Rhenium(V) oxo complexes with Schiff base ligands containing four or five coordination sites. X-ray molecular structure of [*N*,*N*′-3-azapentane-1,5-diylbis(salicylideneiminato)(3 −)-*O*,*O*′,*N*,*N*′,*N*″]oxorhenium(V)

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Abstract

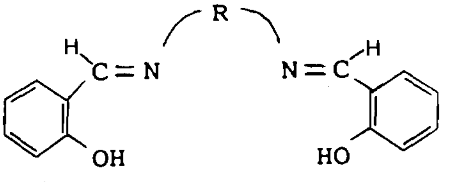
The reactions of $[ReOCl_4]^-$ with Schiff base ligands derived from salicylaldehyde and 1,5-diaminopentane (H_2L^{1a}), -hexane (H_2L^{1b}), -heptane (H_2L^{1c}) or diethylentriamine (H_3L^2) have been investigated. The complexes $ReOCl_2(EtOH)HL^{1n}$ (I) (n = a, b or c), $Re_2O_2(MeOH)_2Cl_4HL^2$ (II), $ReOClL^{1n}$ (III) and $ReOL^2$ (IV), have been synthesized and characterized with the usual physicochemical measurements. The crystal structure of $ReOL^2$ was determined by single crystal X-ray methods. Crystals are monoclinic, space group $P2_1/c$, with $a = 9.470(7)$, $b = 9.358(8)$, $c = 21.859(12)$ Å, $\beta = 99.23(8)°$ and $Z = 4$. X-ray diffraction provides 5601 observed reflections (up to $2\theta = 60°$) and the structure has been refined by full-matrix least-squares methods to $R = 0.061$. The monomeric structure consists of distorted octahedral $ReOL^2$ units. One oxygen atom of the N_3O_2 pentadentate ligand is located *trans* to the rhenium–oxo-oxygen bond, while the remaining four coordinating atoms lie on the equatorial plane of the octahedron assuming that the oxo-oxygen occupies an apex. The arrangement of the two iminophenolate groups is explained as a function of the length of the aliphatic chain joining the two imine groups.

Introduction

Rhenium(V) complexes contain mainly the $[Re{=}O]^{3+}$ core [1]. Many X-ray structures depict the hexacoordination around the rhenium metal as a distorted octahedron [2, 3]. Usually, an oxygen or a chloro atom is coordinated *trans* to the Re=O bond.

Schiff base ligands stabilize the $[Re{=}O]^{3+}$ core in several ways. Tetradentate N_2O_2 Schiff bases containing up to four carbon atoms between the imino groups were found to coordinate symmetrically in the equatorial plane with respect to Re=O [4–7]. But, in bis bidentate NO Schiff base Re(V) oxo complexes an asymmetric fashion of the two ligands is observed, one being in the equatorial plane and the other showing a phenolate group *trans* to the Re=O moiety [8].

This paper deals with the reactions of the potentially N_2O_2 tetradentate and N_3O_2 pentadentate Schiff bases, listed in Scheme 1, with $[ReOCl_4]^-$ in alcohols. These ligands have more than four atoms in the bridge chain between the two imine nitrogens.



H_2L^1 R = $-(CH_2)_n-$
$n = 5$ (L^{1a}), 6 (L^{1b}) or 7 (L^{1c})
H_3L^2 R = $-(CH_2)_2-NH-(CH_2)_2-$

Scheme 1. The ligands.

Monomeric and dimeric complexes were obtained depending on the type of ligand and on the experimental conditions. The species $ReOL^2$ was characterized by X-ray analysis, while the other products were characterized by routine determinations and spectroscopical measurements.

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Experimental

Materials

$[NBu_4][ReOCl_4]$ was prepared as already reported in the literature [9]. The starting products were reagent grade chemicals. The ligands were prepared by mixing salicylaldehyde and amines in a 2:1 stoichiometric ratio, and recovering the Schiff bases as yellow solid or oil by filtration or solvent evaporation. They were used without further purification in the reactions with $[ReOCl_4]^-$.

