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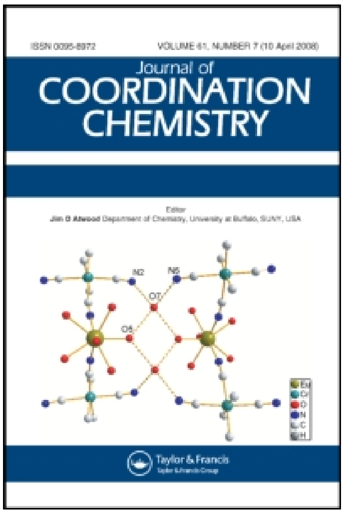

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Synthesis and structural characterization of cationic octahedral oxorhenium(V) complexes with bidentate imidazole derivatives

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Online publication date: 12 May 2010

To cite this Article Gerber, T. I. A. , Tshentu, Z. R. and Mayer, P.(2003) 'Synthesis and structural characterization of cationic octahedral oxorhenium(V) complexes with bidentate imidazole derivatives', Journal of Coordination Chemistry, 56: 16, 1357 — 1366

To link to this Article: DOI: 10.1080/00958970310001617049

URL: http://dx.doi.org/10.1080/00958970310001617049

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J. Coord. Chem., Vol. 56, No. 16, 10 November 2003, pp. 1357–1366

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CATIONIC OCTAHEDRAL OXORHENIUM(V) COMPLEXES WITH BIDENTATE IMIDAZOLE DERIVATIVES

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(Received 28 April 2003; In final form 11 August 2003)

Cationic distorted octahedral complexes [ReOCl(OEt)(L)(PPh$_3$)]X {L = 2-(1-ethylaminomethyl)-1-methylimidazole (eami), 2-(1-methylaminomethyl)-1-methylimidazole (mami), 2-(1-ethylthiomethyl)-1-methylimidazole (etmi); X=ReO$_4$, PF$_6$} were prepared by reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a twofold molar excess of L in ethanol under anaerobic conditions. X-ray structure determinations of [ReOCl(OEt)(eami)(PPh$_3$)](ReO$_4$) (**1a**) and its etmi equivalent (**3a**) were performed. In **1a** coordination of the chloride occurs *trans* to the imidazole nitrogen. However, in **3a** the chloride is coordinated *trans* to the ethereal sulfur donor of etmi.

Keywords: Cationic complexes; Oxorhenium(V); Bidentate imidazole derivatives; X-ray structure

INTRODUCTION

The chemistry of oxorhenium(V) complexes has attracted increasing interest in recent years because of the attractive nuclear properties of the ^{186}Re and ^{188}Re isotopes, which may make them useful as potential radiotherapeutic agents for cancer [1]. Additional interest to rhenium arose from the similarity of its chemical behaviour to that of technetium, its second row congener, which has found major applications in diagnostic nuclear medicine [1].

In the course of a systematic study of rhenium(V) complexes with nitrogen heterocycles as ligands, we now report several cationic octahedral oxorhenium(V) complexes with the *N*,*N* and *N*,*S*-donor ligands 2-(1-ethylaminomethyl)-1-methylimidazole (eami), 2-(1-methylaminomethyl)-1-methylimidazole (mami) and 2-(1-ethylthiomethyl)-1-methylimidazole (etmi). Complexes of the type [ReOCl(OEt)(L)(PPh$_3$)]X (L = eami, mami, etmi; X = ReO$_4$, PF$_6$) were isolated and characterised.

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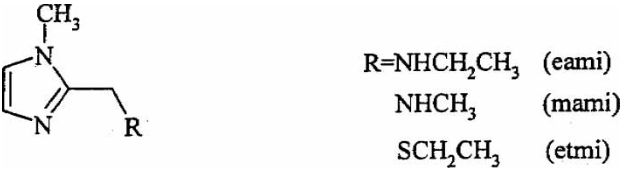
ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/00958970310001617049



Cationic rhenium(V) complexes have potential applications in radiotherapy due to their ability to permeate lipophilic membranes. While cationic dioxo complexes of the type *trans*-$[ReO_2L'_4]^+$ [L′ = pyridine, picolines, primary amines, 1/2{ethylenediamine (en), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen)}] are common and well studied [2], cationic octahedral monooxo complexes are relatively rare. A recent report [3] has shown the cation $[ReOCl_2(OPPh_3)(biimH_2)]^+$ ($biimH_2$ = 2,2′-biimidazole), with a chloride counterion hydrogen-bonded to the NH protons of $biimH_2$. Cationic complexes of rhenium(V) with the tridentate *N*-(2-oxidophenyl)salicylideneiminate ($OPhsal^{2-}$) and the bidentate ligands bipy and phen (NN), with the general formula $[ReO(OPhsal)(NN)]PF_6$, have also been reported [4]. Other examples are $[ReOCl_2(tacn)]BPh_4$ (tacn = triazacyclononane) [5], $[ReOCl_2(tu)_2(H_2O)]Cl$ (tu = thiourea) [6] and $[ReO(cyclam)(H_2O)]Cl_3$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [7].

