

Mixed Tri- and Bi-dentate Schiff-base Complexes of Technetium(v) and Rhenium(v). The Crystal Structure of *N*-(2-Oxidophenyl)salicylideneiminato-*NOO'*)oxo(8-quinolinolato-*NO*)technetium(v)†

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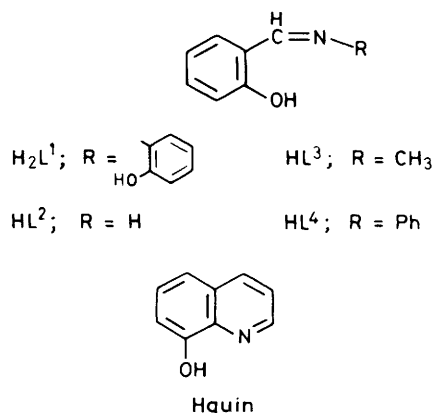
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Six-co-ordinate complexes of technetium(v) and rhenium(v) containing the MO^{3+} core with tri- and bi-dentate Schiff-base ligands were synthesized and characterized. The complexes with general formula $[\text{MO}(\text{L}^1)\text{L}]$ [$\text{M} = \text{Tc}$ or Re ; $\text{L}^1 = N$ -(2-oxidophenyl)salicylideneimine; $\text{L} = \text{salicylideneimine}$, *N*-methyl- and *N*-phenyl-salicylideneimine, or 8-quinolinolato (quin)] were characterized by elemental analysis, i.r., ^1H n.m.r., and mass spectroscopy. The structure of $[\text{TcO}(\text{L}^1)(\text{quin})]$ was also determined by *X*-ray analysis. The co-ordination around the metal is approximately octahedral. The phenolic oxygen of the quin ligand is *trans* to the $\text{Tc}=\text{O}$ group. The tridentate Schiff-base ligand lies on the equatorial plane with respect to $\text{Tc}=\text{O}$. The complex crystallizes in monoclinic space group $P2_1/n$ with $a = 15.496(8)$, $b = 10.355(4)$, $c = 12.122(5)$ Å, $\beta = 109.03(6)^\circ$, and $Z = 4$. The structure has been refined to $R = 0.054$ for 2 025 observed reflections.

In the production of new radiopharmaceuticals labelled with technetium-99m, one of the main problems is the stabilization of the technetium centre in a complex in which all the co-ordination sites are occupied by groups forming bonds thermodynamically and kinetically stable toward the substitution by substances which the complex meets when injected in the blood. The properties of such complexes can be changed by varying the lateral chains of the complex ligands.

One of the most common cores in technetium(v) complexes is TcO^{3+} . This central group dictates the chemical properties of the whole complex, its main characteristic being the weakening effect on the position *trans* to the 'yl' oxygen atom. For this reason many technetium(v) complexes show five-co-ordination in a square-pyramidal configuration.¹ Those with polydentate Schiff-base ligands show either five- or six-co-ordination. Bi-dentate ligands always result in six-co-ordination, e.g. with a phenolic oxygen *trans* to $\text{Tc}=\text{O}$,^{2,3} and when two different ligands are involved they do not lie in equivalent positions in the complex. On the contrary, tri- and quadri-dentate ligands, owing to their higher resonance effect and steric effects, co-ordinate around technetium on the plane perpendicular to $\text{Tc}=\text{O}$. Thus six-co-ordination is possible only when a compromise is reached between two properties of the group *trans* to $\text{Tc}=\text{O}$: the length of the bond to the metal and the nucleophilic character of the group. In fact the steric hindrance *trans* to $\text{Tc}=\text{O}$ is very high.^{4,5}

With the aim of finding other possible stable configurations around technetium(v) containing the TcO^{3+} core, complexes with mixed tri- and bi-dentate Schiff-base ligands were synthesized and characterized. In particular, the tridentate ligand derived from salicylaldehyde and *o*-aminophenol (H_2L^1) and the bidentate ligands salicylideneimine (HL^2), *N*-methylsalicylideneimine (HL^3), *N*-phenylsalicylideneimine (HL^4), and 8-quinolinol (Hquin) were used. For comparison, the rhenium analogues were also prepared and studied. The



complexes of the type $[\text{MO}(\text{L}^1)\text{L}]$ ($\text{M} = \text{Tc}$ or Re ; $\text{L} = \text{L}^2$, L^3 , L^4 , or quin) were isolated and characterized by means of elemental analysis, i.r., ^1H n.m.r., and mass spectroscopy. The structure of $[\text{TcO}(\text{L}^1)(\text{quin})]$ was also defined by *X*-ray analysis.

Experimental

Materials.—Ammonium pertechnetate, $[\text{NH}_4][\text{TcO}_4]$, was obtained from the Radiochemical Centre, Amersham; $[\text{NBu}_4][\text{TcOCl}_4]$ and $[\text{NBu}_4][\text{ReOCl}_4]$ were prepared by methods reported elsewhere.^{6,7} All the ligands were prepared by mixing salicylaldehyde and ammonia, methylamine, aniline, or *o*-aminophenol in ethanol following the procedure detailed for *N*-phenylsalicylideneimine (HL^4). To a stirred solution of salicylaldehyde (0.5 g, 4.2 mmol) in ethanol (20 cm³) was added a solution of aniline (0.4 g, 4.2 mmol) in ethanol (10 cm³); the solution became intensely yellow in a few minutes. After 2 h, bright yellow crystals were collected and washed with a small portion of ethanol and diethyl ether (yield 90%). When methylamine was used the product was a yellow oil. It was collected by evaporation of the reaction solvent. All the ligands were characterized by elemental analysis, i.r. and ^1H

† Supplementary data available (No. SUP 56534, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

n.m.r. spectra. 8-Quinolinol was commercially available. The starting complexes $[\text{TcO}(\text{Cl})\text{L}^1]$ and $[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$ were synthesized as previously reported.^{8,9} Other materials were reagent-grade chemicals.

