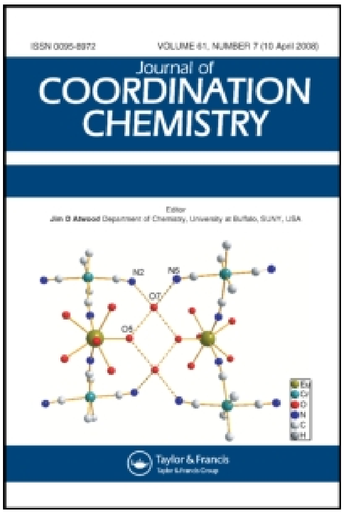

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A. Abrahams[a]; G. Bandolp[a]; S. Gatto[a]; T. I. A. Gerber[a]; J. G. H. Du Preez[a]
[a] Department of Chemistry, University of Port Elizabeth, Port Elizabeth, South Africa

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A SYNTHETIC AND STRUCTURAL STUDY OF OXORHENIUM(V) COMPLEXES WITH MIXED DIDENTATE (*O,O*)-TERDENTATE(*O,N,N*) LIGANDS

A. ABRAHAMS[a], G. BANDOLI[b,*], S. GATTO[b], T.I.A. GERBER[a] and J.G.H. DU PREEZ[a]

[a]*Department of Chemistry, University of Port Elizabeth, P.O. Box 1600, 6000 Port Elizabeth, South Africa*[a]; [b]*Department of Pharmaceutical Sciences, University of Padova, Via Marzolo 5, 35131 Padova, Italy*

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The reaction of *cis*-$[ReOCl_2(L_3)]$ (L_3^- = terdentate *O,N,N*-donor ligand 2-[[{2-(2-pyridinyl)ethyl}amino]methyl]phenolate) with ethylene glycol (H_2eg) in acetonitrile led to the isolation of $[ReO(L_3)(eg)]$. The analogous complexes $[ReO(L_3)(cat)]$ (H_2cat = 1,2-dihydroxybenzene) and $[ReO(L_3)(ox)]$ (H_2ox = oxalic acid) could not be prepared by this method. $[ReO(L_3)(cat)]$ was synthesized by the one-pot reaction of $[ReOCl_4^-]$ with a twofold molar excess of HL_3 and H_2cat in ethanol, and $[ReO(L_3)(ox)]$ was isolated from the reaction of $[ReO(L_3)(eg)]$ and H_2ox in acetonitrile. All complexes were characterized by various physical techniques, including IR and NMR. The X-ray crystal structure of $[ReO(L_3)(cat)\cdot 1/2EtOH]$ was determined. Crystals are triclinic, $P\bar{1}$, a = 8.920(2), b = 11.209(5), c = 11.735(5)Å, α = 78.00(4), β = 68.93(3), γ = 86.49(3)°, Z = 2. The structure was solved by the Patterson method and refined by full-matrix least-squares procedures to R = 0.047 (R_w = 0.066) for 2321 reflections with $F_0 > 3\sigma(F_0)$.

Keywords: oxorhenium(V); mixed di-/terdentate ligands; X-ray structure

INTRODUCTION

The promise of ^{186}Re as possible radionuclide for incorporation into therapeutic agents [1, 2] has rekindled the interest in the coordination chemistry of this metal. As part of a programme to synthesize new complexes with possible nuclear

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[*] Corresponding author.

medicinal applications, we are currently studying the formation of oxorhenium(V) complexes containing both di- and terdentate ligands. Oxocomplexes of this metal with multidentate ligands have been extensively studied during the last few years, but these ligands were mainly derivatives of *N*-phenylsalicylideneimine [3-5] and *S*-methyldithiocarbazate [6-8]. With didentate *N,O*-donor Schiff bases (HL_2) complexes of the type $ReOCl(L_2)_2$ and $ReOCl_2(L_2)(PPh_3)$ [9, 10], and with terdentate *O,N,O*-donors (H_2L_3) the six-coordinate compounds $ReOCl(MeOH)(L_3)$ were isolated [5].

