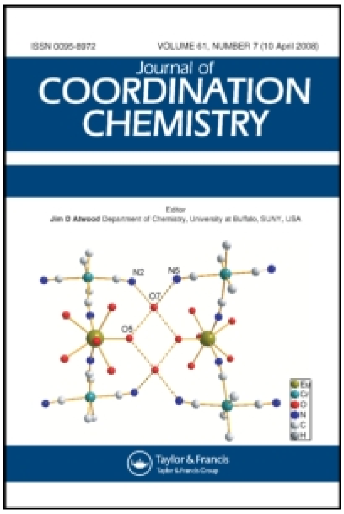

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COMPLEXES OF OXORHENIUM(V) WITH AROMATIC 2-AMINO-ALCOHOLS

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Monooxo complexes of rhenium(V) with 2-aminophenol and some of its derivatives (H_2nod), containing the *N*,*O* donor-atom set, have been synthesized. Square-pyramidal complexes $[ReO(nod)_2]^-$ were isolated by reaction with (*n*-Bu_4N) $[ReOCl_4]$ in ethanol. In benzene the neutral species $[ReOCL(Hnod)_2]$ were obtained. In the presence of hydrochloric acid in ethanol, the anionic complexes (*n*-Bu_4N) $[ReOCl_3(Hnod)]$ were produced. *Trans*-$[ReOCl_3(PPh_3)_2]$ was also reacted with some of the H_2nod ligands to yield $[ReOCL_2(Hnod)(PPh_3]$. The crystal structure of $[ReOCl_2(Hmap)(PPh_3)]$ (H_2map = 2-aminobenzylalcohol) was determined; crystals are monoclinic, $P2_1/n$, with $a = 15.065(6)$, $b = 11.253(7)$, $c = 15.850(7)$ Å, $\beta = 94.27(4)^\circ$, $U = 2680(2)$ Å^3 and $Z = 4$. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques to $R = 0.042$. The monoanionic $Hmap^-$ ligand is coordinated as a bidentate through a neutral amino nitrogen and an anionic alcoholate oxygen atom, with the latter *trans* to the oxo group.

Keywords: Rhenium(V); Bidentate ligands; X-ray structure

INTRODUCTION

The chemistry of oxorhenium(V) has attracted increasing interest in recent years because of the attractive nuclear properites of the ^{186}Re and ^{188}Re isotopes, which make them useful as potential radiotherapeutic agents against cancer [1]. These two isotopes are strong β-emitters (2.12 and 1.07 MeV respectively) and radiopharmaceuticals based on these isotopes have shown potential for the treatment of malignant tumours of the liver, kidney, skeleton, and other organs in the pelvic cavity [1].

We are currently interested in the coordination chemistry of oxorhenium(V) complexes with bidentate *N*,*O*-donor ligands containing an aromatic amino nitrogen as the *N*-donor. This study centres on oxorhenium(V) complexes formed with the following aromatic 2-amino-alcohols shown below.

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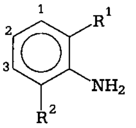


R^1	R^2	
OH	H	H_2amp
OH	NO_2	H_2anp
OH	CH_3	H_2pma
CH_2OH	H	H_2map
CH_2CH_2OH	H	H_2eap

The study of rhenium(V) with *N*,*O*-donor chelates has largely been limited to Schiff base ligands, which are relatively polarizeable and able to stabilize the rather acidic ReO^{3+} core. Bidentate aromatic *N*,*O*-donor Schiff bases, containing an imine nitrogen and phenolic oxygen, always give complexes with the phenolate oxygen *trans* to the oxo group in a distorted octahedral geometry around the ReO^{3+} core [2]. The reaction of *trans*-$ReOCl_3(PPh_3)_2$, for example, with *N*-methylsalicylideneimine (MesalH) yields the six-coordinate complexes [$ReOCl_2$(Mesal)(PPh_3)] and [ReOCl$(Mesal)_2$] under various conditions. Oxorhenium(V) complexes with *N*,*O*-donor ligands containing the amino group (NH_2) as one of the donor groups have not been well studied. The only report in the literature concerns the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with vinyl amides (NOH) that give products of the type [$ReOCl_2$(NO)(PPh_3)], in which these ligands act as monoanionic bidentate chelates with a neutral amino group [3].

