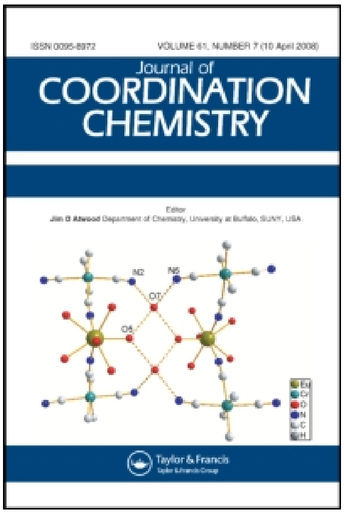

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

2,2'-dipyridylamine complexes of rhenium(V)

T. I. A. Gerber[a]; A. Abrahams[a]; P. Mayer[b]; E. Hosten[a]
[a] Department of Chemistry, University of Port Elizabeth, 6000 Port Elizabeth, South Africa [b] Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

To cite this Article Gerber, T. I. A. , Abrahams, A. , Mayer, P. and Hosten, E.(2003) '2,2'-dipyridylamine complexes of rhenium(V)', Journal of Coordination Chemistry, 56: 16, 1397 — 1407

To link to this Article: DOI: 10.1080/00958970510001641691

URL: http://dx.doi.org/10.1080/00958970510001641691

J. Coord. Chem., Vol. 56, No. 16, 10 November 2003, pp. 1397–1407

2,2′-DIPYRIDYLAMINE COMPLEXES OF RHENIUM(V)

T.I.A. GERBER[a,]*, A. ABRAHAMS[a], P. MAYER[b] and E. HOSTEN[a]

[a]*Department of Chemistry, University of Port Elizabeth, P.O. Box 1600, 6000 Port Elizabeth, South Africa;* [b]*Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany*

(Received in final form 25 August 2003)

The reactivity of oxorhenium(V) precursors with the potentially *N*,*N*-donor ligand 2,2′-dipyridylamine (dpa) has been investigated. Reaction of a two-fold molar excess of dpa with *trans*-[ReO(OEt)Cl$_2$(PPh$_3$)$_2$] in ethanol led to the isolation of [ReOCl$_2$(OEt)(dpa)] (**1**). Spectroscopic measurements indicate that dpa is coordinated as a bidentate in the equatorial plane *cis* to the oxo group, with the ethoxide in the *trans* position. Treatment of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a tenfold molar excess of dpa in ethanol at reflux yielded the *trans*-dioxo complex [ReO$_2$(dpa)$_2$]Cl (**2**), but with a twofold molar excess (μ-O)[{ReOCl$_2$(dpa)}$_2$] (**3a**) was isolated. The latter reaction with (*n*-Bu$_4$N)[ReOCl$_4$] as starting material in ethanol at room temperature led to a dark green product, also with the formulation (μ-O)[{ReOCl$_2$(dpa)}$_2$] (**3b**). These compounds were characterised by common spectroscopic techniques, and the crystal structures of **2** · 3H$_2$O, **3a** and **3b** · 2DMSO were determined. The structure of **3b** presents a nearly linear O=Re–O–Re=O group, with the two [ReOCl$_2$(dpa)] halves of the dimer rotated by 180.0° about the Re–O–Re fragment away from an eclipsed conformation. In **3a**, the two halves are only rotated by 61.4°.

Keywords: Dipyridylamine; Rhenium(V); Crystal structures; Oxo-bridge

INTRODUCTION

Due to potential applications in radiotherapy [1], there is currently considerable interest in the coordination chemistry of rhenium, especially in its +V oxidation state. The most prevalent complexes in this oxidation state are those that contain the [ReO]$^{3+}$, *trans*-[ReO$_2$]$^{+}$ and [Re$_2$O$_3$]$^{4+}$ moieties, although complexes with multiple rhenium–nitrogen bonds are also common [2].

We have studied Re(V) complexes with bidentate heterocyclic nitrogen-donor ligands for some time [3–8]. As an extension of these studies we have investigated Re(V) complexes formed with 2,2′-dipyridylamine (dpa). The ability of dpa to coordinate as a bidentate to transition metal ions is well established [9–11]. The two

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970510001641691

ring-nitrogen atoms act as electron-pair donors in most complexes, although some examples exist in which the bridging amino nitrogen has donor properties [12]. Also, dpa displays several configurations in its coordination; *anti*-*anti* (where *anti* refers to the relation of the pyridyl nitrogens to the amine hydrogen) [13,14], *syn*-*syn* [15,16], and *anti*-*syn* configurations in the dimer of the free ligand [17] are all known.

