ 9.33 [d, 1 H, $J(H^5H^{12})$ = 10.7, H^5], 9.08 [dd, 1 H, $J(H^{11}H^{10})$ = 4.2, $^4J(H^{11}H^9)$ = 1.6, H^{11}], 8.28 [dd, 1 H, $J(H^9H^{10})$ = 8.3, $^4J(H^9H^{11})$ = 1.6, H^9], 8.07 [d, 1 H, $J(H^{4'}H^{4''})$ = 7.6, H$^{4'}$], 7.83 [d, 1 H, $J(H^6H^7)$ = 7.7, H^6], 7.74 [t, 1 H, $J(H^7H^6) = J(H^7H^8)$ = 7.7, H^7], 7.73 [d, 1 H, $J(H^1H^2)$ = 9.5, H^1], 7.68 [d, 1 H, $J(H^8H^7)$ = 7.7, H^8], 7.63 [d, 1 H, $J(H^{3'}H^{3''})$ = 7.6, H$^{3'}$], 7.58 [dd, 1 H, $J(H^{10}H^{11})$ = 8.3, $J(H^{10}H^9)$ = 4.2, H^{10}], 7.52 [t, 1 H, $J(H^{4''}H^{4'}) = J(H^{4''}H^{3''})$ = 7.6, H$^{4''}$], 7.31 [t, 1 H, $J(H^{3''}H^{4''}) = J(H^{3''}H^{3'})$ = 7.6, H$^{3''}$], and 6.87 [d, 1 H, $J(H^2H^1)$ = 9.5 Hz, H^2].

N-(8'-*Quinolyl*)*salicylideneimine*, HL^2. This is a deep orange oil collected from the reaction solution after drying at a vacuum pump. The oil is soluble in all common organic solvents (Found: C, 77.10, H, 5.10; N, 11.75. Calc. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.85; N, 11.30%). I.r. (KBr): 1 625, 1 287, 1 159, 1 124, 1 063, 985, 920, 796, 761, 589, and 465 cm^{-1}. Electronic spectrum (MeOH): $\lambda_{\text{max.}}$ 456 (ε 1 400), 340 (11 000), and 228 nm (60 000 dm^3 mol^{-1} cm^{-1}). ^{1}H N.m.r. (CDCl$_3$): δ 12.64 (br, 1 H, H^{12}), 8.97 [dd, 1 H, $J(H^{11}H^{10})$ = 4.2, $^4J(H^{11}H^9)$ = 1.7, H^{11}], 8.92 (s, 1 H, H^5), 8.18 [dd, 1 H, $J(H^9H^{10})$ = 8.3, $^4J(H^9H^{11})$ = 1.7, H^9], 7.72 [d, 1 H, $J(H^6H^7)$ = 8.1, H^6], 7.57 [t, 1 H, $J(H^7H^6) = J(H^7H^8)$ = 8.1, H^7], 7.49 [d, 1 H, $J(H^8H^7)$ = 8.1, H^8], 7.44 [dd, 1 H, $J(H^{10}H^9)$ = 8.3, $J(H^{10}H^{11})$ = 4.2, H^{10}], 7.43 [d, 1 H, $J(H^1H^2)$ = 7.9, H^1], 7.39 [t, 1 H, $J(H^2H^1) = J(H^2H^3)$ = 7.9, H^2], 7.07 [d, 1 H, $J(H^4H^3)$ = 7.9, H^4], and 6.94 [t, 1 H, $J(H^3H^4) = J(H^3H^2)$ = 7.9 Hz, H^3].

Table 1. Final atomic positional co-ordinates for non-hydrogen atoms of [$TcOCl_2L^1$] (**1**)

Atom	X/a	Y/b	Z/c
Tc	0.571 33(3)	0.394 57(10)	0.326 44(5)
Cl(1)	0.513 9(1)	0.667 0(3)	0.289 4(2)
Cl(2)	0.630 7(1)	0.131 6(4)	0.320 8(2)
O(1)	0.575 1(3)	0.399 5(9)	0.471 4(4)
O(2)	0.632 5(2)	0.530 4(8)	0.270 7(5)
N(1)	0.494 7(3)	0.236 6(8)	0.319 9(5)
N(2)	0.544 8(2)	0.337 2(7)	0.140 5(5)
C(1)	0.470 9(4)	0.193 4(12)	0.415 0(7)
C(2)	0.420 5(4)	0.090 3(13)	0.408 3(8)
C(3)	0.392 4(4)	0.037 1(11)	0.301 3(8)
C(4)	0.415 3(3)	0.080 5(10)	0.197 0(7)
C(5)	0.388 5(3)	0.033 8(10)	0.082 3(7)
C(6)	0.413 3(3)	0.084 6(10)	−0.012 9(6)
C(7)	0.464 4(3)	0.187 0(10)	0.001 5(6)
C(8)	0.492 2(3)	0.235 6(9)	0.111 4(6)
C(9)	0.466 8(3)	0.183 0(9)	0.210 4(6)
C(10)	0.574 2(3)	0.377 6(9)	0.055 0(6)
C(11)	0.627 7(3)	0.474 8(9)	0.065 8(6)
C(12)	0.654 6(3)	0.510 1(9)	−0.039 1(6)
C(13)	0.630 6(3)	0.453 0(10)	−0.152 9(6)
C(14)	0.657 9(4)	0.491 1(12)	−0.249 4(7)
C(15)	0.710 3(4)	0.587 6(12)	−0.236 1(7)
C(16)	0.733 8(3)	0.645 6(11)	−0.126 1(8)
C(17)	0.707 6(3)	0.609 3(10)	−0.026 0(7)
C(18)	0.732 8(3)	0.674 4(11)	0.087 5(7)
C(19)	0.707 8(3)	0.646 4(11)	0.184 4(7)
C(20)	0.654 7(3)	0.545 7(10)	0.174 4(7)

Table 2. Selected interatomic bond distances (Å) and angles (°) in [$TcOCl_2L^1$] (**1**)

