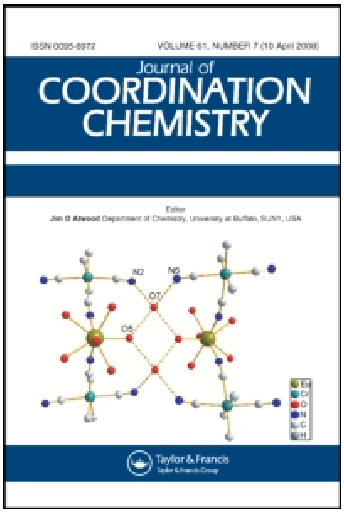

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SYNTHESIS AND CRYSTAL STRUCTURE OF A MONONUCLEAR COMPLEX OF OXORHENIUM (V) WITH 2,2′-DIPYRIDYLAMINE

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The complex [ReOCl$_2$(OEt)(dpa)] was prepared by reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a twofold molar excess of 2,2′-dipyridylamine (dpa) in ethanol under an inert atmosphere. Its X-ray crystal structure shows that the *N*,*N*-chelated dpa ligand is coordinated in the equatorial plane *cis* to the oxo and ethoxo groups, which are in *trans* positions relative to each other. The two pyridine rings of dpa are folded around the bridging nitrogen atom away from the oxo oxygen atom.

Keywords: Rhenium(V); 2,2′-Dipyridylamine; *trans* Oxo-ethoxo; X-ray structure

INTRODUCTION

The ability of 2,2′-dipyridylamine (dpa) to coordinate as a bidentate ligand to transition metal ions is well established [1–3]. The two ring nitrogen atoms act as the donors in the majority of complexes, although some examples exist in which the bridging amino nitrogen has donor properties [4].

We have previously described the syntheses and structures of the rhenium(V) complexes *trans*-[ReO$_2$(dpa)$_2$]Cl and two polymorphs of (μ-O)[{ReOCl$_2$(dpa)}$_2$] [5]. We have now also managed to isolate the monomeric monooxo complex [ReOCl$_2$(OEt)(dpa)], and in this account its preparation and structure are reported.

EXPERIMENTAL

Trans-[ReOCl$_3$(PPh$_3$)$_2$] was synthesised by a literature method [6]. 2,2′-Dipyridylamine (dpa) was obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. All manipulations were done

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under nitrogen using standard Schlenk and cannula techniques. Infrared spectra were obtained using KBr discs and ^{1}H NMR spectra (300 MHz) were run at room temperature in d_6-DMSO. The instrumentation used is the same as reported earlier [7].

Synthesis of [ReOCl$_2$(OEt)(dpa)] (1)

Dpa (137 mg, 800 μmol) was added to a stirred suspension of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] (300 mg, 360 μmol) in 10 cm^3 of ethanol and the mixture was heated under reflux for 30 mins. After about 10 mins heating, the lime-green colour of the starting material changed to purple, and after heating was stopped and the solution cooled to room temperature, a purple solid was filtered off. Recrystallization from dichloromethane/ethanol gave dark blue crystals. Yield = 58%, mp 299–301°C. Anal. Calcd. for $C_{12}H_{14}N_3O_2Cl_2Re$ (%): C, 29.45; H, 2.88; N, 8.59. Found: C, 29.68; H, 2.72; N, 8.56. IR(cm^{-1}): ν(Re=O) 954s, ν(C=C) 1587s, ν(C=N) 1630s, ν(N–H) 3216w, δ(OCH$_2$) 916vs, ν(Re–N) 524m, ν(Re–Cl) 318m. ^{1}H NMR δ(ppm): 11.04 (s, 1H, N*H*), 9.26 (d, 2H, *H*(1), *H*(10), *J* 6.1), 8.15 (t, 2H, *H*(3), *H*(8), *J* 7.3), 7.54 (d, 2H, *H*(4), *H*(7), *J* 7.3), 7.47 (t, 2H, *H*(2), *H*(9), *J* 6.1), 3.28 (q, 2H, C*H*$_2$, *J* 7.1), 0.77 (t, 3H, C*H*$_3$, *J* 7.1). Conductivity (DMF, 10^{-3} M): 8 Ω^{-1}cm^{2}mol^{-1}.

Crystallography

Intensity data were collected on a Nonius Kappa CCD diffractometer at 200(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å). Further details are given in Table I. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically. Selected bond lengths and angles are given in Table II.