Apparatus

Elemental analyses were performed on a Carlo Erba elemental analyzer model 1106. IR spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer PE580B spectrophotometer, using KBr 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.* 1.12×10^{-17} J; 200 A). Magnetic susceptibility measurements were performed in the solid state with the Faraday method. Conductivity measurements were collected in dimethylformamide at 25 °C using a Metrohm Herison conductometer, model E518. UV–Vis spectra were recorded in dichloromethane using a Cary 17D spectrophotometer.

Syntheses

$ReOCl_2(EtOH)HL^{1n}HCl$ (I)

The same procedure was used for the syntheses of the complexes containing L^{1a}, L^{1b} and L^{1c} ligands. $[NBu_4][ReOCl_4]$ (0.293 g, 0.5 mmol) was dissolved in ethanol (20 cm^3). An ethanol solution containing the appropriate ligand in a 1:1 molar ratio was added to the previous solution and the mixture was left to stir at room temperature for 10 min. A light brown solid immediately precipitated from the reaction mixture and its amount increased with time. The solid was then filtered off, washed with ethanol and dried *in vacuo*. For all the complexes the yields ranged from 31 to 45%, based on $[ReOCl_4]^-$.

The recovered products are stable under nitrogen but decompose slowly in air as well as in solution.

$ReOClL^{1n}$ (III)

The same preparation procedure was followed using H_2L^{1a}, H_2L^{1b} or H_2L^{1c} ligand.

$[NBu_4][ReOCl_4]$ (0.293 g, 0.5 mmol) was dissolved in 20 cm^3 of ethanol and mixed with an ethanol solution of H_2L^{1n} ligand in a 1:2 molar ratio. The reaction mixture was refluxed for 3 h. The initial brown precipitate dissolved slowly and a bright yellow–green solution was present at the end. After cooling, the addition of 50 cm^3 of diethyl ether gave a pale green precipitate that was collected by filtration (yield 65–74%). The products were recrystallized from dichloromethane/diethyl ether.

The complexes were also prepared starting from $[ReO(eg)_2]^-$ (eg = ethyleneglycole)*, or by adding triethylamine to the reaction mixture at room temperature.

$Re_2O_2Cl_4(MeOH)_2HL^2$ (II)

A solution of $[NBu_4][ReOCl_4]$ (0.293 g, 0.5 mmol) in 25 cm^3 of methanol was added to 20 cm^3 of a methanol solution of H_3L^2 (0.310 g, 1 mmol) at room temperature. The reaction mixture gave a yellow–brown powder that was filtered off and washed with methanol and diethyl ether (yield 32%). The solid slowly decomposes upon standing in air or in solution.

$ReOL^2$ (IV)

$[NBu_4][ReOCl_4]$ (0.293 g, 0.5 mmol) was treated in 25 ml of methanol with H_3L^2 (0.310 g, 1 mmol) and refluxed for 4 h. The initial yellow–brown solid dissolved with time and the resulting bright green solution was left to cool. A light brown solid precipitated by concentration of the reaction mixture. The reaction mother liquors, after slow evaporation at room temperature, yielded brown crystal plates which were used for X-ray single crystal determination (yield 12%).

Crystal data

$C_{18}H_{18}N_3O_3Re \cdot MeOH$, $M = 542.6$, monoclinic, $a = 9.470(7)$, $b = 9.358(8)$, $c = 21.859(12)$ Å, $\beta = 99.23(8)°$, $U = 1912.1(2.4)$ Å^3, D_m (by flotation) 1.87, $Z = 4$, $D_c = 1.885$ g cm^{-3}, $F(000) = 1056$. Space group $P2_1/c$. Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 64.7 cm^{-1}.