Tc–Cl(1)	2.396(3)	N(1)–C(9)	1.375(9)
Tc–Cl(2)	2.371(3)	C(9)–C(8)	1.410(10)
Tc–O(1)	1.648(5)	C(3)–N(2)	1.425(9)
Tc–O(2)	1.923(6)	N(2)–C(10)	1.312(9)
Tc–N(1)	2.115(6)	C(10)–C(11)	1.421(9)
Tc–N(2)	2.162(5)	C(11)–C(20)	1.401(10)
C(1)–N(1)	1.333(11)	C(20)–O(2)	1.293(10)
Cl(1)–Tc–Cl(2)	167.9(1)	C(9)–C(8)–N(2)	114.0(6)
O(2)–Tc–O(1)	113.4(3)	Tc–N(2)–C(8)	115.7(4)
O(1)–Tc–N(1)	87.7(3)	Tc–N(2)–C(10)	118.2(6)
N(1)–Tc–N(2)	75.5(2)	C(8)–N(2)–C(10)	118.2(6)
N(2)–Tc–O(2)	83.4(2)	N(2)–C(10)–C(11)	126.9(6)
N(1)–Tc–O(2)	158.8(2)	C(10)–C(11)–C(20)	121.7(6)
Tc–N(1)–C(9)	117.6(5)	C(11)–C(20)–O(2)	122.8(7)
N(1)–C(9)–C(8)	117.2(6)	C(20)–O(2)–Tc	137.9(5)

3-*Methoxy*-N-(8′-*quinolyl*)*salicylideneimine*, HL^3. This is a red powder soluble as HL^1 (Found: C, 73.60; H, 4.90; N, 10.05. Calc. for $C_{17}H_{14}N_2O$: C, 73.35; H, 5.05; N, 10.05%). I.r. (KBr): 1 621, 1 462, 1 246, 1 095, 971, 832, 795, 734, and 731 cm^{-1}. Electronic spectrum (MeOH): $\lambda_{max.}(\varepsilon)$ 472 (3 800), 344 (11 600), and 230 nm (33 400 dm^3 mol^{-1} cm^{-1}). ^1H N.m.r. ($CDCl_3$): δ 12.60 (br, 1 H, H^{12}), 8.97 [dd, 1 H, $J(H^{11}H^{10}) = 4.2$, $J(H^{11}H^9) = 1.6$, H^{11}], 8.93 (s, 1 H, H^5), 8.18 [dd, 1 H, $J(H^9H^{10}) = 8.3$, $^4J(H^9H^{11}) = 1.7$, H^9], 7.73 [d, 1 H, $J(H^6H^7) = 7.7$, H^6], 7.58 [t, 1 H, $J(H^7H^6) = J(H^7H^8) = 7.7$, H^7], 7.54 [d, 1 H, $J(H^8H^7) = 7.7$, H^8], 7.45 [dd, 1 H, $J(H^{10}H^9) = 8.3$, $J(H^{10}H^9) = 4.2$, H^{10}, 7.07 [d, 1 H, $J(H^2H^3) = 7.8$, H^2], 6.98 [d, 1 H, $J(H^4H^3) = 7.8$, H^4], 6.85 [t, 1 H, $J(H^3H^2) = J(H^3H^4) = 7.8$ Hz, H^3], and 3.95 (s, 3 H, H^1).

N-(2′-*Dimethylaminoethyl*)*salicylideneimine*, HL^4. This is a yellow oil recovered from the reaction mixture after drying at a vacuum pump. The oil is soluble in all common organic solvents. Found: C, 69.10; H, 8.05; N, 14.55. Calc. for $C_{11}H_{16}N_2O$: C, 68.70; H, 8.40; N, 14.55%). I.r. (KBr): 1 642, 1 505, 1 470, 1 288, 1 159, 1 048, and 763 cm^{-1}. Electronic spectrum (MeOH): $\lambda_{max.}(\varepsilon)$ 397 (1 000), 312 (3 600), 252 (10 400), and 212 nm (22 000 dm^3 mol^{-1} cm^{-1}). ^1H N.m.r. ($CDCl_3$): δ 13.36 (br, 1 H, H^{12}), 8.39 (s, 1 H, H^5), 7.36—7.22 (m, 2 H, H^1, H^2), 6.95 [d, 1 H, $J(H^4H^3) = 8.0$, H^4], 6.87 [t, 1 H, $J(H^3H^4) = J(H^3H^2) = 8.0$, H^3], 3.77 (t, 2 H, $^2J_{AB} = 6.9$ Hz, H^6), 2.72 (t, 2 H, $^2J_{AB} = 6.9$ Hz, H^7), and 2.38 (s, 6 H, H^8).

Syntheses of Complexes.—[$TcOCl_2L^1$]. A methanolic solution of HL^1 (36 mg, 0.12 mmol) was added under stirring at room temperature to a pale green solution of [NBu_4][$TcOCl_4$] (60 mg, 0.12 mmol) in MeOH (10 cm^3). The solution became immediately red and after a few minutes a dark solid appeared. The precipitate was filtered off and the resulting green product washed with Et_2O. The solid was soluble in dmf and slightly soluble in MeCN, CH_2Cl_2, and Me_2CO maintaining the green colour, while in alcohols the solutions slowly turned red. Green crystals deposited from both green and red solutions after slow evaporation of the solvent; all attempts to recover the red solid failed. The yield of green complex was 65%. Green crystals suitable for *X*-ray analysis were collected from Me_2CO–MeCN (1:1) solutions.

