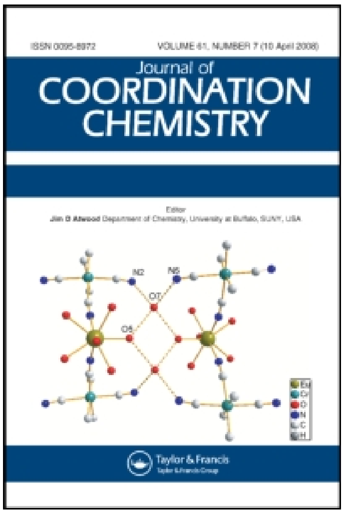

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF OXORHENIUM(V) COMPLEXES WITH LIGANDS OF THE PYRIDYLAMINOPHENOL TYPE CONTAINING THE ONN DONOR ATOM SET

A. Abrahams[a]; G. Bandoli[b]; S. Gatto[b]; T. I. A. Gerber[a]; J. G. H. Du Preez[a]
[a] Department of Chemistry, University of Port Elizabeth, Port Elizabeth, South Africa [b] Department of Pharmaceutical Science, University of Padova, Padova, Italy

To cite this Article Abrahams, A. , Bandoli, G. , Gatto, S. , Gerber, T. I. A. and Preez, J. G. H. Du(1997) 'SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF OXORHENIUM(V) COMPLEXES WITH LIGANDS OF THE PYRIDYLAMINOPHENOL TYPE CONTAINING THE ONN DONOR ATOM SET', Journal of Coordination Chemistry, 42: 4, 303 — 320

To link to this Article: DOI: 10.1080/00958979708022860

URL: http://dx.doi.org/10.1080/00958979708022860

J. Coord. Chem., 1997, Vol. 42, pp. 303–320
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF OXORHENIUM(V) COMPLEXES WITH LIGANDS OF THE PYRIDYLAMINOPHENOL TYPE CONTAINING THE ONN DONOR ATOM SET

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;* [b]*Department of Pharmaceutical Science, University of Padova, Via Marzolo 5, 35131 Padova, Italy*

(Received 9 October 1996)

Monooxo complexes of rhenium(V) with 2-[[[(2-pyridinyl)ethyl]amino]methyl]phenol (HL_2) and some of its derivatives, containing the ONN donor-atom set, have been synthesized. The complexes with general formula $[ReOCl_2(L_n)]$ were characterized by various physical techniques, including IR and NMR. X-ray structures of $[ReOCl_2(L_n)]$ (n = 2,3,5; HL_3 = 2-[[[2-(dimethylamino)ethyl]amino]methyl]phenol; HL_5 = 2-[[(2-pyridinylmethyl)ethylamino]methyl]phenol) were determined. Crystals of $[ReOCl_2(L_2)]$ (**2**) are rhombohedral, $R3$, a = 13.915(2)Å, α = 81.76(2)°, Z = 6; those of $[ReOCl_2(L_3)]$ (**3**) are monoclinic, $C2/c$, a = 25.92(2), b = 9.426(8), c = 28.38(2)Å, β = 100.33(9)°, Z = 16. $[ReOCl_2(L_5)]$, (**5**), is monoclinic, $P2_1$, a = 7.380(4), b = 11.743(7), c = 8.346(5)Å, β = 94.74(5)°, Z = 2. The structures were solved by the Patterson method and refined by full-matrix least-squares to R = 0.038, 0.036 and 0.062 for complexes **2**, **3** and **5**, respectively. In all three complexes the multidentate L_n^- ligands act as terdentate ONN-donors, with the phenolate oxygen occupying the site *trans* to the oxo oxygen.

Keywords: rhenium(V); terdentate ligands; X-ray structures

INTRODUCTION

Due to the interest in correlations of rhenium and technetium chemistry and the potential radiotherapeutical applications of ^{186}Re and ^{188}Re [1], we are studying the interaction of potentially terdentate ligands with the oxorhenium(V) core.

---

*Authors for correspondence.

During the last few years complexes of oxorhenium(V) and oxotechnetium(V) with dianionic terdentate ONX (X=O or S) donor Schiff base ligands (containing an imino nitrogen) have been well studied [2-4]. In the case of oxorhenium(V) the ligand is completely bonded to the metal on the equatorial plane with respect to the Re=O linkage, with a *halogen atom or small oxygenated molecule* (H_2O, MeOH) *trans* to Re=O in distorted octahedral products of the type ReOCl(ONX)(MeOH).

Only one study of oxorhenium(V) complexes containing terdentate Schiff base ligands with the ONN donor-atom set has appeared in the literature [5]. Six-coordinate complexes of the type [$ReOCl_2$(ONN)] were obtained from the ligand exchange reactions of $ReOCl_4^-$ with HONN. X-Ray diffraction and spectrophotometric analyses showed that the ONN ligands are coordinated to the metal in an unusual fashion, with the central *imino nitrogen* located *trans* to the oxo oxygen. It was intimated that the *trans*-labilizing effect of the oxo oxygen seems to be inactive in these complexes.

In this account we report on complexes that were isolated from the reactions of *trans*-$ReOCl_3(PPh_3)_2$ or $ReOCl_4^-$ with terdentate ligands of the pyridylaminophenol type (Figure 1). These chelates are very similar to the abovementioned ONN donor Schiff base ligands, except that they contain an amino nitrogen in place of the imino nitrogen.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used as received. Solvents were purified and dried before use. Literature methods were used for the syntheses of *trans*-$ReOCl_3(PPh_3)_2$ [6] and (*n*-Bu_4N)[$ReOCl_4$] [7]. The synthesis of ligands HL_1-HL_4 was based on a literature method [8]. HL_5 and HL_6 were prepared from the reaction of HL_1 with ethyl bromide and benzyl bromide, respectively, by using a published procedure [9].

Instrumentation

Scientific instrumentation used in this study is the same as reported elsewhere [10]. Infrared spectra were obtained in KBr discs and ^1H n.m.r. 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.