The reaction of neutral bidentate *N*,*N*-donor ligands like en, bipy and phen (L′) with the monooxorhenium(V) core generally gives $[ReOCl_3(L')]$ [8,9]. With the monodentate nitrogen-donor ligands 7-azaindole (Haza) [10] and pyridine [11] the complexes $[ReO(OEt)Cl_2(Haza)_2]$ and $[ReO(OEt)Cl_2(pyr)_2]$ have been isolated.

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EXPERIMENTAL

Reagents

Trans-$[ReOCl_3(PPh_3)_2]$ [12] and the ligands eami, mami and etmi [13] were prepared as stated previously. All chemicals were of reagent grade and used as received from commercial sources. Solvents were purified and dried by standard procedures. All reactions were carried out under an inert argon atmosphere.

Instrumentation

Infrared spectra were recorded on a Nicolet 20 DXC FTIR spectrophotometer in the 4000–200 cm^{-1} range in KBr pellets. ^1H-NMR spectra were recorded in d_6-DMSO at 300 MHz on a Bruker AMX-300 spectrometer at 298 K, with peak positions relative to $SiMe_4$. Conductivity measurements were carried out in DMF at 293 K on a Phillips PW 9509 digital conductometer. Melting points were determined with an Electrothermal 1A9100 apparatus. Elemental analyses for carbon, hydrogen, nitrogen and sulfur were carried out at the Department of Chemistry at the University of the Western Cape in Cape Town.

Synthesis of Complexes

General Method

Some 0.24 mmol of eami, mami or etmi was dissolved in 5 cm^3 of ethanol, and this solution was added to 0.12 mmol of *trans*-$[ReOCl_3(PPh_3)_2]$ in 5 cm^3 of ethanol under argon. The mixture was stirred for 5 min, and then heated gently under reflux conditions for 30 min, during which time the yellow-green solution changed colour to purple. To the hot purple solution was added 0.13 mmol of either NH_4ReO_4 or NH_4PF_6 in 5 cm^3 of warm ethanol, and then the mixture was stirred for 30 min and cooled to room temperature while a purple precipitate (brown for etmi) formed. The precipitate was filtered off and washed with ethanol, acetone and diethylether. The mother liquor was allowed to stand at room temperature and, after several hours, bright purple crystals (brown for etmi complexes) were obtained.

*[ReOCl(OEt)(eami)(PPh$_3$)](ReO$_4$) (**1a**)* Yield = 76%, m.p. = 195°C. Anal. Calcd.: C, 34.70; H, 3.55; N, 4.49. Found: C, 35.08; H, 3.40; N, 4.48%. IR: ν(NH) 3140; ν(C=N) 1591; ν(C=C) 1493; ν(Re=O) 957; ν(Re–N) 457; ν(Re–Cl) 331 cm^{-1}. ^{1}H-NMR (ppm): 1.08 (3H, t, NCH_2CH_3), 1.31 (3H, t, OCH_2CH_3), 3.50 (4H, q, $OCH_2CH_3 + NCH_2CH_3$), 3.98 (3H, s, NCH_3), 4.05 (2H, s, CH_2N), 6.17 (1H, s, N*H*), 7.50–7.70 (15H, m, P*Ph*$_3$), 7.76 (1H, d, *H*(4)), 7.85 (1H, d, *H*(3)). Conductivity (10^{-3} M) = 246 ohm^{-1} cm^2 mol^{-1}.

*[ReOCl(OEt)(eami)(PPh$_3$)]PF$_6$ (**1b**)* Yield = 68%, m.p. = 193°C. Anal. Calcd.: C, 39.11; H, 4.01; N, 5.07. Found: C, 38.97; H, 3.97; N, 5.07%. IR: ν(NH) 3144; ν(C=N) 1584; ν(C=C) 1507; ν(Re=O) 957; δ(OEt) 923; ν(P–F) 849; ν(Re–N) 461; ν(Re–Cl) 318 cm^{-1}. ^{1}H-NMR (ppm): 0.44 (3H, t, OCH_2CH_3), 1.00 (3H, t, NCH_2CH_3), 3.90 (3H, s, CH_3N), 4.68 (2H, s, CH_2N), 7.60–7.80 (15H, m, P*Ph*$_3$), 7.80 (d, 1H, *H*(4)), 7.87 (d, 1H, *H*(3)). Conductivity (10^{-3} M) = 257 ohm^{-1} cm^2 mol^{-1}.