[$TcOCl_2L^1$] (**1**) (Found: C, 49.00; H, 2.45; N, 5.40, Tc, 19.35. Calc. for $C_{20}H_{13}Cl_2N_2O_2Tc$: C, 49.70; H, 2.70; N, 5.80; Tc, 20.50%). I.r. (Nujol): 1 615, 1 600, 1 534, 1 210, 956 [ν(Tc=O)], 834, 765, and 296 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$580, 440, and 250 nm. ^1H N.m.r. (dmf): δ 10.51 [dd, 1 H, $J(H^{11}H^{10}) = 5.2$, $^4J(H^{11}H^9) = 1.2$, H^{11}) 10.10 (s, 1 H, H^5), 9.02 [dd, 1 H, $J(H^9H^{10}) = 8.3$, $^4J(H^9H^{11}) = 1.1$, H^9], 8.94 [d, 1 H, $J(H^{4'}H^{4''}) = 8.3$, $H^{4'}$], 8.83 [d, 1 H, $J(H^6H^7) = 7.7$, H^6], 8.46 [d, 1 H, $J(H^1H^2) = 9.2$, H^1], 8.30—8.23 (m, 2 H, H^{10}, $H^{3'}$) 8.17 [d, 1 H, $J(H^8H^7) = 7.8$, H^8], 8.05 [t, 1 H, $J(H^7H^8) = J(H^7H^6) = 7.8$, H^7], 7.81 [t, 1 H, $J(H^{4'}H^{4''}) = J(H^{4''}H^{3''}) = 8.3$, $H^{4''}$], 7.70 [d, 1 H, $J(H^2H^1) = 9.3$, H^2], and 7.63 [t, 1 H, $J(H^{3''}H^{3'}) = J(H^{3''}H^{4''}) = 8.0$ Hz, $H^{3''}$].

[$TcOCl_2(OMe)L^1$]$^-$ (**2**), *red solution*. Electronic spectrum (MeOH): $\lambda_{max.}$ 510, 390, and 315 nm. Conductivity in MeCN–MeOH: $\Lambda_{eq} = 155$ Ω^{-1} cm^2 mol^{-1}. ^1H N.m.r. spectrum (MeOH): δ 9.91 (s, 1 H^5), 9.11 (m, 1 H, H^{11}), 8.52 [d, 1 H, $J(H^{4'}H^{4''}) = 7.8$, $H^{4'}$], 8.40 (m, 1 H, H^9), 8.24 [d, 1 H, $J(H^1H^2) = 7.0$, H^1], 7.84—7.70 (m, 3 H, $H^{10'}$ $H^{6'}$ $H^{3'}$), 7.60 [t, 1 H, $J(H^6H^7) = J(H^7H^8) = 7.8$, H^7], 7.47 [d, 1 H, $J(H^8H^7) = 7.8$, H^8], 7.33 [t, 1 H, $J(H^{4'}H^{4''}) = J(H^{4''}H^{3''}) = 7.8$, $H^{4''}$], 7.08 [t, 1 H, J $(H^{3''}H^{4''}) = J(H^{3''}H^{3'}) = 7.8$, $H^{3''}$], and 6.96 [d, 1 H, $J(H^1H^2) = 7.0$ Hz, H^2].

[$TcOCl_2L^2$]. The orange oil HL^2 (53 mg, 0.21 mmol) was dissolved in a few drops of methanol and added with stirring at room temperature to a solution of [NBu_4][$TcOCl_4$] (106 mg, 0.21 mmol) in MeOH (20 cm^3). The solution became red and after 20 min a deep red solid appeared. It was filtered off, washed with a few drops of MeOH and then with Et_2O. The red solid is soluble in dmf, slightly soluble in alcohols, MeCN, Me_2CO, CH_2Cl_2, and $CHCl_3$, and insoluble in Et_2O and maintains the red colour in all solvents. The complex was recrystallized from dmf–Et_2O (1:3) as a red powder (Found: C, 43.85; H, 2.15; N, 6.70; Tc, 15.80. Calc. for $C_{16}H_{11}Cl_2N_2O_2Tc$: C, 44.35; H, 2.55; N, 6.45; Tc, 16.35%). I.r. (Nujol): 1 606, 1 595, 1 528, 1 152, 953 [ν(Tc=O)], 831, 754, 337, and 293 cm^{-1}. Electronic spectrum (dmf): $\lambda_{max.}$ 560, 370, and 322 nm. ^1H N.m.r. spectrum (dmf): δ 10.48 [d, 1 H, $J(H^{11}H^{10}) = 5.7$, H^{11}], 9.53 (s, 1 H, H^5), 8.97 [d, 1 H, $J(H^9H^{10}) = 7.7$ H^9], 8.55 [d, 1 H, $J(H^6H^7) = 7.7$, H^6], 8.31—8.15 (m, 3 H, H^1, H^8, H^{10}), 8.03 [t, 1 H, $J(H^7H^6) = J(H^7H^8) = 7.7$, H^7], 7.93 [t, 1 H, $J(H^2H^1) = J(H^2H^3) = 7.9$, H^2], 7.35 [d, 1 H, $J(H^4H^3) = 8.5$, H^4], and 7.23 [t, 1 H, $J(H^3H^4) = J(H^3H^2) = 8.1$ Hz, H^3].

The complexes [$TcOCl_2L^3$] and [$TcOCl_2L^4$] were synthesized following the method below. The yields of the three

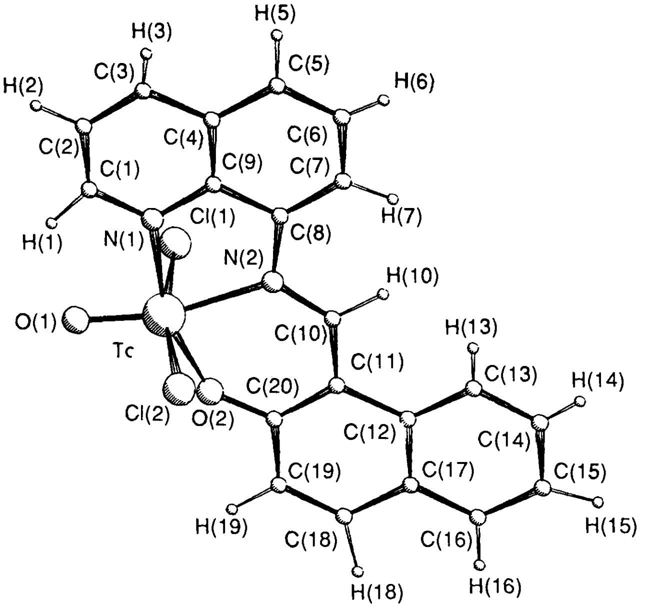


Figure 1. Drawing of [TcOCl$_2$L^1] (**1**) viewed along the *b* axis (PLUTO, S. Motherwell, A Program for Plotting Molecular and Crystal Structures, Cambridge, 1976)

technetium complexes (L^n, n = 2—4) range from 60 to 80%.