Apparatus.—Infrared spectra were obtained from Nujol mulls between CsI pellets or KBr pellets and recorded on a Perkin-Elmer 580B spectrophotometer in the range 4000–200 cm^{-1} . Proton n.m.r. spectra were recorded on a Varian FT80 instrument using CD_2Cl_2 as solvent. Mass spectroscopic measurements were carried out on a WG ZAB2F instrument operating in electron-impact mode (70 eV, *ca.* 1.12×10^{-17} J; 200 A). Magnetic susceptibility measurements were performed in solution *via* the Evans n.m.r. method¹⁰ using a Varian FT80 spectrometer. Conductivity measurements were made in methanol or acetonitrile at 25 °C using a Metrohm Herison conductometer, model E518. Liquid chromatographic analyses were performed on a Hewlett-Packard high-performance liquid chromatograph, model 1090, with a u.v. detector using a C_{18} reversed-phase column.

Technetium-99 is a β -emitter (0.292 keV, half-life 2.12×10^5 years); therefore, all manipulations were carried out in protected areas using glove-boxes under a slight vacuum.

Synthesis of Complexes.—*Technetium and rhenium mixed-ligand complexes* $[\text{MO}(\text{L}^1)\text{L}]$. The same procedure was followed for all the complexes. The $[\text{TcO}(\text{Cl})\text{L}^1]$ or $[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$ starting compound (0.1 mmol) was dissolved in EtOH (30 cm^3). Twice the stoichiometric amount (0.2 mmol) of ligand (HL^2 , HL^3 , HL^4 , or Hquin) was added after 10 min with stirring at room temperature. The solution immediately became dark red and after a few minutes a solid appeared. One hour later the precipitate was filtered off and washed with EtOH and a small volume of Et_2O . No recrystallization was necessary to obtain a pure sample. The solid products are soluble in common organic solvents such as CH_2Cl_2 , Me_2CO , and C_6H_6 , slightly soluble in MeOH, EtOH, MeCN, and Et_2O , and insoluble in hydrocarbons.

A second method can be used to prepare rhenium mixed-ligand complexes with L^1 and $\text{L} = \text{L}^2$, L^3 , or L^4 . The preparation of $[\text{ReO}(\text{L}^1)\text{L}^4]$ reported here can be used also when $\text{L} = \text{L}^2$ or L^3 .

Synthesis of $[\text{ReO}(\text{L}^1)\text{L}^4]$. $[\text{NBu}_4][\text{ReOCl}_4]$ (0.094 g, 0.16 mmol) in methanol (15 cm^3) was added to a stirred solution of H_2L^1 (0.102 g, 0.48 mmol) and HL^4 (0.095 g, 0.48 mmol) in methanol (20 cm^3). The reaction solution turned immediately from green to deep red. After 2 h a red precipitate was collected by filtration and washed with a few drops of methanol and diethyl ether. The yield was 95%.

X-Ray Analysis.—Dark red crystals of $[\text{TcO}(\text{L}^1)(\text{quin})]$ were obtained by slow evaporation (2 d) of a solution in CH_2Cl_2 –MeCN. A transparent irregularly shaped crystal with dimensions *ca.* $0.12 \times 0.16 \times 0.08$ mm was mounted on a glass capillary and transferred to a Philips PW1100 computer-controlled diffractometer. Cell constants were based on a least-squares fit of 25 reflections with 2θ values ranging between 22 and 32° (graphite-monochromated Mo-K_α radiation, $\lambda = 0.7107$ Å).

Crystal data. $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}_4\text{Tc}$, $M = 470.3$, monoclinic, $a = 15.496(8)$, $b = 10.355(4)$, $c = 12.122(5)$ Å, $\beta = 109.03(6)^\circ$, $U = 1838.8(1.6)$ Å³, $Z = 4$, $D_c = 1.70$ g cm^{-3} , $F(000) = 944$, $\mu(\text{Mo-K}_\alpha) = 7.9$ cm^{-1} , space group $P2_1/n$ from systematic absences: $0k0 \neq 2n$, $h0l \neq l \neq 2n$.

A unique data set was collected at 20 °C by using a ω – 2θ scan mode for all reflections for which $3 < 2\theta < 52^\circ$, a scan range of 1.2° , a scan rate of $0.04^\circ \text{ s}^{-1}$, and a total background time of 16 s; no reflection was sufficiently strong to require the

insertion of an attenuator filter. Three standard reflections were measured every 2 h the intensities of which did not exhibit any systematic trend throughout the data collection. The intensities of 4101 independent reflections were measured, of which 2025 obeyed the condition $I > 3\sigma(I)$ and were used in subsequent calculations. The data were then corrected for Lorentz and polarization effects, but not for extinction or absorption.