*[ReOCl(OEt)(mami)(PPh$_3$)](ReO$_4$) (**2**)* Yield = 58%, m.p. = 185°C. Anal. Calcd.: C, 33.77; H, 3.37; N, 4.54. Found: C, 33.56; H, 3.38; N, 4.51%. IR: ν(NH) 3146; ν(C=N) 1585; ν(C=C) 1504; ν(Re=O) 958; ν(Re–N) 458; ν(Re–Cl) 316 cm^{-1}. ^{1}H-NMR (ppm): 1.05 (3H, t, OCH_2CH_3), 2.37 (2H, q, OCH_2CH_3), 3.80 (3H, s, CH_3N), 4.04 (2H, s, CH_2N), 6.12 (1H, s, N*H*), 7.50–7.70 (16H, m, P*Ph*$_3$, H(4)), 7.78 (1H, d, *H*(3)). Conductivity (10^{-3} M) = 213 ohm^{-1} cm^2 mol^{-1}.

*[ReOCl(OEt)(etmi)(PPh$_3$)](ReO$_4$) (**3a**)* Yield = 68%, m.p. = 191°C. Anal. Calcd.: C, 34.08; H, 3.39; N, 2.95; S, 3.37. Found: C, 34.56; H, 3.38; N, 2.96; S, 3.39%. IR: ν(C=N) 1635; ν(C=C) 1494; ν(Re=O) 955; ν(Re–Cl) 324 cm^{-1}. ^{1}H-NMR (ppm): 0.45 (3H, t, SCH_2CH_3), 0.84 (3H, t, OCH_2CH_3), 2.84 (2H, q, SCH_2CH_3), 3.08 (2H, q, OCH_2), 3.92 (3H, s, CH_3N), 4.68 (2H, s, CH_2S), 7.62–7.68 (15H, m, P*Ph*$_3$), 7.85 (1H, d, *H*(4)), 7.87 (1H, d, *H*(3)). Conductivity (10^{-3} M) = 230 ohm^{-1} cm^2 mol^{-1}.

*[ReOCl(OEt)(etmi)(PPh$_3$)](PF$_6$) (**3b**)* Yield = 64%, m.p. = 196°C. Anal. Calcd.: C, 38.32; H, 3.81; N, 3.31; S, 3.79. Found: C, 38.57; H, 3.83; N, 3.23; S, 3.68%. IR: ν(C=N) 1624; ν(C=C) 1503; ν(Re=O) 956; δ(OEt) 918; ν(P–F) 840; ν(Re–Cl) 320 cm^{-1}. ^{1}H-NMR (ppm): 1.05 (3H, t, SCH_2CH_3), 1.14 (3H, t, OCH_2CH_3), 3.44 (2H, q, SCH_2CH_3), 3.98 (3H, s, CH_3N), 4.03 (2H, s, CH_2S), 7.52–7.67 (15H, m, P*Ph*$_3$), 7.77 (1H, d, *H*(4)), 7.85 (1H, d, *H*(3)). Conductivity (10^{-3} M) = 230 ohm^{-1} cm^2 mol^{-1}.

X-ray Structure Determinations

Data collections were performed at 200 K on a Stoe IPDS using Mo Kα radiation. The structure of **1a** was solved by direct methods and was refined by full-matrix least-squares procedures using SHELXL-97 [14]. All non-hydrogen atoms except

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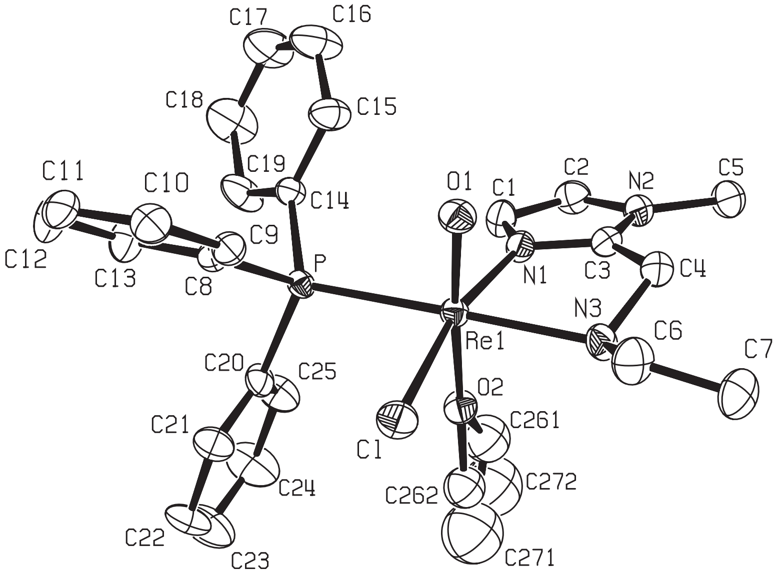

FIGURE 1 An ORTEP view of [ReOCl(OEt)(eami)(PPh$_3$)](ReO$_4$) (**1a**) showing the atom labelling scheme and 50% probability ellipsoids.

