

Synthesis, Characterization and Electrochemical Studies on Technetium(V) and Rhenium(V) Oxo-complexes with *N,N'*-2-Hydroxypropane-1,3-bis(salicylideneimine)

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Abstract

Ligand-exchange reactions of potential quinque-dentate Schiff base ligands derived from salicylaldehyde and 1,3-diamino-2-hydroxypropane (H_3L) with $[MOCl_4]^-$ ($M = Tc$ and Re) have been investigated. The complexes $[MOCl_2(R-OH)(H_2L \cdot HCl)]$ (I) ($R = Me, Et$), $[ReOCl(HL)]$ (II) and $\mu-O[MO(HL)]_2$ (III) were synthesized and characterized by the usual physicochemical measurements. Cyclic voltammeteries for both III complexes reveal two separate and single-electron redox processes. The crystal structure of $\mu-O[TcO(HL)]_2$ was determined by single-crystal X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/c$, with $a = 9.423(6)$, $b = 19.666(9)$, $c = 22.785(11)$ Å, $\beta = 99.41(4)^\circ$ and $Z = 4$. X-ray diffraction provides 2842 observed reflections (up to $\theta = 40^\circ$) and the structure has been refined by full-matrix least-squares methods to $R = 0.10$. The 'dimeric' structure of $\mu-O[TcO(HL)]_2$ consists of two distorted octahedral $TcO(HL)$ moieties bridged by an oxygen atom which occupies the sixth coordination site of each moiety with the $Tc-O-Tc$ angle nearly linear (173°).

Introduction

The development of the knowledge on the coordination chemistry of the fifth oxidation state of technetium (the first relatively stable oxidation state reducing pertechnetate(VII)) is one of the bases for the synthesis of new radiopharmaceuticals. One example is the production of the stable, neutral and lipophilic complex $[Tc(V)OPn(AO)_2]$ ($Pn(AO)_2 = 3,3,9,9$ -tetramethyl-4,8-diazaundecane-2,10-dione di-oxime) [1] showing a promising brain uptake for SPECT studies [2–4]. To date the chemistry of technetium(V) is chiefly the chemistry of tech-

netium oxo-complexes. There are only a few compounds, such as TcF_5 , $K[TcF_5]$ and $[Tc(diars)_2Cl_4]^+$, which do not present any oxo group bonded to the metal. Technetium(V) oxo-complexes are clearly categorized on the basis of their oxo-technetium cores: TcO^{3+} , *trans*- TcO^{2+} and $Tc_2O_3^{4+}$ [5].

Polydentate Schiff base ligands appear to be suitable systems to surround and stabilize the above mentioned technetium(V) cores. At present, several X-ray structure determinations of technetium complexes with Schiff base ligands are reported, mainly containing the TcO^{3+} core. The geometry of these complexes depends on the nature of the ligand (number and type of coordinating atoms, chain-length between the coordinating groups, etc.). For example, $[TcOCl(OPhsal)]$ ($OPhsal = N$ -(2-oxido-phenyl)salicylideneimine) [6] and $[TcOCl(SPhsal)]$ ($SPhsal = N$ -(2-sulphidophenyl)salicylideneimine) [7] are five-coordinate complexes containing the TcO^{3+} core in a square-pyramidal configuration, while $[TcO(OPhsal)(8\text{-quinolinate})]$ [8] and $[TcOCl(Phsal)_2]$ ($Phsal =$ phenylsalicylideneimine) [9] are six-coordinate compounds containing the TcO^{3+} core in a distorted octahedral environment and $\mu-O[TcO(sal_2pn)]_2$ ($sal_2pn = N,N'$ -propane-1,3-bis(salicylideneimine) [10] is a six-coordinate complex containing the $Tc_2O_3^{4+}$ core with a quasi-linear bridge $O=Tc-O-Tc=O$. There are no structural examples of complexes containing the *trans*- TcO_2^+ core and Schiff base ligands. This is reasonable, because the TcO^{3+} core is present in complexes containing π -donor ligands (as Schiff base ligands) in the equatorial plane, while the *trans*- TcO_2^+ moiety is shown with π -acceptor ligands or with ligands that do not form π -bonds [5, 11–13]. In this paper we report on the reactions of $[MOCl_4]^-$ ($M = Tc$ and Re) with the Schiff base ligand derived from condensation between salicylaldehyde and 1,3-diamino-2-hydroxypropane. A single X-ray structure determination of the $\mu-O[TcO(HL)]_2$ complex has established

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the presence of a μ -oxo bridge between the two technetium centres.

Experimental

Materials

Technetium as $[\text{NH}_4][\text{TcO}_4]$ in 0.1 mol dm^{-3} ammonia solution was purchased from the Radiochemical Centre, Amersham, U.K. The $[\text{NBu}_4][\text{TcOCl}_4]$ and $[\text{NBu}_4][\text{ReOCl}_4]$ compounds were prepared by the methods reported in the literature [14, 15]. Other materials were reagent grade chemicals.