Synthesis of the Complexes

Cis-[ReOCl$_2$(L$_1$)] (1)

The salt (n-Bu$_4$N)[ReOCl$_4$] (102 mg, 170 μmol) was dissolved in 10 cm^3 of acetone, and an equimolar amount of HL$_1$ (37.3 mg), dissolved in acetone (10 cm^3), was added to the yellow solution. The colour of the solution changed immediately to apple green, and it was heated under reflux for 6h. After cooling to room temperature, the solution was filtered. Slow evaporation of the filtrate at room temperature deposited fine green needles, which were removed by

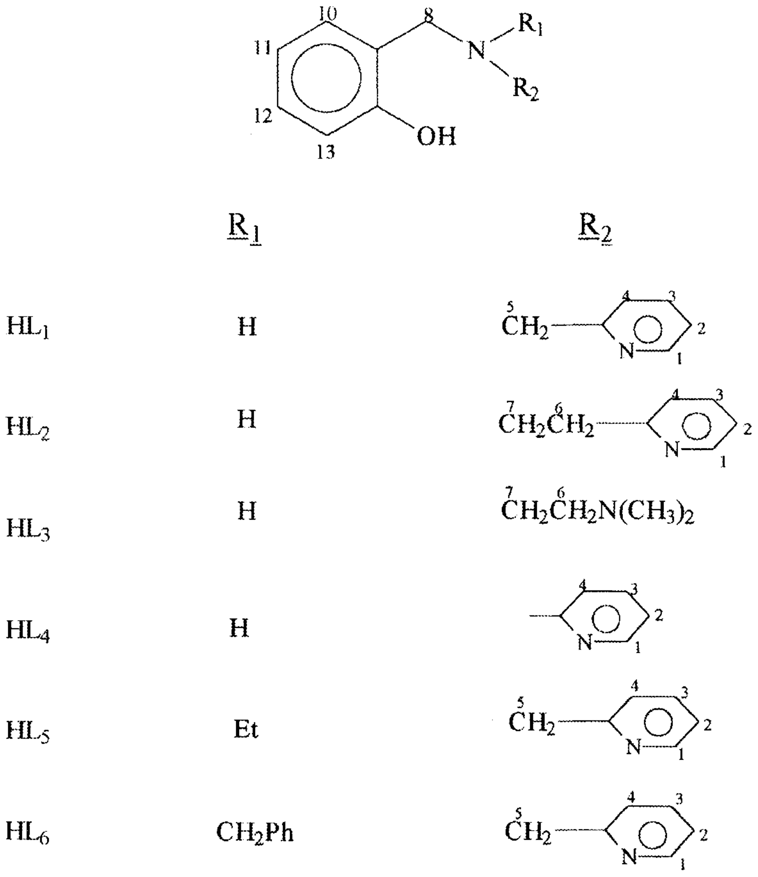

FIGURE 1 Ligands used in this study; (HL$_1$ = 2-[[(2-pyridinylmethyl)amino]methyl]phenol; HL$_2$ = 2-[[[(2-pyridinyl)ethyl]amino]methyl]phenol; HL$_3$ = 2-[[[2-(dimethylamino)ethyl]amino]methyl-]phenol; HL$_4$ = 2-[[(2-pyridyl)amino]methyl]phenol; HL$_5$ = 2-[[(2-pyridinylmethyl)ethylamino]methyl]phenol; HL$_6$ = 2-[[(2-pyridinylmethyl)benzylamino]methyl]phenol.)

filtration, washed with acetone (3 × 2 cm^3), and dried under vacuum. Yield 64%; m.p. > 350° C. *Anal.*: calcd.: C, 32.10; H, 2.69; N, 5.76%. Found: C, 32.21; H, 2.53; N, 5.88%. IR: ν(Re=O) 966(vs); ν(N-H) 3156(s); δ(py) 1615(s); ν(C-O) 1273(vs); ν(Re-Cl) 322(m), 311(m) cm^{-1}. ^1H n.m.r.: δ9.29 (d, 1H, H^1); 7.98 (t, 1H, H^3); 7.78 (t, 1H, H^2); 7.62 (d, 1H, H^4); 7.14 (d, 1H, H^{13}); 6.83 (t, 1H, H^{12}); 6.69 (t, 1H, H^{11}); 5.96 (d, 1H, H^{10}); 5.05 (d, 1H, H^{5a}); 4.67 (dd, 1H, H^{5b}); 4.39 (d, 1H, H^{8a}); 4.09 (dd, 1H, H^{8b}) ppm. Electronic spectrum: 344(9800), 255(22500).

Cis-[$ReOCl_2(L_2)$] (2)

To a solution of HL_2 (55.3 mg, 240 μmol) in acetone (10 cm^3) was added *trans*-$ReOCl_3(PPh_3)_2$ (103 mg, 120 μmol) in 10 cm^3 of acetone. The mixture was gently heated under reflux for 24h, and during this time the colour changed from yellow-green to very dark green. After cooling to room temperature, a green precipitate was filtered from the solution, and it was washed with benzene and diethylether. The mother liquor yielded a batch of green needles on slow evaporation. Crystals suitable for X-ray analysis were grown from acetonitrile. Total yield 63%; m.p. 199° C. *Anal.*: calcd.: C, 33.60; H, 3.02; N, 5.60%. Found: C, 33.99; H, 3.11; N, 5.62%. IR: ν(Re=O) 966(vs); ν(N-H) 3176(s); δ(py) 1617(s); ν(C-O) 1277(vs); ν(Re-Cl) 315(m), 301(m) cm^{-1}. ^1H n.m.r.: δ9.43 (br s, 1H, NH); 9.32(d, 1H, H^1); 7.91 (t, 1H, H^3); 7.78 (t, 1H, H^2); 7.61 (d, 1H, H^4); 7.08 (d, 1H, H^{13}); 6.98 (t, 1H, H^{11}); 6.72(t, 1H, H^{12}); 6.35 (d, 1H, H^{10}); 3.46 (s, 2H, H^8); 3.11-3.17(m, 3H, H^6 and H^7); 2.85(br s, 1H, H^6) ppm. Electronic spectrum: 340 (5300), 250 (11000).

Cis-[$ReOCl_2(L_3)$] (3)

A solution of *trans*-$ReOCl_3(PPh_3)_2$ (103 mg) in acetone (10 cm^3) was added to 48 mg of HL_3 (250 μmol) in 10 cm^3 of acetone, and the mixture was heated under reflux for 6h. During this time the solution changed colour from yellow-green to green, and a green precipitate formed. The solid was removed and washed with acetone (3 × 2 cm^3), and dried under vacuum; yield 91%; m.p. 278° C. *Anal.*: calcd.: C, 28.33; H, 3.67; N, 6.01%. Found: C, 28.10; H, 3.57; N, 6.10%. IR: ν(Re=O) 961(s); ν(N-H) 3150(m); ν(C-O) 1277(s); ν(Re-N) 436(s); ν(Re-Cl) 313(m), 307(m) cm^{-1}. ^1H n.m.r.: δ9.28 (br s, 1H, NH); 7.63(d, 1H, H^{13}); 7.45(t, 1H, H^{11}); 7.28(t, 1H, H^{12}); 6.60 (d, 1H, H^{10}); 3.78 (t, 2H, H^6); 3.61 (d, 2H, H^8); 3.34 (t, 2H, H^7); 2.85(s, 6H, CH_3) ppm. Electronic spectrum: 338(3700), 242(7700).