EXPERIMENTAL

Materials

All chemicals were of reagent grade and were used as received. Solvents were purified and dried. Literature methods were used for the syntheses of (*n*-Bu_4N)[$ReOCl_4$] [4] and *trans*-$ReOCl_3(PPh_3)_2$ [5]. The ligands 2-aminophenol (H_2amp), 2-amino-3-nitrophenol (H_2amp), 2-amino-3-methylphenol (H_2pma), 2-aminobenzylalcohol (H_2map) and 2-aminophenethylalcohol (H_2eap) were obtained commercially (Aldrich).

Instrumentation

Scientific instrumentation used is the same as reported elsewhere [6]. Infrared spectra were obtained using KBr discs and ^{1}H NMR. spectra were run in d_6-DMSO. Electronic spectra and conductivity measurements (in units cm^2 ohm^{-1} mol^{-1}) were all obtained in acetonitrile, and the spectroscopic data are given as λ_{max} with extinction coefficients (in units M^{-1} cm^{-1}) in parentheses.

Synthesis of the Complexes

(n-Bu_4N)[ReO$(anp)_2$]

A mixture of 0.100 g of (*n*-Bu_4N)[$ReOCl_4$] (171 μmol) and 0.0527 g of H_2anp (342 μmol) in 25 cm^3 of ethanol was heated under reflux for 2 h. The dark green solution was cooled to room temperature, filtered, and left to evaporate slowly at room temperature. After two days an orange crystalline precipitate was collected, was washed with water, cold ethanol and diethyl ether, and dried under vacuum. Yield = 62%; m.p. 143°C. Anal. Calcd. for $C_{28}H_{44}N_5O_7Re$(%): C, 44.91; H, 5.92; N, 9.35. Found: C, 44.87; H,5.87; N, 9.47. Infrared: ν(N–H) 3387(m); ν(N–Bu) 2961(m); $\nu_s(NO_2)$ 1348(s); ν(Re=O) 913(s). ^{1}H NMR: 1.01(t, 12H, 4x CH_3); 1.38(m, 8H, 4x CH_2); 1.64(br m, 8H, 4x CH_2); 3.23(br m, 8H, 4x CH_2N); 10.52 (br s, 2H, 2x N*H*); 7.54 (d, 2H, H^1); 6.98(d, 2H, H^3); 6.56 (t, 2H, H^2). Conductivity = 121. Electronic spectrum: 426(2100), 348(6000), 298(56000).

(n-Bu$_4$N)[ReO(amp)$_2$]

Yield = 73%; m.p. 168°C, colour = red. Anal. Calcd. for $C_{28}H_{46}N_3O_3Re$(%): C, 51.04; H, 7.04; N, 6.38. Found: C, 51.12; H, 7.31; N, 6.25. Infrared: ν(N–H) 3393(m); ν(N–Bu) 2952(m); ν(Re=O) 914(s). ^{1}H NMR: 0.86(t, 12H); 1.25(m, 8H); 1.51(br m, 8H); 3.09(br m, 8H); 10.39 (br s, 2H); 6.67 (d, 2H, H^1); 6.41 (d, 2H, H^4); 6.57(t, 2H H^2); 6.42 (t, 2H, H^3). Conductivity = 124. Electronic spectrum: 440(4000), 328(5200), 282(44800).

(n-Bu$_4$N)[ReO(pma)$_2$]

Yield = 77%; m.p. 138°C, colour = orange. Anal. Calcd. for $C_{30}H_{50}N_3O_3Re$(%): C, 52.45; H, 7.34; N, 6.12. Found: C, 52.68; H, 7.51; N, 6.41. Infrared: ν(N–H) 3391(m); ν(N–Bu) 2961(m); ν(Re=O) 915(vs). ^{1}H NMR: 0.98(t, 12H); 1.34(m, 8H); 1.62(br m, 8H); 3.26(br m, 8H); 10.36 (br s, 2H); 6.61 (d, 2H, H^1); 6.52 (d, 2H, H^3); 6.39(t, 2H, H^2); 2.28 (s, 6H, CH_3). Conductivity = 123. Electronic spectrum: 436(3400), 317(7000), 285(54000).

[ReOCl(Hanp)$_2$]

To a suspension of 0.100 g of (*n*-Bu$_4$N)[ReOCl$_4$] in 20 cm^3 of benzene was added 0.0527 g of H$_2$anp. The mixture was heated under reflux for 2 h. The green solution was cooled to room temperature, and filtered. It was left to evaporate slowly at room temperature, and after two days small maroon-coloured crystals were collected by filtration. The product was washed with ethanol and acetone, and dried under vacuum. Yield = 71%, m.p. 174°C. Anal. Calcd. for $C_{12}H_{10}N_4O_4ClRe$(%): C, 29.06; H, 2.03; N, 11.30. Found: C, 29.11; H, 2.07; N, 11.12. Infrared: ν(N–H) 3391(m), 3402(m); $\nu_s(NO_2)$ 1363(s); ν(Re=O) 921(s); ν (Re–Cl) 321(m). ^{1}H NMR: 10.42 (br s, 4H, 2x NH_2); 7.39(d, 2H, H^1), 6.84(d, 2H, H^3); 6.42(t, 2H, H^2). Conductivity = 13. Electronic spectrum: 429(2900), 344(8400), 298(34000).

