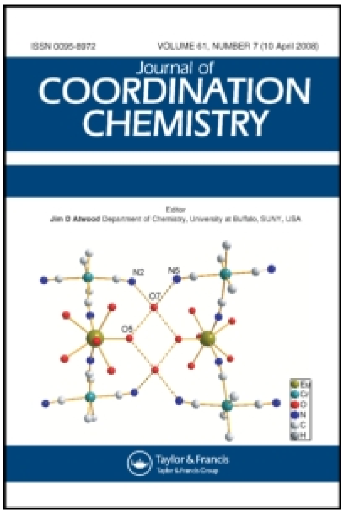

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Synthesis and Structural Characterization of Dinuclear Oxorhenium(V) Complexes with Bidentate Imidazole Derivatives

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

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The oxo-bridged dinuclear complexes $[(\mu\text{-O})\{ReOCl_2(L)\}_2]$ [L = 2-(1-ethylaminomethyl)-1-methylimidazole (eami); 2-(1-methylaminomethyl)-1-methylimidazole (mami); 2-(1-ethylthiomethyl)-1-methylimidazole (etmi)] were prepared by reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ with L in acetone. X-ray crystallographic studies of the eami and etmi complexes show that these ligands coordinate in a bidentate manner, and that the *cis*, *cis*-N_2Cl_2 and *cis*, *cis*-$NSCl_2$ equatorial planes are nearly orthogonal to the O=Re–O–Re=O backbone.

Keywords: Oxo-bridge; Dinuclear; Rhenium(V); Bidentate *N,N*; *N,S*; Imidazole; Crystal structure

INTRODUCTION

Recent interest in the coordination chemistry of rhenium was initially sparked by the development of technetium radiopharmaceuticals as diagnostic agents in nuclear medicine [1]. Initially, rhenium acted as a safe and non-radioactive substitute for its second row congener, technetium, in chemical studies. However, with the β-emitting radionuclides ^{186}Re and ^{188}Re finding their own applications as therapeutic agents in nuclear medicine, and the discovery of subtle differences in chemical behaviour between these two metals, a blossoming of activity in rhenium coordination chemistry has occurred [2–5].

These research efforts concentrate mainly on oxidation state V, since it is easily obtained from the reduction of perrhenate and easily stabilised by a large variety of ligands. A distinctive feature of most stable Re(V) complexes is the existence of multiple

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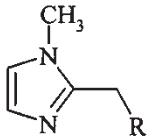
bonds to sulfur, nitrogen and, especially, oxygen [6]. The latter examples are mostly octahedral and contain one of the $[ReO]^{3+}$, $[ReO_2]^{+}$ or $[Re_2O_3]^{4+}$ moieties. Complexes of Re(V) which lack such multiple bonds are rare and unusual. In general, the monooxo core is formed with charged π-donor ligands such as Schiff bases, while the dioxo moiety is obtained with π-acceptor ligands or ligands that do not form π bonds.

The factors determining the formation of the $Re_2O_3^{4+}$ complexes have not been formalised. Most $Re_2O_3^{4+}$ complexes contain at least one basic N-donor atom in the equatorial plane *cis* to the oxo ligands [7–9]. Water is in most cases the source of the bridging oxo group, intimating that the production or presence of hydroxide is crucial. If no *N*-donors are present, triethylamine is added, or the synthesis is carried out at a pH of 9 or more. In the absence of water or a base, dimerization *via* the oxo group is prevented [9,10]. Also, when "flexible" N_2O_2-donor ligands are, for example, used, one of the anionic oxygen-donor atoms of the tetradentate ligand coordinates *trans* to the oxo group in the monomeric species, and dimerisation is prevented [11].

The chemistry of rhenium(V) with both aliphatic [12] and aromatic N,N-donor ligands [10,13,14] has been studied extensively, but bidentate N,N-donors containing an aliphatic nitrogen and a heterocyclic nitrogenous core have not been studied. Also, the potential of thioether ligands to coordinate to technetium and rhenium in a stable and bidentate fashion has been demonstrated [15]. In this account, the preparation and characterisation of oxo-bridged dimeric rhenium(V) complexes with the ligands 2-(1-ethylaminomethyl)-1-methylimidazole (eami), 2-(1-methylaminomethyl)-1-methylimidazole (mami) and 2-(1-ethylthiomethyl)-1-methylimidazole (etmi) are reported. The basic structure of the ligands is as follows.



R = $NHCH_2CH_3$ (eami)
$NHCH_3$ (mami)
SCH_2CH_3 (etmi)

EXPERIMENTAL

Reagents

trans-$[ReOCl_3(PPh_3)_2]$ [16] and the ligands eami, mami and etmi were prepared as stated previously [17]. All chemicals were of reagent grade and were used as received. Solvents were purified and dried before use.