Trans-$[ReOCl_2(L_4)(PPh_3)]$ (4)

An acetone solution of *trans*-$ReOCl_3(PPh_3)_2$ (101 mg in 10 cm^3) was added to 51 mg of HL_4, dissolved in 10 cm^3 of acetone. After the mixture was heated under reflux for 3h and cooled to room temperature, a light green solid was removed by filtration, and it was washed with benzene, diethylether and acetone, and dried under vacuum. The yield was 71%; m.p. 197° C. *Anal.*: calcd.: C, 49.05; H, 3.57; N, 3.81%. Found: C, 49.55; H, 3.39; N, 3.78%. IR: ν(Re=O) 970(s); ν(N-H) 3177(s); δ(py) 1630(s); ν(C-O) 1284(s); ν(Re-N) 430(s); ν(P-C) 1099(s); ν(Re-Cl) 308 cm^{-1}. ^1H n.m.r.: δ8.98 (br s, 1H, $\mathrm{N}H$); 7.95 (d, 1H, H^1); 7.52-7.69 (m, 17H, $\mathrm{P}Ph_3$, H^3, H^{13}); 7.43 (t, 1H, H^2); 7.26 (d, 1H, H^4); 7.16 (t, 1H, H^{11}); 6.88 (d, 1H, H^{10}); 6.82 (t, 1H, H^{12}); 4.51 (d, 2H, H^8) ppm. Electronic spectrum: 309(3300), 272(4400).

Cis-$[ReOCl_2(L_5)]$ (5)

A mixture of 101 mg of *trans*-$ReOCl_3(PPh_3)_2$ and 61 mg of HL_5 (250 μmol) in 20 cm^3 of ethanol was heated under reflux for 18h. After cooling to room temperature, the dark green solution was filtered, and left to evaporate slowly overnight at room temperature. The green paralellepipeds that deposited were removed by filtration, washed with benzene, diethylether and acetone, and dried under vacuum. They were suitable for X-ray diffraction studies. The yield was 57%; m.p. 242° C. *Anal.*: calcd.: C, 32.02; H, 3.33; N, 5.45%. Found: C, 35.13; H, 3.27; N, 5.39%. IR: ν(Re=O) 961(s); δ(py) 1613(s); ν(C-O) 1270(s); ν(Re-N) 432(s); ν(Re-Cl) 321(m), 310(m) cm^{-1}. ^1H n.m.r.: δ9.18 (d, 1H, H^1); 7.94 (t, 1H, H^3); 7.72 (t, 1H, H^2); 7.51 (d, 1H, H^4); 7.16 (d, 1H, H^{13}); 6.82 (t, 1H, H^{11}); 6.64 (t, 1H, H^{12}); 5.94 (d, 1H, H^{10}); 5.29 (d, 1H, H^{5a}); 4.79 (d, 1H, H^{5b}); 4.14 (d, 1H, H^{8a}); 3.97 (d, 1H, H^{8b}); 4.36 (q, 2H, $\mathrm{C}H_2^{Et}$); 1.51 (t, 3H, $\mathrm{C}H_3$) ppm. Electronic spectrum: 340(3400), 258(8150).

Cis-$[ReOCl_2(L_6)]$ (6)

This complex was synthesized following the same procedure as for **5**. The yield was 68%; m.p. 254° C. *Anal.*: calcd.: C, 41.67; H, 3.32; N, 4.86%. Found: C, 41.59; H, 3.29; N, 4.71%. IR: ν(Re=O) 965(s); δ(py) 1611(s); ν(C-O) 1269(vs); ν(Re-N) 430(s); ν(Re-Cl), 324(m), 329(m) cm^{-1}. ^1H n.m.r.: δ9.19 (d, 1H, H^1); 7.90 (t, 1H, H^3); 7.79 (d, 1H, H^{13}); 7.71 (t, 1H, H^2); 7.50-7.61 (m, 6H, H^4, C_6H_5); 6.79 (t, 1H, H^{11}); 6.53 (t, 1H, H^{12}); 5.93 (d, 1H, H^{10}); 5.52 (d, 1H, H^{5a}); 5.04 (d, 1H, H^{5b}); 5.31 (d, 1H, H^{8a}); 4.85 (d, 1H, H^{8b}); 3.39 (s, 2H, $\mathrm{C}H_2$) ppm. Electronic spectrum: 342(3900), 262(11300).

Crystallographic Measurements and Structure Resolution of $[ReOCl_2(L_2)]$ (2), $[ReOCl_2(L_3)]$ (3) and $[ReOCl_2(L_5)]$ (5)

Details of the crystal data, intensity measurements and data processing for the three complexes are summarized in Table I.Final unit-cell parameters were obtained by least-squares fits of the setting angles for 50 reflections with $2\theta > 17°$ for **2**, and from 30 high angle data with $2\theta > 21°$ for **3** and **5**. For the structure factors, corrections for Lorentz and polarization effects and absorption were made. The structures were solved by standard heavy-atom methods with subsequent Fourier difference maps yielding the positions of the light atoms. To ensure an acceptable observation/variable ratio the phenyl ring in **3** was treated as a rigid body and anisotropy was applied only to Re and Cl atoms. In all cases refinement proceeded routinely and no anomalies in temperature factors or excursions of election 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. For **3** the peaks were broad; the crystal was a weak diffractor and its metrical data (Table III) should be interpreted with caution. The SHELXTL-PLUS package of computer programs [11] was employed for the solution and refinement of the structures and ORTEP [12] used to plot the structures. Additional material comprises anisotropic thermal parameters (Table A), bond lengths (Table B) and angles (Table C), and a listing of observed/calculated structure factors (Table D), and is available from the authors upon request.

RESULTS AND DISCUSSION

The reactions between $(n\text{-}Bu_4N)[ReOCl_4]$ or *trans*-$ReOCl_3(PPh_3)_2$ with the HL_n ligands containing the ONN donor-atom set in acetone or ethanol led to the isolation of neutral six-coordinated complexes of general formula $[ReOCl_2(L_n)]$ ($n \neq 4$), as described in equations (*1*) and (*2*).

$$(n\text{-}Bu_4N)[ReOCl_4] + HL_n \rightarrow [ReOCl_2(L_n)] + (n\text{-}Bu_4N)Cl + HCl \qquad (1)$$

$$ReOCl_3(PPh_3)_2 + HL_n \rightarrow [ReOCl_2(L_n)] + 2PPh_3 + HCl \qquad (2)$$

The ligands HL_n ($n \neq 4$) act as terdentate chelates. However, ligand HL_4 reacts to form the complex $[ReOCl_2(L_4)(PPh_3)]$ (**4**), in which L_4^- is coordinated in a didentate mode.

TABLE I Structure determination summary*.