[ReOCl(Hamp)$_2$]

Yield = 78%; m.p.177°C, colour = dark red. Anal. Calcd. for $C_{12}H_{12}N_2O_3Cl$ Re(%): C, 31.75; H, 2.66; N, 6.17. Found: C, 31.87; H, 2.83; N, 6.33. Infrared: ν(N–H) 3386(m), 3411(m); ν(Re=O) 923(s); ν(Re–Cl) 322(m). ^{1}H NMR: 10.34(br s, 4H); 6.47(d, 2H); 6.34(d, 2H); 6.29(t, 2H); 6.17(t, 2H). Conductivity = 13. Electronic spectrum: 418(1700), 321(10100), 284(28000).

[ReOCl(Hpma)$_2$]

Yield = 73%; m.p.169°C, colour = red-brown. Anal. Calcd. for $C_{14}H_{16}N_2O_3ClRe$(%): C, 34.89; H, 3.35; N, 5.81. Found: C, 34.73; H, 3.61; N, 5.73. Infrared: ν(N–H) 3382(m), 3409(m); ν(Re=O) 924(vs); ν(Re–Cl)322(m). ^{1}H NMR: 10.78(br s, 4H); 7.17(t, 2H, H^2); 6.98(d, 2H, H^1); 6.79(d, 2H, H^3); 2.42(s, 6H, CH_3). Conductivity = 11. Electronic spectrum: 440(5000), 361(5100), 277(36000).

(n-Bu$_4$N)[ReOCl$_3$(Hanp)]

To an ethanolic solution (20 cm^3) containing 0.100 g of (*n*-Bu$_4$N)[ReOCl$_4$] and 0.0264 g of H_2anp was added 0.5 cm^3 of concentrated hydrochloric acid. The reaction mixture was heated under reflux for 2 h, during which time the orange-brown solution changed colour to dark green. The solution was cooled to room temperature and filtered. It was left to evaporate slowly overnight, and the dark red crystalline precipitate that formed was removed by filtration, washed with small quantities of cold ethanol (4 × 2 cm^3) and diethyl ether, and dried under vacuum. Yield = 61%, m.p. 161°C(dec.). Anal. Calcd. for $C_{22}H_{41}N_3O_4Cl_3Re$(%): C, 37.53; H, 5.87; N, 5.97; Cl, 15.10. Found: C, 37.68; H, 5.93; N, 5.68; Cl, 15.55. Infrared: ν(N–H) 3387(m), 3371(m); ν(N–Bu) 2962(m); $\nu_s(NO_2)$ 1348(s); ν(Re=O) 923(vs); ν(Re–Cl) 316(m), 322(m). ^{1}H NMR: 0.84(t, 12H); 1.23(m, 8H); 1.51(br m, 8H); 3.08 (br m, 8H); 10.34 (br s, 2H); 7.37(d, 1H, H^1); 6.83(d, 1H, H^3); 6.39(t, 1H, H^2). Conductivity: 118. Electronic spectrum: 425(6700), 335(12500), 273(66000).

(n-Bu$_4$N)[ReOCl$_3$(Hamp)]

Yield = 72%, m.p. 147°C, colour = orange. Anal. Calcd. for $C_{22}H_{42}N_2O_2Cl_3Re$(%): C, 40.09; H, 6.42; N, 4.25; Cl, 16.14. Found: C, 40.31; H, 6.46; N, 4.35; Cl, 16.35. Infrared: ν(N-H) 3394(m), 3380(m); ν(N–Bu) 2963(m); ν(Re=O) 926(vs); ν(Re–Cl) 316(m), 324(m). ^{1}H NMR: 0.98(t, 12H); 1.37 (m, 8H); 1.65(br m, 8H); 3.26(br m, 8H); 6.57(d, 1H); 6.38(d, 1H); 6.48(t,1H); 6.29(t,1H). Conductivity = 121. Electronic spectrum: 428(2100), 318(9800), 262(64000).