Data collection, solution and refinement of the structure

Intensity data were collected for an hexagonal brown plate of dimensions *c.* $0.24 \times 0.18 \times 0.05$ mm on a Stoe automatic four-circle diffractometer. A total of 5601 independent reflections ($2\theta < 60°$) was measured by use of 2θ–θ scan technique and 2642 reflections having $I > 3\sigma(I)$ were used in the subsequent calculations. To the data Lorentz and polarization corrections were applied and an empirical absorption correction based on ψ-scans gave the transmission factors ranging from 0.26–0.99. An un-

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*$[ReO(eg)_2]^-$ was prepared according to the method already reported for the analogous $[TcO(eg)_2]^-$ [10].

sharpened three-dimensional Patterson map revealed the positions of the rhenium atom, refinement of which gave $R=0.22$. The positions of the non-hydrogen atoms were found from two subsequent difference syntheses. Two cycles of block-diagonal least-squares refinement of the parameters, with only the 'inner core' anisotropic, lowered R to 0.08. The subsequent difference map showed two peaks higher than background which were successfully attributed to a methanol molecule. Two cycles of full-matrix least-squares refinement, including the methanol molecule isotropically treated, lowered R to 0.061. The function minimized in the refinement was $\Sigma w|F_o| - |F_c|)^2$, with w derived from counter statistics, and R_w was 0.064. A final difference-Fourier map showed two symmetrically disposed peaks around the rhenium atom, 0.9 Å apart with a height of 1.2 e $Å^{-3}$, but no other peaks of any importance. The reasons for the relatively high R factor are the presence of some disorder at the MeOH and perhaps an improper treatment of the atomic-scattering factors for rhenium. See also 'Supplementary material'.

The solution and refinement of the structure were carried out by the use of Sheldrick's SHELX'76 program system.

Results and discussion

By mixing salicylaldehyde with an aliphatic diamine of the type $H_2N-(CH_2)_n-NH_2$ ($n=5$, 6 or 7) or the triamine $H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$, the Schiff base ligands H_2L^{1n} and H_3L^2 are obtained. The reaction of $[ReOCl_4]^-$ with these ligands follows different pathways depending on whether the chain between the imino groups is aliphatic or contains another facultative coordinating atom.

Reactions of $[ReOCl_4]^-$ with H_2L^{1n} ligands

The reaction of $[ReOCl_4]^-$ with an N_2O_2 chelating ligand leads to the formation of $ReOClL^{1n}$ type complexes (**III**) according to the following equation:

$$[Bu_4N][ReOCl_4] + 2H_2L^{1n} \xrightarrow{EtOH}$$

$$ReOClL^{1n} + [Bu_4N]Cl + H_2L^{1n} \cdot 2HCl$$

At room temperature the reaction stands at an intermediate step and $ReOCl_2(EtOH)L^{1n} \cdot HCl$ complexes precipitate from the reaction mixtures. To promote the next step, that is the whole coordination of the ligand, the heating, the presence of a deprotonating agent such as sodium acetate or triethylamine, or an excess of ligand is required.

The use of at least 1:2 metal/ligand ratio as well as the use of a basic medium helps to remove the HCl released in the substitution reaction. H_2L^{1n} ligands buffers the reaction medium producing $H_2L^{1n} \cdot 2HCl$.

The $ReOCl_2(EtOH)L^{1n} \cdot HCl$ (**I**) complexes have been characterized by means of elemental analyses (Table 1), consistent with a 1:1 rhenium/ligand and 1:3 rhenium/chlorine ratios. IR spectra (Table 2) show the presence of the chloride salt of the complexes resulting in the characteristic bands around the 3100–2600 cm^{-1} region, the presence of a free phenolic group at $\nu(OH)=3500$ cm^{-1} and the $\nu(Re=O)$ stretches falling in the usual range at 973 cm^{-1}. The imine groups show two different stretch frequencies at 1660 cm^{-1}, for the non-coordinated nitrogen, and at 1604–1607 cm^{-1} for the coordinated one. EI mode mass spectra of the powders show the highest peaks at 510, 524 and 538 m/z, corresponding to the $ReOL^{1n}$ fragment for the H_2L^{1a}, H_2L^{1b} and H_2L^{1c} ligand, respectively, all exhibiting the typical pattern of rhenium isotopes. No fragmentation peaks are detectable.