	(2)	(3)	(5)
Crystal Data:			
Empirical Formula	$C_{14}H_{15}Cl_2N_2O_2Re\cdot 1/3CH_3CN\cdot 1/3H_2O$	$C_{15}H_{17}N_2O_2Cl_2Re$	$C_{11}H_{17}N_2O_2Cl_2Re$
M	520.1	514.4	466.4
Colour; Habit	violet spheroids	green lozenges	green paralellepipeds
Crystal Size (mm)	radius *ca* 0.12 mm	0.05 × 0.10 × 0.20	0.05 × 0.10 × 0.10
Crystal System	rhombohedral	monoclinic	monoclinic
Unit Cell Dimensions:			
a/Å	13.915(2)	25.92(2)	7.380(4)
b/Å		9.426(8)	11.743(7)
c/Å		28.38(2)	8.346(5)
α/°	81.76(2)	90	90
β/°	90	100.33(9)	94.74(5)
γ/°	90	90	90
U/Å^3	2618(1)	6821(6)	720.8(7)
D_c/Mgm^{-3}	1.979	2.004	2.149
μ/mm^{-1}	7.28	74.5	87.9
Z	6	16	2
Space Group	RR-3	$C2/c$ (No. 15)	$P2_1$ (No. 4)
Data Collection:			
2θ Range/°	4.5-50.0°	4.5-44.0°	4.5-45.0°
Index Ranges, $h\ k\ l$	0 to 16, − 16 − 16, − 16 − 16	− 27 to 27, 0 − 9, − 29 to 29	0 − 7, 0 − 12, − 8 to 8
Independent Reflections	2179	4203(R_{int} = 0.040)	998(R_{int} = 0.061)
Observed Reflections	1484($F_o > 4\sigma(F_o)$)	2710($F_o > 3\sigma(F_o)$)	850 ($F_o > 3\sigma(F_o)$)
Solution and Refinement:			
Weighting Scheme (w^{-1})	$\sigma^2(F) + 0.0154F^2$	$\sigma^2(F) + 0.0074F^2$	$\sigma^2(F) + 0.1463F^2$
Number of Parameters Refined	198	301	75
Final R, R' indices (observed data)	0.038, 0.055	0.036, 0.049	0.062, 0.080
Goodness-of-fit	0.41	0.54	0.50

*Details in common: Nicolet-Siemens R3m/V diffractometer, MoKα radiation (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 reflections every 150; function minimized $\Sigma w(|F_o| - |F_c|)^2$; H atoms undetectable from ΔF.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$).

		(2)		
	x/a	*y/b*	*z/c*	U(*)
Re	−455(1)	1971(1)	4942(1)	28(1)
Cl(1)	492(3)	3254(3)	4299(3)	42(1)
Cl(2)	162(3)	1188(3)	3509(3)	45(1)
O(1)	329(6)	1275(7)	5643(7)	46(4)
O(2)	−1549(6)	2631(6)	4309(6)	32(3)
N(1)	−1115(7)	2734(8)	6157(8)	34(4)
N(2)	−1440(8)	834(8)	5425(8)	35(4)
C(1)	−1193(11)	3744(11)	6020(12)	48(6)
C(2)	1536(12)	4290(12)	6780(11)	50(6)
C(3)	−1791(12)	3791(14)	7656(14)	63(7)
C(4)	−1768(12)	2831(13)	7824(12)	53(6)
C(5)	−1457(10)	2300(11)	7039(9)	34(5)
C(6)	−1478(11)	1217(11)	7143(10)	51(6)
C(7)	−2018(10)	892(11)	6386(10)	37(5)
C(8)	−2064(10)	718(10)	4673(11)	40(5)
C(9)	−2793(9)	1602(9)	4454(10)	32(5)
C(10)	−3749(11)	1532(11)	4402(10)	43(6)
C(11)	−4432(10)	2326(11)	4173(11)	44(6)
C(12)	−4098(10)	3261(11)	3975(10)	41(5)
C(13)	−3156(9)	3348(9)	4060(9)	34(5)
C(14)	−2491(8)	2525(9)	4249(9)	27(4)
N(3)	3355(10)	3355(10)	3355(10)	67(7)
C(15)	2931(10)	2931(10)	2931(10)	48(7)
C(16)	2393(10)	2393(10)	2393(10)	56(7)
O(3)	827(14)	827(14)	827(14)	184(16)
		(3)		
	x	*y*	*z*	U(*)
Re	8436(1)	10000	9382(1)	24
Cl(1)	7422(14)	8080(9)	9636(12)	37
Cl(2)	9859(16)	9449(10)	7014(12)	44
O(1)	10254(49)	9993(61)	10 452(38)	81
O(2)	6345(32)	10438(20)	7975(26)	28
N(1)	8798(37)	11847(27)	9125(30)	17
N(2)	6950(39)	10614(28)	11421(31)	26
C(1)	5686(34)	11195(19)	6919(27)	29
C(2)	3921	11127	6187	51
C(3)	3272	11971	5111	62
C(4)	4389	12882	4768	39
C(5)	6154	12950	5500	34
C(6)	6803	12106	6576	34
C(7)	8773(68)	12163(45)	7376(57)	53
C(8)	7531(57)	12456(43)	10215(48)	35
C(9)	7505(60)	11769(44)	11768(49)	47
C(10)	4941(51)	10438(34)	11167(43)	34
C(11)	7667(52)	10020(80)	13035(42)	50

TABLE II *(continued)* Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$).

		(5)		
	x	*y*	*z*	*U*(*)
Re(1)	3386(1)	2481(1)	3896(1)	30
Cl(1)	2689(2)	2896(5)	4320(2)	49
Cl(2)	3958(2)	2111(5)	4632(1)	44
O(1)	3229(4)	795(11)	3700(4)	46
O(2)	3567(4)	4506(11)	3940(3)	32
N(1)	4026(4)	2349(13)	3476(4)	29
N(2)	2968(4)	3191(14)	3218(4)	28
C(1)	3706(6)	5400(17)	3619(6)	37
C(2)	3462(6)	6705(18)	3492(6)	42
C(3)	3632(7)	7586(19)	3141(7)	50
C(4)	4050(8)	7152(23)	2925(7)	66
C(5)	4314(8)	5858(23)	3064(7)	65
C(6)	4125(6)	5007(15)	3407(6)	28
8C(7)	4403(6)	3602(16)	3553(7)	48
C(8)	3743(6)	2268(18)	2945(6)	44
C(9)	3259(6)	3147(18)	2869(5)	34
C(10)	3099(7)	3881(20)	2429(6)	48
C(11)	2634(7)	4602(21)	2379(7)	55
C(12)	2323(8)	4678(22)	2730(8)	65
C(13)	2527(7)	3954(21)	3158(6)	53
C(14)	4334(6)	983(19)	3591(6)	43
C(15)	4720(8)	641(21)	3248(7)	61
Re(2)	8734(1)	1857(1)	6235(1)	32
Cl(1A)	8657(2)	4018(5)	6653(2)	53
Cl(2A)	9331(2)	1109(5)	6930(1)	47
O(1A)	8183(4)	1089(13)	6334(4)	51
O(2A)	9324(4)	2612(10)	5964(4)	35
N(1A)	8820(5)	−17(12)	5779(4)	31
N(2A)	8324(5)	2559(14)	5557(4)	33
C(1A)	9407(6)	2531(17)	5511(5)	29
C(2A)	9473(6)	3776(18)	5240(6)	39
C(3A)	9546(6)	3597(16)	4768(6)	35
C(4A)	9545(6)	2243(17)	4552(6)	42
C(5A)	9478(6)	1034(19)	4820(6)	43
C(6A)	9410(6)	1168(17)	5295(6)	33
C(7A)	9350(6)	−77(16)	5624(6)	37
C(8A)	8382(6)	51(16)	5366(6)	44
C(9A)	8270(5)	1584(16)	5203(5)	30
C(10A)	8106(6)	1941(20)	4720(6)	43
C(11A)	7994(6)	3376(18)	4606(6)	41
C(12A)	8041(7)	4369(19)	4964(7)	50
C(13A)	8207(6)	3950(19)	5443(6)	36
C(14A)	8764(8)	−1368(22)	6057(8)	66
C(15A)	8842(13)	−2681(35)	5855(12)	69
C(15B)	9104(39)	−1775(108)	6333(34)	124

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

TABLE III Selected bond lengths (Å) and angles (°).