[TcOCl$_2$L^3]. Purple red powder. (Found: C, 43.10; H, 3.10; N, 6.50; Tc, 14.20. Calc. for $C_{17}H_{13}Cl_2N_2O_3Tc$: C, 44.05; H, 2.80; N, 6.05; Tc, 15.30%). I.r. (Nujol): 1 619, 1 601, 1 544, 1 264, 950 [ν(Tc=O)], 831, 774, 336, and 295 cm^{-1}. Electronic spectrum (dmf): $\lambda_{max.}$ 560, 410, and 350 nm. ^{1}H N.m.r. (dmf): δ 10.51 [d, 1 H, J(H^{11}H^{10}) = 5.3, H^{11}], 9.55 (s, 1 H, H^5), 8.98 [d, 1 H, J(H^{9}H^{10}) = 8.2, H^9], 8.57 [d, 1 H, J(H^{6}H^7) = 7.7, H^6], 8.21—8.35 (m, 2 H, H^8, H^{10}), 8.04 [t, 1 H, J(H^{7}H^8) = J(H^{7}H^6) = 7.6, H^7], 7.77 [d, 1 H, J(H^{2}H^3) = 8.0, H^2], 7.53 [d, 1 H, J(H^{4}H^3) = 7.9, H^4], 7.18 [t, 1 H, J(H^{3}H^4) = J(H^{3}H^2) = 7.9 Hz, H^3], and 4.00 (s, 3 H, H^1).

[TcOCl$_2$L^4]. Violet powder (Found: C, 35.80; H, 4.35; N, 8.00; Tc, 24.90. Calc. for $C_{11}H_{15}Cl_2N_2O_2Tc$: C, 35.00; H, 4.00; N, 7.40; Tc, 26.25%). I.r. (Nujol): 1 613, 1 560, 1 300, 953 [ν(Tc=O)], 763, 629, and 308 cm^{-1}. Electronic spectrum (dmf): $\lambda_{max.}$ 492, 395, 350, and 290 nm. ^{1}H N.m.r. (dmf): δ 9.08 (s, 1 H, H^5), 7.54 [d, 1 H, J(H^{1}H^2) = 6.7, H^1], 7.40 [t, 1 H, J(H^{2}H^1) = J(H^{2}H^3) = 6.7, H^2], 7.06 [t, 1 H, J(H^{3}H^2) = J(H^{3}H^4) = 7.0, H^3], 6.70 [d, 1 H, J(H^{4}H^3) = 7.0, H^4], 4.68 [t, 2 H, J = 5.7, H^6], 4.14 [t, 2 H, J = 5.9 Hz, H^7], and 3.19 (s, 6 H, H^8).

Rhenium complexes[18] were synthesized following the same procedure as for the technetium ones. The reactions involving the ligands HL^2 and HL^4 require higher temperatures (refluxing methanol). The yields range from 70 to 90%. All the rhenium complexes are non-conducting both in acetonitrile and acetonitrile–methanol solutions.

[ReOCl$_2$L^1]. Bright brown powder (Found: C, 42.15; H, 2.20; N, 4.85. Calc. for $C_{20}H_{13}Cl_2N_2O_2Re$: C, 42.10; H, 2.30; N, 4.9%). I.r. (KBr): 1 599, 1 533, 1 510, 1 371, 1 210, 969 [ν(Re=O)], 827, 764, and 308 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 565, 455, 320, and 255 nm. ^{1}H N.m.r. (dmf) δ 9.70 (s, 1 H, H^5), 9.60 [dd, 1 H, J(H^{11}H^{10}) = 5.3, ^4J(H^{11}H^9) = 1.3, H^{11}], 9.08 [d, 1 H, J(H^{6}H^7) = 7.7, H^6], 9.02 [d, 1 H, J(H$^{4'}$H$^{4''}$) = 8.2, H$^{4'}$], 8.49 [dd, 1 H, J(H^{9}H^{10}) = 8.3, ^4J(H^{9}H^{11}) = 1.3, H^9], 8.35—8.09 (m, 5 H, H^1, H$^{3'}$, H^7, H^8, H^{10}), 7.83 [d, 1 H, J(H^{2}H^1) = 9.2, H^2], 7.79 [t, 1 H, J(H$^{4''}$H$^{4'}$) = J(H$^{4''}$H$^{3''}$) = 8.3, H$^{4''}$], and 7.65 [t, 1 H, J(H$^{3''}$H$^{4''}$) = J(H$^{3''}$H$^{3'}$) = 8.2 Hz, H$^{3''}$].

[ReOCl$_2$L^2]. Brown powder (Found: C, 36.95; H, 2.05; N, 5.30. Calc. for $C_{16}H_{11}Cl_2N_2O_2Re$: C, 36.95; H, 2.15; N, 5.40%). I.r. (KBr) 1 606, 1 528, 1 512, 1 404, 1 152, 963 [ν(Re=O)], 826, 762, 327, and 307 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 565, 415, 365, 275, and 245 nm. ^{1}H N.m.r. (DMF): δ 9.41 [dd, 1 H, J(H^{11}H^{10}) = 5.1, ^4J(H^{11}H^9) = 1.2, H^{11}], 9.20 (s, 1 H, H^5), 8.73 [dd, 1 H, J(H^{9}H^{10}) = 7.9, ^4J(H^{9}H^{11}) = 1.1, H^9], 8.30—8.26 (m, 3 H, H^6, H^8, H^{10}) 8.14 [t, 1 H, J(H^{7}H^6) = J(H^{7}H^8) = 7.8, H^7], 8.07 [d, 1 H, J(H^{1}H^2) = 9.5, H^1], 7.70 [t, 1 H, J(H^{2}H^1) = J(H^{2}H^3) = 9.4, H^2], 7.40 [d, 1 H, J(H^{4}H^3) = 9.4 H^4], and 7.14 [t, 1 H, J(H^{3}H^4) = J(H^{3}H^2) = 9.5 Hz, H^3].