(n-Bu$_4$N)[ReOCl$_3$(Hpma)]

Yield = 68%, m.p. 138°C, colour = orange. Anal. Calcd. for $C_{23}H_{44}N_2O_2Cl_3Re$(%): C, 41.04; H, 6.59; N, 4.16; Cl, 15.80. Found: 41.12; H, 6.71; N, 4.33; Cl, 15.96. Infrared: ν(N–H) 3396(m), 3383(m); ν(N–Bu) 2964(m); ν(Re=O) 922(vs); ν(Re–Cl) 318(m), 323(m).^{1}H NMR: 0.99(t, 12H); 13.5(m, 8H); 1.66(br m, 8H); 3.24(br m, 8H); 6.68(d, 1H, H^1); 6.54(d, 1H, H^3); 6.41(t, 1H, H^2); 2.36(s, 3H, CH_3). Conductivity = 122. Electronic spectrum: 424(7700), 306(12700), 274(44000).

[ReOCl$_2$(Hmap)(PPh$_3$)]

A mixture of 0.100 g (120 µmol) of *trans*-ReOCl$_3$(PPh$_3$)$_2$ and 0.0160 g (129 μmol) of H_2map in 25 cm^3 of benzene was heated under reflux for 2 h. During this time the colour of the solution changed from yellow to dark red. After cooling the mixture to room temperature, a reddish-purple precipitate was collected by filtration, washed with benzene and diethyl ether, and dried under vacuum. Yield = 68%, m.p. 181°C. Anal. Calcd. for $C_{25}H_{23}NO_2Cl_2$ PRe(%): C, 45.67; H, 3.53; N, 2.13. Found: C, 45.55; H, 3.68; N, 2.22. Infrared: ν(NH) 3204(m), 3136(m); ν(Re=O) 933(vs); ν(Re–Cl) 326(m). ^{1}H NMR: 4.58(s, 2H, CH_2); 5.84(br s, 2H, NH_2); 7.32–7.44(m, 4H); 7.45–7.70(m, 15H, PPh_3); Conductivity = 14. Electronic spectrum: 641(200), 276(11100), 250(23900). The complexes [ReOCl$_2$(Hamp)(PPh$_3$)] and [ReOCl$_2$(Heap)(PPh$_3$)] were prepared in exactly the same manner as [ReOCl$_2$(Hmap)(PPh$_3$)].

[ReOCl$_2$(Hamp)(PPh$_3$)]

Yield = 78%, m.p. 196°C, colour = purple. Anal. Calcd. for $C_{24}H_{21}NO_2Cl_2$ PRe(%): C, 45.94; H, 3.37; N, 2.23. Found: C, 45.79; H, 3.38; N, 2.42. Infrared: ν(NH) 3233(m), 3162(m); ν(Re=O) 927(s); ν(Re–Cl) 299(m), 322(m). ^{1}H NMR: 6.93(t, 1H, H^2); 7.05(d, 1H, H^4); 7.22(d, 1H, H^1); 7.30–7.90(m, 16H, H^3, PPh_3); 5.86(br s, 2H, NH_2). Conductivity = 14. Electronic spectrum: 648(200), 366(600), 262(34200).

[ReOCl$_2$(Heap)(PPh$_3$)]

Yield = 68%, m.p. 181°C, colour = blue. Anal. Calcd. for $C_{25}H_{23}NO_2Cl_2$ PRe(%): C, 46.50; H, 3.75; N, 2.09. Found: C, 46.68; H, 3.83; N, 2.16. Infrared: ν(NH) 3220(m), 3143(m); ν(Re=O) 931(vs); ν(Re–Cl) 317(m). ^{1}H NMR: 2.79(t, 2H, CH_2); 3.63(t, 2H, CH_2O); 5.84(br s, 2H, NH_2); 7.22–7.43(m, 4H); 7.45–7.60(m, 15H, PPh_3). Conductivity = 14. Electronic spectrum: 625(150), 378(500), 266(30400).