Structure determination and refinement. A three-dimensional Patterson map revealed the position of the technetium atom and least-squares refinement based on Tc alone gave $R = 0.36$. A number of cycles of least-squares refinement, with anisotropic thermal parameters only for Tc, followed by difference syntheses, enabled location of all non-hydrogen atoms and led to convergence with $R = 0.074$, but the refinement yielded a model which was chemically unacceptable, showing a very short $\text{N}(2)$ – $\text{C}(16)$ double bond (1.02 Å) accompanied by a long $\text{C}(15)$ – $\text{N}(2)$ distance (1.60 Å). Moreover, the $\text{N}(2)$ and $\text{C}(16)$ atoms were affected by high thermal motion ($U = 0.10$ and 0.12 Å², respectively). However, at this stage, a Fourier difference map showed relevant electron-density peaks in the neighbourhood of the bridge (up to $1.7 \text{ e } \text{Å}^{-3}$), suggesting a positional disorder resembling that found in other similar compounds.¹¹ On splitting the N and C bridge atoms and also refining their occupancy factors, we were able to refine the model to $R = 0.054$ and the two orientations showed a population ratio of *ca.* 1.1. Thermal motions for these atoms were no greater than those observed in the core of the complex. The refined occupancy factors for $\text{N}(2)$, $\text{C}(16)$, $\text{N}(2')$, and $\text{C}(16')$ were 0.52(4), 0.49(4), 0.45(5), and 0.60(4), respectively. Finally, the Fourier difference map in the vicinity of the bridge showed no spurious peaks and the bridge, in the two orientations, exhibited acceptable geometry (Table 1), although the $\text{N}(2)$ – $\text{C}(17)$ and $\text{N}(2')$ – $\text{C}(15)$ distances appear to be too long (1.57 and 1.50 Å, respectively) and the bridge angles differ from the expected value of 120° . In conclusion, the tridentate ligand has two orientations about the $-\text{CH}=\text{N}-$ bridge (see Figure 2), without any preference for either of the two possibilities.

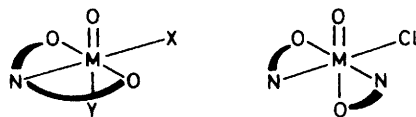
In the last refinement cycles (including alternate occupancy and thermal parameters for the disordered atoms) hydrogen atoms were placed at calculated positions and held invariant, with fixed isotropic thermal parameters ($U = 0.07$ Å²). Isotropic parameters were maintained for $\text{N}(2)$, $\text{C}(16)$, $\text{N}(2')$, $\text{C}(16')$, and also for $\text{C}(1)$ – $\text{C}(9)$ to assure a good 'observations/parameters' ratio (2025/215). The function $\sum w(F_o - F_c)^2$ was minimized, with unit weights. A weighting scheme based on counter statistics was unsuccessful, probably owing to systematic errors, and did not improve the model. The maximum shift in the last cycle was 0.04σ and a final difference synthesis showed two major maxima (1.4 and $0.8 \text{ e } \text{Å}^{-3}$) in the vicinity of the Tc atom. Final atomic positional parameters are listed in Table 1, bond lengths and angles in Table 2, and some other geometrical data in Table 3. The atom numbering scheme is shown in Figure 1.

The major calculations were made with the SHELX 76 program package.¹²

Results and Discussion

Reactions between TcOCl_4^- or ReOCl_4^- and individual tridentate^{8,9} or bidentate^{2,3} Schiff bases have already been studied. While only one tridentate ligand was found to co-ordinate around the metals, two bidentate ligands also can co-ordinate. The only differences between technetium and rhenium are the possibility with rhenium of co-ordination of a molecule of methanol or water when a tridentate ligand is used, and the

lower reaction rate to form $[\text{ReOCl}(\text{L})_2]$ starting from ReOCl_4^- compared with the technetium analogue. The resulting products have the following configurations.



M = Tc or Re

ON = L

ONO = L¹

X = Cl for M = Tc; Cl or MeOH for M = Re

Y = nothing for M = Tc; MeOH, Cl, or H₂O for M = Re

When the two types of Schiff base are used together in the above reactions, mixed complexes have been obtained. The possible reactions when MOCl_4^- (M = Tc or Re) is treated with H_2L^1 and HL are summarized in Scheme 1.

