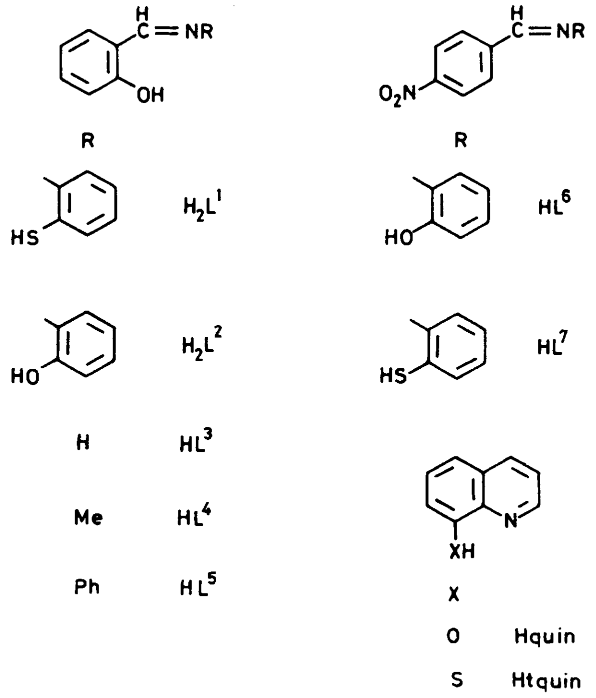
Technetium(v) and Rhenium(v) Complexes with *N*-(2-Mercaptophenyl)-salicylideneiminate. Crystal Structure† of Chloro(oxo)[*N*-(2-sulphidophenyl)-salicylideneiminato-*NOS*]technetium(v)

Francesco Tisato,* Fiorenzo Refosco, and Ulderico Mazzi
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R. Area della Ricerca, C. so Stati Uniti 4, 35020 Padova, Italy
Giuliano Bandoli and Marino Nicolini
Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo 5, 35131 Padova, Italy

The reactions of the tridentate Schiff-base ligand derived from salicylaldehyde and *o*-aminothiophenol (H_2L^1) with $[MOCl_4]^-$ (M = Tc or Re) have been investigated. The complexes $[MOCl(L^1)]$, $[ReOCl_2(L^1)]^-$, and $[ReOCl(X)(L^1)]$ (X = MeOH or EtOH) were synthesized and characterized by elemental analysis, i.r., ^{1}H n.m.r., and u.v.–visible spectroscopy, mass spectrometry, magnetic susceptibility, conductivity, and thermogravimetric measurements and the complete configurations of the complexes were determined. *X*-Ray crystallographic investigation on $[TcOCl(L^1)]$ shows the molecular structure to be a distorted square pyramid having the ligand L^1 in the equatorial plane with respect to Tc=O. The molecule is in the monoclinic space group $P2_1/a$, with a = 14.255(9) b = 12.495(7), c = 7.865(6) Å, β = 105.22(5)°, and Z = 4. The structure has been refined to R = 0.068 for 2 184 observed reflections. The reactions of $[MOCl(L^1)]$ (M = Tc or Re) or $[ReOCl(X)(L^1)]$ (X = MeOH or EtOH) with the bidentate Schiff-base ligands (HL) salicylideneimine (HL^3), *N*-methylsalicylideneimine (HL^4), *N*-phenylsalicylideneimine (HL^5), *N*-(2-hydroxyphenyl)-*p*-nitrobenzylideneimine (HL^6), quinolin-8-ol (Hquin), quinoline-8-thiol (Htquin), and *N*-(2-mercaptophenyl)-*p*-nitrobenzylideneimine (HL^7) lead to the 'mixed' compounds $[MO(L^1)(L)]$. The products with L = tquin or L^7 were obtained only for $[ReOCl(X)(L^1)]$ (X = MeOH or EtOH). All these complexes were characterized by the physicochemical techniques listed above.

Recently we devoted our efforts to the synthesis of several Schiff-base complexes with technetium and rhenium,[1–4] to obtain information on the chemical behaviour of the metals with these ligands in order to produce stable complexes suitable for the preparation of new radiopharmaceuticals labelled with technetium-99m. In particular we have investigated the reactions of the tridentate Schiff bases *N*-(2-mercaptophenyl)salicylideneimine (H_2L^1) or *N*-(2-hydroxyphenyl)salicylideneimine (H_2L^2) with $[TcOCl_4]^-$, producing the complexes $[TcOCl(L^n)]$ (n = 1 or 2).[2] We have also studied the behaviour of H_2L^2 with $[ReOCl_4]^-$ and obtained a series of compounds of the type $[ReOCl(X)(L^2)]^n$ (X = MeOH or PMe_2Ph, n = 0; X = Cl, n = 1 −).[3] Mixed complexes with technetium and rhenium with the formulation $[MO(L^2)(L)]$ [M = Tc or Re, L = bidentate Schiff-base anion L^3, L^4, L^5 (see below), or quinolin-8-olate], prepared starting from $[TcOCl(L^2)]$ or $[ReOCl(MeOH)(L^2)]$, have been described previously.[4]

In this paper we report the behaviour of $[MOCl_4]^-$ (M = Tc or Re) with respect to the tridentate Schiff base (H_2L^1), derived from the condensation reaction between salicylaldehyde and *o*-aminothiophenol, and the reactions of $[MOCl(L^1)]$ (M = Tc or Re) and $[ReOCl(X)(L^1)]$ (X = MeOH or EtOH) with the following bidentate Schiff bases (HL): salicylideneimine (HL^3), *N*-methylsalicylideneimine (HL^4), *N*-phenylsalicylideneimine (HL^5), *N*-(2-hydroxyphenyl)-*p*-nitrobenzylideneimine (HL^6), quinolin-8-ol (Hquin), quinoline-8-thiol (Htquin), and *N*-(2-mercaptophenyl)-*p*-nitrobenzylideneimine (HL^7). The complexes were characterized by elemental analysis, i.r., ^{1}H n.m.r., u.v.–visible spectroscopy, mass spectrometry, magnetic suceptibility, conductivity, and thermogravimetric measurements. The structure of the complex $[TcOCl(L^1)]$ was also determined by *X*-ray analysis.