Crystallography

Crystals of [ReOCl$_2$(Hmap)(PPh$_3$) · ½Me$_2$CO suitable for X-ray crystallography were grown from an acetone solution. Details of the crystal data, measurement of intensities and data processing are summarised in Table I. Data were measured at room temperature on a Nicolet R3m/V diffractometer and, as the crystal was a rather weak diffractor, the collection was restricted to $2\theta = 42.0°$. A total of 2888 reflections were collected of which 2290 were unique with $I > 2\sigma(I)$. Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by heavy-atom methods and refined using the SHELXTL/PC [7] and SHELXL-93 [8] suite of programs. The refinement was performed using weighted full-matrix least-squares on F^2. During refinement it became apparent that the Me$_2$CO molecule was disordered. However, efforts to identify partial occupancies for the atoms were unsuccessful and hence the positions, derived from ΔF, were not refined. In the final least-squares cycles the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined as riding atoms using the SHELXL-93 default parameters. The final R factor was 0.042, $wR2 = 0.102$ and goodness of fit = 1.080 for all observed reflections. The final Fourier-difference map did not show any significant features. Selected bond lengths and angles are listed in Table II and final atomic coordinates for the non-hydrogen atoms in Table III.

Tables giving complete crystallographic experimental details, bond distances and angles, positional parameters for all atoms, anisotropic thermal parameters, and hydrogen atom coordinates are available from the authors upon request.

TABLE I Crystal data and structure refinement details for $[ReOCl_2(Hmap)(PPh_3)] \cdot ½ Me_2CO$

Empirical Formula	$C_{26.50}H_{26}Cl_2NO_{2.50}PRe$
Formula weight	686.55
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 15.065(6)$ Å $b = 11.253(7)$ Å, $\beta = 94.27(4)°$ $c = 15.850(7)$ Å
Volume, z	2680(2) $Å^3$, 4
Density (calculated)	1.702 $Mg^{-3}m$
Absorption coefficient	4.820 mm^{-1}
F (000)	1344
Crystal size	0.30 × 0.10 × 0.08 mm
θ range for data collection	2.22–21.04°
Limiting indices	$0 \leq h \leq 15$, $0 \leq k \leq 11$, $-16 \leq l \leq 15$
Reflections collected	3039
Independent reflections	2888 ($R_{int} = 0.0405$)
Absorption correction	psi-scan
Max. and min. transmission	0.61 and 0.39
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0417$, $wR2 = 0.1018$
R indices (all data)	$R1 = 0.0649$, $wR2 = 0.1205$

TABLE II Selected bond distances (Å) and angles (°)

Re–Cl(1)	2.328(3)	Re–O(1)	1.671(8)
Re–Cl(2)	2.447(4)	Re–O(2)	1.861(8)
Re–P(1)	2.414(4)	Re–N(1)	2.158(9)
O(1)–Re–Cl(1)	91.4(3)	Cl(1)–Re–Cl(2)	89.8(1)
O(1)–Re–Cl(2)	92.0(3)	Cl(1)–Re–N(1)	169.1(3)
O(1)–Re-P(1)	90.1(3)	Cl(1)–Re–P(1)	90.3(1)
O(1)–Re–N(1)	86.2(3)	Cl(2)–Re–P(1)	177.8(1)
O(1)–Re–O(2)	166.2(3)	(Re)–N(1)–C(1)	122.4(7)
O(2)–Re–N(1)	80.0(3)	Re–O(2)–C(7)	138.8(8)

RESULTS AND DISCUSSION

Reactions with $[ReOCl_4]^-$

The simple reaction of $(n\text{-}Bu_4N)[ReOCl_4]$ with a twofold molar excess of the ligands H_2anp, H_2amp and H_2pma (H_2nod) in boiling ethanol gave the anions $[Re(nod)_2]^-$, which precipitated as the $n\text{-}Bu_4N^+$ salts in good yields (1)

$$(n\text{-}Bu_4N)[ReOCl_4] + 2H_2\ \text{nod} \xrightarrow{\text{EtOH}} (n\text{-}Bu_4N)[ReO(nod)_2](\mathbf{1}) + 4HCl \qquad (1)$$

Experimental evidence suggests that both the nod^{2-} ligands act as dianionic bidentate *N*,*O*-donor chelates, with both the amino and phenolic groups singly deprotonated, in a square-pyramidal coordination geometry around the rhenium(V) ion.

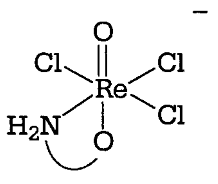
TABLE III Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for the complex U(eq) is defined as one third of the trace of the orthogonalized $U_{ij\ \text{tensor}}$