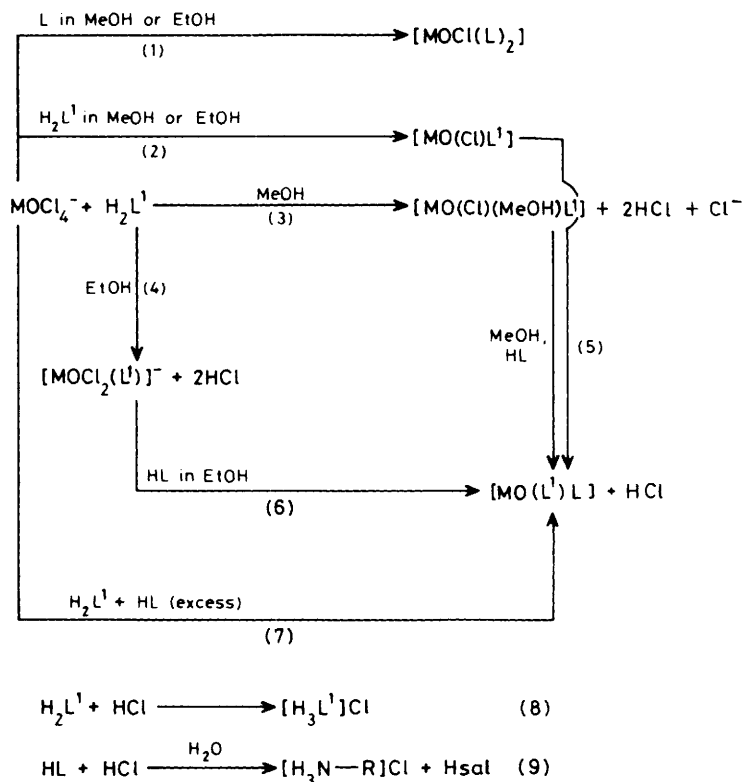
When TcOCl_4^- is mixed with both tridentate (H_2L^1) and bidentate (HL^2 , HL^3 , HL^4 , or Hquin) Schiff-base ligands, the reaction follows different pathways depending on the stoichiometric ratios and the conditions. By adding both the ligands in excess, the only products collected were $[\text{TcOCl}(\text{L})_2]$. By using the three starting products in the ratios 1:1:1 or 1:3:1, only not well defined compounds were collected. The mixed-ligand compound $[\text{TcO}(\text{L}^1)\text{L}]$ was obtained only when, after adding H_2L^1 to the TcOCl_4^- starting complex, the ligand HL was added at least 1 h later.

		Yield / %
$\text{ReOCl}_4^- + \text{H}_2\text{L}^1 + \text{HL}^4$	1:1:1	$[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$ 65
	1:1:3	$[\text{ReO}(\text{L}^1)\text{L}^4]$ 85
	1:2:1	$[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$ 80
	1:3:1	$[\text{ReO}(\text{L}^1)\text{L}^4]$ 80
	1:3:3	$[\text{ReO}(\text{L}^1)\text{L}^4]$ 95

Scheme 2. Products and yields for reaction (7) in methanol at various ratios of the reagents

Rhenium analogues follow the same behaviour only when HL = Hquin. The reactions involving ReOCl_4^- , H_2L^1 , HL^2 , HL^3 , and HL^4 follow a more specific pathway. The reaction with HL^4 was studied in detail. The investigated parameters were: stoichiometric ratio of reagents, reaction time, nature of reaction solvent, and nature of starting reagents. The reactions performed for long times in methanol gave the results in Scheme 2. The hydrochloric acid salt of H_2L^1 was always produced, but collected only when this ligand was used in excess. The hydrolysis products of HL^4 were identified by liquid chromatography.

The first assumption made about the behaviour of the ligands with respect to MOCl_4^- (M = Tc or Re) is that when M = Tc and HL = Hquin, reaction (1) is predominant, whereas when M = Re and the other HL ligands the first reaction is (3) or (4). Secondly, the formation of the HCl salt of H_2L^1 is thermodynamically and kinetically favoured [reaction (8)]: 1 mol of H_2L^1 produces 2 mol of HCl by co-ordination to the metal. In agreement with these assumptions, when the reagent ratio is 1:1:1 the only product is $[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$. In fact, the hydrochloric acid produced is sufficient to hydrolyse the



Scheme 1. General scheme for the reactions between MOCl_4^- and tri- and bi-dentate Schiff bases. Reaction (3) occurs only when M = Re. R = H, Me, or Ph; Hsal = salicylaldehyde

Table 1. Final fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations (e.s.d.s) in parentheses, for $[\text{TcO}(\text{L}^1)(\text{quin})]$

Atom	x	y	z	Atom	x	y	z
Tc	1 288(1)	5 150(1)	3 732(1)	C(9)	2 362(6)	6 684(8)	5 824(7)
O(1)	180(4)	5 314(7)	3 518(4)	C(10)	1 436(7)	2 426(8)	4 228(9)
O(2)	2 651(4)	5 331(6)	4 449(5)	C(11)	1 445(8)	1 305(11)	4 866(9)
O(3)	1 496(5)	3 561(6)	4 730(6)	C(12)	1 384(8)	116(11)	4 385(9)
O(4)	1 438(5)	6 608(7)	2 718(5)	C(13)	1 324(8)	-36(13)	3 241(11)
N(1)	1 466(5)	6 441(7)	5 221(5)	C(14)	1 294(8)	1 068(14)	2 572(9)
N(2)*	1 353(11)	4 272(16)	2 224(15)	C(15)	1 355(7)	2 269(12)	3 038(9)
N(2')*	1 347(10)	3 652(15)	2 667(13)	C(16)*	1 354(14)	3 104(20)	2 065(19)
C(1)	824(6)	6 981(9)	5 574(8)	C(16)*	1 273(14)	3 859(20)	1 555(19)
C(2)	1 032(7)	7 827(11)	6 526(9)	C(17)	1 263(6)	5 152(11)	1 133(8)
C(3)	1 926(7)	8 071(10)	7 155(9)	C(18)	1 128(8)	4 976(12)	-60(10)
C(4)	2 630(6)	7 503(8)	6 808(8)	C(19)	1 049(8)	6 000(14)	-750(9)
C(5)	3 582(7)	7 696(10)	7 383(9)	C(20)	1 118(7)	7 261(11)	-332(8)
C(6)	4 198(7)	7 069(10)	6 988(9)	C(21)	1 255(7)	7 431(9)	837(9)
C(7)	3 933(7)	6 241(10)	5 986(9)	C(22)	1 318(6)	6 386(10)	1 578(8)
C(8)	3 009(6)	6 051(8)	5 412(7)				