Examples of oxorhenium(V) complexes containing both di- and terdentate ligands are rare in the literature. Among the few examples are ReO(ONS)(NS) (ONS^{2-} = *N*-(2-mercaptophenyl)salicylideneiminate; NS^- = *N*-(2-mercaptophenyl)-*p*-nitrobenzylideneiminate) [5], and *cis*-$ReO(PO_2)(PO)$ (H_2PO_2 = bis(*o*-hydroxyphenyl)phenylphosphine; HPO = (*o*-hydroxyphenyl)diphenylphosphine) [11]. In both examples, a deprotonated phenolic oxygen occupies the coordination site *trans* to the oxo group. In this paper we present synthetic and structural work on mixed didentate-terdentate complexes of oxorhenium(V) with an O_3N_2 donor set.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used as received. Solvents were purified and dried before use. The starting complex $[ReOCl_2(L_3)]$ (HL_3 = 2-[[{2-(2-pyridinyl)ethyl}amino] methyl]phenol) was prepared from the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with HL_3 in acetone as described earlier [12], and (*n*-Bu_4N)$[ReOCl_4]$ was synthesized by a literature method [13].

Instrumentation

Infrared and electronic spectra were obtained on a Nicolet 20 DXC and a Shimadzu UV-3100 spectrophotometer, respectively. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer, and peak positions are relative to $SiMe_4$ as external reference. Conductivity data were obtained with a Phillips PW 9509 conductometer, and melting points were performed with an Electrothermal 9100 apparatus. Infrared spectra were obtained in KBr discs and ^1H NMR spectra were run in d_6-DMSO. Electronic spectra were all obtained in acetonitrile, and data are given as λ_{max} with extinction coefficients (in units $M^{-1}cm^{-1}$) in parentheses. Microanalyses were performed by Mrs M. Maksa of the Materials Science and Technology Division of the CSIR in Pretoria, South Africa.

Synthesis of the Complexes

[ReO(L$_3$)(cat)]·1/2;EtOH (1)

The salt (n-Bu$_4$N)[ReOCl$_4$] (104 mg, 170 μmol) was dissolved in ethanol (5 cm^3), and a solution of 2-[[{2-(2-pyridinyl)ethyl}amino]methyl]phenol (HL$_3$) (56 mg in 2 cm^2 of ethanol) was added. The colour of this mixture changed immediately from light green to dark brown, without the formation of a precipitate. A mass of 44 mg (400 μmol) of 1,2-dihydroxybenzene (H$_2$cat) in 4 cm^3 ethanol was then added, without any colour change occurring. After stirring for 2h at room temperature, a brown solid was filtered from the solution, and it was washed with ethanol (2 × 5 cm^3), and dried under vacuum. Good crystals, suitable for X-ray structure determination, were obtained as brown plates from slow evaporation of the mother liquor at room temperature. The yield of product was 65%; m.p. 301°C. *Anal.*: calcd.: C, 44.99; H, 3.96; N, 5.00%. Found: C, 44.70; H, 4.08; N, 4.80%. IR: ν(Re=O) 951(vs); ν(N-H) 3165(m); δ(py) 1611(s); ν(C-O) 1287(s), 1240(vs), 1231(vs); ν(Re-O) 362(m), 358(m), 350(m) cm^{-1}. ^{1}H n.m.r.: δ9.64 (s, 1H, N*H*); 9.08(d, 1H, H^{14}); 7.95(t, 1H, H^{12}); 7.76(t, 1H, H^{13}); 7.70(d, 1H, H^{11}); 7.07(t, 1H, H^3); 6.99(d, 1H, H^5); 6.50-6.95 (m, 5H, H^2, $H^{16\text{-}19}$); 6.19(d, 1H, H^4); 3.86(t, 2H, H^8); 3.71(s, 2H, H^7); H^9 and CH_2^{Et} protons obscured by DMSO signals; 1.07(t, 1.5H, CH_3^{Et}) ppm. Electronic spectrum: 357(6200), 318(6000), 271(15000).