	x/a	*y/b*	*z/c*	*U(eq)*
Re	4763(1)	194(1)	8306(1)	36(1)
Cl(1)	5120(2)	1502(3)	7245(2)	59(1)
Cl(2)	4333(2)	1878(3)	9164(2)	53(1)
P(1)	5130(2)	−1473(3)	7439(2)	39(1)
O(1)	5735(5)	45(6)	8877(5)	38(2)
O(2)	3581(5)	134(7)	7876(5)	42(2)
N(1)	4199(6)	−829(9)	9286(6)	38(3)
C(1)	3474(8)	−1661(10)	9109(7)	38(3)
C(2)	3508(9)	−2741(11)	9523(8)	44(3)
C(3)	2851(10)	−3552(13)	9341(9)	63(4)
C(4)	2160(10)	−3278(12)	8772(9)	58(4)
C(5)	2121(9)	−2188(13)	8394(9)	58(4)
C(6)	2779(7)	−1370(11)	8552(8)	41(3)
C(7)	2759(9)	−202(12)	8137(10)	59(4)
C(1A)	6247(9)	−1507(12)	7154(8)	50(4)
C(2A)	6585(11)	−2545(14)	6827(12)	90(6)
C(3A)	7443(15)	−2621(19)	6632(15)	116(8)
C(4A)	7958(12)	−1714(22)	6746(14)	101(7)
C(5A)	7675(11)	−669(21)	7036(12)	98(6)
C(6A)	6820(10)	−551(15)	7231(10)	70(4)
C(1B)	4422(10)	−1531(11)	6490(8)	50(4)
C(2B)	3543(10)	−1822(12)	6543(9)	61(4)
C(3B)	2970(12)	−1797(15)	5799(12)	81(5)
C(4B)	3269(18)	−1521(18)	5058(12)	112(8)
C(5B)	4167(15)	−1270(18)	5009(11)	100(7)
C(6B)	4723(12)	−1275(15)	5730(10)	82(5)
C(1C)	5080(8)	−2896(11)	7961(8)	40(3)
C(2C)	5545(8)	−2997(11)	8728(8)	44(3)
C(3C)	5592(9)	−4071(13)	9162(8)	54(4)
C(4C)	5119(9)	−5000(12)	8826(11)	62(4)
C(5C)	4659(10)	−4918(12)	8022(11)	65(4)
C(6C)	4635(8)	−3871(11)	7628(8)	44(3)
C(8)	4000	−4460	5600	200
C(9)	3730	−4300	4680	200
C(10)	4430	−4030	4030	200
O(3)	3080	−4470	4340	200

In the presence of hydrochloric acid in ethanol, the orange-coloured compounds (n-$\mathrm{Bu_4N}$)[$\mathrm{ReOCl_3}$(Hnod)] were isolated (2).

$$(n\text{-}\mathrm{Bu_4N})[\mathrm{ReOCl_4}] + \mathrm{H_2}\ \mathrm{nod} \xrightarrow{\mathrm{HCl/EtOH}} (n\text{-}\mathrm{Bu_4N})[\mathrm{ReOCl_3(Hnod)}](\mathbf{2}) + \mathrm{HCl} \qquad (2)$$

All experimental data support the following arrangement of donor atoms around the oxorhenium(V) centre:



In benzene, direct reaction of a twofold molar excess of H_2nod gave complexes of the type [ReOCl(Hnod)$_2$] (**3**). Experimental evidence suggests the bidentate coordination of the monoanionic Hnod ligands through a neutral amino group and a deprotonated phenolate oxygen, with one of the latter occupying the site *trans* to the oxo group in a distorted octahedral environment around the metal.

All prepared complexes are diamagnetic (formally d^2), and **1** and **2** are **1** : **1** electrolytes in acetonitrile. They are weakly soluble, but stable, in polar solvents like DMSO, DMF and acetonitrile.

In the infrared spectra asymmetric Re=O stretching frequencies appear as sharp strong bands in the narrow ranges 913–915 cm^{-1} (for **1**) and 921–926 cm^{-1} for **2** and **3**, which fall in regions normally observed for anionic square-pyramidal [9] and distorted octahedral [10] (with an anionic phenolate oxygen *trans* to the oxo group) oxorhenium(V) complexes, respectively. For complexes **1**, only one peak of medium intensity around 3390 cm^{-1} is observed for ν(N–H), and a single peak near 412 cm^{-1}, due to ν(Re–O), is indicative of the equivalence of the anionic oxygen interaction with the metal. The presence of a neutral amino group in complexes **2** is shown by two medium-intensity peaks at about 3390 and 3380 cm^{-1}, in addition to two signals due to the Re–Cl bonds at about 316 and 323 cm^{-1}. These latter values suggest that the chloride ions are coordinated equatorially to the oxo group in **2**. In complexes **3** the neutral amino groups produce two peaks at about 3390 and 3410 cm^{-1}, and two medium-intensity peaks are observed for ν(Re–O) at around 410 and 424 cm^{-1}. The latter value is assigned to the anionic oxygen coordinated in the equatorial plane *cis* to the oxo group. The ν(Re–Cl) stretch appears at about 322 cm^{-1} in **3**, a value that was previously assigned to a chloride to the oxo oxygen [10].