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the disordered carbon atoms of the ethoxy group were refined anisotropically. An ORTEP [15] view of the asymmetric unit of **1a**, along with the atom numbering scheme, is given in Fig. 1. Relevant crystallographic data are listed in Table I. Table II summarises selected bond distances and angles.

The structure of **3a** was also solved by direct methods and was refined by full-matrix least-squares procedures using SHELXL-97. All non-hydrogen atoms were refined anisotropically. An ORTEP diagram of **3a** is shown in Fig. 2. Selected bond distances and angles are given in Table III. Full lists of crystallographic data are available from the authors.

RESULTS AND DISCUSSION

Synthesis

Reaction of a twofold molar excess of the ligands eami, mami and etmi (L) with *trans*-[ReOCl$_3$(PPh$_3$)$_2$] in dry ethanol under argon led to the isolation of the cationic hexacoordinate complexes [ReOCl(OEt)(L)(PPh$_3$)]$^+$ as their perrhenate or hexafluorophosphate salts as follows:

$$\mathrm{ReOCl_3(PPh_3)_2} + 2\mathrm{L} + \mathrm{EtOH} + \mathrm{NH_4X} \rightarrow [\mathrm{ReOCl(OEt)(L)(PPh_3)}]\mathrm{X} + \mathrm{LH^+Cl^-} + \mathrm{PPh_3} + \mathrm{NH_4Cl}$$

$(\mathrm{X} = \mathrm{ReO_4}, \mathrm{PF_6})$.

Pure crystalline products could not be isolated without the addition of the counterions $\mathrm{ReO_4^-}/\mathrm{PF_6^-}$. In these efforts no precipitate of the complexes formed on cooling, and

TABLE I Crystal data and structure refinement for [ReOCl(OEt)(eami)(PPh$_3$)](ReO$_4$) (**1a**) and [ReOCl(OEt)(etmi)(PPh$_3$)](ReO$_4$) (**3a**)

Empirical formula	$C_{27}H_{32}ClN_3O_6PRe_2$	$C_{27}H_{33}ClN_2O_6SPRe_2$
Formula weight	933.40	952.47
Temperature (K)	200	200
Radiation (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å, °)	$a = 9.0535(8)$	$a = 9.7139(4)$
	$b = 12.0860(11)$	$b = 31.840(2)$
	$c = 15.7198(13)$	$c = 10.3154(5)$
	$\alpha = 68.797(10)$	
	$\beta = 75.038(10)$	$\beta = 94.287(6)$
	$\gamma = 81.056(11)$	
Volume (Å^3)	1545.6(3)	3181.5(3)
Z	2	4
Density (calc.) (Mg/m^3)	2.006	1.988
Crystal size (mm)	0.04 × 0.15 × 0.28 mm	0.03 × 0.05 × 0.35
Absorption coefficient (μ) (mm^{-1})	8.006	7.843
F(000)	890	1820
Theta Min–Max	2.3–27.9°	2.1–28.0°
Limiting indices	$-11 \le h \le 11$	$-12 \le h \le 12$
	$-15 \le k \le 15$	$-41 \le k \le 41$
	$-20 \le l \le 20$	$-12 \le l \le 13$
Reflections collected/unique	13415/6838 [*R*(int) = 0.041]	27464/7477 [*R*(int) = 0.059]
Observed data [$I > 2.0\,\sigma(I)$]	5110	5416
*N*ref, *N*par	7477, 361	7477, 361
R, *wR*2, *S*	0.0373, 0.0807, 0.94	0.0288, 0.0528, 0.87
Min. and max. resd. dens. (eÅ^{-3})	−4.57, 3.19	−0.86, 0.82