---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

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

Experimental

Materials.—Technetium as $[NH_4][^{99}TcO_4]$ was purchased from the Radiochemical Centre, Amersham. $[NBu_4][TcOCl_4]$ and $[NBu_4][ReOCl_4]$ were prepared by the methods described previously.[5,6] The ligands HL and H_2L^2 were prepared by mixing in ethanol salicylaldehyde (or *p*-nitrobenzaldehyde) and the corresponding amine (ammonia, methylamine, aniline, or *o*-aminophenol) following the procedure described previously.[4] Quinolin-8-ol and quinoline-8-thiol hydrochloride were used as commercially available.

The ligand H_2L^1 was prepared by mixing salicylaldehyde (0.5 cm^3, 4.65 mmol) and *o*-aminothiophenol (0.52 cm^3, 4.65 mmol) in ethanol (30 cm^3). The solution became immediately yellow and after 30 min a white powder appeared. It was collected by filtration and washed with EtOH and Et_2O. The yellow mother-liquors gave yellow crystals after 2 d by slow evaporation of the solvent; these were washed several times with EtOH and then with Et_2O. The 'white form' is very soluble in Me_2CO, soluble in MeCN and CH_2Cl_2, slightly soluble in EtOH or MeOH, and insoluble in Et_2O and water (Found: C, 68.2; H, 4.8; N, 6.0. Calc. for $C_{13}H_{11}NOS$: C, 68.1; H, 4.8; N, 6.1%). I.r.: ν(N–H) at 3 259 cm^{-1}. The 'yellow form' is very soluble in CH_2Cl_2, soluble in Me_2CO, and practically insoluble in other organic solvents (Found: C, 68.4; H, 4.4; N, 6.1. Calc. for $C_{13}H_{11}NOS$: C, 68.1; H, 4.8; N, 6.1%). I.r.: ν(C=N) at 1 616 cm^{-1}.

All other materials were reagent grade chemicals.

Apparatus.—Elemental analyses were performed on a Carlo Erba 1106 elemental analyser; technetium quantitative determinations were carried out on a Rackbeta II (model 1215) instrument, with Insta-gel, a ready-for-use xylene-based liquid scintillation cocktail (Packard Instrument Int., Zürich). Infrared spectra were recorded in the range 4 000—200 cm^{-1} on a Perkin-Elmer PE 580B spectrometer using KBr pellets or Nujol mulls between CsI pellets. ^1H N.m.r. spectra were obtained on a Varian FT80 instrument using CD_2Cl_2 as solvent and $SiMe_4$ as internal reference. Mass spectrometric measurements were carried out on a WG ZABZF instrument operating in electron impact mode (70 eV, 200 A).

Magnetic susceptibility measurements were performed in solution by the Evans n.m.r. method using a Varian FT80 spectrometer for technetium compounds and in the solid state with an assembled Oxford instrument (DN 700S with N177 magnet and Cahn 200 microbalance) using the Faraday system for those of rhenium. All the complexes were found to be diamagnetic in character, in agreement with the data reported previously for Tc^V and Re^V complexes containing the M=O group, both in distorted octahedral and square pyramidal environments. Conductivity measurements were made in acetonitrile at 25 °C using a Metrohm Herison E518 conductometer. The complexes were found to be non-conductive, except for the product characterized as $[ReOCl_2(L^1)]^-$. U.v.-visible spectra were recorded in different solvents using a Cary 17D spectrophotometer. Thermogravimetric measurements were performed in air using a Netzsch STA-429 thermoanalytical instrument (N_2 flux rate 250 cm^3 min^{-1}, heating rate 5 °C min^{-1}, reference material Al_2O_3).

^{99}Tc is a weak β emitter ($E_{\beta_{max.}}$ = 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 moderate vacuum for the synthesis and recovery operations.

Synthesis.—$[TcOCl(L^1)]$. This complex was prepared using a modified version of a previously described procedure.[2] A methanolic solution of either the yellow or white form of H_2L^1 (97 mg, 0.42 mmol) was added under stirring at room temperature to a pale green solution of $[NBu_4][TcOCl_4]$ (210 mg, 0.42 mmol) in MeOH (15 cm^3). The solution became immediately dark red and after a few minutes (for the yellow form) a solid appeared; the reaction required 2 h for completion when the white form was used. The precipitate was filtered off and washed with a few drops of MeOH. No recrystallization was necessary to obtain a pure sample (yield 82%). The solid product is soluble in CH_2Cl_2, $CHCl_3$, dimethylformamide (dmf), and Me_2CO, slightly soluble in MeOH, EtOH, and MeCN, and insoluble in Et_2O and hydrocarbons. Crystals for *X*-ray study of the complex were obtained by slow evaporation of a solution in CH_2Cl_2–EtOH (1:1).

$[ReOCl(X)(L^1)]$ (X = MeOH *or* EtOH). Following the same procedure as that above, $[ReOCl_4]^-$ produces different compounds on changing the reaction solvent. When MeOH or EtOH was employed the complex $[ReOCl(MeOH)(L^1)]$ or $[ReOCl(EtOH)(L^1)]$ was isolated. The solids precipitated from the reaction mixture and were collected by filtration and washed with the reaction solvent (yields 80% or 50% respectively). The compounds are soluble in CH_2Cl_2, Me_2CO, and MeCN, and slightly soluble in alcohols. The MeOH derivative is insoluble in Et_2O while the EtOH derivative changes colour from red to yellow-brown, the product being characterized as $[ReOCl(L^1)]$.