Instrumentation

Scientific instrumentation used is the same as reported elsewhere [18]. Infrared spectra were obtained in KBr discs and ^1H NMR spectra were run in d_6-DMSO. Electronic spectra and conductivity measurements ($cm^2\,ohm^{-1}\,mol^{-1}$) were all obtained in DMF, and spectroscopic data are given as λ_{max} (nm) with extinction coefficients ($M^{-1}\,cm^{-1}$) in parentheses.

Synthesis of Complexes

[(μ-O){ReOCl$_2$(eami)}$_2$] (1)

Some 0.24 mmol of eami was dissolved in 5 mL of dried acetone and this solution was added to 0.12 mmol of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] in 5 mL of acetone. The mixture was heated under reflux for one hour, during which the green solution changed to light blue in colour. The solution was cooled to room temperature and the blue precipitate was collected by vacuum filtration. The blue product was washed with water and acetone and then dried under vacuum. Recrystallisation was from a CH$_3$CN/MeOH/acetone mixture (2 : 1 : 2), which was allowed to evaporate slowly in a desiccator. After two days, bright-blue crystals developed. They were collected and washed with acetone. The complex is insoluble in alcohols and hydrocarbons. Yield = 59% (based on Re), m.p. > 400 °C. Anal. Calcd. (%): C, 20.00; H, 3.12; N, 9.99. Found: C, 20.14; H, 3.18; N, 9.78. IR: ν(NH) 3168; ν(C=N) 1630; ν(C=C) 1505; ν(Re=O) 958; ν(Re–O–Re) 716; ν(Re–Cl) 307, 315 cm^{-1}. ^{1}H NMR (295 K) ppm: 1.38(3H, t, NCH$_2$CH_3), 3.85 (5H, m, CH_3–N, CH_2–N), 4.00 (1H, s, NH), 6.84 (1H, d, H(2)), 7.57 (1H, d, H(3)). UV-Vis: 409(3400), 649(2400). Conductivity (10^{-3} M) = 42.

[(μ-O){ReOCl$_2$(mami)}$_2$] (2)

This complex was prepared in a similar way to **1**. Yield 76% (based on Re), m.p. > 400 °C. Anal. Calcd. (%): 23.01; H, 3.54; N, 6.71. Found: C, 22.87; H, 3.39; N, 6.86. IR: ν(NH) 3162; ν(C=N) 1617; ν(C=C) 1505; ν(Re=O) 937; ν(Re–O–Re) 719; ν(Re–Cl) 311, 318 cm^{-1}. ^{1}H NMR (295 K) ppm: 3.82 (3H, s, N–CH_3), 3.93 (3H, s, CH_3–N), 4.52(2H, s, CH_2–N), 3.99 (1H, s, NH), 6.83 (1H, d, H(2)), 7.75 (1H, d, H(3)). UV-Vis: 397 (4200), 655(1900). Conductivity (10^{-3} M) = 38.

[(μ-O){ReOCl$_2$(etmi)}$_2$] (3)

A 0.24-mmol aliquot of etmi was dissolved in 5 mL of dried acetone and this solution was added to 0.12 mmol of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] in 5 mL of acetone. The mixture was refluxed gently for one hour, during which time a green precipitate formed. The solution was cooled, filtered, and the precipitate washed with water and acetone. Suitable crystals were obtained by recrystallising the product from DMF. Yield 68% (based on Re), m.p. > 400 °C. Anal. Calcd. (%): C, 21.88; H, 3.24; N, 6.01; S, 6.87. Found: C, 21.81; H, 3.07; N, 6.29; S, 6.82. IR: ν(C=N) 1618; ν(C=C) 1496; ν(C–S–C) 1273; ν(Re=O) 974; ν(Re–O–Re) 694; ν(Re–Cl) 305, 325 cm^{-1}. ^{1}H NMR (295 K) ppm: 1.15 (3H, t, SCH$_2$CH_3), 3.82 (3H, s, CH_3N), 3.87 (2H, q, SCH_2CH$_3$), 4.16 (2H, s, CH_2–S), 7.63 (1H, d, H(2)), 7.74 (1H, d, H(1)). UV-Vis: 352(2150), 648 (300). Conductivity (10^{-3} M) = 33.

X-ray Structure Determinations

Data collection for Complex **1** was performed at 120 K on a Nonius Kappa CCD single crystal diffractometer using Cu Kα radiation. The crystal detector distance was fixed at 29 mm, and a total of 32 images were collected using the oscillation method, with 2° oscillation and 20 s exposure time per image. Data collection strategy was performed by the program COLLECT [19]. Data reduction and cell refinement were performed with the programs DENZO and SCALEPACK [20].