[ReOCl$_2$L^3]. Brown powder (Found: C, 36.15; H, 2.40; N, 5.00. Calc. for $C_{17}H_{13}Cl_2N_2O_3Re$: C, 37.10; H, 2.40; N, 5.10%). I.r. (KBr): 1 599, 1 543, 1 262, 964 [ν(Re=O)], 830, and 319 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 545, 435, 375, 270, and 238 nm. ^{1}H N.m.r. (dmf): δ 9.45 [d, 1 H, J(H^{11}H^{10}) = 5.2, H^{11}], 9.16 (s, 1 H, H^5), 8.75 [d, 1 H, J(H^{9}H^{10}) = 7.8, H^9], 8.33—8.25 (m, 3 H, H^6, H^8, H^{10}), 8.13 [t, 1 H, J(H^{7}H^6) = J(H^{7}H^8) = 8.0, H^7], 7.60 [d, 1 H, J(H^{2}H^3) = 7.9, H^2], 7.24 [d, 1 H, J(H^{4}H^3) = 7.9, H^4], 7.06 [t, 1 H, J(H^{3}H^4) = J(H^{3}H^2) = 7.9 Hz, H^3] and 3.98 (s, 3 H, H^1).

Results and Discussion

The reactions of $[MOCl_4]^-$ (M = Tc or Re) with tridentate Schiff-base ligands containing the ONX (X = O or S) donor-atom set have already been studied.[3,4,9] Two types of products were usually obtained: five-co-ordinated oxo-complexes of Tc showing square-pyramidal configuration and six-co-ordinated oxo-complexes of Re exhibiting distorted octahedral environments. In both cases the ligand is completely bonded to the metal on the equatorial plane, with respect to the M=O linkage. In this study the reactions between $[MOCl_4]^-$ and HL ligands containing the ONN donor atom set lead to the formation of neutral six-co-ordinated complexes of general formula [MOCl$_2$L^n], as described in equation (1).

$$[NBu_4][MOCl_4] + HL^n \longrightarrow [MOCl_2L^n] + [NBu_4]Cl + HCl \quad (1)$$

The ligands always act as tridentate but exhibit an unusual co-ordination around the metal centre (see below). The complexes [MOCl$_2$L^n] are air stable, having elemental analyses and spectroscopic data in agreement with the formulae (see Experimental section); ν(Tc=O) and ν(Re=O) are found in the i.r. spectra within the usual ranges 956—950 and 969—963 cm^{-1}, respectively. Anaalysis of ^{1}H n.m.r. spectra shows the ligands to be completely co-ordinated: the absence of O–H phenolic proton signals supports the phenolate co-ordination; furthermore, the signals of the protons close to the ONN co-ordinating atoms are all shifted downfield with respect to those of the free ligands (Table 3). The technetium metal centre induces more marked variations of the proton chemical shifts than does that of rhenium. This is clearly seen for the proton H^{11}, closest to the metal (Table 3). Conductivity measurements in acetonitrile showed non-conducting complexes.

The molecular geometry and atom numbering of [TcOCl$_2$L^1] are shown in Figure 1. The structure consists of discrete molecules and the technetium environment is distorted octahedral, with the equatorial plane formed by the tridentate N$_2$O chelate ligand and by the Tc=O oxygen in the fourth position, whereas the two chlorine atoms are *trans* to each other in axial positions. The octahedral geometry around Tc is severely distorted and, for example, the small [75.5(2)°] angle N(1)–Tc–N(2) corresponds to the very large [113.4(3)°] angle O(2)–Tc–O(1). The chelate ligand, as a whole, is very nearly planar [maximum deviation from the best plane 0.02 Å, except

Table 3. Chemical shifts of selected protons [δ referred to $SiMe_4$ (δ = 0.0)] relative (variations in parentheses) to those of the free ligand[a]

	H^1	H^5	H^6	H^{11}
$[TcOCl_2L^1]$	8.46 (+0.73)	10.10 (+0.77)	8.83 (+1.00)	10.51 (+1.43)
$[TcOCl_2(OMe)L^1]^-$ [b]	8.24 (+0.51)	9.91 (+0.58)	n.i.[c]	9.11 (+0.03)
$[TcOCl_2L^2]$	n.i.	9.53 (+0.61)	8.55 (+0.83)	10.48 (+1.51)
$[TcOCl_2L^3]$	—	9.55 (+0.60)	8.57 (+0.84)	10.51 (+1.54)
$[TcOCl_2L^4]$	n.i.	9.08 (+0.69)	—	—
$[ReOCl_2L^1]$	n.i.	9.70 (+0.37)	n.i.	9.60 (+0.52)
$[ReOCl_2L^2]$	8.07 (+0.64)	9.20 (+0.28)	8.28 (+0.56)	9.41 (+0.44)
$[ReOCl_2L^3]$	—	9.16 (+0.21)	8.33 (+0.60)	9.45 (+0.48)