	(2)		
Re-Cl(1)	2.368 (4)	Re-N(2)	2.21 (1)
Re-Cl(2)	2.401 (4)	O(2)-C(14)	1.36 (2)
Re-O(1)	1.676 (9)	N(2)-C(7)	1.47 (2)
Re-O(2)	1.921 (9)	N(2)-C(8)	1.49 (2)
Re-N(1)	2.15 (1)		
Cl(1)-Re-Cl(2)	88.7 (1)	O(1)-Re-N(1)	90.6 (4)
Cl(1)-Re-O(1)	99.4 (3)	O(1)-Re-N(2)	86.4 (4)
Cl(1)-Re-O(2)	91.4 (3)	O(2)-Re-N(1)	84.9 (4)
Cl(1)-Re-N(1)	91.5 (3)	O(2)-Re-N(2)	83.0 (4)
Cl(1)-Re-N(2)	174.0 (3)	N(1)-Re-N(2)	89.8 (4)
Cl(2)-Re-O(1)	94.4 (3)	Re-O(2)-C(14)	139.6 (7)
Cl(2)-Re-O(2)	90.0 (3)	Re-N(2)-C(7)	116.0 (9)
Cl(2)-Re-N(1)	174.9 (3)	Re-N(2)-C(8)	113.5 (8)
Cl(2)-Re-N(2)	89.5 (3)	C(7)-N(2)-C(8)	111 (1)
O(1)-Re-O(2)	168.4 (4)		
	(5)		**(3)**
Re-Cl(1)	2.375 (5)	2.383 (5)	2.39 (1)
Re-Cl(2)	2.360 (5)	2.383 (5)	2.40 (1)
Re-O(1)	1.71 (1)	1.67 (1)	1.55 (3)
Re-O(2)	1.96 (1)	1.96 (1)	1.93 (2)
Re-N(1)	2.21 (1)	2.22 (1)	2.20 (3)
Re-N(2)	2.14 (1)	2.13 (1)	2.22 (3)
O(2)-C(1)	1.34 (2)	1.34 (2)	1.32 (3)
N(1)-C(7)	1.52 (2)	1.52 (2)	1.50 (4)
N(1)-C(8)	1.55 (3)	1.48 (2)	1.53 (4)
N(2)-C(9)	1.35 (2)	1.35 (2)	1.44 (5)
O(1)-Re-O(2)	164.8 (5)	166.5 (5)	164 (2)
Cl(1)-Re-Cl(2)	89.4 (2)	86.7 (2)	88.9 (4)
Cl(1)-Re-N(1)	173.5 (3)	173.8 (3)	168.8 (8)
Cl(2)-Re-N(2)	168.1 (3)	169.5 (4)	174.6 (8)
N(1)-Re-N(2)	80.9 (4)	78.8 (5)	80 (1)
Re-O(2)-C(1)	131 (1)	128.7 (9)	145 (2)
N(1)-C(7)-C(6)	112 (1)	110 (1)	110 (3)
C(7)-N(1)-C(8)	111 (1)	112 (1)	120 (3)
Re-N(1)-C(8)	104.9 (8)	106.5 (9)	108 (2)
Re-N(2)-C(9)	113.0 (9)	115 (1)	108 (2)
N(1)-C(8)-C(9)	111 (1)	111 (1)	108 (3)
N(2)-C(9)-C(8)	119 (1)	115 (1)	111 (3)

Characterization of the Complexes

All the complexes are green in colour, air stable, diamagnetic and non-electrolytes in acetonitrile and DMF. The infrared spectra of the complexes prove that the multidentate ligands are coordinated, as were shown by shifts in absorptions relative to those of the free ligands. The spectra are characterized by a very strong absorption in the range 961-970 cm^{-1}, which is assigned to ν(Re=O). A strong band around 3150 cm^{-1} has been assigned to ν(NH), proving that the amino nitrogen remains protonated in the complexes **1**-**4**. Deprotonation of the phenolic OH group is suggested by the absence of a band in the region 3200-3500 cm^{-1}, and coordination of the deprotonated phenolic oxygen to rhenium is reflected in ν(C-O) around 1275 cm^{-1}. Two frequencies in the region 300-330 cm^{-1} are ascribed to rhenium(V)-chlorine stretches. Only one Re-Cl stretch was observed for **4**, implying that the two chlorides are in equivalent *trans* positions to each other in $[ReOCl_2(L_4)(PPh_3)]$.

Analyses of the ^1H NMR spectra show the ligands L_n ($n \neq 4$) to be completely coordinated; the absence of O-H phenolic proton signals for all the complexes supports phenolate coordination. Furthermore, signals of protons close to the ONN coordinating atoms are all shifted downfield with respect to those of the free ligands. The appearance of the N*H* proton as a broad singlet the furthest downfield around δ9.30 ppm in complexes **1**-**3** suggests that the ligands L_n^- ($n \neq$ **4**) act as terdentate monoanionic chelates. Although the spectrum of complex **4** is complicated by the overlapping of the phenyl protons of PPh_3, it does provide information on the chelation of L_4^-. The signal of proton H^1, on the carbon adjacent to the pyridinic nitrogen, is in fact shifted slightly upfield to δ7.95 ppm on coordination to the metal, from δ8.06 ppm in the free ligand HL_4. This suggests that the pyridinic nitrogen is not coordinated in complex **4**, since the spectra of all the other complexes ($\neq$**3**) show a downfield shift of H^1 on coordination. L_4^- thus acts as a monoanionic didentate chelate.