The crystal structure of **1** was solved by direct methods, using the program SHELXS-97 [21]. Anisotropic least-squares refinement was carried out with SHELXL-97 [21]. The hydrogen atoms were geometrically placed. During the final stages of the refinement the non-hydrogen atoms were anisotropically refined. The hydrogen atoms were isotropically refined with a common thermal parameter for each group of hydrogen atoms riding on the same atom. Atom scattering factors for **1** and **3** were taken from *International Tables for X-ray Crystallography* [22]. Geometrical calculations of **1** were made with PARST [23]. The crystallographic plots were made with EUCLID [24].

A green rod-like crystal of Complex **3** was used for data collection at 200 K on a Nonius Kappa CCD, using Mo Kα radiation. Unit cell and space group determinations were carried out in the usual manner [25]. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-96 [26]. The oxygen atom of acetone could not be localised, so all acetone atoms were isotropically refined as carbon with one common *U*. All other non-hydrogen atoms were refined anisotropically. The hydrogen atoms of acetone were omitted.

ORTEP views of the asymmetric units of **1** and **3**, along with the atom-numbering schemes, are given in Figs. 1 and 2, respectively. Summaries of crystal data and refinement details are shown in Table I for **1** and **3**. Tables II and IV give atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atom for the two complexes. Bond distances and angles for **1** are shown in Table III and those for **3** in Table V.

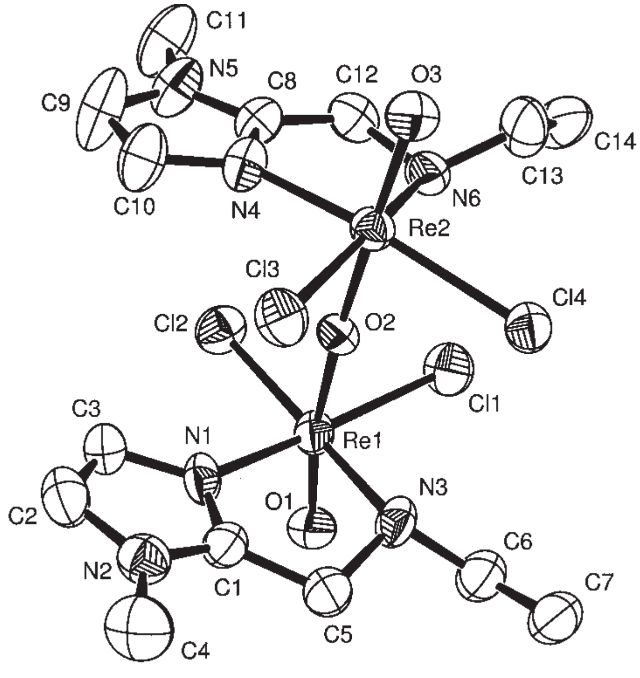


FIGURE 1 An ORTEP view of $[(\mu\text{-O})\{\text{ReOCl}_2(\text{eami})\}_2]$ (**1**), showing the atom labelling scheme and 50% probability ellipsoids.

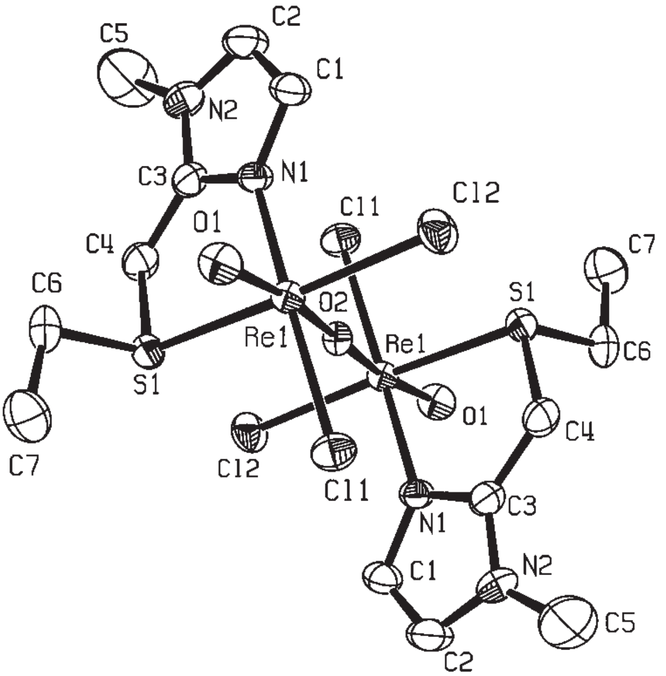


FIGURE 2 ORTEP view (at 50% probability) of [(μ-O){ReOCl$_2$(etmi)}$_2$] (**3**). The acetone molecule is omitted for clarity.