The **I** products are conducting in dimethylformamide with a $\Lambda_{eq} \simeq 30$ Ω^{-1} cm^2 mol^{-1}, lower than that required for a 1:1 electrolyte. The value is consistent with a partial ionization of the chloride salt of the free imino group.

UV–Vis measurements in dimethylformamide show the change of the spectra of the brown solutions of **I** to the spectra of $ReOClL^{1n}$ (**III**) green complexes. Owing to the decomposition with time of species **I**, ^1H NMR spectra only reveal the presence of a free ethanol molecule. By comparison with previous complexes [7] and from our present spectroscopic data, we have tentatively attributed the $ReOCl_2(EtOH)(HL^{1n})$ formulation for complexes of type **I** even though each experiment could not establish the purity of the samples, owing to the instability of the product.

$ReOClL^{1n}$ products are pale green powders with elemental analyses consistent with the formula (Table 1). IR spectra show $\nu(Re=O)$ at 963–961 cm^{-1} and two values for $\nu(C=N)$ stretches at 1623–1620 and 1606–1605 cm^{-1} (Table 2). The two $\nu(C=N)$ values support the coordination of the imino nitrogens in a different chemical environment, one having a chlorine *trans* to it and the other a phenolate oxygen atom. Consequently the other phenolate group must be *trans* to the Re=O linkage. Indeed $\nu(Re=O)$ fall at the same values already found for similar bis NO bidentate Schiff base Re(V) oxo complexes [3, 7, 11]. The **III** products are diamagnetic, in agreement with all other known d^2 Re(V) oxo species in a distorted octahedral environment.

Reactions of $[ReOCl_4]^-$ with H_3L^2 ligand

The reaction of oxotetrachlororhenate with the pentadentate ligand H_3L^2 leads to a complex in which

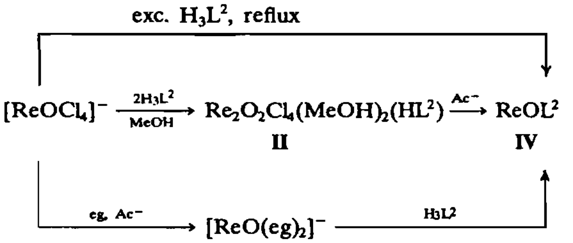
TABLE 1. Elemental analysis and general properties of the complexes

Compound	Yield (%)	Colour	Analysis: found (Calc.) (%)			
			C	H	N	Cl
H_2L^{1a}	95	yellow	74.2 (74.0)	6.7 (6.5)	8.8 (9.1)	
H_2L^{1b}	96	yellow	74.2 (74.5)	7.1 (7.0)	8.6 (8.7)	
H_2L^{1c}	91	yellow	74.5 (74.7)	7.6 (7.2)	8.3 (8.3)	
H_3L^2	92	yellow	68.1 (68.9)	6.0 (6.2)	13.2 (13.6)	
$ReOCl_2(EtOH)(HL^{1a}\cdot HCl)$	45	yellow–brown	37.8 (38.1)	4.1 (4.0)	4.5 (4.2)	15.8 (16.1)
$ReOCl_2(EtOH)(HL^{1b}\cdot HCl)$	38	yellow–green	38.9 (39.1)	4.3 (4.2)	4.1 (4.1)	15.3 (15.7)
$ReOCl_2(EtOH)(HL^{1c}\cdot HCl)$	31	mustard	37.9 (40.0)	4.4 (4.4)	3.9 (4.1)	15.9 (15.4)
$ReOCl(L^{1a})$	74	pea-green	41.6 (41.7)	3.8 (3.3)	4.8 (5.1)	6.0 (6.5)
$ReOCl(L^{1b})$	70	bright pea-green	43.1 (42.8)	3.8 (3.6)	5.1 (5.0)	5.7 (6.3)
$ReOCl(L^{1c})$	65	olive–green	43.6 (43.8)	3.5 (3.8)	4.8 (4.9)	6.3 (6.2)
$Re_2O_2Cl_4(MeOH)_2(HL^2)$	32	yellow–brown	26.8 (26.2)	3.0 (2.6)	4.0 (4.6)	16.1 (15.5)
$ReOL^2\cdot MeOH$	12	brown	42.2 (42.0)	4.1 (4.3)	7.6 (7.7)	