In this article, we describe the preparation of [ReOCl$_2$(OEt)(dpa)] (**1**), *trans*-[ReO$_2$(dpa)$_2$]Cl (**2**), and two polymorphs of (μ-O)[{ReOCl$_2$(dpa)}$_2$], (**3a** and **3b**), and present the crystal structures of **2** · 3H$_2$O, **3a** and **3b** · 2DMSO.

EXPERIMENTAL

Reagents

trans-[ReOCl$_3$(PPh$_3$)$_2$] was synthesised by a literature method [18]. 2,2′-Dipyridylamine (dpa) was obtained commercially (Aldrich), and was used without further purification after its purity was verified by ^{1}H NMR and melting point (95°C). Solvents were of reagent grade, and were purified and dried before use. All other chemicals were obtained commercially.

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

A mixture of 338 mg (401 μmol) of *trans*-[ReO(OEt)Cl$_2$(PPh$_3$)$_2$] and 144 mg (841 μmol) of 2,2′-dipyridylamine (dpa) in 15 cm^3 of ethanol was heated under reflux for 30 min. The solution was then cooled to room temperature and a purple precipitate was filtered off. The solid was washed with ethanol (2 × 2 cm^3), dried under vacuum, and subsequently recrystallised from acetonitrile. Yield = 68%, mp 301°C. Anal. Calcd. for $C_{12}H_{14}N_3O_2Cl_2Re$ (%): C, 29.45; H, 2.88; N, 8.59. Found: C, 29.76; H, 2.69; N, 8.58. IR (cm^{-1}): ν(Re=O) 954 s; δ(OCH$_2$) 916 vs; ν(C=C) 1587s; ν(C=N) 1630s; ν(N–H) 3216 w; ν(Re–N) 522 m; ν(Re–Cl) 316 m. ^{1}H NMR δ(ppm): 11.04 (s, 1H, N*H*), 9.26 (d, 2H, *H*(3), *H*(3′), *J* = 6.1 Hz), 8.15 (t, 2H, *H*(5), *H*(5′), *J* = 7.3 Hz), 7.56 (d, 2H, *H*(6), *H*(6′), *J* = 7.3 Hz), 7.46 (t, 2H, *H*(4), *H*(4′), *J* = 6.1 Hz), 3.28 (q, 2H, CH_3CH_2O, *J* = 7.0 Hz), 0.77 (t, 3H, CH_3CH_2O, *J* = 7.0 Hz). Conductivity (DMF, 10^{-3} M): $8\ \Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$.

Synthesis of *trans*-[ReO$_2$(dpa)$_2$]Cl (2)

A mixture of 626 mg (3.65 mmol) of dpa and 331 mg (400 μmol) of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] in 15 cm^3 of ethanol was heated under reflux for 30 min. During this time the solution changed from yellow–green to brown, and after 20 min a bright orange precipitate formed. After cooling the mixture to room temperature the solid was filtered off, washed with ethanol (2 × 2 cm^3) and dried under vacuum. Crystals of the 3H$_2$O solvate, suitable for X-ray diffraction, were obtained by slow evaporation of the mother liquor from the synthetic solution. Yield = 72%, mp 229°C. Anal. Calcd. for **2** · 3H$_2$O (%): C, 36.95; H, 3.72; N, 12.93. Found: C, 37.12; H, 3.49; N, 12.69. IR (cm^{-1}): ν(O=Re=O) 814 vs; ν(C=C) 1582s; ν(C=N) 1637s; ν(N–H) 3232 w; ν(Re–N)

540 m. ^{1}H NMR δ (ppm): 11.24 (s, 2H, N*H*), 8.06 (m, 8H, *H*(3), *H*(3′), *H*(5), *H*(5′)), 7.61 (d, 4H, *H*(6), *H*(6′), $J = 8.1$ Hz), 7.21 (t, 4H, *H*(4), *H*(4′), $J = 6.5$ Hz). Conductivity (DMF, 10^{-3} M): 81 Ω^{-1} cm^2 mol^{-1}.

Synthesis of (μ-O)[{ReOCl$_2$(dpa)}$_2$] (3a)

Dpa (137 mg, 800 µmol) was added to a stirred suspension of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] (300 mg, 400 µmol) in ethanol (10 cm^3). The mixture was heated to reflux for 30 min, generating a brown solution from which a green solid precipitated. The mixture was cooled to room temperature and the green product was filtered off after standing overnight. It was then washed with cold ethanol and diethyl ether, and vacuum dried. Recrystallisation was from acetonitrile. Yield = 76%, mp 274°C. Anal. Calcd. for $C_{20}H_{18}N_6O_3Cl_4Re_2$ (%): C, 26.55; H, 2.01; N, 9.29. Found: C, 26.62; H, 2.11; N, 9.13. IR (cm^{-1}): ν(Re=O) 913 m; ν(Re–O–Re) 697 vs; ν(N–H) 3297 m; ν(Re–N) 529 m; ν(C=N) 1632 s; ν(C=C) 1585 s; ν(Re–Cl) 317 m, 322 m. ^{1}H NMR: identical to **3b**.