^{1}H NMR spectra clearly establish the presence of the n-Bu_4N^+ group and the amidophenolates in complexes **1** and **2**. The cation protons lead to a series of signals of the form triplet (12 protons), multiplet (8 protons), another multiplet (8 protons) and a broad multiplet (8 protons) near δ0.95, 1.30, 1.60 and 3.20 ppm, respectively. Integration of the signals of n-Bu_4N^+ and those of the bidentate ligands shows a molar ratio of 1 : 2 in complexes **1** and **1** : **1** in **2**. In addition to the ring protons in the aromatic region, there is a broad singlet, integrating for two protons, around δ10.4 ppm in the spectra of **1**, assigned to the coordinated N*H* of each chelate ligand. For the complex [ReOCl(Hanp)$_2$] the three ring protons give a two-proton pattern of a doublet (δ7.39 ppm), doublet (δ6.84 ppm) and triplet (δ6.42 ppm), with the electronegative nitro group in the 3-position, the pattern is different: a triplet (δ7.17 ppm), doublet (δ6.98 ppm) and a doublet at δ6.79 ppm.

The low solubilities of all these complexes made the growing of crystals for X-ray crystallographic studies impossible. Crystals obtained from the slow evaporation of the mother liquors of the synthetic solutions were too small and imperfect for X-ray analyses.

Impure products of incomprehensible elemental analyses were obtained when the aminoalcohols H_2map and H_2eap were used as potential chelates in reactions with (n-Bu_4N)[ReOCl$_4$]. However, this problem was not experienced in their reactions with *trans*-ReOCL$_3$(PPh$_3$)$_2$.

Reactions with trans-ReOCl$_3$(PPh$_3$)$_2$

The reaction of *trans*-ReOCl$_3$(PPh$_3$)$_2$ with the ligands 2-aminophenol (H_2amp), 2-aminobenzylalcohol (H_2map) and 2-aminophenethylalcohol (H_2eap) in boiling benzene resulted in the complexes of general formula $ReOCl_2(Hnod)(PPh_3)$, according to (3).

$$ReOCl_3(PPh_3)_2 + H_2\,nod \xrightarrow{C_6H_6} ReOCl_2(Hnod)(PPh_3) + HCl + PPh_3 \qquad (3)$$

The $Hnod^-$ ligands coordinate as bidentate monoanionic *N*,*O*-donor chelates to the ReO^{3+} core. These complexes are diamagnetic and are non-electrolytes in DMF and acetonitrile. They are reasonably soluble in chloroform, acetone, acetonitrile, DMF and DMSO, and insoluble in ethanol, toluene, THF and benzene.

Infrared spectra display the Re=O stretching frequencies as a sharp band in the 927–933 cm^{-1} range. Two bands of medium intensity around 3220 and 3150 cm^{-1} are indicative of the presence of a coordinated neutral NH_2 group. The ν(Re–O) stretch appears near 410 cm^{-1}, which intimates that the anionic alcoholate oxygen is coordinated *trans* to the oxo group.

Full assignment of the peaks in the ^1H NMR spectrum of $ReOCl_2(Hmap)(PPh_3)$ was not possible due to overlapping of signals in the aromatic region. The broad singlet at δ5.84 ppm is attributed to the protons of the NH_2 group. The protons of the methylene group appear as a singlet at δ4.58 ppm. The multiplet observed from δ7.32–7.44 ppm integrates for four protons and is assigned to the aromatic protons of the ligand Hmap. The multiplet at δ7.45–7.70 ppm integrates for the 15 protons of the triphenylphosphine.

The two triplets at δ3.63 and 2.79 ppm in the spectrum of $ReOCl_2(Heap)(PPh_3)$ are assigned to the two methylene CH_2 groups, while the rest of the spectrum, as well as the spectrum of $ReOCl_2(Hmap^-)(PPh_3)$, is as expected.

Description of the Structure of $ReOCl_2(Hmap)(PPh_3)$

The crystal structure of this complex (Fig. 1) exhibits distorted octahedral geometry around the rhenium(V) centre. The basal plane is defined by the amino nitrogen of the Hmap ligand, two chlorides and the phosphorus atom of PPh_3, with the phenolate and oxo oxygens in *trans* axial positions. The two chlorides are coordinated to the metal centre *cis* to each other, with the Cl(1)–Re–Cl(2) angle practically orthogonal at 89.8(1)°.