* Occupancy factor: 0.5.

imino group of HL^4 . The yield is similar to that of the reaction of ReOCl_4^- and H_2L^1 in 1:1 ratio.⁹ On increasing the amount of HL^4 the mixed-ligand compound was obtained: with a 1:1:3 ratio the yield was very high. On the other hand, on increasing the amount of tridentate ligand a ratio of 1:3:1 must be used to produce $[\text{ReO}(\text{L}^1)\text{L}^4]$.

These results demonstrate the higher rate of reaction of H_2L^1 and HCl with respect to the hydrolysis of HL^4 ; in fact, when sufficient H_2L^1 is present to react with all the HCl produced (1:3:1), the mixed-ligand compound is obtained in high yield. The highest yield of mixed-ligand compound was obtained when both the ligands were added in excess or when HL^4 was added in excess to the isolated intermediate $[\text{ReO}(\text{Cl})(\text{MeOH})\text{L}^1]$. Similar behaviour was observed when HL^2 or HL^3 was used.

The same reactions in ethanol show some differences depending on the different intermediate compounds produced. As reported elsewhere,⁹ in ethanol the tridentate ligand yields $[\text{ReOCl}_2(\text{L}^1)]^-$ [reaction (4)]. In Scheme 3 the yields of the products are reported under different reaction conditions.

		Yield / %
$\text{ReOCl}_4^- + \text{H}_2\text{L}^1 + \text{HL}^4$	1:1:1 $\rightarrow [\text{ReOCl}_2(\text{L}^1)]^-$	60
	1:1:1 $\rightarrow [\text{ReOCl}_2(\text{L}^1)]^-$	45
	long time $\rightarrow [\text{ReO}(\text{L}^1)\text{L}^4]$	10
	1:1:2 $\rightarrow [\text{ReO}(\text{L}^1)\text{L}^4]$	54
	1:1:3 $\rightarrow [\text{ReO}(\text{L}^1)\text{L}^4]$	80

Scheme 3. Products and yields for reaction (7) in ethanol at various ratios of the reagents

The formation of the mixed-ligand compound starting from $[\text{ReOCl}_2(\text{L}^1)]^-$ is kinetically favoured with respect to reaction (3); in fact, $[\text{ReO}(\text{L}^1)\text{L}^4]$ is formed even when the reagent ratio is 1:1:1 and the reaction time is long. This difference can be attributed to the chlorine atom which behaves as a better leaving group than MeOH . The latter is also forced to bond to a rhenium centre, being present as solvent. Owing to the higher rate of co-ordination of ligand HL^4 , it seems that this reaction competes with the hydrolysis reaction and produces, though in low yield, the mixed-ligand compound. In conclusion, from the above results it is possible by identifying the products and determining their yield to indicate qualitatively

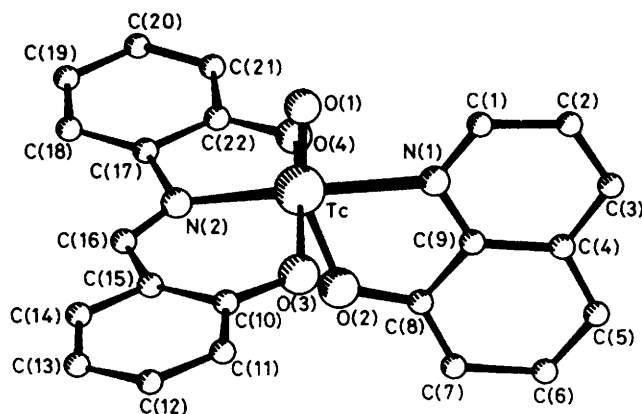
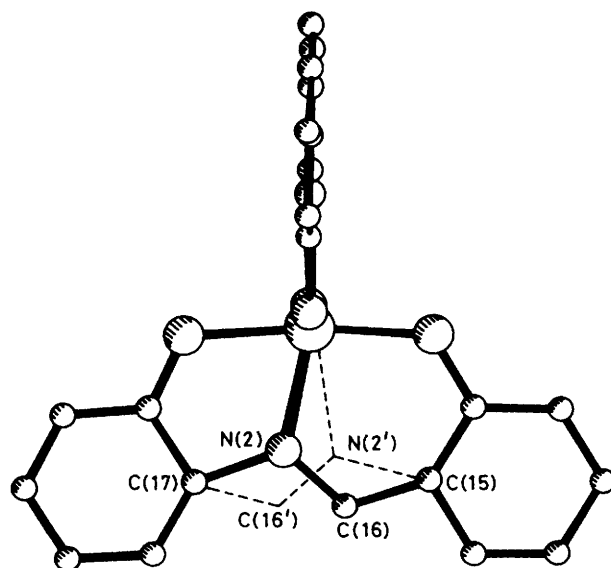
**Figure 1.** Perspective view of $[\text{TcO}(\text{L}^1)(\text{quin})]$ showing the atom numbering**Figure 2.** The complex viewed perpendicular to the $\text{O}(3)\text{N}(1)\text{O}(4)$ plane. Dashed lines indicate the second, equipopulated orientation