TABLE I Crystal and structure refinement data for [(μ-O){ReOCl$_2$(eami)}$_2$] (**1**) and [(μ-O){ReOCl$_2$(etmi)}$_2$] (**3**)

Property	*1*	*3*
Empirical formula	$C_{14}H_{26}Cl_4N_6O_3Re_2$	$C_{14}H_{24}Cl_4N_4O_3S_2Re_2 \cdot C_3H_6O$
Formula weight	840.61	932.80
Temperature (K)	120 (2)	200
Wavelength (Å)	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 17.1991\,(6)$	$a = 8.4658(2)$
	$b = 16.7701\,(4)$	$b = 11.9025\,(3)$
	$c = 16.8039\,(4)$	$c = 13.3491\,(3)$
	$\beta = 81.488\,(2)$	$\beta = 97.6566\,(9)$
Volume (Å^3)	4793.4 (2)	1333.12 (6)
Z	8	2
Density (calc.) (Mg/m^3)	2.330	2.299
Crystal size (mm)	0.18 × 0.03 × 0.03	0.04 × 0.05 × 0.17
Absorption coefficient (μ) (mm^{-1})	23.797	9.661
F(000)	3152	868
Theta range for data collection	3.70–69.67°	3.2–27.5°
Index ranges	$-20 \le h \le 20$,	$-10 \le h \le 10$
	$0 \le k \le 20$,	$-15 \le k \le 15$
	$0 \le l \le 20$	$-17 \le l \le 17$
Reflections collected/unique	8952/8952 [R(int) = 0.096]	29477/3045 [R(int) = 0.061]
Data/restraints/parameters	8952/0/523	30450/0/143
Goodness-of-fit on F^2	0.983	1.10
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0441$, $wR2 = 0.0882$	$R1 = 0.0289$, $wR2 = 0.0707$
Largest diff. peak and hole (e Å^{-3})	1.905 and − 1.460	1.55 and − 1.30

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Re(1)	4116 (1)	6967 (1)	2215 (1)	37 (1)
Re(2)	3470 (1)	9098 (1)	1881 (1)	35 (1)
Cl(1)	4609 (2)	7522 (1)	3383 (1)	57(1)
Cl(2)	5384 (1)	7176(1)	1454 (1)	52 (1)
Cl(3)	2499 (1)	8656 (1)	1112 (1)	47 (1)
Cl(4)	2533 (1)	8912(1)	3097 (1)	43(1)
O(1)	4212 (3)	6029 (3)	2530 (4)	50 (2)
O(2)	3797 (3)	8027 (3)	2013 (3)	37 (1)
O(3)	3344 (3)	10092 (3)	1839 (3)	48 (2)
N(1)	3580 (4)	6674 (4)	1238 (4)	40 (2)
N(2)	2524 (4)	6483 (4)	700 (4)	46 (2)
N(3)	2905 (4)	6904 (4)	2766 (4)	42 (2)
N(4)	4364 (4)	9080 (4)	926 (4)	43 (2)
N(5)	5611 (5)	9163 (5)	445 (5)	60 (2)
N(6)	4475 (4)	9274 (4)	2504 (4)	43 (2)
C(1)	2809 (5)	6540 (5)	1385 (5)	39 (2)
C(2)	3129 (6)	6582 (5)	77 (6)	53 (2)
C(3)	3781 (6)	6702 (5)	410 (5)	48 (2)
C(4)	1694 (6)	6386 (6)	618 (6)	65 (3)
C(5)	2424 (5)	6468 (6)	2233 (5)	53 (2)
C(6)	2744 (6)	6611 (6)	3612 (5)	56 (3)
C(7)	1943 (6)	6778 (6)	4026 (6)	59 (3)
C(8)	5086 (5)	9203 (5)	1102 (5)	41 (2)
C(9)	5206 (6)	8985 (8)	−194 (6)	78 (4)
C(10)	4447 (6)	8935 (6)	108 (5)	58 (3)
C(11)	6458 (6)	9266 (8)	409 (6)	81 (4)
C(12)	5230 (5)	9355 (6)	1940 (5)	50 (2)
C(13)	4403 (6)	9857 (7)	3166 (6)	62 (3)
C(14)	5022 (6)	9768 (7)	7236 (6)	69 (3)

U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE III Selected bondlengths (Å) and angles (°) for **1**