TABLE 2. General properties of rhenium complexes

Compound	MM (m/z)	ν(Re=O) (cm^{-1})	ν(C=N) (cm^{-1})	Λ_{eq} (DMF) (Ω^{-1} cm^2 mol^{-1})	UV (CH_2Cl_2) (nm)
$ReOCl_2(EtOH)(HL^{1a}\cdot HCl)$	510	973	1660 1604	27.6	460, 345sh, 320
$ReOCl_2(EtOH)(HL^{1b}\cdot HCl)$	524	973	1660 1604	30.4	455, 340sh, 320
$ReOCl_2(EtOH)(HL^{1c}\cdot HCl)$	538	973	1660 1607	37.1	455, 345sh, 315
$ReOCl(L^{1a})$	510	963	1621sh 1606	2.8	410sh, 325, 280, 250
$ReOCl(L^{1b})$	524	962	1623 1605	3.1	410sh, 325, 285, 255
$ReOCl(L^{1c})$	538	961	1620sh 1605	4.0	405sh, 320, 285
$Re_2O_2Cl_4(HL^2)(EtOH)_2$		969	1612		
$ReOL^2\cdot MeOH$	510	915	1621 1608	3.2	465, 405, 295, 260

the ligand is completely coordinated around the metal. However, the reaction must be forced to avoid the formation of an intermediate compound, as reported in the following reaction scheme.



The intermediate dimer, the $Re_2O_2Cl_4$-$(MeOH)_2(HL^2)$ complex, can be obtained from $[ReOCl_4]^-$ in methanol using a 1:2 metal ligand ratio at room temperature. The yellow–brown solid rearranges to the monomer $ReOL^2$ (**IV**) in basic media.

$ReOL^2$ can also be synthesized using an excess of ligand in refluxing methanol or by adding H_3L^2 to a basic reaction mixture containing $[ReO(eg)_2]^-$ (eg = ethyleneglycolate). Both the temperature and/or the basicity of the medium allow the complete coordination of the ligand around the metal centre through the amine group deprotonation.

The intermediate $Re_2O_2Cl_4(MeOH)_2(HL^2)$ complex was characterized by elemental analyses, consistent with one molecule of ligand per two Re=O moieties. The compound is sparingly soluble in the common organic solvents and does not fly in the mass spectrometer, somewhat supporting the dimer formulation. The IR spectrum shows $\nu(C=N)$ at 1608 cm^{-1} consistent with the presence of the coordinated ligand, $\nu(Re=O)$ at 969 cm^{-1} and $\nu(Re-Cl)$ at 325, 302 cm^{-1}.

Elemental analyses, IR and UV–Vis spectroscopic measurements of $ReOL^2$ have already been reported [12]. It is interesting to note the low value of $\nu(Re=O)$, found at 915 cm^{-1}. Other hexacoordinated Schiff base Re(V) oxo complexes exhibiting a phenolate group *trans* to the rhenium–oxygen multiple bond (see Tables 2 and 5) show the Re=O stretching vibration in the 958–978 cm^{-1} region. This peculiar behaviour can be explained in terms of the high nucleophilic power of the N-iminate group, which supplies the metal with high electron density and consequently weakens the rhenium–oxygen multiple bond.