Table 2. Elemental analysis and mass spectral data for technetium and rhenium mixed-ligand compounds with calculated values in parentheses

Compound	Analysis (%)				<i>m/e</i>
	C	H	N	Tc	
[TcO(L ¹)L ²]	54.2 (53.8)	3.3 (3.4)	6.0 (6.3)	22.1 (22.2)	446 (446.34)
[TcO(L ¹)L ³]	54.8 (54.8)	3.5 (3.7)	5.9 (6.1)	21.7 (21.5)	461 (460.37)
[TcO(L ¹)L ⁴]	60.1 (59.7)	3.7 (3.6)	5.5 (5.4)	19.1 (18.9)	522 (522.43)
[TcO(L ¹)(quin)]	56.0 (56.2)	3.0 (3.2)	5.7 (5.9)	20.7 (21.0)	470 (470.36)
[ReO(L ¹)L ²]	45.6 (45.0)	2.7 (2.8)	5.2 (5.1)		533 (533.54)
[ReO(L ¹)L ³]	45.8 (46.0)	3.2 (3.1)	5.0 (5.1)		547 (547.57)
[ReO(L ¹)L ⁴]	50.5 (51.1)	3.4 (3.3)	4.4 (4.5)		610 (610.63)
[ReO(L ¹)(quin)]	47.4 (47.4)	2.8 (2.7)	5.1 (5.0)		557 (557.56)

Table 3. Principal i.r. bands (cm⁻¹) and ¹H n.m.r. signals (δ with respect to SiMe₄) of technetium and rhenium mixed-ligand compounds

Compound	I.r.		N.m.r.	
	ν(M=O)	ν(C=N)	imine	methyl
[TcO(L ¹)L ²]	940	1 603, 1 586	8.83	
[TcO(L ¹)L ³]	935	1 620	8.80, 8.52	4.03, 4.04
[TcO(L ¹)L ⁴]	931	1 610, 1 593	8.77, 8.64	
[TcO(L ¹)(quin)]	948	1 607, 1 584	8.92	
[ReO(L ¹)L ²]	953	1 610, 1 598	8.86	
[ReO(L ¹)L ³]	955	1 600	8.88	3.84, 3.85
[ReO(L ¹)L ⁴]	964	1 608	8.82	
[ReO(L ¹)(quin)]	971	1 608, 1 592	8.93	

[ReOCl(L)₂] needs high temperatures and long reaction times. The mixed-ligand complex is produced when reactions (2), (3), or (4) are allowed to occur before adding ligands HL.

Using ReOCl₄⁻, with H₂L¹ and HL² or HL³ or HL⁴, reaction (3) or (4) predominates over the others. In methanol, reaction (3) is followed by (8), then (9) and (5) can occur only if the ligand is in sufficient amount. In ethanol, reaction (4) is favoured over (8), thus (6) and (9) are competitive.

While high yields of technetium mixed-ligand complexes can be prepared only by starting from [TcO(Cl)L¹], the rhenium analogue can also be prepared directly from ReOCl₄⁻ and the two ligands in excess, with the exception of Hquin.