TABLE II Selected bond distances (Å) and angles (°) for **1a**

Re(1)–Cl	2.3917(17)	N(2)–C(3)	1.338(9)
Re(1)–P	2.4403(17)	N(2)–C(2)	1.360(10)
Re(1)–O(1)	1.697(5)	N(2)–C(5)	1.462(10)
Re(1)–O(2)	1.866(5)	N(3)–C(6)	1.502(10)
Re(1)–N(1)	2.106(5)	N(3)–C(4)	1.494(9)
Re(1)–N(3)	2.226(6)	C(1)–C(2)	1.347(10)
P–C(8)	1.822(6)	C(3)–C(4)	1.488(10)
O(2)–C(262)	1.38(3)	C(6)–C(7)	1.516(11)
O(2)–C(261)	1.447(17)	C(8)–C(9)	1.397(9)
N(1)–C(1)	1.385(9)	N(1)–C(3)	1.324(9)
Cl–Re(1)–P	88.75(6)	O(1)–Re(1)–N(1)	91.2(2)
Cl–Re(1)–O(1)	96.49(17)	O(1)–Re(1)–N(3)	90.7(2)
Cl–Re(1)–O(2)	88.19(15)	O(2)–Re(1)–N(1)	83.7(2)
Cl–Re(1)–N(1)	168.03(16)	O(2)–Re(1)–N(3)	86.3(2)
Cl–Re(1)–N(3)	93.09(16)	N(1)–Re(1)–N(3)	77.6(2)
P–Re(1)–O(1)	91.96(16)	C(1)–N(1)–C(3)	106.3(5)
P–Re(1)–O(2)	90.88(15)	Re(1)–N(1)–C(3)	114.6(4)
P–Re(1)–N(1)	100.15(15)	Re(1)–N(1)–C(1)	138.3(4)
P–Re(1)–N(3)	176.61(16)	C(2)–N(2)–C(5)	126.7(6)
O(1)–Re(1)–O(2)	174.6(2)	Re(1)–N(3)–C(6)	116.8(4)
		Re(1)–N(3)–C(4)	109.0(4)

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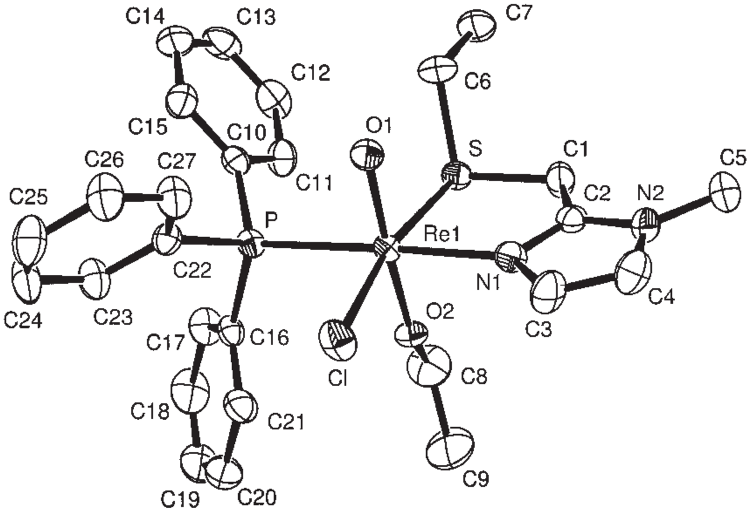

FIGURE 2 ORTEP view (at 50% probability) of [ReOCl(OEt)(etmi)(PPh$_3$)](ReO$_4$) (**3a**).

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TABLE III Selected bond distance (Å) and angles (°) for **3a**

Re(1)–Cl	2.3710(13)	S–C(1)	1.826(5)
Re(1)–S	2.4621(12)	O(2)–C(8)	1.419(7)
Re(1)–P	2.4711(10)	N(1)–C(3)	1.386(7)
Re(1)–O(1)	1.703(3)	N(1)–C(2)	1.334(6)
Re(1)–O(2)	1.863(3)	N(2)–C(4)	1.378(8)
Re(1)–N(1)	2.127(4)	N(2)–C(5)	1.450(7)
S–C(6)	1.812(5)	N(2)–C(2)	1.346(6)
Cl–Re(1)–S	169.54(4)	O(2)–Re(1)–N(1)	88.79(14)
Cl–Re(1)–P	88.72(4)	Re(1)–S–C(6)	108.12(16)
Cl–Re(1)–O(1)	98.24(10)	Re(1)–O(2)–C(8)	154.2(3)
Cl–Re(1)–O(2)	92.48(10)	Re(1)–N(1)–C(2)	121.4(3)
Cl–Re(1)–N(1)	90.68(11)	C(2)–N(1)–C(3)	106.3(4)
S–Re(1)–P	99.98(4)	C(4)–N(2)–C(5)	127.0(4)
S–Re(1)–O(1)	87.91(10)	C(2)–N(2)–C(5)	125.8(5)
S–Re(1)–O(2)	81.87(9)	C(2)–N(2)–C(4)	107.2(4)
S–Re(1)–N(1)	80.45(11)	N(1)–C(2)–N(2)	110.3(4)
P–Re(1)–O(1)	88.28(10)	N(1)–C(2)–C(1)	124.6(4)
P–Re(1)–O(2)	89.50(9)	N(1)–C(3)–C(4)	108.9(5)
P–Re(1)–N(1)	178.16(11)	N(2)–C(4)–C(3)	107.4(5)
O(1)–Re(1)–O(2)	169.00(13)	O(2)–C(8)–C(9)	112.2(6)
O(1)–Re(1)–N(1)	93.53(15)		