$[ReOCl(L^1)]$. This complex was produced when higher alcohols such as Pr^{n}OH or Bu^{n}OH were used. The solid precipitated from the reaction mixture as a yellow-brown powder (yield 30%). The yield was improved (to 70%) by refluxing for 1 h. The complex is soluble in CH_2Cl_2 and MeCN (yellow solutions). With solvents such as Me_2CO, dmf, and tetrahydrofuran (thf) the solution becomes red.

$[NBu_4][ReOCl_2(L^1)]$. A solution of the white form of H_2L^1 (60 mg, 0.26 mmol) was added under stirring at room temperature to a pale yellow solution of $[NBu_4][ReOCl_4]$ (153 mg, 0.26 mmol) in MeCN or Me_2CO (10 cm^3). The solution immediately became dark red, without any solid product after 2 h. It was then treated with Et_2O and a precipitate appeared. This was filtered off, washed with Et_2O, and recrystallized by dissolving in MeCN and adding Et_2O until the solution was saturated (yield 78%).

$[MO(L^1)(L)]$ (M = Tc *or* Re). The same procedure was followed for the preparation of all the complexes. The $[MOCl(L^1)]$ (M = Tc or Re) or $[ReOCl(X)(L^1)]$ (X = MeOH or EtOH) starting compound (0.1 mmol) was dissolved in EtOH (20 cm^3). A double stoicheiometric amount (0.2 mmol) of the bidentate ligand (HL = HL^3, HL^4, HL^5, HL^6, or Hquin) was added after stirring for 10 min at room temperature. The solution changed from red to dark red and after 30 min a solid appeared. After a further 2 h the precipitate was filtered off and washed with EtOH and a little Et_2O. No recrystallization was necessary to obtain a pure sample (yield >80%). The solid products are generally soluble in CH_2Cl_2 and Me_2CO, slightly soluble in alcohols and MeCN, and insoluble in Et_2O and hydrocarbons.

$[ReO(L^1)(tquin)]$. An ethanolic solution of quinoline-8-thiol hydrochloride (48 mg, 0.25 mmol) was added under stirring to $[ReOCl(MeOH)(L^1)]$ (128 mg, 0.25 mmol) dissolved in EtOH (20 cm^3) and left at room temperature. The solution became orange-red and after 10 min a solid appeared. After a further 1 h the precipitate was filtered off and washed with EtOH and Et_2O. No recrystallization was necessary to obtain a pure sample. The solid products are soluble in CH_2Cl_2 and dmf, slightly soluble in Me_2CO, MeOH, EtOH, and MeCN, and insoluble in Et_2O and hydrocarbons (yield 80%).

$[ReO(L^1)(L^7)]$. The product was prepared by following the same method as that above and the properties were very similar (yield 70%).

X-Ray Analysis.—A dark red, transparent crystal of [TcOCl(L^1)], irregularly shaped with dimensions *ca.* 0.15 × 0.12 × 0.08 mm, was mounted on a Philips PW 1100 computer-controlled diffractometer. Cell constants were based on a least-squares fit of 25 reflections with 2θ values ranging from 16 to 36° (Mo-K_α radiation, λ = 0.7107 Å). The structure is shown in Figure 1.

Crystal data. $C_{13}H_9ClNO_2STc$, M = 377.6, monoclinic, a = 14.255(9), b = 12.495(7), c = 7.865(6) Å, β = 105.22(5)°, U = 1 351.7(1.6) Å^3, Z = 4, D_c = 1.86 g cm^{-3}, $F(000)$ = 744, μ(Mo-K_α) = 13.8 cm^{-1}, space group $P2_1/a$.

A unique data set was collected at 20 °C using a ω–2θ scan mode for all reflections in the range 3 < 2θ < 56°, with a scan range of 1.3°, a scan rate of 0.03° s^{-1}, and a total background time of 20 s. Three standard reflections were measured every 3 h and the intensities did not exhibit any systematic trend throughout the data collection. The intensities of 3 445 independent reflections were measured, of these 2 184 obeyed the condition $I \geqslant 3\sigma(I)$ and were used in subsequent calculations. An experimental absorption correction based on ψ scans was applied.

Structure determination and refinement. The structure was solved by using direct methods to find the co-ordinates of the Tc, Cl, S, and O(1) atoms. A number of cycles of least-squares refinement, followed by difference synthesis, enabled location of all non-hydrogen atoms and led to convergence with R = 0.18; refinement yielded a model chemically acceptable, but the 19 atoms exhibited rather high thermal parameters and a difference Fourier map showed eight relevant electron-density peaks, suggesting a positional disorder similar to that found in the six-co-ordinate [TcO(L^2)(quin)] complex[4] in which disorder is restricted only to the –CH=N– bridge atoms.

On treating the phenyl rings as 'rigid bodies' (C–C 1.395 Å), the bridge atoms were assigned two orientations corresponding to the positions and peak heights on the difference map. Subsequent least-squares refinement (including alternately normalized occupancies and isotropic thermal parameters for the 'disordered atoms') was successful (R = 0.068 with anisotropic heavy atoms), the L^1 ligand showing two orientations [(A) and (B)] about the –CH=N– bridge (Figure 2); the first is slightly preferred. In the final calculations each atom of (A) and (B) was given an individual occupancy of 0.6 and 0.4, respectively. A difference electron-density map based on the final parameters of all atoms was virtually featureless, except two peaks (up to 1.3 e Å^{-3}) in the vicinity of the Tc atom. Final

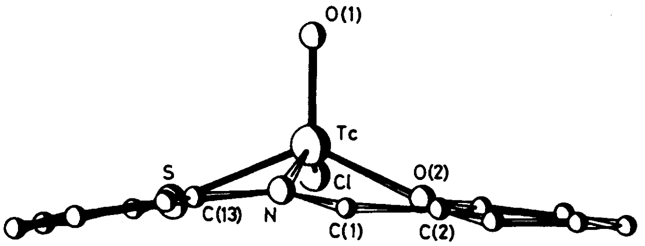


Figure 1. Perspective view of the co-ordination around the technetium atom in [TcOCl(L^1)]