Re(1)–O(1)	1.676 (6)	N(5)–C(8)	1.320 (11)
Re(1)–O(2)	1.905 (5)	N(5)–C(9)	1.396 (13)
Re(1)–N(1)	2.058 (7)	N(5)–C(11)	1.459 (12)
Re(1)–N(3)	2.154 (7)	N(6)–C(13)	1.473 (11)
Re(1)–Cl(2)	2.386 (2)	N(6)–C(12)	1.496 (11)
Re(1)–Cl(1)	2.434 (2)	C(1)–C(5)	1.483 (11)
Re(2)–O(3)	1.684 (6)	C(2)–C(3)	1.340 (12)
Re(2)–O(2)	1.905 (5)	N(2)–C(1)	1.320 (10)
Re(2)–N(4)	2.052 (7)	N(2)–C(2)	1.374 (11)
Re(2)–N(6)	2.169 (7)	N(2)–C(4)	1.464 (11)
Re(2)–Cl(3)	2.376 (2)	N(3)–C(6)	1.491 (10)
Re(2)–Cl(4)	2.427 (2)	N(3)–C(5)	1.497 (11)
N(1)–C(1)	1.332 (10)	N(4)–C(8)	1.336 (10)
N(1)–C(3)	1.383 (10)	N(4)–C(10)	1.383 (11)
O(1)–Re(1)–O(2)	167.5 (3)	Cl(2)–Re(1)–Cl(1)	88.65 (8)
O(1)–Re(1)–N(1)	96.0 (3)	O(3)–Re(2)–O(2)	168.7 (3)
O(1)–Re(1)–N(3)	87.2 (3)	O(3)–Re(2)–N(4)	93.9 (3)
O(2)–Re(1)–N(3)	80.6 (2)	O(3)–Re(2)–N(6)	90.2 (3)
N(1)–Re(1)–N(3)	79.2 (3)	O(2)–Re(2)–N(6)	78.6 (2)
O(1)–Re(1)–Cl(2)	100.5 (2)	N(4)–Re(2)–N(6)	79.7 (3)
N(1)–Re(1)–Cl(2)	95.1 (2)	O(3)–Re(2)–Cl(3)	100.4 (2)
O(1)–Re(1)–Cl(1)	92.4 (2)	N(4)–Re(2)–Cl(3)	94.3 (2)
O(2)–Re(1)–Cl(1)	86.09 (16)	O(3)–Re(2)–Cl(4)	95.2 (2)
N(1)–Re(1)–Cl(1)	170.05 (19)	N(4)–Re(2)–Cl(4)	169.6 (2)
N(3)–Re(1)–Cl(1)	95.90 (18)	N(6)–Re(2)–Cl(4)	95.09 (19)
Cl(3)–Re(2)–Cl(4)	89.14 (7)	Re(1)–O(2)–Re(2)	176.4 (3)

TABLE IV Atomic coordinates and equivalent isotropic displacements ($\mathrm{\AA}^2$) for **3**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Re(1)	0.05604 (2)	0.10406 (1)	0.60953 (1)	0.0221 (1)
C1(1)	– 0.20893 (14)	0.18323 (11)	0.57032 (10)	0.0332 (4)
C1(2)	0.15192 (16)	0.24111 (11)	0.50211 (11)	0.0365 (4)
S(1)	– 0.02276 (14)	– 0.06017 (11)	0.70392 (10)	0.0270 (3)
O(1)	0.0968 (4)	0.1760 (3)	0.7188 (3)	0.0333 (11)
O(2)	0	0	½	0.0226 (12)
N(1)	0.2748 (4)	0.0218 (4)	0.6306 (3)	0.0259 (11)
N(2)	0.4378 (6)	– 0.1178 (4)	0.6742 (4)	0.0430 (16)
C(1)	0.4241 (6)	0.0522 (5)	0.6122 (4)	0.0327 (17)
C(2)	0.5252 (6)	– 0.0322 (6)	0.6389 (5)	0.0432 (19)
C(3)	0.2868 (6)	– 0.0824 (5)	0.6691 (4)	0.0312 (17)
C(4)	0.1488 (6)	– 0.1498 (5)	0.6937 (4)	0.0334 (17)
C(5)	0.5001 (10)	– 0.2266 (8)	0.7093 (9)	0.096 (4)
C(6)	0.0076 (7)	– 0.0225 (5)	0.8371 (4)	0.0389 (17)
C(7)	– 0.1429 (8)	0.0336 (6)	0.8627 (5)	0.048 (2)
C(8)	½	0	0	0.122 (4)
C(9)[a]	0.548 (3)	0.0986 (13)	0.0630 (16)	0.122 (4)
C(10)[a]	0.411 (3)	0.005 (2)	– 0.1042 (9)	0.122 (4)
C(11)[a]	0.523 (3)	– 0.1158 (11)	0.0495 (17)	0.122 (4)

U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.
[a]Acetone of crystallisation; see text.