Apparatus

Elemental analyses were performed on a Carlo Erba elemental analyzer model 1106. Technetium quantitative determinations were carried out on a Rackbeta II instrument, model 1215, using Insta-gel: a ready-for-use xylene-based liquid scintillation cocktail (Packard Instrument Int., Zurich). Infrared spectra were recorded in the range $4000\text{--}250 \text{ cm}^{-1}$ on a Perkin-Elmer PE580B spectrophotometer, using KBr pellets or nujol mulls between CsI pellets. ^1H NMR spectra were obtained on a Varian FT80 instrument using different solvents and SiMe_4 as internal reference. Mass spectroscopy measurements were carried out on a WG ZABZF instrument operating in the electron impact mode (70 eV c. $1.12 \times 10^{-17} \text{ J}$; 200 A). Magnetic susceptibility measurements were performed in the solid state with the Faraday method for rhenium compounds. Conductivity measurements were collected in acetonitrile at 25°C using a Metrohm Herison conductometer, model E518. UV-Vis spectra were recorded in dichloromethane using a Cary 17D spectrophotometer. Thermogravimetric measurements were performed in air using a Netzsch STA-429 thermoanalytical instrument (N_2 flux rate $250 \text{ cm}^3 \text{ min}^{-1}$, heating rate 5°C min^{-1} , reference material Al_2O_3). Cyclic voltammetry 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 three electrodes: platinum spiral wire working electrode (area about 3.3 cm^2), a platinum auxiliary foil electrode which was isolated inside a salt bridge by a medium glass frit, and a saturated calomel reference electrode. All measurements were done in dry and degassed DMF (Aldrich gold label solvent) with tetraethylammonium perchlorate (TEAP, 0.10 M) as supporting electrolyte. Potentials were recorded versus the saturated calomel electrode (SCE). Couples potentials were calculated at the mid point between the anodic and cathodic

peaks of the cyclic voltammetric waveform scanned at 0.2 V s^{-1} . Low temperature measurements were made in liquid nitrogen/ethanol slurries.

^{99}Tc is a weak β -emitter ($E_{\beta_{\text{max}}} = 292 \text{ KeV}$ with $t_{1/2} = 2.12 \times 10^5 \text{ y}$) All manipulations of this material were carried out in laboratories approved for low level radioactivity using glove-boxes under slight vacuum for the synthesis and recovery operations.

Synthesis

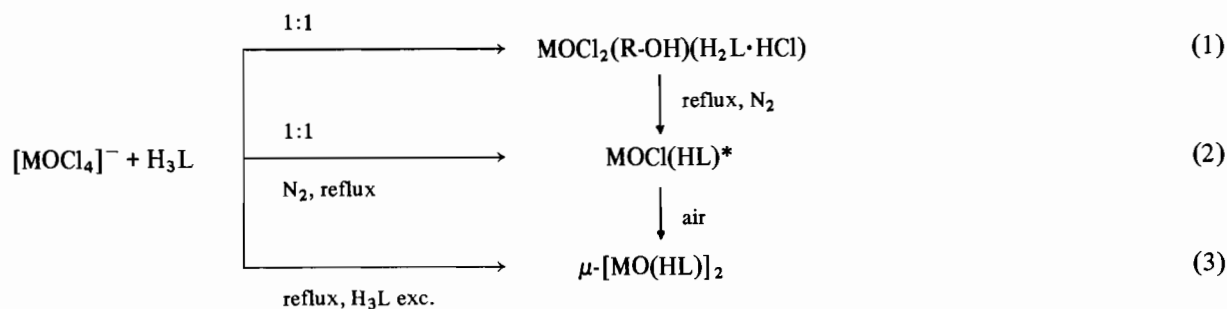
Synthesis of the ligand

N,N' -2-Hydroxypropane-1,3-bis(salicylideneimine) (H_3L) was prepared by mixing in ethanol (20 ml) salicylaldehyde (1 g; 8.02 mmol) and 1,3-diamino-2-hydroxypropane (361 mg, 4.01 mmol). The solution became immediately bright yellow and after 10 min a spongy yellow precipitate appeared. It was collected by filtration and washed with a few drops of EtOH and then with Et_2O . The same product was obtained using the reagents in stoichiometric ratio and by adding water to the ethanolic solution until the yellow solid appeared. No recrystallization was necessary to obtain a pure sample. The spongy yellow solid is soluble in MeOH, DMF, Me_2CO , MeCN and CH_2Cl_2 , slightly soluble in EtOH, insoluble in Et_2O and H_2O . Elemental analysis is in agreement with the formula $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3$ (Found: C, 68.38; H, 6.11; N, 9.34. Calc. C, 68.44; H, 6.08; N, 9.39%). The UV-Vis spectrum in dichloromethane shows absorption at 218, 258, 318 and 400 nm while mass spectrum presents the peak parent ion at 298 m/z . (IR and ^1H NMR data are given in Table 3).