only oils were isolated. It is therefore obvious that chloride is not an ideal counterion for these large cations. With equimolar metal-to-ligand ratios, only the oxo-ethoxide species [ReOCl$_2$(OEt)(PPh$_3$)$_2$] was isolated, suggesting that the first step in the formation of the complexes is the substitution of the *trans* chloride by ethoxide. It is also intimated that the ligand L assists in the deprotonation of ethanol. The species [ReOCl$_2$(L)(PPh$_3$)]X could never be isolated, even in different solvents. In toluene the complexes [ReOCl$_3$(L)] were formed, and in acetone the dimeric oxo-bridged [Re$_2$O$_3$Cl$_4$(L)$_2$] species were isolated. The complexes **1**–**3** are only soluble in polar solvents such as water, DMF and acetonitrile. They are 1 : 1 electrolytes in DMF, and are stable for months in the solid state and for days in solution.

Spectroscopic Characterisation

In the infrared spectra of the complexes **1**–**3** a strong band around 957 cm^{-1} is assigned to ν(Re=O). Monooxorhenium(V) complexes with an anionic oxygen atom *trans* to the oxo group typically display ν(Re=O) in the range 950–968 cm^{-1} [16]. The presence of ethoxide *trans* to oxo is shown by broad and intense bands around 915 cm^{-1}, which corresponds to the ethoxy bending mode. Coordination of the imidazole nitrogen is shown by the shift of ν(C=N) from about 1670 cm^{-1} in the free ligands to around 1585 cm^{-1} for **1** and **2**, and to 1630 cm^{-1} in **3**. Coordination of the aliphatic nitrogen atom in **1** and **2** is shown by ν(Re–N) around 460 cm^{-1}, and the ν(N–H) that decreases from about 3310 cm^{-1} in the free ligands to around 3140 cm^{-1} in the complexes. Coordination of a single chloride is supported by a single band of medium intensity around 320 cm^{-1} in the spectra of all complexes. A decrease in the energy of the asymmetric ν(C–S–C) from 1285 cm^{-1} in the free ligand etmi to 1270 and 1268 cm^{-1} in **3a** and **3b** suggests that the ethereal sulfur atom is coordinated. The hexafluorophosphate and perrhenate salts show very strong broad bands around 850 cm^{-1} (ν(P–F)) and 910 cm^{-1} (ν(Re=O)), respectively.

^{1}H-NMR spectra were run in d_6-DMSO. The presence of the two imidazole ring protons is established by two single proton doublets in the narrow range δ 7.75–7.90 ppm. The 15 protons of the PPh_3 ligand appear in the range δ 7.50–7.70 ppm as a multiplet. The methylene protons of the ethoxide, which should give rise to a quartet signal, are obscured by the solvent peak, as are the proton signals of the methylene group of the ethyl substituent in **1**. All other details are given in the Experimental Section, and the data confirm the neutral bidentate coordination mode of the ligands eami, mami and etmi to rhenium in the complexes **1**–**3**.

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Description of the Structures

[ReOCl(OEt)(eami)(PPh$_3$)](ReO$_4$) (1a)

Single crystals of **1a** of X-ray quality were obtained by slow evaporation of the ethanolic mother liquor of the synthetic solution. An ORTEP perspective view of the asymmetric unit, along with the atom numbering scheme, is given in Fig. 1. The ethoxide molecule is distorted, but it has very little influence on any of the parameters of the structure. The rhenium atom is at the centre of a distorted octahedral environment. The basal plane is defined by the two nitrogen donor atoms of the eami ligand, the phosphorus atom of triphenylphosphine and chloride. The ethoxide oxygen and the oxo group are in *trans* axial positions. The chloride is coordinated *trans* to the imidazolyl nitrogen atom N(1). The eami moiety acts as a neutral bidentate ligand.