TABLE V Selected bondlengths (Å) and angles (°) for **3**

Re(1)–Cl(1)	2.4251(12)	N(1)–C(1)	1.368(6)
Re(1)–Cl(2)	2.3846 (14)	N(2)–C(3)	1.341 (7)
Re(1)–S(1)	2.4652 (13)	N(2)–C(2)	1.379 (8)
Re(1)–O(1)	1.687 (4)	N(2)–C(3)	1.339 (7)
Re(1)–O(2)	1.9267 (2)	N(2)–C(5)	1.452 (11)
Re(1)–N(1)	2.081 (4)	C(1)–C(2)	1.337 (9)
S(1)–C(4)	1.822 (6)	C(3)–C(4)	1.489 (8)
S(1)–C(6)	1.818 (5)	C(6)–C(7)	1.517 (9)
Cl(1)–Re(1)–Cl(2)	89.06 (5)	S(1)–Re(1)–O(2)	79.75 (3)
Cl(1)–Re(1)–S(1)	96.48 (4)	S(1)–Re(1)–N(1)	81.63 (12)
Cl(1)–Re(1)–O(1)	93.79 (12)	O(1)–Re(1)–O(2)	169.68 (12)
Cl(1)–Re(1)–O(2)	87.64 (3)	O(1)–Re(1)–N(1)	92.65 (16)
Cl(1)–Re(1)–N(1)	173.29 (12)	O(2)–Re(1)–N(1)	85.69 (12)
Cl(2)–Re(1)–S(1)	170.66 (5)	Re(1)–O(2)–Re(1)_a	180.00
Cl(2)–Re(1)–O(1)	97.23 (13)	C(1)–N(1)–C(3)	106.8 (4)
Cl(2)–Re(1)–O(2)	93.01 (3)	C(2)–N(2)–C(3)	107.6 (5)
S(1)–Re(1)–O(1)	89.92 (13)	S(1)–C(6)–C(7)	108.4 (4)

RESULTS AND DISCUSSION

Synthesis

The complexes $[(\mu\text{-O})\{\mathrm{ReOCl_2(L)}\}_2]$ (L = eami, mami, etmi) were synthesised by the reaction of *trans*-$[\mathrm{ReOCl_3(PPh_3)_2}]$ with a two-fold molar excess of the ligands L in dry acetone in a system that was open to the atmosphere. Not surprisingly, the source of the bridging oxo group is atmospheric water. This reaction does not, however, occur under equimolar conditions, when only the mononuclear complexes $(\mathrm{ReOCl_3(L)}]$

could be isolated from acetone. This indicates that the second mole of L is involved in deprotonation of the coordinated water molecule. The reaction is given by the following equation.

$$2[\mathrm{ReOCl_3(PPh_3)_2}] + 4\mathrm{L} + \mathrm{H_2O} \rightarrow (\mu\text{-O})\{\mathrm{ReOCl_2(L)}\}_2 + 2\mathrm{LH^+Cl^-} + 4\mathrm{PPh_3}$$

The sensitivity of high oxidation state 4d and 5d transition metal ions to hydrolysis has been observed. For example, the oxo chemistry of Mo(V) is dominated by dinuclear complexes that contain single and double oxo bridges, due to its ability to abstract an oxo group from water [27]. It was also found that the shortening of the substituent on the aliphatic nitrogen has a dramatic influence on the yield of these reactions, raising it from 59% in **1** (ethyl substituent) to 76% in **2**. Complexes **1**–**3** are air-stable and non-electrolytes in DMF. They are very insoluble and only in DMF, DMSO and acetonitrile was solubility significant.

Spectroscopic Characterization

The dominant feature in the IR spectra of the dimeric Complexes **1**–**3** is the presence of a strong and intense absorption band in the region 700–740 $\mathrm{cm^{-1}}$, ascribed to the asymmetric Re–O–Re stretching mode [10, 28, 29]. For **1**, **2** and **3**, ν(Re=O) is evidenced by weak absorptions at 958, 937 and 974 $\mathrm{cm^{-1}}$, respectively. A weak or medium absorption corresponding to ν(Re=O) has been observed for dimeric species containing the imidazole ligand [10]. Complexes **1** and **2** exhibit medium absorption bands at 3168 and 3162 $\mathrm{cm^{-1}}$, respectively, assigned to ν(N–H). The presence of this band in both complexes verifies that the secondary amine nitrogen remains protonated. Coordination of the imidazolyl nitrogen [30] is indicated by the shift in ν(C=N) from around 1670 $\mathrm{cm^{-1}}$ in the free ligands to about 1620 $\mathrm{cm^{-1}}$ in the spectra of the complexes. For Complex **3**, coordination of the thioethereal sulfur is indicated by the lowering of the asymmetric C–S–C stretching mode from 1285 $\mathrm{cm^{-1}}$ in the spectrum of the free ligand to 1275 $\mathrm{cm^{-1}}$ in the complex [31]. A medium intensity band around 307 $\mathrm{cm^{-1}}$ with a shoulder at about 320 $\mathrm{cm^{-1}}$ [ν(Re–Cl)] indicates the presence of the two inequivalent *cis* chlorides in the complexes.

Complexes **1**–**3** show sharp, well-resolved peaks in their ^{1}H NMR spectra. There are no detectable paramagnetic shifts or line broadening of the signals. The proton signals of the imidazole ring in **1** and **2** are practically identical at δ 6.84 and 7.57 ppm, while those of **3** appear further downfield. The signals of the methylene $\mathrm{CH_2}$ protons of the ethyl group in **1** and **3** are obscured by the solvent peak. All the other signals are as expected, and support the coordination of the ligands L to rhenium(V) in a bidentate mode.