Synthesis of (μ-O)[{ReOCl$_2$(dpa)}$_2$] (3b)

A solution of dpa (190 mg, 1110 µmol) in ethanol (10 cm^3) was added dropwise to a stirred suspension of 324 mg (552 µmol) of (*n*-Bu$_4$N) [ReOCl$_4$] in 10 cm^3 of ethanol. An intense purple solution was obtained in a few minutes, and after stirring for 30 min a dark green crystalline precipitate was filtered off, washed rapidly with water, acetone and diethyl ether, and dried under vacuum. Recrystallisation was from DMSO/*n*-hexane. Yield = 74%, mp 246°C. Anal. Calcd. for $C_{24}H_{30}N_6O_5Cl_4S_2Re_2$ (%): C, 27.17; H, 2.85; N, 7.92. Found: C, 27.38; H, 2.71; N, 7.79. IR (cm^{-1}): ν(Re=O) 923 m; ν(Re–O–Re) 697 s; ν(N–H) 3301 m; ν(Re–N) 534 m; ν(C=N) 1628 s; ν(C=C) 1585 s; ν(Re–Cl) 319 m. ^{1}H NMR δ (ppm): 10.89 (s, 1H, N*H*), 8.82 (d, 2H, *H*(3), H(3′)), 8.18 (t, 2H, *H*(5), *H*(5′)), 7.56 (d, 2H, *H*(6), *H*(6′)), 7.23 (t, 2H, *H*(4), *H*(4′)). Conductivity (DMF, 10^{-3} M): 19 Ω^{-1} cm^2 mol^{-1}.

Physical Measurements

The instrumentation used was the same as reported earlier [19]. IR spectra were obtained in KBr discs, and ^{1}H NMR spectra (300 MHz) were run at room temperature in d_6-DMSO; chemical shifts are reported with respect to Me$_4$Si.

X-ray Data Collection, Structure Solution and Refinement

Crystals of **3a** were grown from an acetonitrile solution and those with formulation **3b** · 2DMSO were obtained from a DMSO solution of **3b** that was layered with *n*-hexane. Intensity data for **2** · 3H$_2$O, **3a** and **3b** · 2DMSO were collected on a Nonius Kappa CCD diffractometer with MoKα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. Crystal data and details of the structure determinations are given in Table I, with selected bond distances and angles shown below in Tables II–IV for **2** · 3H$_2$O, **3a** and **3b** · 2DMSO, respectively.

TABLE I Crystal data and structure refinement for $[ReO_2(dpa)_2]Cl \cdot 3H_2O$ ($\mathbf{2} \cdot 3H_2O$), (μ-O)$[\{ReOCl_2(dpa)\}_2]$ (**3a**) and (μ-O)$[\{ReOCl_2(dpa)\}_2] \cdot 2DMSO$ (**3b** · 2DMSO)

	2 · *3H$_2$O*	**3a**	**3b** · *2DMSO*
Empirical formula	$C_{20}H_{24}ClN_6O_5Re$	$C_{20}H_{18}Cl_4N_6O_3Re_2$	$C_{24}H_{30}Cl_4N_6O_5S_2Re_2$
Formula weight	650.1	904.6	1060.9
Temperature (K)	200	200	200
Radiation (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Tetragonal	Triclinic
Space group	$P\bar{1}$	$I4_1/a$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.3141(3)	13.8640(6)	9.0089(11)
b (Å)	11.2706(4)	13.8640(6)	9.2570(11)
c (Å)	13.8906(6)	25.5319(17)	10.9635(14)
α (°)	85.435(1)	90	100.817(15)
β (°)	87.597(1)	90	108.613(14)
γ (°)	77.210(2)	90	104.831(14)
Volume (Å^3)	1112.7(1)	4907.5(4)	800.6(2)
Z	2	8	1
Density (calcd., Mg/m^{-3})	1.940	2.449	2.200
Absorption coefficient (mm^{-1})	5.626	10.330	8.063
F(000)	636	3376	506
Crystal size (mm)	0.07 × 0.10 × 0.12	0.07 × 0.13 × 0.20	0.05 × 0.10 × 0.14
Theta min–max	3.2–27.4	2.6–28.0	2.0–28.1
Limiting indices			
h	−9, 9	−17, 17	−11, 11
k	−14, 14	−18, 18	−12, 12
ℓ	−17, 17	−33, 33	−14, 14
Reflections collected/unique/*R*(int)	17652/5004/0.064	21330/2957/0.038	7362/3563/0.033
Observed data [$I > 2.0\sigma(I)$]	3934	2508	2981
*N*ref, *N*par	5004/325	2957/163	3563/200
R, *wR*2	0.0367, 0.0756	0.0181, 0.0403	0.0272, 0.0591
Min, max resd. density (e Å^{-3})	−2.32, 0.89	−1.35, 0.51	−1.46, 2.88
S	1.00	1.00	0.95