[ReO(L$_3$)(eg)] (2)

A solution of 98 mg of ReOCl$_2$(L$_3$) (188 μmol) in 7 cm^3 of acetonitrile was mixed with ethylene glycol (H$_2$eg; 0.04 cm^3) and triethylamine (0.11 cm^3), and the mixture was heated under reflux for 8h. During this time the colour changed from green to purple. The acetonitrile was removed on a rotary evaporator, and the residue taken up in 5 cm^3 of dichloromethane. The purple solution was then washed with water (2 × 4 cm^3) to remove triethylammonium chloride and ethylene glycol, and then dried over anhydrous Na$_2$SO$_4$. After removal of Na$_2$SO$_4$ by filtration, the dichloromethane solution was left to evaporate slowly at room temperature, yielding violet needles; yield 32 mg (35%); m.p. 178°C. *Anal.*: calcd.: C, 39.26; H, 3.91; N, 5.72%. Found: C, 39.24; H, 3.88; N, 5.71%. IR: ν(Re=O) 951(vs); ν(N-H) 3083(m); δ(py) 1611(m), ν(C-O) 1291(vs), 1269(m); ν(Re-O) 386(m), 352(m) cm^{-1}. ^{1}H n.m.r.: δ9.12 (d, 1H, H^{14}); 8.34(br s, 1H, N*H*); 7.87(t, 1H, H^{12}); 7.69(t, 1H, H^{13}); 7.63(d, 1H, H^{11}); 6.91(d, 1H, H^5); 6.81(t, 1H, H^3); 6.45(t, 1H, H^4); 6.04(d, 1H, H^2); 4.40-4.60(m, 4H, OCH_2CH_2O); 4.21(br s, 2H, H^7); 4.00(t, 2H, H^8); H^9 obscured; ppm. Electronic spectrum: 384(1800), 297(6400), 265(12200).

[ReO(L_3)(ox)] (3)

A mixture of [ReO(L_3)(eg)] (135 mg, 276 μmol) and an equimolar amount of oxalic acid dihydrate (34 mg, H_2ox) in 15 cm^3 of acetonitrile was heated under reflux for 24 h. After heating was stopped and the solution cooled to room temperature, a blue precipitate was removed by suction filtration, and washed with acetonitrile (2 × 2 cm^3). Slow evaporation of the mother liquor gave another batch of dark blue needles; yield 75%; m.p. 185°C (decomp). *Anal.*: calcd.: C, 37.13; H, 2.92; N, 5.41%. Found: C, 36.66; H, 2.65; N, 5.33%. IR: ν(Re=O) 986(vs); ν(N-H) 3122(m); ν(C=O) 1738, 1729(vs), 1688(s); ν(C-O) 1287(s), 1271(m); ν(Re-O) 376(w), 354(m) cm^{-1}. ^{1}H n.m.r.: δ9.33(br s, 1H, N*H*); 8.95(d, 1H, H^{14}); 8.11(t, 1H, H^{12}); 7.85(t, 1H, H^{13}); 7.84(d, 1H, H^{11}); 7.19(d, 1H, H^5); 7.05(t, 1H, H^3); 6.79(t, 1H, H^4); 6.39(d, 1H, H^2); 4.41(br d, 2H, H^8); 3.97(d, 2H, H^7); 3.68(t, 2H, H^9) ppm. Electronic spectrum: 338(6200), 278sh, 249(10100).

Crystallographic Measurements and Structure Resolution of [ReO(L_3)(cat)] (1)

Details of crystal data, intensity measurements and data processing are summarized in Table I. Cell parameters were determined from 30 high-angle data ($2\theta > 21°$). For the structure factors, corrections for Lorentz and polarization effects and absorption, using an empirical method based on ψ-scan of six reflections at χ *ca.* 90°, were made. The structure was solved by standard heavy-atom methods with subsequent Fourier difference maps yielding the positions of the light atoms. Refinement proceeded routinely and no anomalies in the temperature factors or excursions of electron density in the final Fourier maps were observed. Final fractional atomic coordinates are given in Table II, and selected bond distances and angles in Table III. The SHELXTL PLUS [14] package of computer programs was employed for the solution and refinement of the structure and ORTEP [15] used to plot the molecular structure. Additional material available from the authors includes thermal parameters and a full listing of bond lengths and angles.

RESULTS AND DISCUSSION

Synthesis

It was argued that the oxodichloride complex $ReOCl_2(L_3)$ would provide a convenient entry into the synthesis of 'mixed' di- and terdentate ligand

TABLE I Structure determination summary* for [ReO(L_3)(cat)·1/2EtOH].