Description of the Structures

[(μ-O){ReOCl$_2$(eami)}$_2$] (1)

Complex **1** consists of two independent [(ReOCl$_2$(eami)] units bridged by an oxygen atom (Fig.1). There are two molecules in the asymmetric unit, one which is ordered [Re(1)Re(2)] and another which shows some disorder. For this discussion, the molecule that is labelled Re(1)Re(2) will be used. The characteristic feature is the presence of the O=Re–O–Re=O backbone which shows considerable deviation from linearity [O(1)–

Re(1)–O(2)=167.5(3)°; O(3)–Re(2)–O(2) = 168.7(3)°; Re(1)–O(2)–Re(2) = 176.4(3)°]. In this respect the structure of **1** is comparable to those found for corresponding rhenium complexes (μ-O)[ReO(Meim)$_2$Cl$_2$]$_2$ (Meim = 1-methylimidazole) [32], (μ-O) [ReO(en)Cl$_2$]$_2$ (en = ethylenediamine) [33] and (μ-O)[ReO(biimMe$_2$)Cl$_2$]$_2$ (biimMe$_2$ = *N*,*N*′−dimethylbiimidazole) [10].

Each rhenium atom is centred in an octahedron with the equatorial plane formed by the N$_2$Cl$_2$ donor set. The octahedra are appreciably distorted, with the four equatorial ligands being displaced away from the Re=O bonds. The effect is small for the donor atoms Cl(1), N(4), N(6) and Cl(4), with the O–Re–X angles ranging from 90.2(3)° to 95.2(2)° (Table III). This deviation is large for the atoms N(1), Cl(2) and Cl(3), falling in the range 96.0(3)–100.5(2)°. However, the O(1)–Re(1)–N(3) angle is only 87.2(3)°. These distortions, typical of such systems, is due to the relatively high double-bond character of the terminal bonds [Re(1)–O(1) = 1.676(6) Å; Re(2)–O(3) = 1.684(6) Å] compared to the bridging Re–O bonds (both 1.905(5) Å), which are definitely on the single-bond side. Re–N(imidazole) bond distances [average = 2.055(7) Å] are shorter than the average Re–N(amine) bonds [2.162(7) Å]. This reflects considerable π-character in the Re–N(imidazole) bonds, with only σ-character in the Re–N(aliphatic) bonds. The Re–Cl bonds [mean = 2.406(2) Å] are slightly longer than in (μ-O)[ReOCl$_2$(biim)]$_2$ [average = 2.397(2) Å] [10] and in the *cis*, *cis* dimer (μ-O)[ReOCl$_2$(py)$_2$]$_2$ (average = 2.375 Å) [32]. Also, the Re–Cl(1) and Re–Cl(4) bondlengths are longer [average = 2.431(2) Å] than the Re–Cl bonds *trans* to the aliphatic nitrogen donor atoms [mean = 2.381(2) Å].

The molecule adopts a staggered conformation in which the ReN$_2$Cl$_2$ planes are mutually rotated by 168.7° about the O=Re–O–Re=O axis, so that the chlorines of one ReOCl$_2$N$_2$ unit almost eclipse the nitrogen atoms of the other part of the molecule. The bondlengths of the Re=O cores of 1.676(6) Å and 1.684(6) Å are shorter than is commonly observed for nitrogen-coordinated dimers of the type Re$_2$O$_3^{4+}$, which fall in the range 1.688(5)–1.706(7) Å [34]. The bridging Re–O distance of 1.905(5) Å is similar to what was observed earlier in (μ-O)[ReOCl$_2$(biim)]$_2$ [1.905(1) Å] [10] and in (μ-O)-[ReOCl$_2$(py)$_2$]$_2$ [1.912(5) Å].

The average bite angle of the eami ligands equals 79.5(3)° and this introduces little strain in the eami molecule, with the N(1)–C(1)–C(5) bond angle [118.9(7)°] deviating little from the ideal of 120°. In the imidazole rings, C(1)–N(1) and C(1)–N(2) bonds are not localised double and single bonds as expected, but are delocalised, with bond distances of 1.332(10) and 1.320(10) Å, respectively. The C(2)–N(2) and C(3)–N(1) bonds are localised single bonds [1.374(11) and 1.383(10) Å], with the C(2)–C(3) bond a double bond with a distance of 1.340(12) Å. The same phenomenon is observed for the eami ligand coordinated to Re(2).

[(μ-O){ReOCl$_2$(etmi)}$_2$] (3)

Dark blue crystals with the formulation **3** · acetone, suitable for X-ray analysis, were obtained by slow evaporation of a DMF solution. The molecular structure of **3** is illustrated in Fig. 2 and bondlengths and angles are listed in Table V. The axis of the molecule is formed by the O=Re–O–Re=O moiety, with the bridging O(2) atom lying on a crystallographic inversion centre. Therefore, the Re–O–Re angle is exactly 180°, and the two O–Re=O angles are equal [169.68(12)°] showing a significant deviation from linearity.