TABLE II Selected bond lengths (Å) and angles (°) for $\mathbf{2} \cdot 3H_2O$

Re–O(1)	1.764(3)	N(1)–C(5)	1.343(6)
Re–O(2)	1.760(3)	N(2)–C(5)	1.397(6)
Re–N(1)	2.140(4)	N(2)–C(6)	1.392(6)
Re–N(3)	2.150(4)	N(5)–C(16)	1.399(7)
Re–N(4)	2.137(4)	C(1)–C(2)	1.364(7)
Re–N(6)	2.137(4)	C(2)–C(3)	1.402(8)
C(3)–C(4)	1.369(8)	C(4)–C(5)	1.407(6)
O(1)–Re–O(2)	179.16(14)	O(2)–Re–N(1)	88.99(14)
O(1)–Re–N(1)	90.10(13)	O(2)–Re–N(3)	89.88(13)
O(1)–Re–N(3)	90.25(13)	O(2)–Re–N(4)	90.74(14)
O(1)–Re–N(4)	90.08(13)	O(2)–Re–N(6)	89.42(13)
O(1)–Re–N(6)	90.45(13)	N(1)–Re–N(3)	83.95(15)
N(1)–Re–N(4)	179.65(14)	N(4)–Re–N(6)	83.64(15)
N(3)–Re–N(6)	179.30(13)	C(5)–N(2)–C(6)	126.1(4)
N(1)–Re–N(6)	96.15(15)	C(15)–N(5)–C(16)	125.4(4)
N(3)–Re–N(4)	96.25(15)	Re–N(1)–C(5)	122.0(3)
Re–N(3)–C(6)	122.6(3)	N(1)–C(5)–N(2)	120.9(4)

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

Re–O(2)	1.692(3)	Re–O(1)	1.9151(3)
Re–Cl(1)	2.398(1)	Re–Cl(2)	2.375(1)
Re–N(1)	2.127(3)	Re–N(3)	2.147(3)
C(5)–N(2)	1.382(4)	C(6)–N(2)	1.376(4)
C(1)–N(1)	1.364(4)	C(5)–N(1)	1.333(4)
C(6)–N(3)	1.342(4)	C(10)–N(3)	1.354(4)
O(2)–Re–O(1)	169.5(1)	Re–O(1)–Re	172.3(2)
Cl(1)–Re–Cl(2)	87.75(3)	N(1)–Re–N(3)	87.6(1)
O(2)–Re–Cl(1)	94.05(9)	O(2)–Re–Cl(2)	96.63(9)
O(2)–Re–N(1)	89.9(1)	O(2)–Re–N(3)	86.3(1)
C(5)–N(2)–C(6)	129.7(3)	Cl(1)–Re–O(1)	91.46(3)
Re–N(1)–C(5)	121.6(2)	Re–N(3)–C(6)	120.6(2)

TABLE IV Selected bond lengths (Å) and angles (°) for **3b** · 2DMSO

Re–O(1)	1.695(5)	Re–O(2)	1.9258(4)
Re–Cl(1)	2.380(2)	Re–Cl(2)	2.405(2)
Re–N(1)	2.127(4)	Re–N(3)	2.132(5)
C(5)–N(2)	1.372(8)	C(6)–N(2)	1.371(8)
C(1)–N(1)	1.358(8)	C(5)–N(1)	1.333(7)
C(6)–N(3)	1.331(7)	C(10)–N(3)	1.363(8)
O(1)–Re–O(2)	171.1(1)	Re–O(2)–Re	180.0
Cl(1)–Re–Cl(2)	88.46(5)	N(1)–Re–N(3)	86.7(2)
O(1)–Re–Cl(1)	96.5(1)	O(1)–Re–Cl(2)	93.5(1)
O(1)–Re–N(1)	88.9(2)	O(1)–Re–N(3)	87.6(2)
C(5)–N(2)–C(6)	129.6(5)	Cl(1)–Re–O(2)	91.35(4)
Re–N(1)–C(5)	122.7(4)	Re–N(3)–C(6)	122.8(4)