Description of the Structures of (2), (3) and (5)

The structures (see Figures 2, 3 and 4) consist of discrete, monomeric and neutral oxorhenium complexes $[ReOCl_2(L)]$ packed with no intermolecular contacts shorter than the van der Waals radii sum. The coordination geometry around the rhenium is highly distorted octahedral; the two nitrogen atoms from the terdentate uninegative N(1), O(2), N(2)-donor ligand lie on the equatorial plane, along with the two *cis*-chlorides, while the phenolate O(2) atom is *trans* to the O(1)-oxo atom. In **5** the asymmetric unit comprises two molecules which are superimposable (Figure 5), the r.m.s being only 0.05Å when the fitting is performed using the eleven atoms nearest to Re; the molecules show no anomalies in structural data and therefore discussion of metrical parameters will refer to the mean values for the two molecules. In **2** the equatorial plane (Figure 2) is strictly planar and in the coordination sphere both the six-membered rings adopt the twist-boat conformation (D_2), the dihedral angle between the two aromatic rings being 81.4°. In the three complexes the O(1)-Re-O(2) axis is non-linear (168.4, 164.0 and 165.6° in **2**, **3** and **5**, respectively), and the rhenium atom is displaced from the mean equatorial plane by 0.11, 0.14 and 0.16Å in **2**, **3** and

5, respectively, towards the 'oxo' oxygen atom. As a measure of the octahedral distortion in the $Cl_2N_2O_2$ polyhedron, the Re atom is +1.09, +1.03 and +1.02Å from the Cl(2)Cl(1)O(1) plane and −1.29, −1.37 and −1.37Å from the N(1)N(2)O(2) one, the angles between the two triangular faces being 9.2, 8.3 and 7.9° for **2**, **3** and **5**, respectively. In **3** and **5** the four donor atoms deviate up to 0.05Å from the mean equatorial plane. The edge distances in **2** are in a rather large range (from 2.69Å for O(1)-N(2) to 3.33Å for Cl(1)-Cl(2)), while the interligand angles in the equatorial plane depart slightly from the ideal 90° (from 88.7° to 91.5°).

Bond lengths and angles within the "inner core" show no unusual features, being within the range expected from the comparison of other six-coordinate monooxorhenium(V) complexes containing the $O_2N_2Cl_2$ donor set, as can be seen in Table IV, and they will not be discussed. Only the Re-N distances deserve a comment. In fact, the Re-N_{py} distances (mean value of 2.15Å in **2** and **5**) are markedly shorter than the bonds from amino-N to Re(V) (2.21Å average).

If the structural data of **3** and **5** are compared (Figure 6), the main differences concern (i) the Re-O(2)-C(1)-C(6) and C(1)-C(6)-C(7)-N(1) torsion angles (−1.1

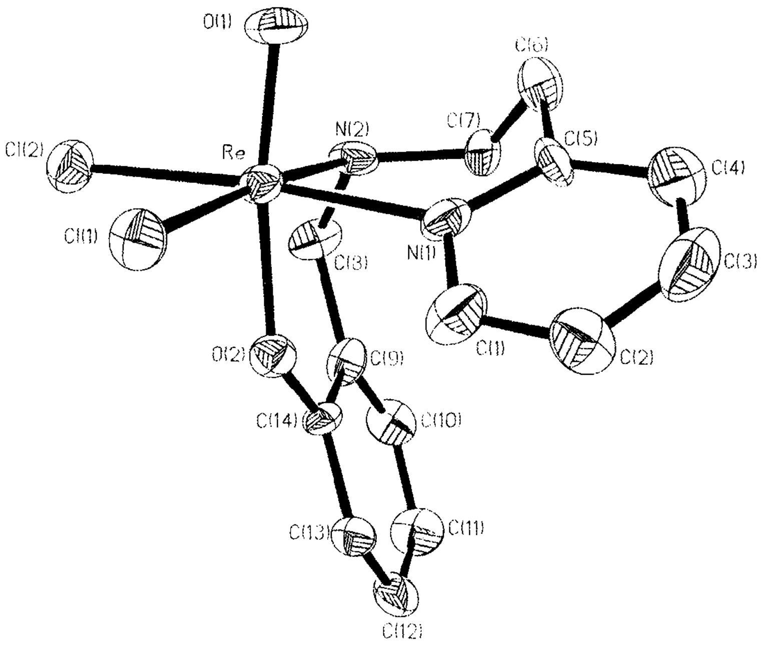

FIGURE 2 ORTEP drawing of the complex $[ReOCl_2(L_2)]$ (**2**). The atom numbering scheme and the thermal ellipsoids at the 40% probability level are shown.

and −43.0° for **3** to be compared with the values −54.1 and 56.9° for **5**), (ii) the dihedral angles between the mean equatorial plane and the six-membered ReO(2)C(1)C(6)C(7)N(1) ring (97.5° in **3** and 74.8° in **5**), (iii) the Re-N(2)-C(9)-C(8) and N(2)-C(9)-C(8)-N(1) torsion angles (45.1 and −56.7° for **3** *vs* 17.5 and −37.3° for **5**), and (iv) the Re-O(2)-C(1) bond angle (145° in **3**) decreases to 130° in **5**, as well as the C(7)-N(1)-C(8) angle (120 and 111° in **3** and **5**, respectively); the N(1)-Re-N(2) bite angle remains unchanged at 80°.

Complexes of rhenium(V) with terdentate ligands have been reasonably well studied [2-5]. With Schiff base ligands containing the ONO donor-atom set, six-coordinated complexes of formula ReOCl(ONO)(MeOH) were isolated, in which the terdentate ligand is completely coordinated to the metal on the equatorial

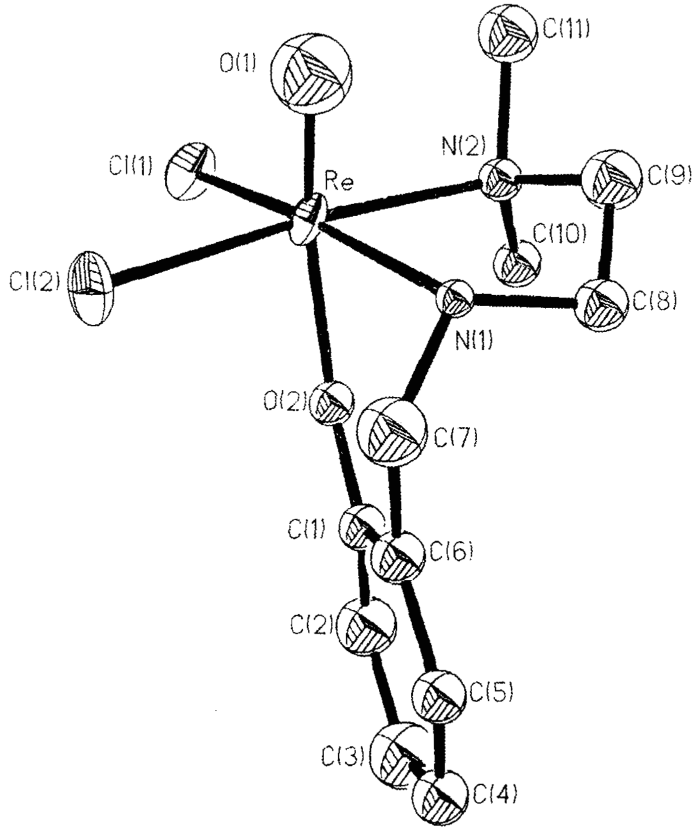

FIGURE 3 An ORTEP view of complex [$ReOCl_2(L_3)$] (**3**), showing the atom labelling scheme and the thermal ellipsoids at 40% probability level.

plane *cis* to the Re=O linkage, and with the solvent molecule MeOH in the *trans* site. With ONN donor-atom Schiff bases the neutral complexes [ReOCl$_2$(ONN)] were obtained. Spectroscopic data and a crystallographic study of a technetium analogue [5] showed that it is the central imino nitrogen of the Schiff base that is located *trans* to the oxo oxygen, with the phenolate oxygen donor atom coordinated on the equatorial *cis* plane.