The Re(V) centre deviates from the means equatorial plane by 0.10 Å towards the oxo oxygen, and the Cl_2NP donor atoms deviate by ± 0.06 Å from this plane as well. The O(1)–Re–O(2) angle deviates considerably from linearity at 166.2(3)°. In the O_2Cl_2NP polyhedron the rhenium ion is -1.07 Å from the Cl(1)–O(1)–Cl(2) plane, and 1.24 Å from P(1)–O(2)–N(1), with the dihedral angle being 7.9°.

The bidentate $Hmap^-$ ligand forms a six-membered ring with a boat formation around the Re ion, with N(1) and C(7) as "bow" and "stern" atoms (up by 0.52 and 0.43 Å respectively, and torsion angles in the range -47.5, 42.0°), and the mean plane is normal to the equatorial one with the dihedral angle being 89.2°.

Re–Cl(2) *trans* to P(1), at 2.447(4) Å, is significantly longer than the chloride *trans* to the amine N(1)[2.328(3) Å], and this result confirms the lower *trans* influence of the amine relative to the phosphine group [11]. The Re–O(2) distance of 1.861(8) Å is somewhat shorter compared to other Re(V)–O(phenolate) distances[12], demonstrating that the oxygen atom acts as a monoanionic donor. Other bond distances and angles are normal (Table II).

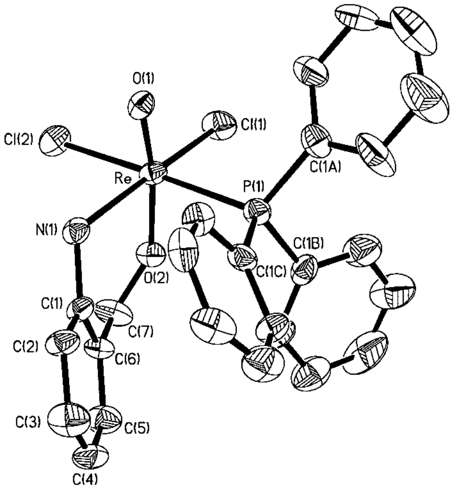


FIGURE 1 An ORTEP view of the structure, showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level. The Me_2CO molecule is omitted for clarity.

Complexes of formula $[ReOCl_2(Rsal)(PPh_3)]$ (RsalH = bidentate *N*,*O*-donor Schiff base) were previously prepared by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with RsalH. It was found that in all these compounds the oxygen donor atom of the Rsal ligands is coordinated in a position *trans* to the Re=O bond [13]. The complex $[ReOCl_2$ $(Mesal)(PPh_3)]$ (Mesal = *N*-methylsalicylideneimino) was isolated in both the *cis* and *trans* forms, which differ in the arrangement of the two chlorine atoms in the equatorial plane.

The first step in complex formation of $[ReOCl_2(Hnod)(PPh_3)]$ is probably the substitution of a PPh_3 group by the ligand H_2nod, which will coordinate to the rhenium(V) centre *via* the amino nitrogen atom. The harder basic character of the amino nitrogen compared to the softer PPh_3 base means that the interaction will be stronger than with PPh_3. The complex $[ReOCl_3(MesalH)(PPh_3)]$ has the Schiff base coordinated as a unidentate ligand through the aldimine nitrogen [10]). The final product, $[ReOCl_2(Hnod)(PPh_3)]$, is then formed by chelation and deprotonation of the alcoholate oxygen by substitution of the more reactive chloride *trans* the Re=O bond.

It was found previously [14] that the reaction of $(n\text{-}Bu_4N)[ReOCl_4]$ with the *N*,*O*-donor 3-hydroxypicolinic acid (HL) in benzene and ethanol yielded $(n\text{-}Bu_4N)$ $[ReOCl_3(L)]$ and $[ReOCl(L)_2l$, respectively. It was also found earlier that $[(C_6H_5)_4$ $As][ReOCl_4]$ reacts with the bidentate ligands RsalH (R = Me, Ph) in THF or EtOH to produce $[(C_6H_5)_4As]^+[ReOCl_3(Rsal]^-$. Prolonged heating of the latter in the presence of the appropriate ligand gave $[ReOCl(Rsal)_2]$ in ethanol. The crystal structure [2] of the $Mesal^-$ derivative has shown an octahedral environment around the metal, with the phenolate oxygen *trans* to the oxo group and the two imine nitrogens *cis* to each other.

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