[a] In dmf solutions. [b] Methanol solution. [c] n.i. = Not identifiable

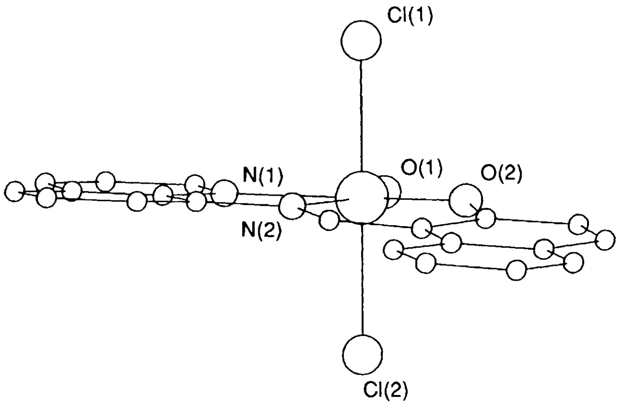
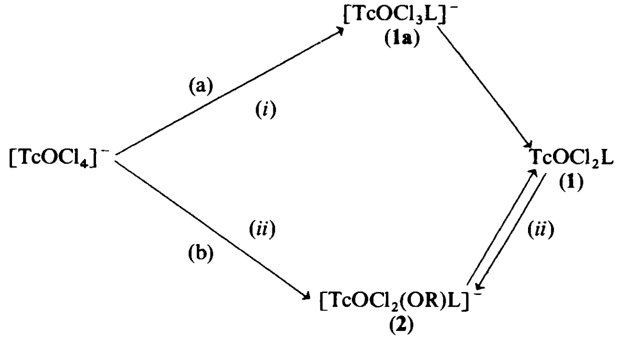


Figure 2. Equatorial co-ordination plane in $[TcOCl_2L^1]$ (**1**)

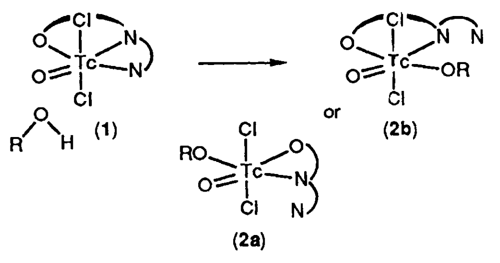


Scheme. R = Me or Et. (a) Strictly anhydrous or non-protonated solvents; (b) anhydrous solvents or alcohols; (*i*) CH_2Cl_2; (*ii*) ROH

for the C(10) which deviates by 0.13 Å], as depicted in Figure 2, and the technetium atom is displaced by only 0.01 Å from the mean plane of the N_2O_2 donor atoms. Consequently, all the dihedral angles approach 0°. Although the Cl(1)–Tc–Cl(2) moiety would be expected to be linear, the observed angle is within 12° of linearity and it is likely that the deviation results from intramolecular steric constraints within the co-ordination sphere. In this regard, atom Cl(2) in general has closer contacts with the other co-ordinated atoms than does Cl(1). The bond lengths [Tc=O 1.648(5), Tc–O 1.923(6), Tc–N(1) 2.115(6), and Tc–N(2) 2.162(5); Tc–Cl mean 2.383(3) Å] and angles in the inner core apart from the somewhat short Tc–N distances do not merit any comment, since they do not differ significantly from expected values.[2,13,18] These are no unusual intermolecular contacts while the shortest (2.18 Å) intramolecular approach involves H(1) and the Tc=O oxygen atom.

The Reaction of $[NBu_4][TcOCl_4]$ *and* HL^1.—This reaction was studied in detail. The Scheme shows it to involve two steps. In strictly anhydrous dichloromethane [route (a)] an intermediate complex (red solution) namely $[TcOCl_3L]^-$ (**1a**) is produced; it quickly rearranges to the final compound $[TcOCl_2L]$ (**1**). This rearrangement is so fast as not to allow the collection and characterization of (**1a**), even in solutions at 0 °C. In the intermediate product the ligand HL^1 could act as in a bidentate manner, *i.e.* with the phenolate oxygen *trans* to the Tc=O group, and the pyridine nitrogen not co-ordinated. Examples of such configurations have been reported in the first step of the synthesis of $[MO(Cl)L_2]$ (L = bidentate ON-Schiff base).[7] In contrast, in alcohols [route (b)] the first step gives another labile intermediate (**2**) (red solution), stable enough to be characterized in solution but not in the solid state. The same product (**2**) is obtained on dissolving green crystals of (**1**) in alcohols. The rate of dissolution depends on the alcohol employed and in particular it is directly related to the inductive effect of the oxygen atom, consistent with the trend H–OH < Me–OH > Et–OH. Protonated solvents interact with complex (**1**) and the high acidity of $[TcOCl_2L^1]$ causes deprotonation of ROH giving rise to complex (**2**)*.

In non-protonated and strictly anhydrous solvents the complex (**1**) maintains the same configuration in solution as in the solid state. Comparison of the green solutions of (**1**) and red solutions of (**2**) shows three differences: (*i*) (**1**) is neutral, since it is non-conducting in acetonitrile, however when a few drops of methanol are added to the acetonitrile solution it produces a 1:1 electrolyte; (*ii*) optical spectra of (**1**) and (**2**) are unambiguously different mainly in the visible region (Figure 3); (*iii*) proton n.m.r. spectra show different co-ordination of the ligand around the metal for (**1**) and (**2**), in particular a consistent change of the chemical shift of H^{11} is in agreement with the release of pyridine nitrogen in (**2**). From the above data one can deduce the formation of a charged compound (**2**) from alcohol



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* The complex $[ReOCl_2L^4]$ was isolated by a procedure identical to that described in the Experimental section for other rhenium compounds. However the microanalytical data fell slightly outside the expected values and also the characterization in solution is not clear. On the other hand, mass spectra undoubtedly show the molecular ion (peak at *m*/*z* 464) with its characteristic isotope distribution pattern, consistent with a species containing the group $ReCl_2$, and fragmentation behaviour (*m*/*z* 429 and 396), consistent with the release of one and two chlorine atoms respectively.