Synthesis of complexes

$[\text{TcOCl}_2(\text{MeOH})(\text{H}_2\text{L}\cdot\text{HCl})]$ (I). To a stirred solution of 150 mg (0.3 mmol) of $[\text{NBu}_4][\text{TcOCl}_4]$ in 20 ml of MeOH, a solution of 89.5 mg (0.3 mmol) of H_3L in 10 ml of MeOH, was added at room temperature. The reaction solution turned immediately from the light green colour of $[\text{TcOCl}_4]^-$ to an intense carrot-red colour and instantly a precipitate appeared. After 15 min the powder was filtered off, washed with a small portion of MeOH and Et_2O . The carrot coloured powder is soluble in DMF, DMSO, slightly soluble in MeCN, MeOH and EtOH, insoluble in Me_2CO and CH_2Cl_2 .

$[\mu\text{-O}\{\text{TcO}(\text{HL})\}_2]$ (III). 173 mg of $[\text{NBu}_4][\text{TcOCl}_4]$ (0.34 mmol) was treated with an excess of H_3L (413 mg; 1.38 mmol) in 30 ml of MeOH and refluxed. The initial carrot coloured precipitate disappeared and after 2 h a deep red crystalline solid was present. It was filtered off and washed with a small amount of MeOH. Red-brown crystals were obtained by slow evaporation of the CHCl_3



Scheme 1. Scheme for reactions between MOC1_4^- and H_3L ligand (R = Me, Et; *technetium derivative was not recovered).

solution. The crystalline product is soluble in DMF, DMSO, CH_2Cl_2 and CHCl_3 , slightly soluble in MeCN, insoluble in hydrocarbons.

Rhenium analogue complexes were prepared following the same procedure detailed above for the technetium ones, but $[\text{ReOCl}_2(\text{EtOH})(\text{H}_2\text{L}\cdot\text{HCl})]$ was prepared using ethanol as reaction solvent.

[ReOCl(HL)] (II). 95 mg (0.16 mmol) of $[\text{NBu}_4]\text{-}[\text{ReOCl}_4]$ solubilized in dry MeOH (15 ml) were treated under nitrogen atmosphere with a solution of 49 mg (0.16 mmol) of H_3L in dry MeOH (10 ml). The pale-green solid immediately produced, as in reaction (1) (Scheme 1), was then refluxed. The initial precipitate disappeared and after 3 h a new green solid was present. It was hot filtered off, washed with dry MeOH and Et_2O . The bright-green crystalline product is soluble in DMF and DMSO, slightly soluble in MeOH, EtOH and MeCN, insoluble in Me_2CO and CH_2Cl_2 . By standing the reaction mixture for some days in air, further deep-green crystalline product was yielded and identified as the rhenium complex of type III.

Crystallographic Data

Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a CHCl_3 solution of $\mu\text{-O}[\text{TcO}(\text{HL})]_2$ at room temperature.

Crystal data

$[\{\text{TcO}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3)\}_2\text{O}]\cdot\text{CHCl}_3$, $M = 957.8$, monoclinic, $a = 9.423(6)$, $b = 19.666(9)$, $c = 22.785(11)$ Å, $\beta = 99.41(4)^\circ$, $U = 4165.5$ Å³; $F(000) = 1920$, $Z = 4$, $D_c = 1.526$ g cm⁻³; space group $P2_1/c$, $\mu(\text{Mo K}\alpha) = 8.9$ cm⁻¹.

Intensity data were recorded on a fully automatic Philips PW 1100 diffractometer, Mo K α radiation. The crystal was cut from a long red needle and, along the needle direction (c) the crystal was 0.5 mm in length. A total of 6820 different reflections in one quadrant was measured within the limit $\theta \leq 40^\circ$. Of these, only 2842 (42%) unique reflections were considered observed [$I > 3\sigma(I)$] and

were used for the structure analysis. The integrated intensities were corrected for Lorentz and polarization effects and for absorption, using an empirical method based on ψ -scans of three reflections near $\chi = 90^\circ$.

Structure determination and refinement

The structure was solved by standard heavy-atom methods. The positions of the two Tc atoms were derived from a three-dimensional Patterson map, and subsequent difference-Fourier syntheses revealed the positions of all 49 non-hydrogen atoms of the complex. A CHCl_3 solvent molecule was then located close to the special position (1,0,0), precluding the possibility of one solvent molecule per complex since this would place two centrosymmetrically related CHCl_3 molecules at an unrealistic short distance from each other. The solvent atoms were accordingly each given an occupancy factor of 0.5 with the solvent molecule being assumed disordered between its two centrosymmetrically related positions. The relative peak heights of these atoms in the electron-density maps also suggested a high degree of disorder. Some peaks of comparable height were observed also in another region of the electron-density maps and these were ascribed to another CHCl_3 molecule with 'tentative' occupancy factor of 0.5. The paucity of diffraction data (mainly the small amount of high-angle data), the high thermal motion also in the 'inner core' of the complex, the high disorder of the solvent molecule and a somewhat deterioration of the crystal during data collection, as pointed out by the intensities of the three standard reflections monitored every two hours, did not allow an accurate structure determination of the complex; however, the stereochemistry at the technetium atoms was unambiguously determined. Full-matrix least-squares refinement, minimizing the function $\sum w(\Delta F)^2$ ($w = 1$), and with anisotropic temperature factors only for the atoms in the 'inner core' of the complex, converged with a reliability index R of 0.10. Some relevant bond distances and angles are reported in Table 1. See also 'Supplementary Material'. Structure determina-