Crystal Data:	
Empirical Formula	$C_{20}H_{19}N_2O_4Re \cdot 1/2EtOH$
M	560.6
Colour; Habit	brown plates
Crystal Size (mm)	0.05 × 0.10 × 0.10
Crystal System	triclinic
Unit Cell Dimensions:	
a/Å	8.920(2)
b/Å	11.209(5)
c/Å	11.735(5)
α/°	78.00(4)
β/°	68.93(3)
γ/°	86.49(3)
U/Å^3	1068.9(8)
D_c/Mgm^{-3}	1.738
μ/mm^{-1}	57.0
F (000); Z	54.6; 2
Space Group	$P\bar{1}$ (No. 2)
Data Collection:	
2θ Range/°	4.5-45.0°
Index Ranges, $h\ k\ l$	0-9, −11 to 12, −11 to 12
Reflections Collected	2826
Independent Reflections	2816(R_{int} = 0.052)
Observed Reflections [$F_o > 3\sigma(F_o)$]	2321
Solution and Refinement:	
Weighting Scheme (w^{-1})	$\sigma^2(F) + 0.0057F^2$
Number of Parameters Refined	257
Final R, R_w indices (observed data)	0.047, 0.066
Goodness-of-fit	0.90
Largest Peak in Final ΔF/eÅ^{-3}	1.7

*Nicolet-Siemens R3m/V diffractometer, Mo-Kα radition (λ = 0.71073 Å), T = 294 K; highly oriented graphite crystal monochromator, ω-2θ scan mode, variable scan speed 4.51-14.65° min^{-1} in ω, scan range (ω) 0.60° + Kα separation; 2 standard reflection every 150; function minimized $\Sigma w(|F_o| - |F_c|)^2$; H atoms undetectable from ΔF.

complexes of rhenium(V), since molecules like 1,2-dihydroxybenzene (H_2cat), ethylene glycol (H_2eg) and oxalic acid (H_2ox) should easily replace the chloride ligands to yield products with an O_3N_2 donor atom set. $ReOCl_2(L_3)$ was prepared earlier [12] from the reaction of (n-Bu_4N)[$ReOCl_4$] or *trans*-$ReOCl_3(PPh_3)_2$ with HL_3 in acetone, and a crystal structure determination has shown that the phenolate oxygen of L_3^- occupies the axial position *trans* to the rhenyl oxo oxygen, with the two neutral nitrogen donor atoms coordinated in the equatorial *cis* plane.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for [ReO(L_3)(cat)·1/2EtOH].

Atom	*x/a*	*y/b*	*z/c*	*U*(*)
Re	728(1)	4856(1)	1968(1)	35
O(1)	2075(13)	4157(10)	919(10)	42
O(2)	−550(11)	5984(9)	2990(9)	37
O(3)	46(13)	3534(11)	3492(13)	53
O(4)	−1331(12)	4343(9)	1811(10)	40
N(1)	1055(14)	6465(11)	477(11)	34
N(2)	2638(15)	5479(11)	2418(11)	38
C(1)	−898(16)	7210(14)	2823(17)	43
C(2)	−1239(20)	7818(16)	3806(15)	47
C(3)	−1665(24)	9033(17)	3641(19)	60
C(4)	−1753(26)	9669(18)	2487(10)	69
C(5)	−1425(20)	9066(16)	1561(19)	56
C(6)	−903(7)	7847(14)	1638(14)	39
C(7)	−433(19)	7175(15)	599(16)	45
C(8)	2427(17)	7293(14)	228(15)	37
C(9)	3958(19)	6573(15)	234(15)	47
C(10)	3896(18)	6177(14)	1613(17)	47
C(11)	5086(20)	6507(18)	1945(18)	56
C(12)	5036(22)	6210(19)	3086(22)	66
C(13)	3740(22)	5539(17)	3987(17)	54
C(14)	2523(20)	5187(16)	3620(15)	46
C(15)	−1390(19)	3011(15)	3628(15)	44
C(16)	−2098(21)	2085(15)	4656(19)	54
C(17)	−3635(25)	1634(17)	4840(19)	63
C(18)	−4329(24)	2094(17)	4016(19)	59
C(19)	−3661(23)	3020(16)	3014(19)	61
C(20)	−2126(18)	3475(14)	2792(15)	37
C(21)	7720(61)	−891(47)	7699(45)	87
C(22)	6733(65)	−102(48)	8237(47)	97
O(5)	7209(62)	−1775(47)	7208(46)	86

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

However, this synthetic method was only successful for the preparation of [ReO(L_3)(eg)]. The reaction of $ReOCl_2(L_3)$ with H_2cat in various solvents, over a period of days, led to the isolation of a mixture of products and very low yields of the required product **1**. Good yields and a pure product were obtained by the one-pot reaction of (n-Bu_4N)[$ReOCl_4$] with HL_3 and H_2cat in a 1:2:2 molar ratio in ethanol.