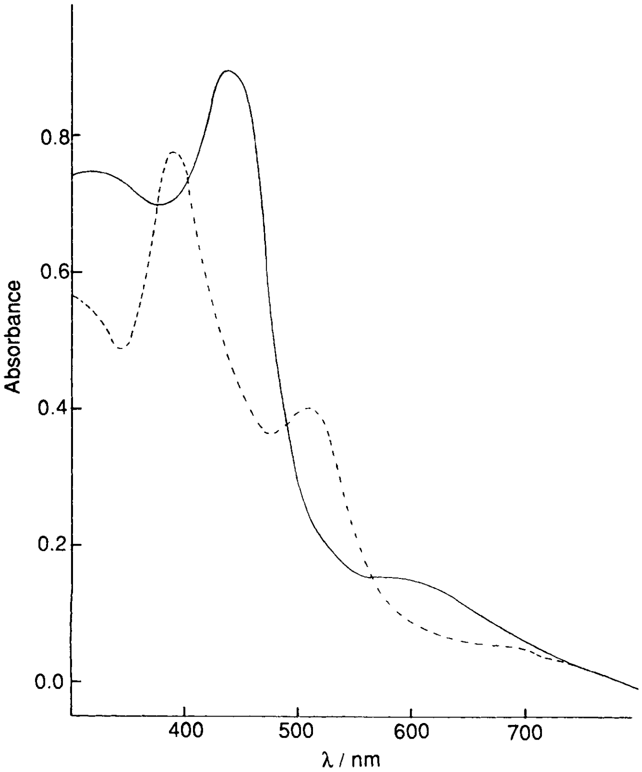


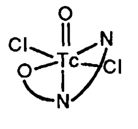
Figure 3. U.v.-visible spectra of a 5×10^{-5} mol dm^{-3} acetonitrile solution of [$TcOCl_2L^1$] (**1**) (——) and a 5×10^{-5} mol dm^{-3} acetonitrile–methanol (100:1 v/v) solution of [$TcOCl_2(OMe)L^1$]$^-$ (**2**) (- - -)

solutions of (**1**). Moreover complex (**2**) is anionic since it is retained on an anionic QAE-Sephadex A-25 resin. The position of the central imino nitrogen of the ligand is not clearly deducible from experimental data, although only the following two configurations are possible. The formation of (**2b**) requires the replacement of the pyridine nitrogen with the alcoholate group and maintains the imino nitrogen *trans* to the Tc=O linkage. On the contrary, the formation of (**2a**), even if this requires a rearrangement of the molecule, is more probable when compared with previous known MO^{3+} (M = Tc or Re) complexes.[7,8]

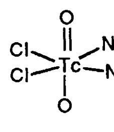
The X-ray crystal structure of [$TcOCl_2L^1$] confirms that the ligand is co-ordinated to the metal in an unusual fashion. The central imino nitrogen of the ligand is located *trans* to the Tc=O group. Only two other examples exhibit a nitrogen atom *trans* to Tc=O: [$TcOCl_2\{HB(pz)_3\}$][19] and [TcO(Cl)(eg)(phen)],[20] where $HB(pz)_3$ = hydrotris(1-pyrazolyl)borato eg = ethylene glycolate, and phen = 1,10-phenanthroline. In the former structure the nature of the tridentate '*fac*' ligand dictates the configuration, so that one pyrazolyl nitrogen must be *trans* to Tc=O.[19] The latter, produced *via* ligand-exchange reaction from [$TcOCl_4$]$^-$ with 1,2-ethanediol and phen in methanol,[20] had a phen nitrogen *trans* to Tc=O. The stability of this configuration is enhanced by proposed valence-bond resonance structures for the ethanediolate moiety.[20] Comparison of the Tc=O stretching frequencies of the three related O–Tc–N compounds (Table 4) confirms the presence of the same atom *trans* to Tc=O.

The Tc–N(2) bond length [2.162(5) Å] *trans* to the Tc=O group merits a comment. Although, as expected, it is longer than Tc–N(1) [2.115(6) Å] *trans* to Tc–O(2), on the basis of previous *X*-ray structures of two complexes[19,20] containing the O=Tc–N^{3+} moiety (Table 4) it seems to be somewhat short. In [TcO(Cl)(eg)(phen)],[20] in which phen (and ethanediolate) provide the same N_2O_2 set in the equatorial plane, the magnitude of the oxo-group on N(2) [and of O$^-$ from the ethanediolato ligand on N(1)], reflected by the bond distances, gives rise to much longer Tc–N bond lengths (2.27 and 2.17 Å) when compared with the corresponding values (2.162 and 2.115 Å) in the present complex. The difference may take into account the planarity (Figure 2) of the HL^1 ligand which accommodates bonding to the Tc atom without any large structural *trans* effect and any large folding of the ligand.

The reason why ONN ligands assume the found configuration (**i**), among the three possible ones, cannot be explained by invoking the rigidity of the ligand since also HL^4, a flexible molecule, shows the same behaviour. Two other effects seem to play a key role in favour of (**i**): (*a*) the high acidity of the MO^{3+} core can be better satisfied by three negatively charged groups;[3,4] (*b*) the *trans*-stabilizing effect of the two chlorine atoms. Moreover the co-ordination of the two lateral atoms O and N of the ligand maintains the remaining central imino nitrogen close to the metal [Tc–N(2) 2.162(5) Å]. As a consequence, in the reported complexes the *trans*-labilizing effect of the oxo-oxygen seems to be inactive.