TABLE 1. Some relevant bond distances (Å) (e.s.d. 0.02 Å) and angles (°) (e.s.d. 1°)

Tc—O	1.92	Tc'—O	1.90
Tc—O1	1.73	Tc'—O1'	1.69
Tc—O2	1.98	Tc'—O2'	1.99
Tc—O3	2.00	Tc'—O3'	2.02
Tc—N1	2.11	Tc'—N1'	2.11
Tc—N2	2.11	Tc'—N2'	2.08
O1—Tc—O	167	O1'—Tc'—O	171
N1—Tc—N2	94	N1'—Tc'—N2'	95
O2—Tc—O3	81	O2'—Tc'—O3'	84
O1—Tc—O2	99	O1'—Tc'—O2'	95
O1—Tc—N1	88	O1'—Tc'—N1'	92
O1—Tc—N2	89	O1'—Tc'—N2'	90
Tc—O—Tc'	173		

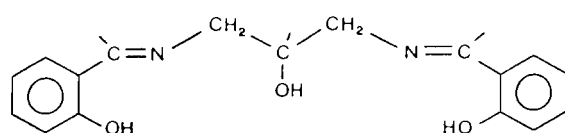


Fig. 1. H₃L ligand.

nation and refinement were performed with the SHELXS-86 program system [16].

Results and Discussion

The H₃L Schiff base ligand contains the potential [N₂O₃]³⁻ donor atom set (Fig. 1), and has therefore the theoretical possibility to surround completely the MO³⁺ core with five coordinating atoms after ligand-exchange reactions with [MOCl₄]⁻. This hypothesis was overcome by the real course of the reactions, in fact stable six-coordinate complexes of general formulation μ-O[MO(HL)]₂, containing the M₂O₃⁴⁺ core with the ligand acting as tetradentate, were produced.

The existence of the quasi-linear O=Re—O—Re=O core has been established by X-ray diffraction in μ-O[ReO(Et₂dtc)₂]₂ (Et₂dtc = diethyldithiocarbamate) [17, 18], μ-O[ReOCl₂(en)]₂ [19] and [Pt-

(NH₃)₄]₂μ-O[ReO(CN)₄]₂ [20]. Furthermore Middleton *et al.* hypothesized, from analytical and spectroscopical data, the presence of the same moiety in complexes of the type μ-O[ReO(L)]₂ (L = quadridentate Schiff base) [21]. By analogy with the corresponding structurally characterized rhenium complexes Trop [22] postulated the presence of the Tc₂O₃⁴⁺ core for μ-O[TcO(Et₂dtc)₂]₂ formed in the reaction between sodium diethyldithiocarbamate and [TcOCl₄]⁻ in acetone. Later the X-ray structure analysis on μ-O[TcO(sal2pn)]₂ established the existence of the Tc₂O₃⁴⁺ core [10]. Our study confirms the presence of the Tc₂O₃⁴⁺ moiety and evidentiates that the ligand binding goes through only four of the five available donor atoms. The central alcoholic group doesn't affect the reaction pathway and stable μ-O[MO(HL)]₂ complexes are obtained.

The reactions of [MOCl₄]⁻ (M = Tc and Re) with the H₃L Schiff base ligand lead to different complexes depending on the reaction conditions, as reported in Scheme 1. At room temperature with a 1/1 metal ligand ratio complexes of type I are obtained in high yield as solid powders only sparingly soluble in common organic solvents. Under reflux in dry alcohols and in a nitrogen atmosphere complexes I re-arrange giving compounds II. Both complexes I and II, in the presence of water and air, change slowly into the corresponding μ-oxo compounds III. Elemental analyses and spectroscopical data (Tables 2, 3 and 4) support the formulations.

Elemental analyses of complexes of type I reveal the 1:1 metal/ligand and the 1:3 metal/chlorine ratios. Both infrared spectra of technetium and rhenium compounds (Table 3), show two intense stretching vibrations in the ν(C=N) region, at higher and lower values with respect to the ν(C=N) of the free ligand. ν(Tc=O) and ν(Re=O) are observed in the usual region with a difference of 15 cm⁻¹, and weak M—Cl bands are evidentiated around 300 cm⁻¹. Furthermore a strong broad band is shown around 3400 cm⁻¹ attributable to the —OH vibration of the non-bonded phenolic group, while the typical bands of chloridate systems are presented close to 3100 and 2600 cm⁻¹.