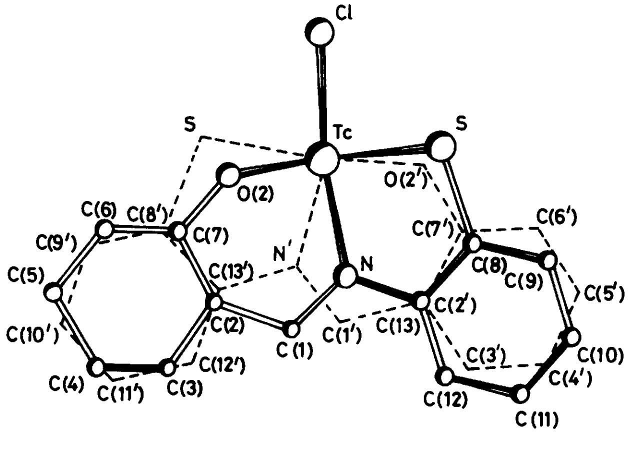


Figure 2. Perspective view of [TcOCl(L^1)], orientation (A), showing the atom numbering, viewed down the Tc–O(1) axis; dashed lines indicate the second orientation (B)

Table 1. Final fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses, for [TcOCl(L^1)]. Orientation (A) denotes atoms with average occupancy 0.6, (B) those with occupancy 0.4

Atom	*x*	*y*	*z*
Tc	3 362(1)	2 196(1)	−2 505(1)
Cl	1 712(2)	1 971(3)	−2 841(5)
O(1)	3 454(6)	2 849(7)	−4 236(10)

Orientation (A)				Orientation (B)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S	3 150(4)	3 281(4)	−221(8)	S′	2 984(5)	337(5)	−3 255(10)
O(2)	3 483(9)	677(9)	−2 754(18)	O(2′)	3 436(16)	2 964(16)	−503(28)
N	4 811(13)	2 190(15)	−785(23)	N′	4 702(16)	1 574(17)	−1 514(27)
C(1)	5 447(15)	1 457(15)	−810(24)	C(1′)	5 382(31)	2 046(33)	−339(52)
C(2)	5 236(11)	469(8)	−1 860(18)	C(13′)	4 977(18)	500(12)	−2 112(29)
C(3)	6 033(11)	−160(8)	−1 930(18)	C(12′)	5 926(18)	121(12)	−1 836(29)
C(4)	5 892(11)	−1 119(8)	−2 871(18)	C(11′)	6 097(18)	−861(12)	−2 542(29)
C(5)	4 954(11)	−1 449(8)	−3 741(18)	C(10′)	5 319(18)	−1 465(12)	−3 524(29)
C(6)	4 157(11)	−820(8)	−3 670(18)	C(9′)	4 370(18)	−1 086(12)	−3 800(29)
C(7)	4 298(11)	139(8)	−2 730(18)	C(8′)	4 199(18)	−103(12)	−3 094(29)
C(8)	4 362(8)	3 615(13)	862(21)	C(7′)	4 240(13)	3 457(19)	522(32)
C(9)	4 565(8)	4 428(13)	2 121(21)	C(6′)	4 184(13)	4 320(19)	1 616(32)
C(10)	5 528(8)	4 695(13)	2 945(21)	C(5′)	5 032(13)	4 764(19)	2 689(32)
C(11)	6 286(8)	4 150(13)	2 509(21)	C(4′)	5 936(13)	4 345(19)	2 669(32)
C(12)	6 083(8)	3 337(13)	1 250(21)	C(3′)	5 992(13)	3 481(19)	1 576(32)
C(13)	5 120(8)	3 069(13)	427(21)	C(2′)	5 144(13)	3 037(19)	502(32)

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Tc–Cl	2.31(1)	Tc–O(1)	1.62(1)
Tc–S	2.33(1)	Tc–S′	2.42(1)
Tc–N	2.15(2)	Tc–N′	2.02(2)
Tc–O(2)	1.92(2)	Tc–O(2′)	1.82(2)
S–C(8)	1.76(1)	S′–C(8′)	1.79(3)
C(13)–N	1.44(2)	C(13′)–N′	1.51(3)
N–C(1)	1.29(3)	N′–C(1′)	1.29(4)
C(1)–C(2)	1.47(2)	C(1′)–C(2′)	1.48(5)
C(7)–O(2)	1.34(2)	C(7′)–O(2′)	1.36(3)
C–C (phenyl)*	1.39	C–C (phenyl)*	1.39
O(1)–Tc–Cl	105.6(3)		
O(1)–Tc–S	114.2(3)	O(1)–Tc–S′	109.9(4)
O(1)–Tc–N	104.6(6)	O(1)–Tc–N′	103.9(7)
O(1)–Tc–O(2)	112.5(5)	O(1)–Tc–O(2′)	117.4(7)
Cl–Tc–S	80.0(2)	Cl–Tc–S′	72.6(2)
Cl–Tc–N	148.3(5)	Cl–Tc–N′	145.9(6)
Cl–Tc–O(2)	89.1(4)	Cl–Tc–O(2′)	89.4(7)
S–Tc–O(2)	133.3(4)	S′–Tc–O(2′)	132.4(7)
S–Tc–N	79.3(5)	S′–Tc–N′	81.5(6)
N–Tc–O(2)	87.9(6)	N′–Tc–O(2′)	92.0(9)
Tc–S–C(8)	101.6(5)	Tc–S′–C(8′)	97.4(7)
C(13)–N–Tc	119.2(1.2)	C(13′)–N′–Tc	121.3(1.5)
C(1)–N–Tc	123.7(1.4)	C(1′)–N′–Tc	123.8(2.3)
C(1)–N–C(13)	117.0(1.7)	C(1′)–N′–C(13′)	115.0(2.6)
Tc–O(2)–C(7)	126.6(9)	Tc–O(2′)–C(7′)	126.7(1.7)
C–C–C (phenyl)*	120.0	C–C–C (phenyl*	120.0

* Phenyl rings treated as rigid bodies.