The crystal structure determinations of complexes **2**, **3** and **5**, containing the ONN donor ligands L_n^- (n = 2,3,5) (see Figure 1), show that the phenolate oxygen donor atom occupies the site *trans* to the oxo oxygen, with the two nitrogen donor atoms coordinated in the *cis* plane. This is to be expected if the repulsion that is exerted by the oxo oxygen on the equatorial ligands is considered. This repulsion originates from the π electron density associated with the multiple Re=O bond, and is greater for ligands connected by formally covalent $L^-: \rightarrow M^+$ bonds than for donor-acceptor $L: \rightarrow M$ bonds [13]. It is thus clear that this repulsion on the equatiorial ligands increases in the order $N < Cl^- < O^-$, which is also the order of increasing hardness of the donor atoms as bases

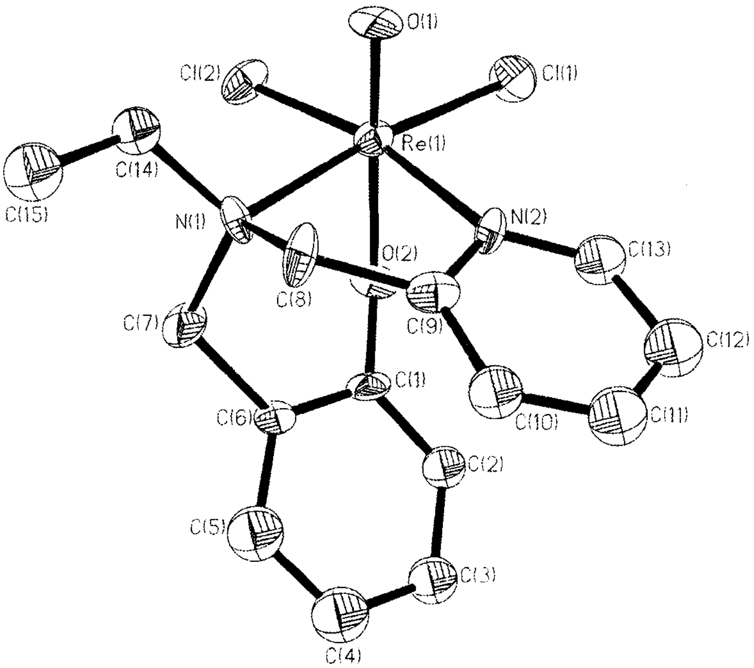

FIGURE 4 An ORTEP view of complex [ReOCl$_2$(L$_5$)] (**5**), showing the atom labelling scheme and the thermal ellipsoids, at 40% probability level.

[14]. This increasing hardness of the bases leads to increasing ionic character of their bonds with the hard acid rhenium(V), with the result that the harder basic groups are repelled more as a consequence of the higher population of their orbitals. This effect will mean that the affinity of the above donor atoms to occupy the coordination site *trans* to the oxo group will decrease in the order O^- > Cl^- > N.

Varying substituents on the amino nitrogen and altering the nature of the terminal nitrogen donor atom (pyridine *vs* $N(CH_3)_2$) have an insignificant effect on the bonding parameters of the complexes. Changing the chain length between the two nitrogen donors only has an effect in complex **4**, where didentate coordination of L_4^- occurs. However, this is not surprising since bond strain and steric effects will prevent the formation of a four-membered metallocycle through *N,N*-coordination.

Deprotonation of the secondary amino nitrogen in ligands L_n^- (n = 1-4) was never observed during this study, and all efforts to induce deprotonation were unsuccessful. In a previous study [15] of technetium(V) amine-oxime complexes,

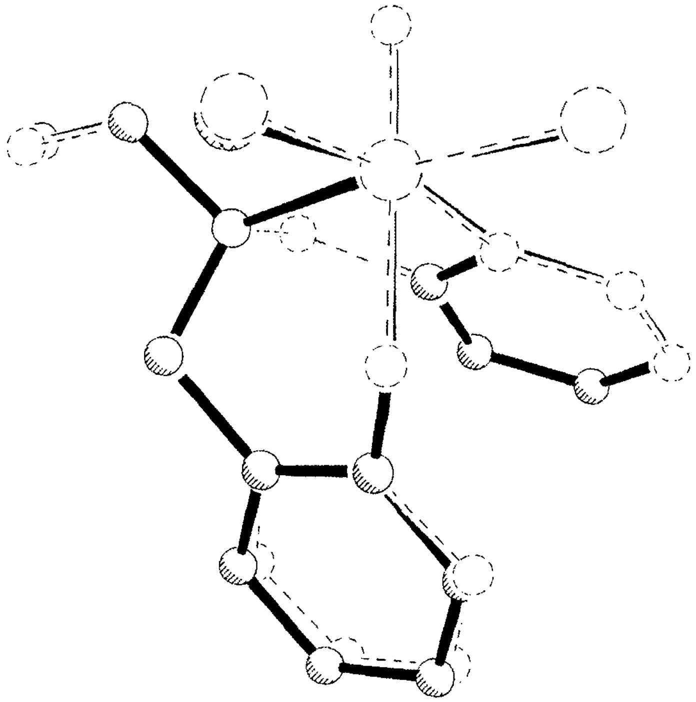

FIGURE 5 Superimposition of the two independent molecules of **5**.