TABLE 2. Elemental analysis and general properties of the complexes

	Yield (%)	Colour	Analysis: found(calc.) (%)				
			C	H	N	Cl	Tc
TcOCl ₂ (MeOH)(H ₂ L·HCl)	81	carrot	38.6(39.2)	3.7(4.0)	5.2(5.1)	18.7(19.3)	17.0(17.9)
μ-O[TcO(HL)] ₂	51	deep-red	49.3(48.7)	3.9(3.8)	6.4(6.7)		22.5(23.6)
ReOCl ₂ (MeOH)(H ₂ L·HCl)	83	pale-green	33.7(33.8)	3.6(3.5)	4.5(4.4)	16.0(16.6)	
ReOCl ₂ (EtOH)(H ₂ L·HCl)	79	pale-green	34.5(34.9)	3.6(3.7)	4.4(4.3)	15.8(16.3)	
ReOCl(HL)	36	bright-green	37.7(38.3)	3.2(3.0)	5.1(5.2)	6.4(6.6)	
μ-O[ReO(HL)] ₂	46	emerald green	39.5(40.3)	3.2(3.2)	5.5(5.5)		

TABLE 3. Principal IR bands (cm^{-1}) and ^1H NMR signals (relative to SiMe_4)

	$\nu(\text{M}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{Cl})$ or others	$\delta(\text{CH}=\text{N})$	$\delta\text{Har.}$	$\delta(\text{CH})$	$\delta(\text{CH}_2)$	$\delta(\text{N}-\text{H})$
H_3L		1635 1612	3398 ^a	8.46(s)	7.40–6.88	4.29(m)	3.87(d)	
$\text{TcOCl}_2(\text{MeOH})(\text{H}_2\text{L}\cdot\text{HCl})$	949	1662 1612	316					
$\mu\text{-O}[\text{TcO}(\text{HL})]_2$	912 625 ^b	1629 1602		7.93(s)	7.71–7.01	4.59(m)	2.83(d)	
$\text{ReOCl}_2(\text{MeOH})(\text{H}_2\text{L}\cdot\text{HCl})$	964	1662 1610	305	8.62(s)	7.74–6.82	4.94(m)	4.07–3.65	1.25(s)
$\text{ReOCl}_2(\text{EtOH})(\text{H}_2\text{L}\cdot\text{HCl})$	963	1660 1611	305	8.59(s)	7.67–6.81	4.98(m)	4.06–3.69	1.23(s)
$\text{ReOCl}(\text{HL})$	959	1604	288 3437 ^a					
$\mu\text{-O}[\text{ReO}(\text{HL})]_2$	911 635 ^b	1625 1603		7.99(s)	7.56–6.43	4.24(m)	2.96(d)	

^a $\nu(\text{OH})$. ^b $\nu_{\text{as}}(\text{M}-\text{O}-\text{M})$.

TABLE 4. UV-Vis bands for $\mu\text{-O}[\text{MO}(\text{HL})]_2$ complexes

	λ_{max} (nm)	ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
$\mu\text{-O}[\text{TcO}(\text{HL})]_2$	230	80600
	260	37800
	325	25200
	462	7100
$\mu\text{-O}[\text{ReO}(\text{HL})]_2$	228	66300
	260	40400
	360	8300
	680	500

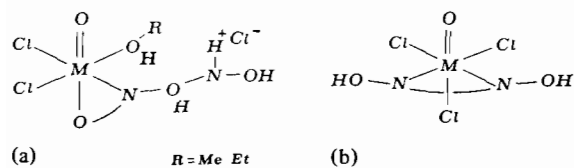


Fig. 2. Proposed configurations for complexes of type I.

The rhenium derivative of type I was studied further to collect more information on the coordination around the metal, the elemental analysis and spectroscopical data not being in agreement with the literature proposals on similar compounds (Fig. 2(b)) [21]. The mass spectrum gave the highest peak at 498 m/z corresponding to the fragment $\text{ReO}(\text{HL})$. Conductivity measurement performed in acetonitrile showed a value ($\Lambda_m = 59 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Λ_m in acetonitrile for 1:1 electrolyte = 120–160 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) indicating a partial ionization due to the hydrochloric salt of the free imino nitrogen (*vide infra*). ^1H NMR spectra in acetonitrile exhibited all

the proton signals of the coordinate ligand, and in particular the N–H proton at $\delta = 1.25$ ppm. Moreover the rhenium product of type I collected in ethanol showed the signals of the ethanol molecule centred at $\delta = 0.96$ (t) and 3.30(q) ppm. Thermogravimetric measurements produced a loss of weight corresponding to the ethanol molecule at 90 °C, followed by total decomposition of the compound, suggesting a metal–alcoholic oxygen weak bond. From the above reported data and by analogy with other similar known rhenium and technetium complexes [9, 23, 24] the proposed octahedral structure of compounds of type I could be as depicted in Fig. 2(a). The complexes contain only half ligand bonded to the metal via one phenolic oxygen (*trans* to $\text{M}=\text{O}$ linkage) and one imino nitrogen. Two chlorine atoms of the starting $[\text{MOCl}_4]^-$ compounds and an hydroxylic oxygen of the alcohol molecule complete the equatorial plane. The presence of an alcohol molecule, located in the *cis* or *trans* position with respect to the MO^{3+} moiety, is not unusual in technetium(V) and rhenium(V) oxo-complexes containing Schiff base ligands [7, 25].