Prolonged heating of $ReOCl_2(L_3)$ with H_2ox in acetonitrile only led to the recovery of starting material. We found, however, that complex **2** is a good precursor for **3**, since the conjugate acid of ox^{2-} is more acidic than ethylene glycol. The oxalate complex **3** was thus formed by heating under reflux a mixture of **2** and two equivalents of oxalic acid in acetonitrile for a day.

TABLE III Selected bond lengths (Å) and angles (°) for [ReO(L_3)(cat)·1/2EtOH].

Re-O(1)	1.67(1)	N(1)-C(7)	1.48(2)
Re-O(2)	1.95(1)	N(1)-C(8)	1.49(2)
Re-O(3)	2.00(1)	N(2)-C(10)	1.34(2)
Re-O(4)	2.04(1)	O(3)-C(15)	1.38(2)
Re-N(1)	2.19(1)	O(4)-C(20)	1.34(2)
Re-N(2)	2.15(1)		
O(1)-Re-O(2)	167.6(4)	Re-N(1)-C(8)	116(1)
O(3)-Re-O(4)	82.5(5)	Re-N(2)-C(10)	125(1)
N(1)-Re-N(2)	90.5(5)	C(7)-N(1)-C(8)	110(1)
Re-O(2)-C(1)	137.2(9)	N(1)-C(8)-C(9)	112(1)
Re-O(3)-C(15)	110(1)	C(8)-C(9)-C(10)	109(1)
Re-O(4)-C(20)	111(1)	N(2)-C(10)-C(9)	117(2)
Re-N(1)-C(7)	113.2(8)		

All the complexes were characterized by elemental analyses, infrared and ^1H NMR spectroscopy, and by X-ray crystallography in the case of complex **1**.

In the infrared spectra of **1** and **2** the Re=O stretching frequencies both appear at 951 cm^{-1}, which is in the expected range (945-965 cm^{-1}) for neutral six-coordinate rhenium(V) complexes with an anionic phenolate oxygen donor coordinated *trans* to the oxo group [16]. In **3** this frequency appears at 986 cm^{-1}, which is surprisingly high for complexes containing the *trans* O=Re-O$^-$ moiety. A medium intensity band around 3100 cm^{-1} has been assigned to ν(NH), proving that the amino nitrogen of ligand L_3^- remains protonated in the complexes. Deprotonation of all the OH groups of the chelate ligands is suggested by the absence of bands in the region 3200-3500 cm^{-1}, and the coordination of the deprotonated oxygens to rhenium(V) is reflected by bands in the regions 1230-1295 cm^{-1} (ν(C-O)) and 350-390 cm^{-1} (ν(Re-O)).

The absence of OH proton signals in the ^1H NMR spectra of the complexes supports the formation of three Re-O bands in **1-3**; furthermore, the signals of the protons close to the coordinating atoms of the di- and terdentate chelates are all shifted downfield with respect to those of the free ligands. The signal due to the N*H* proton of the coordinated ligand L_3^- appears in a wide range in the complexes, but it nevertheless suggests that L_3^- acts as a terdentate monoanionic chelate, as is the case in [ReOCl$_2$(L_3)] [12].

X-ray Structure of [ReO(L_3)(cat)·1/2EtOH] (1)

In the mononuclear complex **1** (Figure 1) the coordination geometry around the rhenium is highly distorted octahedral; the two nitrogen atoms from the terdentate L_3^- ligand and the two oxygen atoms of the catecholate moiety lie on