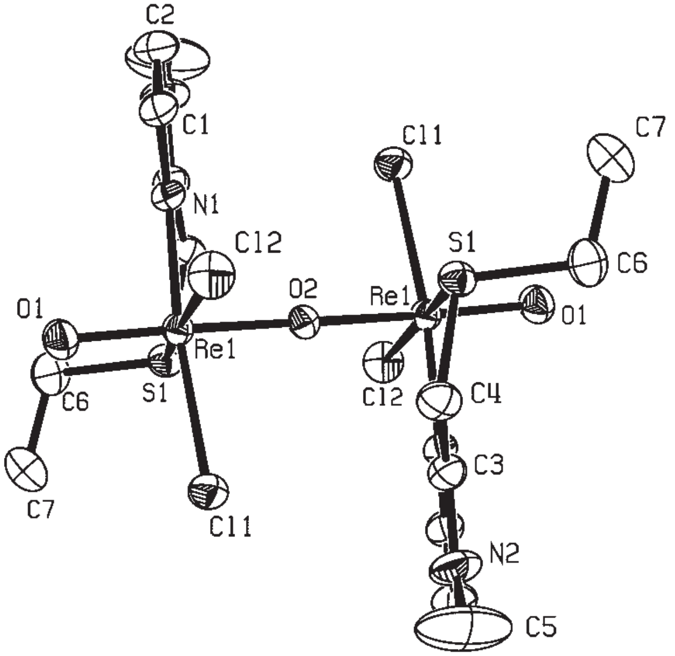


FIGURE 3 An ORTEP view of **3** showing the staggered conformation of the $ReCl_2NS$ planes rotated about the O=Re–O–Re=O axis.

Each rhenium atom is centred in an octahedron with the equatorial plane formed by a Cl_2NS donor set. With respect to the bridging oxygen, the chlorines are placed in an *anti* position [O(2)–Re–Cl(1) = 87.64(3)°; O(2)–Re–Cl(2) = 93.01(3)°]. As usual, the donor atoms in the $ReCl_2NS$ plane are repelled by the Re=O group (except for sulfur; O(1)–Re–S(1) = 89.92(13)°, with O(1)–Re–X angles greater than 90°. The result is that the rhenium atom is displaced from the mean equatorial plane by 0.128 Å towards the O(1) atom. Re=O and Re–O distances of 1,687(4) Å and 1.9267(2) Å are typical of this backbone. The Re–S bondlength of 2.4652(13) Å] is significantly longer than that found for Re(V) thioether complexes of this kind, which varies in the range 2.35–2.44 Å [15]. Re–Cl [2.3846(14) and 2.4251(12) Å and Re–N [2.081(4) Å] distances compare well with those found earlier in similar complexes [Re–Cl averages of 2.368(9) and 2.449(9) Å [15]; Re–N average of 2.109(6) Å [10]]. The molecule adopts a staggered conformation in which the $ReCl_2NS$ planes are mutually rotated by 176.4° about the O=Re–O–Re=O axis (Fig. 3). The bite angle [S(1)–Re–N(1)] of the bidentate etmi ligand is 81.63(12)°. The effect of this larger than normally observed angle is reflected in the strain of the coordinated etmi molecule, with N(1)–C(3)–C(4) [124.1(5)°] and C(3)–C(4)–S(1) [111.0(4)°] angles larger than the ideal values of 120° and 109°, respectively.

The intraligand bond distances in etmi again illustrate π-delocalisation over N(2)–C(3)–N(1), with N(2)–C(3) and N(1)–C(3) equal to 1.339(7) and 1.341(7) Å, respectively, indicating double bonds. The C(1)–C(2) bond is a localised double bond with a distance of 1.337(9) Å, and the N(1)–C(1) and N(2)–C(2) bonds are localised single bonds [1.368(6) and 1.379(8) Å, respectively]. The aromaticity of the imidizole rings is illustrated by its planarity; the C(1)–N(1)–C(3)–N(2) and C(3)–N(1)–C(1)–C(2) torsion angles are only $-0.6(6)^\circ$ and $0.1(6)^\circ$, respectively.

In contrast to the case of $[(\mu\text{-O})\{\text{ReOCl}_2(\text{py})_2\}_2]$ [8] and related systems with monodentate nitrogen-donor ligands [35, 32], the etmi ligand must be perpendicular to the backbone. The two halves of the molecule are related by a crystallographic inversion centre at the central μ-oxo ligand, and the two etmi ligands show no stacking interactions. The distances of the chlorine atoms of one unit from the imidazole plane in the other unit are 3.586(5) and 3.609(6) Å, that is, roughly equal to the sum of the van der Waals radii [36].

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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