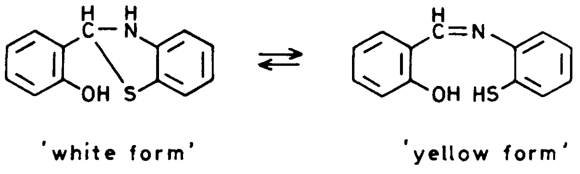


Figure 3. Equilibrium reaction of the H_2L^1 ligand

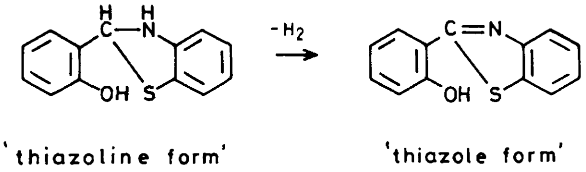


Figure 4. Reduction reaction of the 'thiazoline form' to the 'thiazole form' for H_2L^1

atomic positional parameters are listed in Table 1, bond lengths and angles in Table 2. The major calculations were made with the SHELX 76 program package.[7]

Results and Discussion

The ligand employed, H_2L^1,[8] undergoes a conversion of the type shown in Figure 3. The two forms of the ligand can be isolated and characterized by i.r. spectroscopy. The white form does not show any band around 1 600 cm^{-1} but has ν(N–H) at 3 259 cm^{-1}, the yellow one having ν(C=N) at 1 616 cm^{-1} and no ν(N–H) band.

The $[MOCl_4]^-$ (M = Tc or Re) complexes react in the same way using the white or yellow ligand, reproducing a well known equilibrium template reaction in which the white product changes to the yellow one during the co-ordination reaction.

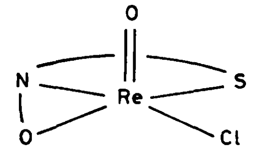


Figure 5. Configuration of $[ReOCl(L^1)]$ derived from experimental data

The complexes obtained both with technetium and rhenium, $[MOCl(L^1)]$, are of similar structure, the ligand acting as tridentate; however, while the technetium analogue can be prepared in different solvents such as methanol, ethanol, dichloromethane, and acetonitrile, the rhenium compound can only be prepared using higher alcohols such as Pr^nOH or Bu^nOH. With solvents such as methanol or ethanol a molecule of solvent was found to bind with rhenium in the sixth co-ordination position *trans* to the Re=O group.

It is interesting to notice that the ligand in the reaction with the starting complex $[TcOCl_4]^-$ must be used in stoicheiometric amount since, when in excess, the products obtained are $[TcOCl_3(\text{'thiazole'})]^-$ or $[TcOCl(\text{'thiazole'})_2]$, as reported by Duatti and Wilcox[9] due to a reaction, shown in Figure 4, involving the ligand which produces another ligand ('thiazole') which is bidentate.

The complex $[TcOCl(L^1)]$ was recrystallized from CH_2Cl_2–EtOH and dark brown plates were collected, suitable for *X*-ray analysis. All other physicochemical measurements were in agreement with those reported in a previous paper.[2] The ^1H n.m.r. spectrum in CH_2Cl_2 shows the imine proton signal at δ 10.14 with respect to $SiMe_4$.

The complex has a distorted square pyramidal geometry with the oxo ligand in the axial position (Figure 1). Thus, the tridentate L^1 ligand occupies three of the four co-ordination sites of the basal plane of this pyramid. In effect, this is one of the anticipated ways in which a tridentate Schiff-base ligand can co-ordinate to a $Tc=O^{3+}$ moiety.[2] Because of the positional disorder for the L^1 ligand, which takes on two orientations [(A) and (B)] with population ratio 0.6:0.4 (see Experimental section), only gross structure features can be derived from the *X*-ray analysis. However, the structure determination establishes that (*i*) the Tc atom is displaced 0.73 Å for (A) and 0.67 Å for (B) from the mean equatorial plane towards the O(1) atom and consequently the angles at Tc are non-orthogonal (Table 2); (*ii*) the donor atoms diametrically opposed are markedly distorted from planarity [S–Tc–O(2) 133.3° in (A) and 132.4° in (B); Cl–Tc–N 148.3° in (A) and 145.9° in (B)]; (*iii*) the angles about the N atom are close to 120°, ranging from 117.0 to 123.7° in (A) and from 115.0 to 123.8° in (B), as expected for the sp^2 hybridization of this atom.

The complex $[ReOCl(L^1)]$ is a yellow-brown, air-stable product with an elemental analysis and mass spectrum consistent with the formulation (Table 3). The i.r. spectrum shows in particular a ν(Re=O) stretching vibration at 995 cm^{-1}, a high value close to the analogous vibration of $[ReOCl_4]^-$[6] and in accordance with five-co-ordination, and ν(Re–Cl) at 348 cm^{-1}, a value suggesting chlorine *cis* to Re=O. The *trans* to Re=O site is confirmed to be empty by thermogravimetric measurement (no loss of weight until decomposition: >230 °C) and by the u.v.–visible spectrum (see below). The ^1H n.m.r. spectrum shows clearly only the chemical shift of the imine proton at δ 9.50 while the phenyl protons show an unresolved multiplet. The proposed configuration is given in Figure 5.