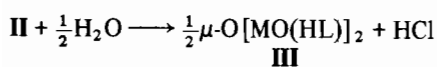
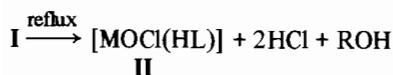
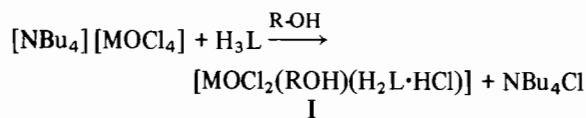
The only recovered complex of type II was $\text{ReOCl}(\text{HL})$. The IR spectrum reveals four indicative absorptions at 3437, 1604, 959 and 288 cm^{-1} , the first consistent with the stretching vibration of the central alcoholic O–H group of the ligand non-bonded to the metal, the second indicative of the coordinate Schiff base C=N stretches, the third assigned to $\nu(\text{Re}=\text{O})$ and the last relative to $\nu(\text{Re}-\text{Cl})$. Elemental analysis supports the formulation with 1/1/1 metal/ligand/chlorine ratios. Conductivity measurements in acetonitrile show the complex to be neutral. No further data were collected owing to the instabil-

ity of the complex that in solution, as well as in the solid state, rearranges with time into the corresponding complex of type **III**. Nevertheless the data are sufficient, along with the comparison of other literature compounds [10, 21], to assign the configuration of a six-coordinate complex (Fig. 3) containing the chlorine atom *trans* to the Re=O linkage and the four coordinating atoms (N₂O₂)²⁻ of the ligand bonded on the equatorial plane. The O-H group in the central chain of the ligand does not bond the metal, as evidenced by the sharp peak at 3437 cm⁻¹ in the IR spectrum. The technetium analogous complex was not recovered because of the higher rearrangement rate.

Compounds of type **III** are stable in the solid state. Elemental analyses (Table 2) are in agreement with the formulation. Conductivity measurements in acetonitrile show the complexes to be neutral. Magnetic susceptibility measurements of the rhenium derivative in the solid state show the compound to be diamagnetic. Spectroscopical data of the μ -oxo-complexes are reported in Tables 3 and 4. Both infrared and proton NMR spectra reveal the coordination of the ligand around the metals. In particular, the IR spectrum of μ -O[ReO(HL)]₂ shows a strong band at 635 cm⁻¹ assigned to $\nu_{as}(\text{Re}-\text{O}-\text{Re})$ and a medium sharp band at 911 cm⁻¹ attributable to $\nu(\text{Re}=\text{O})$, as found in other Re₂O₃⁴⁺ species [18, 20]. Similarly, the IR spectrum of μ -O[TcO(HL)]₂ presents the same finger-printing with a strong band at 625 cm⁻¹ attributable to $\nu_{as}(\text{Tc}-\text{O}-\text{Tc})$ and a sharp band at 912 cm⁻¹ to be assigned to $\nu(\text{Tc}=\text{O})$ [22].

UV-Vis spectra of both μ -oxo-complexes recorded in dichloromethane exhibit intense absorbances at *c.* 230 and 260 nm with a shoulder tailing into the visible region (325–360 nm) of the spectrum (Table 4). The intensity of the *c.* 260 nm band suggests a ligand to metal charge-transfer transition from the orbitals of the amide nitrogens to the empty d_{xz} and d_{yz} orbitals of the metals [1].

In conclusion, all three types of complexes can be obtained from the same reaction mixture through a sequence of reactions, as described below.



The HCl molecule, generated during the first reaction, interacts with the free imino nitrogen of the ligand, to produce, almost quantitatively, com-

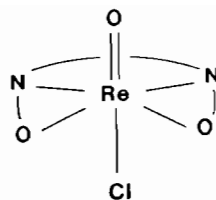


Fig. 3. Proposed configuration for complex of type **II**.

pounds of type **I**. The presence of such a chloridate system prevents the formation, at room temperature, of the complexes of type **II** and moreover the production of dimer complexes, as found for similar compounds containing acac₂en and sal₂en ligands [21]. Refluxing, in dry solvents, the rearrangement of **I** in **II** occurs, but the yield of the reaction is low, since the contemporary production of two equivalents of HCl hydrolyzes part of the ligand yielding salicylaldehyde and diamine detectable by proton NMR spectroscopy. The third reaction gives the most stable compounds of type **III** by simple standing the reaction solutions in contact with the atmosphere. The yield of this last reaction is increased when using an excess of ligand.

The structure of **III** (Fig. 4) involves two octahedrally coordinated atoms bridged by a single oxygen atom with the Tc–O–Tc' group being nearly linear (173°) and having an average Tc–O bond distance of 1.91 Å. The average technetium–yl oxygen bond distance (1.71 Å) is intermediate between the Tc=O distance in TcO³⁺ and TcO₂⁺ complexes (1.65 and 1.75 Å, respectively), while the Tc–O(equatorial) and Tc–N distances are consistent with the values found previously [13, 26, 27]. The Tc and Tc' atoms are displaced by 0.14 and 0.10 Å, respectively, from the mean equatorial plane of the N₂O₂ donor atoms, towards the yl-oxygen, as observed in the strictly parent compound μ -O[TcO(sal₂pd)]₂ [10]. On the other hand, the geometry of the complex does not merit any more comment, since its features parallel those of μ -O[TcO(sal₂pd)]₂ and the introduction of the –OH group in the quadridentate ligand does not modify substantially the overall stereochemistry.