The structure of $ReOL^2 \cdot MeOH$ is isomorphous and isostructural with that of $TcOL^2 \cdot MeOH$ [12]. The atom-numbering system and the configuration of the molecule is illustrated in Fig. 1 and the bond lengths and angles with their standard deviations are given in Tables 3 and 4. The crystal structure

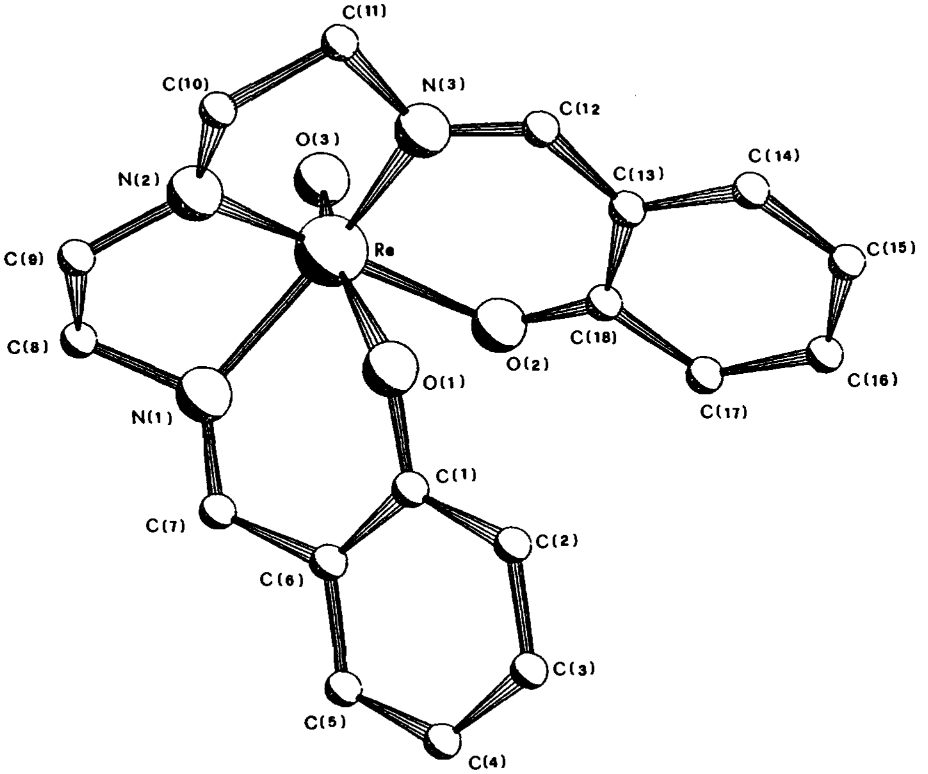


Fig. 1. PLUTO drawing of the $ReOL^2$ molecule showing the atom numbering used in the Tables.

TABLE 3. Bond distances (Å) with e.s.d.s in parentheses

Re–O(1)	2.09(1)	Re–N(1)	2.06(1)
Re–O(2)	2.14(1)	Re–N(2)	1.91(1)
Re–O(3)	1.72(1)	Re–N(3)	2.04(1)
O(1)–C(1)	1.34(2)	O(2)–C(18)	1.26(2)
C(1)–C(6)	1.41(2)	C(13)–C(18)	1.26(2)
C(6)–C(7)	1.46(2)	C(12)–C(13)	1.44(2)
C(7)–N(1)	1.28(2)	C(12)–N(3)	1.26(2)
N(1)–C(8)	1.47(2)	N(3)–C(11)	1.48(2)
C(8)–C(9)	1.54(3)	C(11)–C(10)	1.51(3)
C(9)–N(2)	1.46(3)	C(10)–N(2)	1.51(2)
O(4)–C(19)	1.39(4)	C_{ph}–C_{ph} mean	1.41(2)