The five-co-ordinate compound $[ReOCl(L^1)]$ reacts with methanol or ethanol to yield a six-co-ordinate compound with a molecule of solvent in the sixth co-ordination position *trans* to

Table 3. Elemental analysis (%) and mass spectral results*

Compound	C	H	N	Tc	*m*/*z*
[TcOCl(L^1)]	41.2 (41.3)	2.4 (2.4)	3.7 (3.7)	26.0 (26.2)	378 (377.71)
[TcO(L^1)(L^3)]	52.2 (51.9)	3.4 (3.3)	6.0 (6.1)	21.3 (21.4)	462 (462.39)
[TcO(L^1)(L^4)]	53.0 (52.9)	3.7 (3.6)	5.8 (5.9)	20.6 (20.8)	476 (476.42)
[TcO(L^1)(L^5)]	57.9 (58.0)	3.7 (3.6)	5.2 (5.2)	18.4 (18.4)	538 (538.48)
[TcO(L^1)(quin)]	54.3 (54.3)	3.0 (3.1)	5.7 (5.8)	20.3 (20.4)	486 (486.41)
[ReOCl(L^1)]	33.7 (33.6)	2.1 (2.0)	2.9 (3.0)		465 (484.91)
[ReOCl(MeOH)(L^1)]	34.0 (33.8)	2.7 (2.6)	2.7 (2.8)		465 (496.95)
[ReOCl(EtOH)(L^1)]	35.1 (35.3)	2.9 (3.0)	2.7 (2.7)		465 (510.98)
[NBu$_4$][ReOCl$_2$(L^1)]	46.7 (46.9)	6.2 (6.1)	3.6 (3.8)		
[ReO(L^1)(L^3)]	43.6 (43.7)	2.7 (2.8)	5.1 (5.1)		549 (549.59)
[ReO(L^1)(L^4)]	44.8 (44.7)	2.9 (3.0)	4.9 (5.0)		564 (563.62)
[ReO(L^1)(L^5)]	49.7 (49.9)	3.0 (3.1)	4.9 (4.8)		626 (625.68)
[ReO(L^1)(quin)]	46.1 (46.1)	2.6 (2.6)	4.8 (4.9)		574 (573.61)
[ReO(L^1)(L^6)]	46.5 (46.6)	2.6 (2.7)	6.2 (6.3)		671 (670.68)
[ReO(L^1)(L^7)]	45.3 (45.5)	2.5 (2.6)	6.2 (6.1)		687 (686.73)
[ReO(L^1)(tquin)]	45.0 (44.8)	2.5 (2.6)	4.7 (4.8)		590 (589.66)

* Calculated values are given in parentheses.

Table 4. Principal i.r. bands (cm^{-1}) and ^{1}H n.m.r. signals (δ relative to SiMe$_4$)

Compounds	ν(M=O)	ν(C=N)	δ(CH=N)*	δ(CH$_3$), δ(C$_2$H$_5$)
[TcOCl(L^1)]	979	1 605	10.14	
[TcO(L^1)(L^3)]	947	1 605	8.91	
[TcO(L^1)(L^4)]	932	1 611	8.92	4.12 (s), 4.10 (s)
[TcO(L^1)(L^5)]	920	1 609	8.85	
[TcO(L^1)(quin)]	943	1 611	9.15	
[ReOCl(L^1)]	995	1 608	9.50	
[ReOCl(MeOH)(L^1)]	984	1 608	9.49	3.37 (s)
[ReOCl(EtOH)(L^1)]	984	1 607	9.50	3.60 (q), 1.15 (t)
[NBu$_4$][ReOCl$_2$(L^1)]	955	1 606	8.98	
[ReO(L^1)(L^3)]	953	1 614	9.01	
[ReO(L^1)(L^4)]	962	1 611	8.94	3.99 (s), 3.97 (s)
[ReO(L^1)(L^5)]	949	1 610	8.95	
[ReO(L^1)(quin)]	961	1 610	9.22	
[ReO(L^1)(L^6)]	946	1 609	8.79	
[ReO(L^1)(L^7)]	954	1 606	8.75	
[ReO(L^1)(tquin)]	938	1 606	8.68	

* All singlets.

Re=O. All attempts to obtain a six-co-ordinate compound with a molecule of water or higher alcohol co-ordinated *trans* to Re=O failed even though evidence for such complexes was found in solution by u.v.–visible measurements (see below).

The complexes [ReOCl(MeOH)(L^1)] and [ReOCl(EtOH)(L^1)] are red-violet crystalline products, with elemental analyses in agreement with the formulae (Table 3). The mass spectra exhibit a parent peak at *m*/*e* = 465 consistent with loss of the alcohol molecules. Both the complexes show ν(Re=O) at 984 cm^{-1}, a lower value than for the five-co-ordinate complexes but higher than for other six-co-ordinate compounds, reflecting the low strength of the rhenium–oxygen bond. ^{1}H N.m.r. spectra in CD$_2$Cl$_2$ show the imine protons at δ 9.50 (s) for both the complexes, and the presence in solution of an alcohol molecule [δ(CH$_3$) 3.37 (s) for the methanol complex, δ(CH$_3$) 1.15 (t) and δ(CH$_2$) 3.60 (q) for the ethanol complex]. The methanol complex is air stable while the ethanol analogue in air, or on treatment with diethyl ether, loses ethanol and reverts to the five-co-ordinate compound.

Thermogravimetric measurements produced a loss of weight for both the compounds corresponding to an alcohol molecule at 97 and 82 °C respectively for [ReOCl(MeOH)(L^1)] and [ReOCl(EtOH)(L^1)], suggesting a greater rhenium–oxygen bond strength for the methanol derivative.

The u.v.–visible spectra of the complexes were investigated in dichloromethane, acetonitrile, or alcohols as solvents (Table 5). The complexes [MOCl(L^1)] (M = Tc or Re) in dichloromethane or acetonitrile show the same pattern with a shift to higher frequencies for technetium compared to the rhenium analogue. This pattern can be assumed to be that of five-co-ordinate species. The spectrum of [ReOCl(L^1)] in methanol, ethanol, and also in n-propyl alcohol is the same as those of [ReOCl(MeOH)(L^1)] and [ReOCl(EtOH)(L^1)] in the respective alcohols, and different from the spectra of the five-co-ordinate species in the appearance of a characteristic absorption at 490 nm and of other bands at lower wavelengths. By adding a small amount of water to an acetonitrile solution of [ReOCl(L^1)] the u.v.–visible spectrum changes from the five-co-ordinate type to the six-co-ordinate one. This suggests that the species [ReOCl(Pr^{n}OH)(L^1)] and [ReOCl(H$_2$O)(L^1)] exist in solution and they lose the solvent molecule when the products are collected as solids.