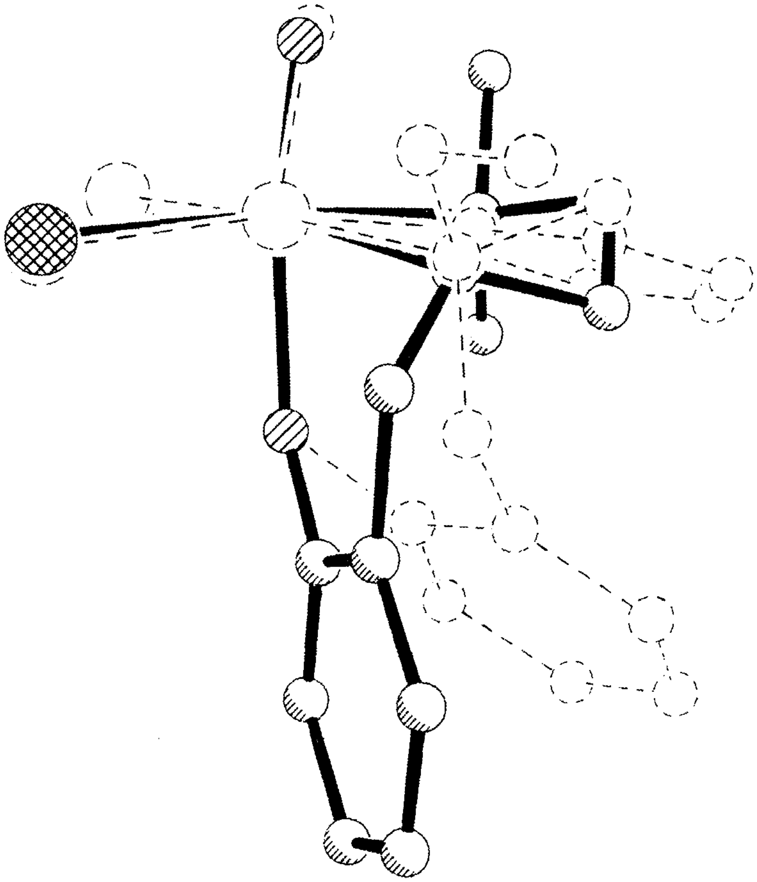

FIGURE 6 Superimposition of **3** (full line) and **5** (dashed line) molecules.

cases were observed in which the amine nitrogens were deprotonated and others in which they remained protonated. This anomalous behaviour was ascribed to electronic effects created by varying the amine-amine backbone length and thereby the overall ring size on complex formation.

Acknowledgements

T.I.A.G. and A.A. are grateful to the Foundation for Research Development and the University of Port Elizabeth for financial assistance.

TABLE IV Bond distances and angles in octahedral oxo-Re(V) complexes containing the $O_2N_2Cl_2$ donor set.

Complex	*Re-Cl*	*Re-O*	*Re = O*	*Re-N*	*O = Re-O*	*N-Re-N*	*Ref.*
$[ReO(OEt)(py)_2Cl_2]$	2.441(3); 2.366(3)	1.896(6)	1.684(7)	2.144(7); 2.132(7)	173.0(3)	178.5(3)	a
$[ReO(OEt)(7\text{-azaindole})_2Cl_2]$	2.414(3)	1.85(1)	1.70(1)	2.136(8)	180	177.2(3)	b
$[ReO(OSiMe_3)(py)_2Cl_2]$	2.393(1); 2.409(1)	1.889(4)	1.679(3)	2.133(4); 2.135(4)	177.0(2)	175.6(1)	c
$[ReO(BBQ{\cdot}OH)Cl_2]^*$	2.365(6); 2.367(5)	1.95(1)	1.69(1)	2.15(1); 2.13(2)	160.1(6)	93.7(6)	d
$[ReO\{(C_5H_4N)_2C(O)(OH)\}Cl_2]$	2.305(4); 2.32(1)	2.00(2)	1.67(2)	2.13(3); 2.14(3)	158(1)	85(1)	e
$[[ReO\{(C_5H_4N)_2C(O)(OH)\}Cl_2]_2Cl]^-$	2.353(3); 2.337(4)	1.966(5)	1.671(6)	2.143(9); 2.16(1)	156.6(3)	86.0(3)	f
(**2**)	2.368(4); 2.401(4)	1.921(9)	1.676(9)	2.15(1); 2.21(1)	168.4(4)	89.8(4)	present work
(**3**)	2.40(1); 2.39(1)	1.93(2)	1.55(3)	2.22(3); 2.20(3)	164(2)	80(1)	present work
(**5**)	2.379(5); 2.371(5)	1.96(1)	1.69(1)	2.22(1); 2.14(1)	165.6(5)	79.8(4)	present work
d	2.37	1.93	1.67	2.16	167		
m	2.37	1.93	1.68	2.14	166		
σ	0.03	0.04	0.04	0.03	8		
q_l	2.36	1.89	1.67	2.13	160		
q_u	2.4	1.96	1.69	2.16	170		

[*] BBQ = 2,3-bis-(2-pyridyl)benzoquinoxaline. [a] C. J. L. Lock and G. Turner, *Can. J. Chem.*, **55**, 333 (1977); [b] A.-M. Lebuis and A. L. Beauchamp, *Can. J. Chem.*, **71**, 2060 (1993); [c] S. Schmid and J. Strähle, *Z. Kristallogr.*, **198**, 49, (1992); [d] G. Bandoli, T. I. A. Gerber, R. Jacobs and J. G. H. du Preez, *Inorg. Chem.*, **33**, 178 (1994); [e] T. I. A. Gerber, H. J. Kemp, J. G. H. du Preez and G. Bandoli, *J. Coord. Chem.*, **28**, 329 (1993); [f] G. Bandoli, A. Dolmella, T. I. A. Gerber, J. G. H. du Preez and H. J. Kemp, *Inorg. Chim. Acta*, **217**, 141 (1994); †d = unweighted sample mean; m = the sample median; σ = the standard deviation; q_l = the lower quartile; q_u = the upper quartile.

References

[1] E. Deutsch, K. Libson, J.-L. Vanderheyden, A. R. Ketring and H. R. Maxon, *Nucl. Med. Biol.*, **13**, 465 (1986).

[2] G. Bandoli, U. Mazzi, B. E. Wilcox and E. Deutsch, *Inorg. Chim. Acta*, **95**, 217 (1984).

[3] U. Mazzi, F. Refosco, G. Bandoli and M. Nicolini, *Transition Met. Chem.*, **10**, 121 (1985).

[4] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1693 (1987).

[5] F. Tisato, F. Refosco, A. Moresco, G. Bandoli, U. Mazzi and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 2225 (1990).

[6] N. P. Johnson, C. J. L. Lock and G. Wilkinson, *Inorg. Synth.*, **9**, 145 (1967).

[7] T. Lis and B. Jezowska-Trzebiatowska, *Acta Cryst.*, **B33**, 1248 (1977).

[8] S. S. Tandon, S. Chander, L. K. Thompson, J. N. Bridson and V. McKee, *Inorg. Chim. Acta*, **219**, 55 (1994).

[9] D. P. Shillington, *PhD Thesis*, University of Port Elizabeth (1984).

[10] J. G. H. du Preez, T. I. A. Gerber and H. J. Kemp, *J. Coord. Chem.*, **25**, 139 (1992).

[11] G. M. Sheldrick, *SHELXTL-PLUS. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data for Nicolet R3m/V*, (University of Göttingen, 1987).

[12] C. K. Johnson, *ORTEP, Report ORNL-5138*, (Oak Ridge National Laboratory, Oak Ridge TN, 1976).

[13] G. Gilli, M. Sacerdoti, V. Bertolasi and R. Rossi, *Acta Cryst.* **B38**, 100 (1982).

[14] V. Bertolasi, M. Sacerdoti, G. Gilli and U. Mazzi, *Acta Cryst.* **B38**, 426 (1982).

[15] S. Jurisson, K. Aston, C. K. Fair, E. O. Schlemper, P. R. Sharp and D. E. Troutner, *Inorg. Chem.*, **26**, 3576 (1987).