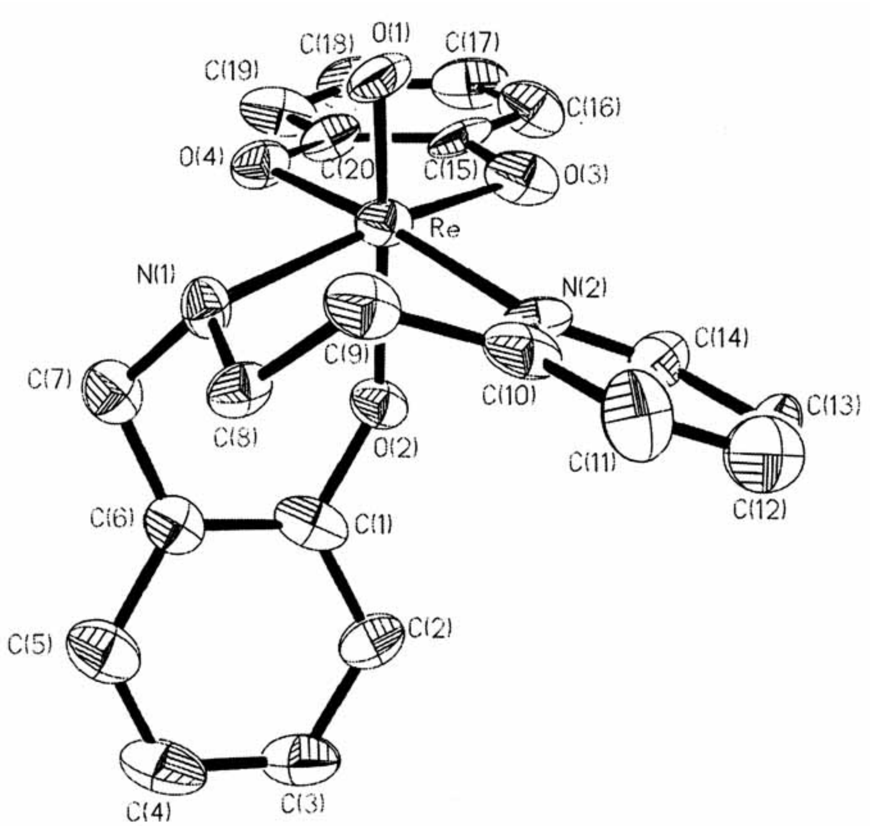

FIGURE 1 An ORTEP view of [ReO(L_3)(cat)·1/2EtOH](**1**), showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level. The EtOH molecule is omitted for clarity.

the equatorial plane, while the phenolate O(2) atom is *trans* to the O(1) oxo atom. In the crystal the molecules are packed individually and interact *via* normal van der Waals contacts. The O(1)-Re-O(2) (phenolate atom) axis is non-linear (167.6°), and the rhenium atom is displaced from the mean equatorial plane by 0.17Å towards the 'oxo' oxygen atom. In the O_4N_2 polyhedron the Re atom is +0.97Å from the O(3)O(4)O(1) plane and −1.30Å from the N(1)N(2)O(2) one, the dihedral angle being 6.0°. In the mean equatorial plane, the four donor atoms deviate only marginally (0.01Å). Bond lengths and angles within the inner core show no unusual features, being within the range expected by comparison to other similar complexes [3-5, 8].

The structures of **1** and the precursor complex [ReOCl_2(L_3)] [12] are superimposable (Figure 2), the r.m.s. deviation, derived from the BMFIT program [17], being only 0.06Å when the fitting is performed using the common atoms. These two complexes differ only marginally also in the periphery and, in particular, in the six-membered ReN(1)C(8)C(9)C(10)N(2) ring, the C(9) and C(10) are above the mean plane defined by ReN(1)C(8)N(2), by 1.09 and 0.46Å in **1**, and by 1.05 and 0.50Å in $ReOCl_2(L_3)$, the major difference being in the dihedral angle between the two rings of the terdentate ligand (103.1° in **1** and 81.4° in $ReOCl_2(L_3)$).

Although a few examples of 'mixed' di- and terdentate ligand complexes of rhenium(V) have been reported in the literature, they were mainly of the Schiff-base type. It was found that the reaction of $ReOCl_4^-$ with the terdentate *ONO*-