The reaction of [NBu$_4$][ReOCl$_4$] with H$_2$L^1 in acetone, acetonitrile, or dichloromethane leads to the formation of the anion [ReOCl$_2$(L^1)]$^-$; the salt [NBu$_4$][ReOCl$_2$(L^1)] was obtained as a dark red-brown crystalline powder. It changes its colour in air after some days to give decomposition products; elemental analysis supports the formulation. The principal i.r. absorption is ν(Re=O) at 955 cm^{-1}, a typical value for a six-co-ordinate compound with a chlorine atom *trans* to Re=O. The value of $\Lambda_{eq.}$ = 132 S cm^2 mol^{-1} in acetonitrile is in agreement with a 1 : 1 electrolyte. A chloride ligand is easily substituted by dissolving the product in alcohols or eliminated by using caesium salts, precipitating insoluble CsCl. A chloride ligand is also added to the five-co-ordinate complex by dissolving it in acetonitrile in the presence of [NBu$_4$]Cl in large excess. The configuration of the six-co-ordinate complexes, as determined from the above data, is shown in Figure 6.

The complete reaction pathway is reported in Scheme 1. It is worth noting the similarity of these reactions with those involving the ligand H$_2$L^2 reported previously.[3] However there are some differences. In particular the [TcOCl(L^n)] (n = 1 or 2) moiety is stable enough to exist as a five-co-ordinate species, while [ReOCl(L^n)] can interact, *via* the site *trans* to the Re=O bonds with nucleophilic agents such as water, alcohols, or chloride to give a six-co-ordinate complex. The reason for this is the effect of M=O (M = Tc or Re) on the stability and geometry of the complex. The electronic effect of the Tc=O core forces the horizontal co-ordination plane to displace from it, as an open 'umbrella', more than for Re=O, so that six-co-ordination is more attainable for rhenium than for technetium also for steric reasons.

Table 5. U.v.-visible bands for some Tc and Re complexes

Complex	Solvent	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
[TcOCl(L^1)]	CH$_2$Cl$_2$	287 (33 700) 355 (16 300) 422 (6 100)
[ReOCl(L^1)]	CH$_2$Cl$_2$	258 (17 300) 335 (8 900) 415 (4 800)
[ReOCl(MeOH)(L^1)]	MeOH	228 (22 500) 322 (12 400) 405 (3 400) 473 (sh) (2 300)
[ReOCl(EtOH)(L^1)]	EtOH	230 (24 500) 325 (12 500) 405 (4 200) 475 (sh) (2 300)
[ReOCl(L^1)]	Pr^{n}OH	230 (25 700) 325 (13 300) 408 (4 700) 475 (sh) (2 300)
[ReOCl(L^1)]	MeCN-H$_2$O (100:1 v/v)	260 (13 200) 335 (9 700) 395 (3 200) 485 (sh) (1 000)
[ReOCl(L^1)(tquin)]	CH$_2$Cl$_2$	260 (23 000) 290 (13 500) 355 (11 500) 510 (sh) (1 000)

For the rhenium complexes of L^1 and L^2 the steric hindrance is very similar and therefore the different behaviour of the two moieties depends only on electronic factors. The possibility of isolating [ReOCl(L^1)] and not the L^2 analogue demonstrates the higher electronic stability of the former. As a consequence of this nucleophilic agents such as water, alcohols, or chloride react with [ReOCl(L^1)], producing complexes less stable than those with [ReOCl(L^2)]. In fact, the [ReOCl(H$_2$O)(L^1)] species is present only in solution and [ReOCl$_2$(L^1)]$^-$ is a labile product, decomposing in air, while the analogous compounds of L^2 are very stable.[1] An exception is the non-isolation of [ReOCl(EtOH)(L^2)], but this can be explained by the formation of the more stable [ReOCl$_2$(L^2)]$^-$ complex. The stability of the complexes of [ReOCl(L^1)] and the oxygenated nucleophilic agents appears to be consistent with the trend of the positive inductive effect on the oxygen atom: H$_2$O < MeOH > EtOH > Pr^{n}OH.

[MOCl(L^1)] (M = Tc or Re) and [ReOCl(X)(L^1)] (X = MeOH or EtOH) react with bidentate Schiff-base ligands to produce 'mixed' complexes of formula [MO(L^1)(L)]. The reactions are reported in Scheme 2. The only exception is that [TcOCl(L^1)] does not react with the bidentate ligands