TABLE I Crystal data and structure refinement data for **1**

Chemical formula	$C_{12}H_{14}N_3O_2Cl_2Re$
Formula weight	489.37
Temperature (K)	200(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions (Å)	$a = 14.8212(4)$ $b = 7.6036(2)$ $c = 13.1638(4)$
Volume (Å^3)	1483.5(1)
Z	4
Density (calc., Mg/m^3)	2.191
Absorption coefficient (mm^{-1})	8.555
$F(000)$	928
Crystal size (mm)	0.18 × 0.03 × 0.02
θ range for data collection (°)	3.15–25.01
Index ranges	$-17 \le h \le 17$, $-8 \le k \le 9$, $-14 \le l \le 15$
Reflections measured	14014
Independent/observed reflections	2501/2248
Data/restraints/parameters	2248/1/185
Goodness of fit on F^2	1.121
R, wR_2	0.0251, 0.0509
Largest diff. peak and hole, (e Å^{-3})	1.206, −0.855

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

Re–O(1)	1.690(5)	Re–O(2)	1.866(5)
Re–N(1)	2.131(4)	Re–N(3)	2.156(7)
Re–Cl(1)	2.384(2)	Re–Cl(2)	2.408(2)
O(2)–C(11)	1.430(9)	C(11)–C(12)	1.502(12)
N(2)–C(5)	1.391(8)	N(2)–C(6)	1.374(9)
C(1)–N(1)	1.365(8)	N(3)–C(6)	1.348(9)
C(5)–N(1)	1.347(8)	N(3)–C(10)	1.357(10)
O(1)–Re–O(2)	169.6(2)	N(1)–Re–N(3)	86.1(3)
O(1)–Re–N(1)	87.9(3)	Cl(1)–Re–Cl(2)	88.3(1)
O(1)–Re–N(3)	85.7(2)	N(3)–C(10)–C(9)	122.0(7)
O(1)–Re–Cl(1)	95.1(2)	C(5)–N(2)–C(6)	129.4(6)
O(1)–Re–Cl(2)	96.0(2)	C(5)–N(1)–Re	121.6(4)
Re–O(2)–C(11)	149.8(5)	C(6)–N(3)–Re	120.3(5)
O(2)–C(11)–C(12)	110.3(9)	N(1)–Re–Cl(1)	93.3(2)
C(1)–N(1)–C(5)	117.6(5)	N(3)–Re–Cl(2)	92.2(2)

RESULTS AND DISCUSSION

The complex [$ReOCl_2(OEt)(dpa)$] (**1**) was prepared by reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a twofold molar excess of 2,2′-dipyridylamine (dpa) at reflux in ethanol under a nitrogen atmosphere. With an equimolar ratio of reactants, coordination of dpa could not be achieved, and only [$ReOCl_2(OEt)(PPh_3)_2$] was isolated. We reported earlier [5] that a twofold molar excess of dpa led to the formation of the μ-oxo dimer [$Re_2O_3Cl_4(dpa)_2$] if the reaction is carried out in air, and that with a tenfold molar excess of dpa the *trans*-dioxo complex [$ReO_2(dpa)_2$]Cl was isolated.

The ^{1}H NMR spectrum of **1** shows that the two pyridine rings are in equivalent positions, with only four signals (that integrate equally) being observed for the eight ring protons. The signal of the proton on the bridging amino nitrogen appears far downfield as a broad singlet at δ 11.04 ppm. The presence of ethoxide is illustrated by the typical quartet-triplet at δ 3.28 and 0.77 ppm respectively. The formulation of complex **1** is further supported by its infrared spectrum, with ν(Re=O) and δ(OCH_2) at 954 and 916 cm^{-1}, respectively. Only one medium intensity peak is observed for both ν(Re–N) and ν(Re–Cl) at 524 and 318 cm^{-1}, respectively, indicating that the two nitrogens and two chlorides are in equivalent coordination environments. The implication of these spectroscopic results is that the ethoxide is coordinated *trans* to the oxo group, with the pyridyl nitrogens and two chlorides bonded in the plane *cis* to the oxo oxygen.

An ORTEP diagram of the asymmetric unit of **1** is shown in Fig. 1. The rhenium atom is at the centre of a distorted octahedron. The basal plane is defined by a N_2Cl_2 donor set. The ethoxide oxygen and the oxo group lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(1)=Re–O(2) axis of 169.6(2)°, accomplished by N(1)–Re–Cl(2) and N(3)–Re–Cl(1) angles of 175.6(2) and 179.0(2)°, respectively. The rhenium atom is shifted out of the mean equatorial plane by 0.0488(1) Å towards O(1), which is the result of the non-orthogonal angles O(1)–Re–N(1) = 87.9(3), O(1)–Re–N(3) = 85.7(2), O(1)–Re–Cl(1) = 95.1(2) and O(1)–Re–Cl(2) = 96.0(2)°. The bite angle (i.e., N(1)–Re–N(3)) of dpa equals 86.1(3)°, which is significantly smaller than in dpa complexes of copper(II) and cobalt(II), where it varies from 88.0(2) to 91.2(2)° [9].