(i)



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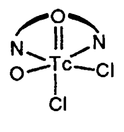

(iii)

Electrochemistry.—Both complexes [$ReOCl_2L^1$] and [$TcOCl_2L^1$) give, at potential scan rates, from 50 to 600 mV and at room temperature, voltammograms of little interest with no apparently reversible systems present. However, in the cathodic region, on decreasing the temperature, reversibility is observed (Figure 4). Furthermore, with the exception of the $E_{\frac{1}{2}}$ values of the redox couples, the shape of the voltammograms is quite similar for both complexes. For the system A/B the peak separation ($E_{pc,pa}$) of the redox couple is comparable with that of the ferrocene internal standard[16] at the same scan rate, tending to 59 mV at low scan rates, thus indicating that quasi-reversible processes are involved. Peak system A/B involves the reduction of [$M^VOCl_2L^1$] to [$M^{IV}OCl_2L^1$]$^-$ (M = Re, $E_{\frac{1}{2}}$ = −1.26; M = Tc, $E_{\frac{1}{2}}$ = −0.69V). Related to this system are two other waves C/D whose intensities rise at room temperature. On the contrary, at −50 °C and increasing scan rate, C/D tends to disappear, while the ratio I_{pB}/I_{pA} approaches one. This behaviour is typical for an electrochemical mechanism: the electrogenerated species [$M^{IV}OCl_2L^1$]$^-$ reacts readily, and the new species is oxidized at peak D and reduced at peak C. Coulometric experiments carried out at peak A show the transfer of one electron per mol of compound.

At more negative potentials there is a quasi-reversible system E/F which, probably, involves a further reduction to M^{III}, however at the potential scan rates studied the ratio I_{pF}/I_{pE} was always found to be less than one. Only the technetium complex shows in this region one more reversible system G/H which can be assigned to the redox couple of a new metal(IV) species generated through an electrochemical mechanism.

In the anodic region both complexes exhibit an irreversible

Table 4. Comparison of some relevant data for complexes of Tc^V containing the $O{=}Tc{-}N^{3+}$ moiety

Complex	$\nu(Tc{=}O)/cm^{-1}$	Bond distance (Å)			
		Tc=O	$Tc{-}N_{trans}$	$Tc{-}N_{cis}$	Tc–Cl
$[TcOCl_2L]$	956	1.65(1)	2.16(1)	2.11(1)	2.396(3)
$[TcOCl_2\{HB(pz)_3\}]$	953	1.656(3)	2.259(4)	2.086(4) 2.088(3)	2.332(1) 2.324(1)
[TcO(Cl)(eg)(phen)]	952	1.661(4)	2.268(4)	2.173(4)	2.418(2)

Table 5. Comparison of $E^r_{\frac{1}{2}}$ values for the couple M^V–M^{IV} (M = Tc or Re)[a]

Complex of M^V [b]	$E_{\frac{1}{2}}/V$		ΔE [c]	Ref.
	Tc	Re		
$[MOCl(L_B)_2]$	−0.91[d]	−1.43[e]	0.52	23,24
$[MO(L_T)(L_B)_2]$	−0.92	−1.38[e]	0.46	23,24
$[MOCl_2L^1]$	−0.69	−1.26	0.57	This work
$[M_2O_3(L_Q)_2]^-$ [f]	−1.03	−1.53	0.50	12

[a] Values of $E_{\frac{1}{2}}$ are measured in acetonitrile *versus* the ferrocenium–ferrocene couple by cyclic voltammetry at 0.2 V s^{-1}. [b] L_B = Bidentate Schiff Base, L_T = tridentate Schiff Base, and L_Q = quadridentate Schiff Base. [c] $\Delta E = E_{\frac{1}{2}}(Tc) - E_{\frac{1}{2}}(Re)$. [d] Measured at −35 °C. [e] Corrected from the reported −1.33V at 20 V s^{-1}. [f] In dmf solutions.

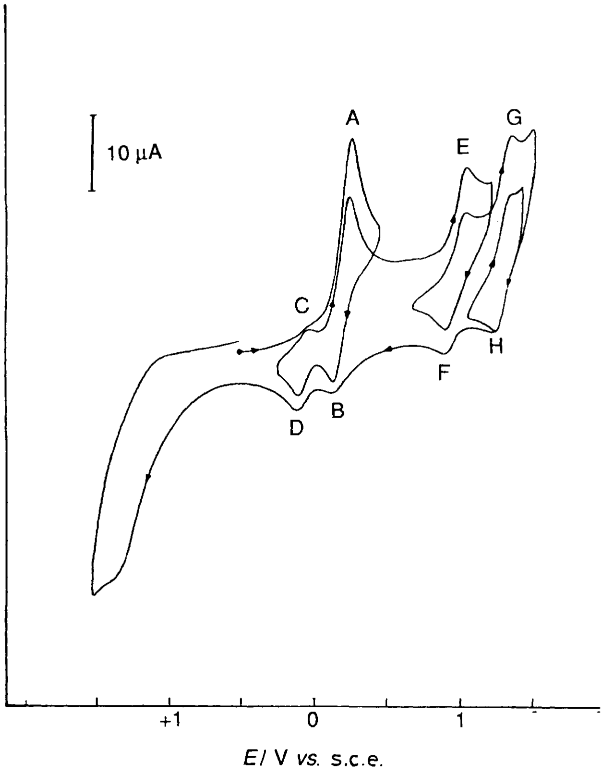

Figure 4. Cyclic voltammetric scan of 1.5×10^{-3} mol dm^{-3} $[TcOCl_2L^1]$ in 0.1 mol dm^{-3} NEt_4ClO_4 in dmf at −50 °C

peak obscured by the solvent background which could be due to oxidation to M^{VI}.

The rhenium complex has a reduction potential for the couple M^V–M^{IV} (Table 5) higher than that for the technetium analogue suggesting that technetium complexes are consistently easier to reduce than their rhenium analogues.[21,22] Previous electrochemical studies on a variety of technetium and rhenium systems, the majority concerning low-valent metal centres, have always shown this trend, but, instead of the usual 200—300 mV reduction-potential differences, the couple M^V–M^{IV} presents larger values within the range 460—570 mV[12,23,24] (Table 5). In a similar way the variation of the chemical shifts of the protons close to the co-ordinated atoms is enhanced in technetium with respect to rhenium complexes (Table 3). Both these measurements (electrochemical and n.m.r.), strictly depending on the ability of the central moiety to attract electron density from the co-ordinated ligands, confirm the greater acidity of the TcO^{3+} moiety with respect to ReO^{3+}.

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