is built up of discrete molecular units of ReOL^2 and MeOH. The rhenium atom resides in a distorted octahedral coordination environment and the methanol molecule, unlike some other methanol adducts, appears to show no significant interaction, apart from the O(1)---O(4) contact of 2.75 Å. The Re atom lies out of the mean N$_3$O equatorial plane by 0.28 Å towards the oxo ligand; O(1)–Re–O$_{oxo}$ departs from linearity by 18°; 'bite' angles range from 76.3–89.9°; the Re–N(2) distance (1.91(1) Å), with N(2) in a near planar geometry, is diagnostic for some pπ–dπ electron donation from ligand to metal, and also the two Tc–N$_{imine}$ distances (2.04 and 2.06 Å) are somewhat shorter than the previously reported values [12], due to their *trans* stabilizing effect.

As found in two other octahedral Re(V) complexes ReOCl[(2-OC$_6$H$_4$CH=NCH$_2$CH$_2$)$_2$S] [13] and ReOCl[(2-OC$_6$H$_4$CH=NCH$_2$CH$_2$OCH$_2$)$_2$] [14], the phenolic oxygen, O(1), of the ligand lies *trans* to the rhenium oxo group, while the phenolic oxygen, O(2), binds *trans* to the imine N(2) nitrogen, the O(2)–Re–N(2) angle being 168.8(5)°. The maximum angular deviation from ideal octahedral values is shown by the N(1)–Re–N(3) angle (150.3(5)°).

The relevant bond lengths of some rhenium(V) and technetium(V) Schiff base oxo complexes are collected in Table 5. The Re=O bond lengths are in agreement with the trend of ν(Re=O) stretches. In fact, all the complexes with a phenolate group *trans* to Re=O show the Re=O distance of 1.68 Å while the value of the ReOL^2 complex is 1.72 Å. The high nucleophilicity of the coordinated N-aminate group, as mentioned above, can also be responsible for the longer single Re–O bond lengths either *cis* or *trans* to Re=O. Technetium analogue complexes behave as rhenium ones, even though the difference in the Tc=O distances is less dramatic.

Conclusions

The peculiarity of the above reported rhenium complexes, in which the ligands are completely coordinated around the metal, is that the *trans* to Re=O coordination site is occupied by a phenolate group. Other authors have recently found (even though for other purposes) the same results using similar ligands having (CH$_2$)$_2$–S–(CH$_2$)$_2$ [13] or (CH$_2$)$_2$–O–(CH$_2$)$_2$ [14] as a chain between the imino groups.

From our results and those already reported in the literature we can conclude that tetradentate N$_2$O$_2$ Schiff base ligands coordinate around the [Re=O]$^{3+}$ core in two different ways in function of the length of the chain between the two imine nitrogens. Chains with less than five atoms lead to a configuration in