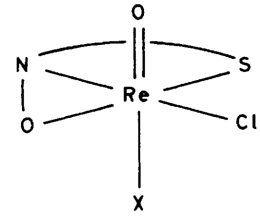
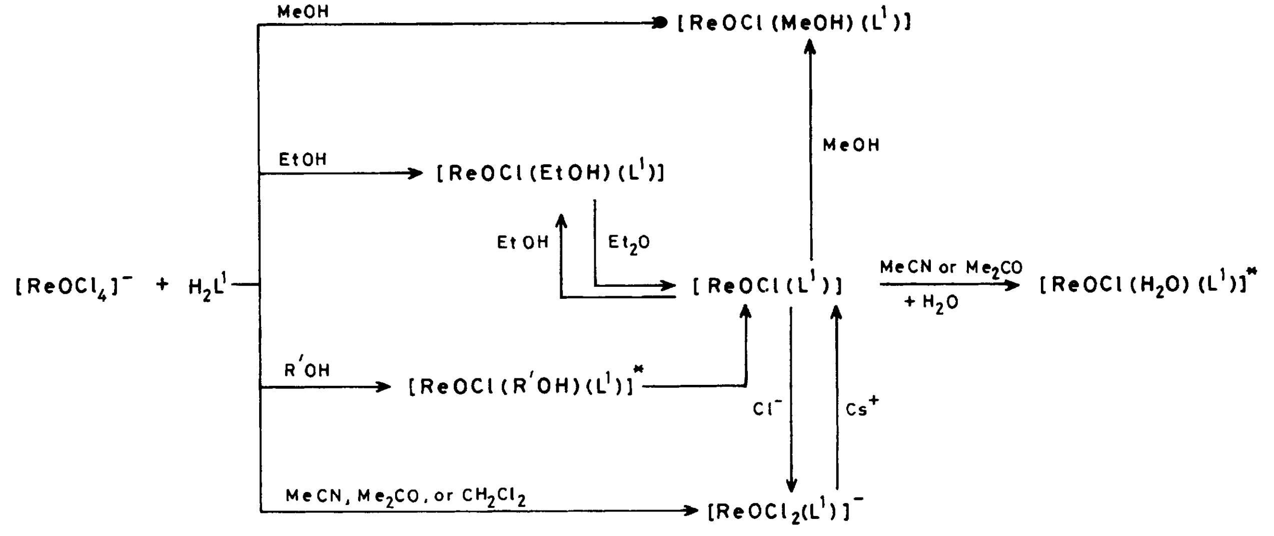


Figure 6. Configurations of [ReOCl(X)(L^1)] (X = MeOH or EtOH) or [ReOCl$_2$(L^1)]$^-$ derived from experimental data



Scheme 1. Summary of the reactions involving [ReOCl$_4$]$^-$ and H$_2$L^1, and their products.* The product exists only in solution; R' = Pr^n or Bu^n

$$[MOCl(X)(L^1)] + HL \xrightarrow{EtOH} [MO(L^1)(L)]$$

Scheme 2. Reactions of rhenium or technetium complexes of the tridentate Schiff-base ligand L^1 with bidentate ones producing 'mixed' complexes. For M = Re: X = MeOH, EtOH, or nothing; L = L^3, L^4, L^5, quin, tquin, L^6, or L^7. For M = Tc: X = nothing; L ≠ tquin or L^7

containing sulphur and the starting compound is recovered unchanged.

All the mixed complexes containing ON donor atoms are air stable, dark red crystalline powders and their formulation is supported by elemental analysis and mass spectral measurements (Table 3). I.r. spectra (Table 4) show ν(Re=O) and ν(Tc=O) in the ranges 962—946 and 947—920 cm^{-1} and ν(C=N) in the ranges 1 614—1 609 and 1 611—1 605 cm^{-1} for the rhenium and technetium complexes respectively, in agreement with the values found for the analogous complexes of L^2.[4] The values of ν(M=O) for these six-co-ordinate complexes are *ca.* 40 cm^{-1} lower than those for the five-co-ordinate starting complexes. The ^1H n.m.r. spectra for all the complexes (Table 4) are similar to those for the mixed complexes of the L^2 analogue with δ(C*H*=N) in the region 8.85—9.22. In particular these values are at higher fields than those of the five-co-ordinate starting compounds, which show δ(C*H*=N) 10.14 for $[TcOCl(L^1)]$ and 9.50 for $[ReOCl(L^1)]$. Mixed complexes containing the ligand L^4 show two single peaks at δ 4.10 and 4.12 and at 3.97 and 3.99 for the technetium and rhenium complexes respectively. The two peaks, attributed to the methyl protons, are due to the presence in solution of two isomers derived from the two possible positions of the tridentate ligand on the horizontal plane with respect to Tc=O, one rotated through 180° relative to the other. This situation has been confirmed in the solid by means of an *X*-ray analysis on $[TcO(L^2)(quin)]$.[4]

The rhenium mixed complexes containing L having an SN donor set are air-stable, orange-red powders with elemental analyses and mass spectral data in agreement with their formulations. Their i.r. spectra show ν(Re=O) at 938 and 954 cm^{-1}, and ν(C=N) at 1 606 cm^{-1} for the tquin and L^7 derivatives. The low value of the ν(Re=O) stretching vibration supports the location of the mercapto sulphur *trans* to the Re=O bond. All mixed complexes showed a configuration as described for the L^2 analogues.[4]

Acknowledgements

We thank Dr. P. Traldi for mass spectral measurements, Mr. F. De Zuane for magnetic susceptibility measurements, and Mrs. A. Moresco for technical assistance.

References

1 G. Bandoli, U. Mazzi, M. Nicolini, and F. Refosco, *J. Chem. Soc., Dalton Trans.*, 1984, 2505.
2 G. Bandoli, U. Mazzi, B. E. Wilcox, S. Jurisson, and E. Deutsch, *Inorg. Chim. Acta*, 1984, **95**, 217.
3 U. Mazzi, F. Refosco, G. Bandoli, and M. Nicolini, *Transition Met. Chem.*, 1985, **10**, 121.
4 U. Mazzi, F. Refoso, F. Tisato, G. Bandoli, and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1986, 1623.
5 F. A. Cotton, A. Davison, V. M. Day, L. G. Gage, and H. S. Trop, *Inorg. Chem.*, 1979, **18**, 3024.
6 T. Lis and B. Jezowska-Trzebiatowska, *Acta Crystallogr., Sect. B*, 1977, **33**, 1248.
7 G. M. Sheldrick, SHELX 76, Program for Structure Determination, University of Cambridge, 1976.
8 W. E. Hill, N. Atabay, C. A. McAuliffe, F. P. McCulloug, and S. M. Razzoki, *Inorg. Chim. Acta*, 1979, **35**, 35.
9 A. Duatti and B. E. Wilcox, personal communication.

Received 27th May 1986; *Paper* 6/1040