Electrochemistry

The electrochemical studies on rhenium and technetium complexes are important because their *in vivo* behaviour is, in most cases, strongly affected by their red.–ox. properties. Nevertheless, to date, few electrochemical studies on MO³⁺ (M = Tc, Re) complexes have been reported [28–30].

The compounds herein investigated present peak separations ($\Delta E_{pc,pa}$), for the considered red.–ox. couples, similar to those of the ferrocene internal standard [31], at the same scan rate, and tend to 59 mV at low scan rates, indicating quasi-reversible processes are involved. The electron transfer reactions

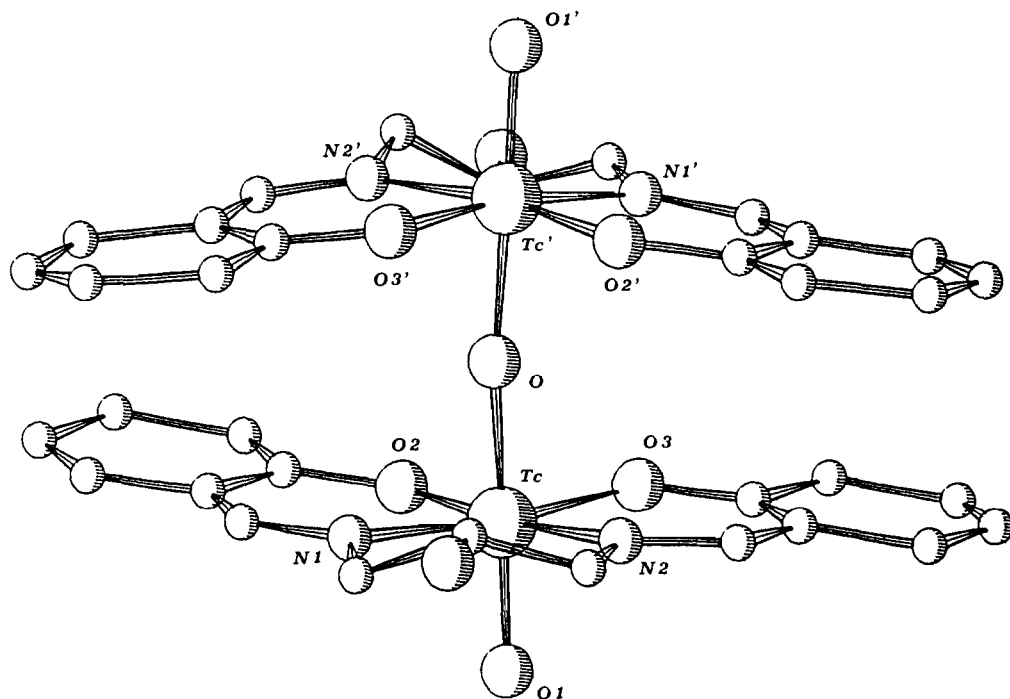


Fig. 4. Perspective view of $\mu\text{-O}[\text{TcO}(\text{HL})]_2$ showing the atom numbering of the 'inner core'.

for the $\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{3+}$ and $\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{5+}$ couples reveal transfer of one electron per mole of compound by means of coulometric measurements. Representative voltammograms of DMF solutions of the $\mu\text{-O}[\text{MO}(\text{HL})]_2$ complexes are shown in Fig. 5.

The voltammogram of $\mu\text{-O}[\text{ReO}(\text{HL})]_2$ shows two quasi-reversible wave systems at $E_{1/2} = +0.70$ and $E_{1/2} = -1.15$ V; however, in the latter an EC mechanism is involved. In fact related with this system, a wave at $E_p = -0.83$ V is present. At this potential the product of the chemical reaction is oxidized. The presence of this wave is confirmed for a scan rate range from 0.02 to 0.60 V s^{-1} . Variations of such a scan rate range show an increasing of the peak separation as high as 20 mV (from 86 to 106 mV) for the peaks system with $E_{1/2} = -1.15$ V and no increase for the $E_{1/2} = +0.70$ V system. The ratio $I_{pa}/I_{pc} = 1$ for the latter peaks system, together with the $\Delta E_{pc,pa}$ value of 74 mV are indicative of a quasi-reversible charge transfer. The voltammogram of $\mu\text{-O}[\text{TcO}(\text{HL})]_2$ shows in reduction a quasi-reversible peaks system with $E_{1/2} = -0.65$ V. Variations of the scan rate between 0.02 and 0.6 V s^{-1} show a constant value for $\Delta E_{pc,pa} = 100$ mV and the ratio $I_{pa}/I_{pc} = 1$ in the same range of scan rate. Both the results are in agreement with a quasi-reversible charge transfer. A further cathodic wave is present at $E_p = -1.43$ V; the value shifts cathodically by increasing the scan rate. An anodic wave is present at $E_p = -1.05$ V (no shift of the potential is observed by varying the scan rate between 0.02 and 0.6 V s^{-1}). Working at $T = -40$ °C, a small cathodic response