Selected bond distances and angles are given in Table II. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(1)=Re–O(2) axis of 174.6(2)°, accomplished by N(1)–Re–Cl and N(3)–Re–P angles of 168.03(16)° and 176.61(16)°, respectively. The rhenium atom is lifted out of the mean equatorial N_2ClP plane by 0.103(1) Å towards O(1), the result of the non-orthogonal angles O(1)–Re–N(1) = 91.2(2)°, O(1)–Re–Cl = 96.49(17)°, O(1)–Re–P = 91.96(16)° and

O(1)–Re–N(3) = 90.7(2)°. The bite angle (i.e. N(1)–Re–N(3)) of eami equals 77.6(2)°. This small bite angle in **1a** is ascribed to the larger steric requirements of the bulky triphenylphosphine group *cis* to the imidazole ring. The smaller bite angle of eami is also the result of the Cl–Re–P angle which is close to orthogonal (88.75(6)°). The orientation of the ligands in the equatorial plane around the rhenium atom is the result of simple σ-donicity and π-acidity considerations. The secondary aliphatic N(3) nitrogen is a good σ-donor atom, and hence a good π-acceptor ligand like PPh_3 occupies the position *trans* to it. Also, the chloride will donate electron density in the sigma region to Re(V), which will position the imidazole nitrogen N(1) *trans* to it, as it has π-acidic properties.

The Re–Cl distance of 2.3917(17) Å is slightly shorter than the average of 2.404 Å in $[ReO(OEt)Cl_2(py)_2]$ [11]. The Re=O(1) bond distance of 1.697(5) Å is statistically exactly the same as the mean of 1.691 Å ($\sigma = 0.025$) in various oxorhenium(V) complexes [17], and compares well with those reported for the $[ReO(OEt)X_2(PPh_3)_2]$ series [18] (X = I, 1.699(4); Cl, 1.678(6); Br, 1.715(9) Å, and $[ReO(OEt)(Ph_2PNPh_2Se)_2]$ (1.70(2) Å) [19]. The Re–O(2) distance of 1.866(5) Å is considerably shorter than in the above compounds (1.880(6)–1.896(6) Å), indicating some considerable multiple bond character, as was discussed by other workers [20]. The Re–P distance equals 2.4403(17) Å, which is short for this type of bond in Re(V) complexes. This is mainly the result of increased π-back bonding in the Re–P bond, which is the result of the good σ-donicity properties of the aliphatic N(3) atom. With a chlordie *trans* to a PPh_3, the average Re–P distance [21] is much shorter at 2.414(4) Å. The Re–N(1) bond (2.106(5) Å) is also shorter than the Re–N(3) bond (2.226(6) Å), thereby reflecting the multibond character of the rhenium to aromatic imidazolyl nitrogen bond.

The ethoxo group is disordered over two equally populated orientations about the axis, with positions for C(261) and C(262) being resolved. This type of disorder has also been observed for the phosphine complexes $[ReO(OEt)X_2(PPh_3)_2]$ (X = Cl, Br) [18, 22]. A broad range (138–176°) is found in the literature for the Re–O–Et angle; our Re–O(2)–Et angles (149.6(7) and 164.6(14)°) for the refined positions lie well within this range.

The imidazole ring is planar, as can be expected from an aromatic system, with torsion angles C(3)–N(2)–C(2)–C(1) = 0.5(8)° and N(1)–C(1)–C(2)–N(3) = 0.2(8)°, for example. The C(1)–C(2) bond is double bond at 1.347(10) Å, with C(1)–N(2) single at 1.385(8) Å. There is a delocalised double bond over the N(1)–C(3)–N(2) part of the ring, with bonds N(1)–C(3) = 1.324(9) Å and C(3)–N(2) = 1.338(9) Å. The bond around C(4) equals 107.4(6)°, which is very close to the ideal expected for an sp^3-hybridised carbon atom. The N(1)–C(3)–C(4)–N(3) torsion angle equals 28.7(9)°.

The perrhenate counterion is also disordered over three equally populated orientations for O(61), O(52) and O(51). The average Re(2)–O distance for the ordered oxo groups equals 1.673(9) Å. The closest contact that this counterion has with the complex is 3.528(19) Å, i.e. between O(61) and H(7B) on C(7).

[ReOCl(OEt)(etmi)(PPh$_3$)](ReO$_4$) (3a)

Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the ethanolic mother liquor of the synthetic solution. An ORTEP perspective view of the asymmetric unit, along with the atom-numbering scheme, is presented in Fig. 2. Selected bond distances and angles are given in Table III.