Table 4. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Tc-O(1)	1.659(7)	N(1)-C(1)	1.33(1)	C(4)-C(9)	1.41(1)	C(14)-C(15)	1.36(2)
Tc-O(2)	2.014(6)	N(1)-C(9)	1.36(1)	C(5)-C(6)	1.36(2)	C(15)-C(16)	1.46(3)
Tc-O(3)	2.005(6)	N(2)-C(16)	1.22(3)	C(6)-C(7)	1.43(1)	C(16)-C(17)	1.43(2)
Tc-O(4)	2.008(7)	N(2)-C(17)	1.57(2)	C(7)-C(8)	1.39(1)	C(17)-C(18)	1.40(2)
Tc-N(1)	2.190(7)	N(2)-C(15)	1.50(2)	C(8)-C(9)	1.42(1)	C(17)-C(22)	1.38(2)
Tc-N(2)	2.07(2)	N(2)-C(16')	1.33(2)	C(10)-C(11)	1.39(1)	C(18)-C(19)	1.33(2)
Tc-N(2')	2.04(2)	C(1)-C(2)	1.40(1)	C(10)-C(15)	1.42(2)	C(19)-C(20)	1.39(2)
O(2)-C(8)	1.34(1)	C(2)-C(3)	1.37(1)	C(11)-C(12)	1.35(2)	C(20)-C(21)	1.37(1)
O(3)-C(10)	1.31(1)	C(3)-C(4)	1.42(2)	C(12)-C(13)	1.37(2)	C(21)-C(22)	1.39(1)
O(4)-C(22)	1.35(1)	C(4)-C(5)	1.42(1)	C(13)-C(14)	1.39(2)		
O(1)-Tc-O(2)	160.8(3)	O(4)-Tc-N(2)	75.0(5)	N(1)-C(1)-C(2)	122.3(9)	O(3)-C(10)-C(15)	123.0(8)
O(1)-Tc-O(3)	97.6(3)	O(4)-Tc-N(2')	98.4(5)	C(1)-C(2)-C(3)	119.6(1.0)	O(3)-C(10)-C(11)	120.2(9)
O(1)-Tc-O(4)	98.5(3)	N(1)-Tc-N(2)	164.8(5)	C(2)-C(3)-C(4)	119.6(1.0)	N(2)-C(15)-C(14)	139.3(1.1)
O(1)-Tc-N(1)	85.0(3)	N(1)-Tc-N(2')	165.1(5)	C(3)-C(4)-C(9)	117.2(9)	N(2)-C(15)-C(10)	100.7(1.2)
O(1)-Tc-N(2)	104.6(5)	Tc-O(2)-C(8)	120.3(6)	C(3)-C(4)-C(5)	124.8(9)	C(14)-C(15)-C(16)	103.0(1.2)
O(1)-Tc-N(2')	103.7(5)	Tc-O(3)-C(10)	118.8(6)	C(5)-C(4)-C(9)	118.0(9)	C(10)-C(15)-C(16)	103.0(1.2)
O(2)-Tc-O(3)	82.9(3)	Tc-O(4)-C(22)	119.5(6)	C(4)-C(5)-C(6)	119.5(1.0)	N(2)-C(16)-C(15)	117.2(1.8)
O(2)-Tc-O(4)	83.1(3)	Tc-N(1)-C(9)	112.7(6)	C(5)-C(6)-C(7)	122.8(1.1)	N(2)-C(16)-C(17)	120.0(1.8)
O(2)-Tc-N(1)	75.8(3)	Tc-N(1)-C(1)	128.0(6)	C(6)-C(7)-C(8)	118.3(1.0)	C(16)-C(17)-C(22)	137.3(1.2)
O(2)-Tc-N(2)	94.3(5)	Tc-N(2)-C(17)	118.1(1.0)	O(2)-C(7)-C(8)	125.5(8)	C(10)-C(15)-C(16)	103.1(1.2)
O(2)-Tc-N(2')	95.0(5)	Tc-N(2)-C(16)	125.1(1.5)	C(7)-C(8)-C(9)	119.4(8)	N(2)-C(17)-C(22)	103.3(9)
O(3)-Tc-O(4)	163.5(4)	C(16)-N(2)-C(17)	116.3(1.6)	O(2)-C(8)-C(9)	115.1(8)	N(2)-C(17)-C(18)	137.1(1.1)
O(3)-Tc-N(1)	92.9(3)	Tc-N(2)-C(16')	120.8(1.3)	C(4)-C(9)-C(8)	121.9(8)	O(4)-C(22)-C(21)	119.0(9)
O(3)-Tc-N(2)	97.3(5)	Tc-N(2)-C(15)	122.3(1.0)	N(1)-C(9)-C(8)	116.0(7)	O(4)-C(22)-C(17)	121.8(9)
O(3)-Tc-N(2')	74.1(5)	C(15)-N(2)-C(16')	116.5(1.5)	N(1)-C(9)-C(4)	122.1(9)	C _{Ph} -C _{Ph} -C _{Ph}	120.0(8) (mean)
O(4)-Tc-N(1)	92.1(3)	C(1)-N(1)-C(9)	119.2(7)				

the mechanism of the complete reaction as a succession of steps involving different competitive reactions.

The reactivity of bidentate Schiff-base ligands with respect to TcOCl₄⁻ and Hquin with respect to ReOCl₄⁻ is considered to be higher than that of tridentate ones. Probably the third chelating group is not bound when another bidentate ligand reacts to produce a bis complex. This assumption is supported by the fact that both [TcOCl(L)₂] and [ReOCl(quin)₂] are immediately produced from MOCl₄⁻ (M = Tc or Re), whereas

The complexes are all air stable and their formulation is supported by elemental analysis and mass spectra (Table 2). The observed diamagnetic character is in accordance with the behaviour of all oxo complexes of Tc^V and Re^V in a distorted octahedral environment. The complexes are non-conducting in both methanol and acetonitrile. Infrared spectra (Table 3) of the rhenium complexes show ν(Re=O) stretching vibrations in the range 953–971 cm⁻¹, in agreement with the values found for six-co-ordinate complexes with a phenolic oxygen *trans* to

Table 5. Other geometrical details

(a) Some torsion angles (°)

Tc—O(2)—C(8)—C(9)	−2.4	C(15)—C(16)—N(2)—C(17)	−174.7
Tc—O(3)—C(10)—C(15)	8.9	C(15)—N(2′)—C(16′)—C(17)	−179.8
Tc—O(4)—C(22)—C(17)	−12.3	C(10)—C(15)—C(16)—N(2)	−7.0
Tc—N(1)—C(9)—C(8)	−1.4	C(10)—C(15)—N(2′)—C(16′)	−179.8
Tc—N(2)—C(16)—C(15)	−3.2	C(22)—C(17)—N(2)—C(16)	−177.7
Tc—N(2′)—C(16′)—C(17)	7.6	C(22)—C(17)—C(16′)—N(2′)	0.5

(b) Least-squares planes with deviations (Å) of relevant atoms in square brackets

Plane

(1) N(1), C(1)—C(9)

[N(1) 0.0, C(1) −0.02, C(2) 0.01, C(3) −0.01, C(4) 0.01, C(5) 0.01, C(6) −0.02, C(7) −0.01, C(8) 0.0, C(9) 0.01, O(2) 0.04, Tc 0.03]