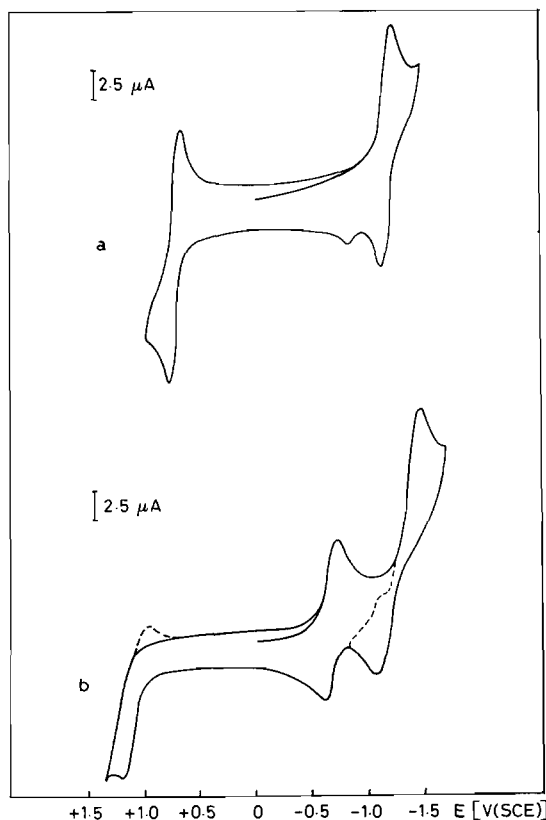


Fig. 5. (a) Cyclic voltammetric scan of $\mu\text{-O}[\text{Re}^{\text{V}}\text{O}(\text{HL})]_2$ in 0.1 M $(\text{Et}_4\text{N})[\text{ClO}_4]$ in DMF at room temperature. (b) Cyclic voltammetric scan of $\mu\text{-O}[\text{Tc}^{\text{V}}\text{O}(\text{HL})]_2$ under the same conditions; the outlined curve shows the behaviour at -40 °C.

TABLE 5. Electrochemical data^a

Complex	Red-Ox change	$E_{1/2}^b$ (V)	ΔE^c
$\mu\text{-O}[\text{ReO}(\text{HL})_2]$	$\text{Re}_2\text{O}_3^{4+}/\text{Re}_2\text{O}_3^{3+}$	-1.53	1.85
	$\text{Re}_2\text{O}_3^{4+}/\text{Re}_2\text{O}_3^{5+}$	+0.32	
$\mu\text{-O}[\text{TcO}(\text{HL})_2]$	$\text{Tc}_2\text{O}_3^{4+}/\text{Tc}_2\text{O}_3^{3+}$	-1.03	1.78
	$\text{Tc}_2\text{O}_3^{4+}/\text{Tc}_2\text{O}_3^{5+}$	+0.75 ^d	
	$\text{Tc}_2\text{O}_3^{3+}/\text{Tc}_2\text{O}_3^{2+}$	-1.81 ^e	

^aConditions: Pt working and auxiliary electrodes, DMF solvent, SCE reference electrode; TEAP 0.1 M supporting electrolyte.

^b $E_{1/2} = 0.5(E_{\text{pc}} + E_{\text{pa}})$ at scan rate 0.2 V s^{-1} and referred to $E_{1/2}$ of the ferrocinium/ferrocene couple used as internal standard.

^c $E = E_{1/2}(\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{3+}) - E_{1/2}(\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{5+})$.

^dValue calculated at -40°C .

^eValue of E_{pc} , EC mechanism involved.

associated to the peak at $E_p = -1.05 \text{ V}$ appears demonstrating that the peak at $E_p = -1.05$ is not the anodic response of the peak at $E_p = -1.43$, thus an EC mechanism occurs. The red-ox changes involving the mixed-valence complexes are given in Table 5.

The technetium complex, once reduced, is more stable than the rhenium analogue which, on the contrary, undergoes an EC mechanism. Once more the technetium complex can be further reduced (wave at $E_p = -1.43 \text{ V}$), while the corresponding rhenium reduction is not visible in the open background window of the solvent. Exactly the same behaviour, but inverted, is observed in the oxidation region, where the rhenium complex becomes more stable than the technetium analogue which undergoes an EC mechanism much better evidenced working at low temperature.

The two analogous complexes present about the same potential differences between the couples $\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{3+}$ and $\text{M}_2\text{O}_3^{4+}/\text{M}_2\text{O}_3^{5+}$, the only change being the shifting of 450 mV of the waves system toward more positive potentials for the technetium complex. This finding is in agreement with the electrochemical behaviour of other technetium and rhenium complexes containing the M=O linkage [30].

Supplementary Material

Final atomic positional and thermal parameters and a table of the observed and calculated structure factors are available from the authors on request.

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