TABLE 4. Bond angles (°) with e.s.d.s in parentheses

O(1)–Re–O(2)	75.7(4)	O(2)–Re–N(2)	168.8(5)
O(1)–Re–O(3)	161.2(5)	O(2)–Re–N(3)	89.9(5)
O(1)–Re–N(1)	80.2(5)	O(3)–Re–N(1)	102.3(5)
O(1)–Re–N(2)	94.2(5)	O(3)–Re–N(2)	104.6(5)
O(1)–Re–N(3)	79.9(5)	O(3)–Re–N(3)	103.6(6)
O(2)–Re–O(3)	85.7(4)	N(1)–Re–N(2)	76.3(5)
O(2)–Re–N(1)	106.2(5)	N(1)–Re–N(3)	150.3(5)
Re–O(1)–C(1)	122.6(8)	N(2)–Re–N(3)	88.4(5)
O(1)–C(1)–C(6)	122.1(1.3)	Re–O(2)–C(18)	122.7(1.0)
C(1)–C(6)–C(7)	120.3(1.5)	O(2)–C(18)–C(13)	127.6(1.4)
C(6)–C(7)–N(1)	122.7(1.7)	C(18)–C(13)–C(12)	124.1(1.4)
Re–N(1)–C(7)	130.1(1.2)	C(13)–C(12)–N(3)	126.5(1.5)
Re–N(1)–C(8)	109.6(1.1)	Re–N(3)–C(12)	127.5(1.2)
C(7)–N(1)–C(8)	118.6(1.5)	Re–N(3)–C(11)	112.3(1.1)
N(1)–C(8)–C(9)	102.2(1.4)	C(12)–N(3)–C(11)	120.1(1.4)
C(8)–C(9)–N(2)	103.6(1.4)	N(3)–C(11)–C(10)	108.4(1.5)
C(9)–N(2)–Re	122.7(1.1)	C(11)–C(10)–N(2)	109.8(1.5)
C(9)–N(2)–C(10)	118.3(1.4)	C(10)–N(2)–Re	116.0(1.0)
C_{ph}–C_{ph}–C_{ph} mean	120.2(1.2)		

TABLE 5. M=O IR stretching vibration and principal bond lengths (Å) in some rhenium and technetium oxo complexes with Schiff base ligands

Complex	ν(M=O)	M=O	(M–O) *trans*	(M–O) *cis*	M–N	Reference
$ReOL^2 \cdot MeOH$	915	1.72(1)	2.09(1)	2.14(1)	2.06(1), 2.04(1)(*trans*) 1.91(1)	this paper
$ReOCl(Mesal)_2$[a]	962	1.680(4)	1.979(4)	1.995(4)	2.120(5), 2.103(5)(*cis*)	6
$ReOCl(sal_2eten)$[b]	960	1.688(6)	1.977(5)	1.983(6)	2.146(7), 2.119(7)(*cis*)	14
$ReOBr_2(PPh_3)phsal$[c]	978	1.683(1)	1.937(5)		2.173(6)	17
$[ReOCl(PPh_3)]_2sal_2en$[d]	968	1.68(1)	1.93(1) 1.92(1)		2.15(1) 2.15(1)	16
$ReOCl_2(salphos)$[e]	958	1.711(13)	1.965(13)		2.109(13)	15
$TcOL^2 \cdot MeOH$	888	1.685(6)	2.120(6)	2.130(6)	2.101(8), 2.044(8)(*trans*) 1.894(8)	12
$TcOCl(Phsal)_2$	940	1.67(1)	1.94(1)	1.99(1)	2.12(1), 2.19(1)(*cis*)	18

M=Re or Tc. [a]mesal=2-[$CH_3N=CH]C_6H_4O$. [b]sal$_2$eten=(2-$OC_6H_4CH=NCH_2CH_2OCH_2)_2$. [c]phsal=2-[$C_6H_5N=CH]C_6H_4O$. [d]sal$_2$en=(2-$OC_6H_4CH=NCH_2)_2$. [e]salphos=2-[$Ph_2P(CH_2)_3N=CH]C_6H_4O$.

which the ligand lies on the equatorial plane with respect to Re=O. Otherwise, chains with five or more atoms make possible a configuration with the ligand twisting the second phenolate group from the equatorial plane, to reach the coordination site *trans* to Re=O. When a fifth potentially coordinating group exists in the chain, and it is not sterically encumbered, it can or cannot coordinate in the equatorial plane in function of its nucleophilicity.

Since bidentate NO Schiff bases assume the twisted configuration around the Re=O group in bisubstituted $ReOCl(ON)_2$ complexes, we can state that the twisted configuration is thermodynamically more stable for these types of complexes, hence the coordination of the ligand on the equatorial plane, when observed, is imposed by sterical reasons.

Supplementary material

Final positional and thermal parameters, the structure factors and details of the least-squares planes, dihedral angles and some interatomic contacts are available from the authors on request.

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