(2) C(10)—C(15)

[C(10) −0.01, C(11) 0.0, C(12) 0.01, C(13) −0.01, C(14) 0.01, C(15) 0.0, O(3) −0.01, N(2) 0.0, N(2′) −0.03, C(16) −0.06, C(16′) 0.04, Tc 0.26]

(3) C(17)—C(22)

[C(17) 0.0, C(18) −0.01, C(19) 0.01, C(20) 0.0, C(21) −0.01, C(22) 0.01, O(4) 0.02, N(2) 0.03, N(2′) 0.11, C(16) −0.01, C(16′) 0.03, Tc 0.40]

(4) Tc, O(3), O(4), N(1), N(2)

[Tc 0.06, O(3) −0.22, O(4) −0.20, N(1) −0.05, N(2) −0.18, O(1) 1.70, O(2) −1.92, C(16′) −0.23, C(16′) −0.12, N(2′) −0.15]

(5) Tc, O(3), O(4), N(1), N(2′)

[Tc 0.06, O(3) −0.21, O(4) −0.21, N(1) −0.05, N(2′) −0.15, O(1) 1.70, O(2) −1.92, C(16) −0.23, C(16′) −0.13, N(2) −0.18]

(c) Dihedral angles (°)

(1)–(2)	90.5	(2)–(4)	0.7
(1)–(3)	93.7	(2)–(5)	0.7
(1)–(4)	90.3	(3)–(4)	4.5
(1)–(5)	90.6	(3)–(5)	4.4
(2)–(3)	3.9	(4)–(5)	0.2

Re=O. The $\nu(\text{C}=\text{N})$ vibrations of the imino groups are in the range 931–948 cm^{-1} , the highest value being shown by the the imino-nitrogen atoms. The stretching vibrations of each ligand are not distinguishable. Infrared spectra of the technetium complexes confirm the position of $\text{Tc}=\text{O}$ *trans* to the phenolic oxygen of a bidentate ligand, showing $\nu(\text{Tc}=\text{O})$ in the range 931–948 cm^{-1} , the highest value being shown by the Hquin derivative, as for the rhenium analogue. The $\nu(\text{C}=\text{N})$ vibrations are not influenced by changes in the central metal, being in the range 1584–1620 cm^{-1} .

The proton n.m.r. spectra show two signals assigned to the $-\text{CH}=\text{N}-$ imino-group protons. However, this assignment could be made only when the signals were in a region far from that of the phenyl protons. The $-\text{CH}=\text{N}-$ imino-group protons of the tridentate ligand were always assigned to the signals in the range $\delta = 8.93\text{--}8.80$ p.p.m., where the signal of the imino-group proton of $[\text{ReO}(\text{Cl})\text{MeOH}]\text{L}^1$ falls.⁸ The imino-group proton of the bidentate ligand could be assigned only for the technetium complexes. The methyl-proton signals of the ligand HL^3 appear as doublets at $\delta = 4.03$ and 3.84 p.p.m. for the technetium and rhenium complexes, respectively. The reason for a doublet can be found in the two different magnetic environments of the methyl group, owing to the two positions assumed by the tridentate ligand, as found in the X-ray structure of $[\text{TcO}(\text{L}^1)(\text{quin})]$ (see below).

The structure of $[\text{TcO}(\text{L}^1)(\text{quin})]$ (Figure 1, Table 4) contains discrete molecules without significant intermolecular interactions, the shortest contact distance being $\text{C}(1) \cdots \text{O}(1)$ (at $-x, 1-y, 1-z$) (3.22 Å). It is emphasized that, because of the lack of an absorption correction to the intensity data, the bond lengths and angles are not sufficiently precise to support arguments based on minor fluctuations in distances or angles and hence only gross structural features will be presented.

The complex consists of the tridentate deprotonated Schiff base and the bidentate deprotonated 8-quinolinolate (quin) and can be regarded as the first technetium(v) complex containing both tri- and bi-dentate Schiff-base ligands. The coordination around technetium is approximately octahedral; the tridentate ligand occupies three equatorial sites and the bidentate ligand bridges the remaining equatorial and one apical site, with the oxygen occupying the sixth position *trans* to TcO^{3+} . The tridentate ligand, as a whole, is roughly planar; it is nearly normal to the quin mean plane (Table 5, Figure 2) and has two orientations about the $-\text{CH}=\text{N}-$ bridge (see Experimental section). As expected,^{1–5} the technetium atom is displaced (by 0.08 Å) from the mean plane of the equatorial ONO N-donor atom set, towards the 'yl' oxygen, and the $\text{O}(1)-\text{Tc}-\text{O}(2)$ angle is significantly non-linear [$160.8(3)^\circ$]. In the distorted octahedron all equatorial bonds are directed away from the $\text{Tc}=\text{O}$ linkage. The bond lengths and angles in the 'inner core' (Table 4) fall within the range reported for other TcO^{3+} complexes,^{1–5} and they do not merit any comment; moreover, the $\text{Tc}-\text{O}(2)$ bond length [2.014(6) Å] seems to exclude considerable *trans* weakening, due to the strong π bonding of the oxo-group, although a structural *trans* effect is present in $[\text{TcO}(\text{mquin})_2\text{Cl}]$ (mquin = 2-methyl-8-quinolinolate).³

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