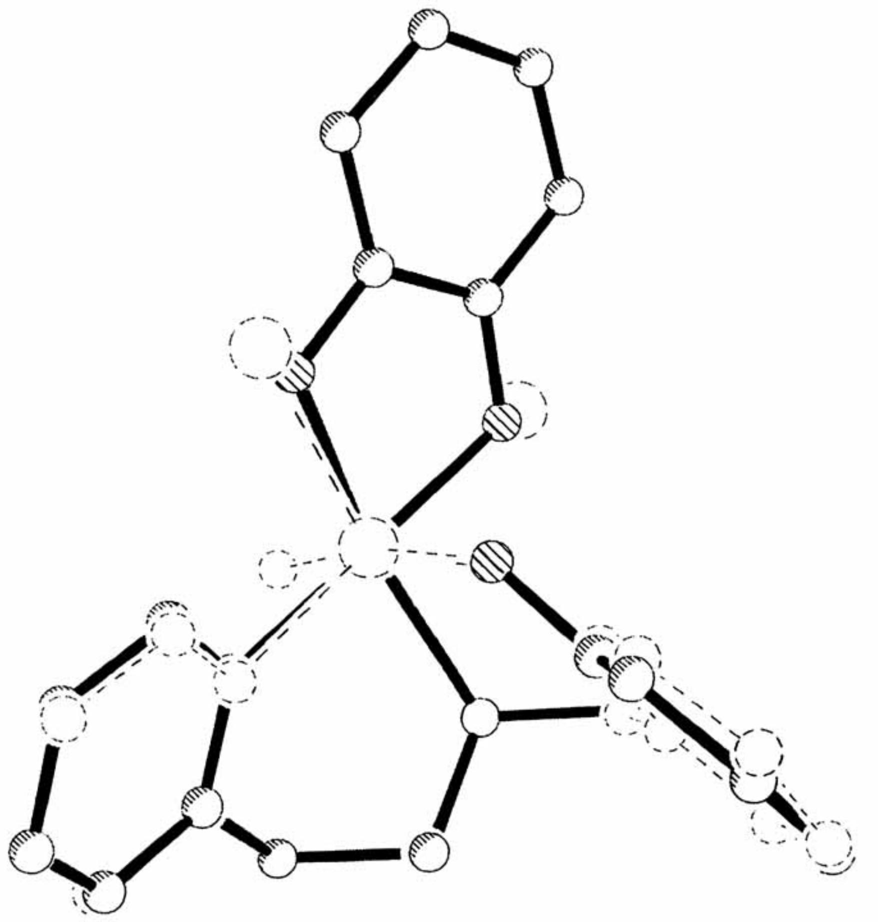

FIGURE 2 Superimposition of **1** and $[ReOCl_2(L_3)]$ (dashed line) molecules.

donor Schiff base ligand *N*-(2-hydroxyphenyl)salicylideneimine (H_2ONO) led to the formation of ReOCl(MeOH)(ONO), in which the terdentate ligand is coordinated in the equatorial plane *cis* to the oxo oxygen with a solvent molecule methanol in the *trans* position. The further reaction with an excess of the didentate *ON* donors *N*-phenylsalicylideneimine or 8-quinolinol (HON) led to the displacement of chloride and methanol to give ReO(ONO)(ON) with the phenolate oxygen atom of the didentate chelate in the *trans* site to Re=O [18].

A previous study with a number of terdentate *ONN*-donor Schiff base ligands gave the products *trans*-[$MOCl_2$(ONN)] (M = Re, Tc) [19]. A crystal structure analysis of a technetium analogue showed that the central imino nitrogen of these Schiff bases is located *trans* to the oxo group. Due to the *trans* arrangement of the two chlorides it is therefore intimated that it would be impossible to prepare oxorhenium(V) complexes containing 'mixed' di- and terdentate chelates by the substitution of the chlorides by dibasic ligands.

We have previously [12] isolated the complex [$ReOCl_2(L_3)$], where L_3^- is an *ONN*-donor ligand containing a phenolate oxygen, secondary amino nitrogen and a pyridine nitrogen as donor atoms. A crystal structure determination showed that it is the phenolate oxygen that occupies the site *trans* to the rhenyl oxo oxygen, and that the two chlorides have a *cis* disposition. In our opinion, [$ReOCl_2(L_3)$] thus presented an ideal starting complex to synthesize new complexes with 'mixed' didentate *OO* donor and terdentate *ONN* donor ligands by simple substitution of the *cis* chlorides. Although this simple synthetic method was successful for **2**, it was unsuitable for complexes **1** and **3**. The latter complex was prepared by the substitution of ethylene glycolate by oxalic acid from **2**, while **1** was isolated from the one-pot reaction of $ReOCl_4^-$ with two-fold molar excesses of HL_3 and H_2cat.

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