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The six bonded ligand atoms form a distorted octahedron about the rhenium atom. The basal plane is defined by the nitrogen and sulfur donor atoms of the etmi ligand, a triphenylphosphine and a chloride. The oxo group and the ethoxide oxygen are in *trans* axial positions. In contrast to the structure of **1a**, the phosphorus atom is coordinated *trans* to the imidazolyl nitrogen, making a nearly linear angle of 178.16(11)° [P–Re–N(1)]. The Cl–Re–S angle deviates appreciably from linearity at 169.54(4)°.

The O(1)–Re–O(2) bond angle deviates significantly from linearity at 169.00(13)°. The two Re(1)–O distances differ as would be expected for a structure of this kind. However, Re(1)–O(1), equal to 1.703(3) Å, lies well within the range of distances (1.60(5)–1.73(6) Å) considered to be representative of Re–O triple bonds [23], and Re(1)–O(2), equal to 1.863(3) Å, is substantially less than 2.04 Å, considered [24] to be representative of an Re(V)–O single bond. The Re(1)–O(2) distance is closer to the Re–O double bond distance of $1.76-1.78$ Å [25–27], and the Re–O (bridging) distance observed in Re–O–Re systems [27, 28], where multiple bonding has been postulated.

The partial multiple bonding in Re(1)–O(2) is consistent with the very large Re–O(2)–C(8) angle of 154.2(3)°, although this cannot be the only cause since, with a Re–O double bond, this bond would be expected to be close to 120°. This deviation may be the result of steric repulsion. The multiple bonding postulated here appears to be a general effect for O≡Re–OR systems. This is in complete contrast to the normal behaviour of formally single-bonded groups *trans* to an oxo-ligand in six-coordinate rhenium(V) compounds [23,24]. Normally the *trans* ligands are at distances from the metal even greater than normal metal–ligand single bond distances [23,24]. The O(2)–C(8) distance (1.419(7) Å) is normal, and the C(8)–C(9) distance of 1.452(10) Å corresponds to a normal single bond.

The rhenium(V) centre deviates from the mean equatorial plane by 0.078(1) Å towards the oxo O(1) oxygen. The smaller deviation of the rhenium from this plane results in the O(1)–Re(1)–N(1) and O(1)–Re(1)–Cl angles being larger than 90° at 93.53(15)° and 98.24(10)°, respectively. However, the O(1)–Re(1)–S and O(1)–Re(1)–P angles are smaller than 90° at 87.91(10)° and 88.28(10)°, respectively. The bite angle of the bidentate etmi ligand is 80.45(11)° [S–Re(1)–N(1)], considerably larger (~ 3°) than that of eami in **1a**.

The Re(1)–Cl bond length of 2.3710(13) Å, *trans* to sulfur, is slightly shorter than that in **1a**. The harder chloride donor is coordinated *trans* to the softer σ-donor and better π-acceptor sulfur donor atom. The Re(1)–P distance of 2.4711(10) Å is within the range expected for Re(V)–P bonds. The Re(1)–S and Re(1)–N(1) bonds of 2.4621(12) and 2.127(4) Å are as expected for these type of bonds.

The imidazole ring is planar, as is clear from the torsion angles C(2)–N(1)–C(3)–C(4) = 0.2(5)° and C(4)–N(2)–C(2)–N(1) = 0.6(5)°, for example. The N(1)–C(2) and N(2)–C(2) bonds differ little (1.334(6) and 1.346(6) Å, respectively), intimating the existence of a delocalised double bond over N(1)–C(2)–N(2). The rest of the ring bond lengths are as observed previously: a C(3)–C(4) double bond (1.339(7) Å), a C(3)–N(1) single bond (1.386(7) Å) and a C(4)–N(2) single bond (1.378(8) Å). The S–C(1)–C(2) bond angle of 111.7(3)° is larger than the ideal of 109.5°, contributing to the larger bite angle of etmi. The average Re–O bond distance for the ReO_4^- counterion is 1.703(5) Å, and the average bond angle between the Re–O bonds is ideal at 109.5(3)°.

A comparison of the structures of **1a** and **3a** reveals that the presence of the sterically bulkier sulfur donor atom in **3a**, instead of the NH group in **1a**, has no influence on the bond distances of the axial oxygen donor atoms; Re=O and the Re–O distances of **1a** and **3a** are identical within experimental error. However, the sulfur's influence on its *cis* ligands is significant, with both the Re–P and Re–N bond distances longer by 0.031(1) Å and 0.021(4) Å, respectively, than in **1a**. The bulky sulfur is also responsible for the distortion of its *cis* neighbours from the mean equatorial plane in **3a**; P moves above this plane towards O(1), and N(1) below the plane towards O(2) (O(1)–Re–P = 88.3(1)°; O(1)–Re–N(1) = 93.5(2)°).

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