The Re=O(1) distance of 1.690(5) Å is statistically the same as for similar *trans* oxo-ethoxorhenium(V) complexes (average = 1.691(2) Å) [10], and it compares well

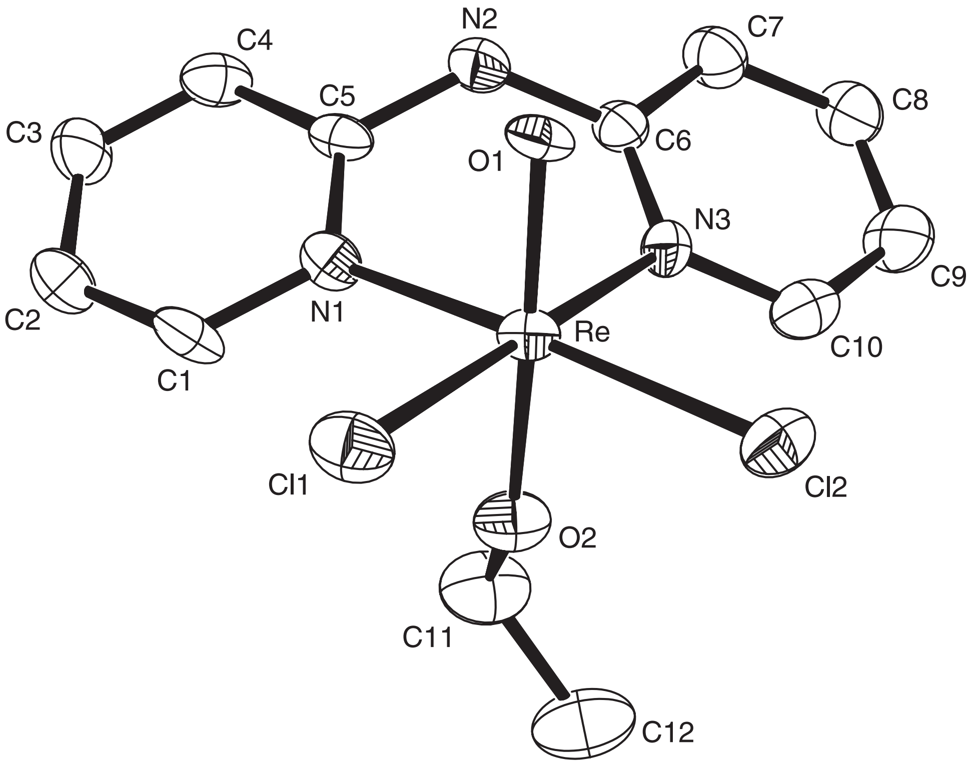

FIGURE 1 ORTEP view of [$ReOCl_2(OEt)(dpa)$], showing the atom labelling scheme. Atomic ellipsoids are drawn at the 40% probability level.

with those reported for the [$ReO(OEt)X_2(PPh_3)_2$] series (X = I, 1.699(4); Br, 1.715(9); Cl, 1.678(6) Å) [11]. The average Re–Cl bond length (2.397(2) Å) is slightly shorter than the 2.404(2) Å value in [$ReOCl_2(OEt)(py)_2$] [12]. Re–N distances are significantly unequal (Re–N(1) 2.131(4), Re–N(3) 2.156(7) Å), a phenomenon that was also observed in (μ-O)[{$ReOCl_2$(dpa)}$_2$] [5]. The Re–O(2)(ethoxo) bond (1.866(5) Å) is identical to this bond in the complex [ReOCl(OEt)(eami)(PPh_3)](ReO_4) (eami=2-(1-ethylaminomethyl)-1-methylimidazole) [13], but is substantially less than 2.04 Å, which is considered to be representative of a Re(V)–O single bond [14]. Partial multiple bonding in Re–O(2) is consistent with the large Re–O(2)–C(11) angle of 149.8(5)°, although this cannot be the only cause, since, with a Re–O double bond, this angle would be expected to be close to 120°. O(2)–C(11) (1.430(9) Å) is normal, and the C(11)–C(12) distance of 1.502(12) Å corresponds to a normal single bond.

In **1** the pyridine rings of dpa are folded around N(2) away from O(1) towards O(2). The two rings make dihedral angles of 32.24° and 31.79° with the mean equatorial plane, and 30.25° with each other. The C(5)–N(2)–C(6) angle of 129.4(6)° is identical to that in (μ-O)[{$ReOCl_2$(dpa)}$_2$] [5]. C–C–N angles at the ring junctions deviate little from 120° [N(1)–C(5)–N(2) = 119.6(6) and N(3)–C(6)–N(2) = 120.4(6)°], and the rhenium atom lies just about on the lone-pair directions [C(5)–N(1)–Re = 121.6(4) and C(6)–N(3)–Re = 120.3(5)°].

Supplementary Material

CCDC-223506 contains the crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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