RESULTS AND DISCUSSION

Synthesis

Reaction of *trans*-[$ReOCl_2(OEt)(PPh_3)_2$] with a twofold molar excess of 2,2′-dipyridylamine (dpa) under reflux in ethanol gave high yields of the product [$ReOCl_2(OEt)$(dpa)] **(1)**. The reaction is described by the equation below.

$$ReOCl_2(OEt)(PPh_3)_2 + dpa \rightarrow ReOCl_2(OEt)(dpa) + 2PPh_3$$

The presence of a single species in the product **1** was established by ^1H NMR spectroscopy, which also indicated the stereochemistry. Only four signals that integrate for two protons each were observed for the eight aromatic protons of dpa, indicating that the two rings of dpa are equivalent. The implication is that complex **1** must be the *fac* isomer, with the ethoxide coordinated in the site *trans* to the oxo oxygen. This was further confirmed by preliminary X-ray diffraction results. Crystals were all twinned and the *R* factor could not be minimised below 16%, but these results unambiguously establish that the composition and ligand arrangement around the Re center correspond to the *fac* isomer. It was found earlier [21] that reaction of 2,2′-bipyridine (bpy) with *trans*-[$ReOCl_3(PPh_3)_2$] or [$ReOCl_3(OPPh_3)(SMe_2)$] yields the pure *mer* isomer of [$ReOCl_3$(bpy)]. However, reduction of a mixture of $HReO_4$ and bpy with H_3PO_2 in HCl–ethanol gave a 40 : 60 ratio of *mer* : *fac* isomers of [$ReOCl_3$(bpy)] [21].

Reaction of a tenfold molar excess of dpa with [$ReOCl_3(PPh_3)_2$] in ethanol gave [$ReO_2(dpa)_2$]Cl (**2**) as the only product as follows.

$$ReOCl_3(PPh_3)_2 + 2dpa + H_2O \rightarrow [ReO_2(dpa)_2]Cl + 2HCl + 2PPh_3$$

Spectroscopic and structural data unambiguously established that the two oxo atoms are in *trans* positions relative to each other.

A twofold molar excess of dpa with [$ReOCl_3(PPh_3)_2$] in ethanol at reflux temperatures led to the isolation of the μ-oxo dimer [$Re_2O_3Cl_4(dpa)_2$] (**3a**). However, a change of the starting material to (*n*-Bu_4N)[$ReOCl_4$] under the same conditions as for **3a** at room temperature gave a green product, also with the formulation [$Re_2O_3Cl_4(dpa)_2$] (**3b**). Spectroscopic and structural characterisation shows that **3a** and **3b** are polymorphic forms of the μ-oxo dimeric complex [$Re_2O_3Cl_4(dpa)_2$]; they differ mainly in the orientation of the two dpa chelates relative to each other. All the complexes are diamagnetic and air-stable, and **2** is a 1 : 1 electrolyte in DMF. They dissolve in polar solvents to give solutions that are stable for days.

Spectroscopic Characterisation

In the IR spectrum of **1** there is a strong absorption at $954\,cm^{-1}$, assigned to the Re=O stretch, and a very intense band at $916\,cm^{-1}$, which corresponds to the ethoxy bending mode. Rhenium(V) complexes with the *trans* oxo–ethoxo arrangement typically display ν(Re=O) in the narrow range 949–960 cm^{-1} [22]. The coordination of the pyridyl nitrogens is shown by the shift of ν(C=N) from about $1670\,cm^{-1}$ in the free ligand to $1630\,cm^{-1}$. The coordination of the two chlorides is supported by a single medium intensity band at $316\,cm^{-1}$, indicating their equivalent coordination environments in *cis* (to the oxo group) positions.

The IR spectra of **2** is dominated by the very strong absorption of the asymmetric O=Re=O stretching frequency at $814\,cm^{-1}$, which falls in the range (810–820 cm^{-1}) normally found for *trans*-dioxo complexes with aromatic nitrogen donor ligands [22–24]. The typical pyridinic C=N and C=C stretching vibrations give rise to strong absorption at 1637 and $1582\,cm^{-1}$, respectively.

IR spectra on **3a** and **3b** · 2DMSO in the solid state are typical of oxo-bridged dimers; a medium absorption at $\sim 920\,cm^{-1}$ attributed to the terminal oxo stretch and a very strong band at $697\,cm^{-1}$ for the Re–O–Re stretch are noted. The spectrum of **3a** displays two medium intensity bands for ν(Re–Cl) at 317 and $322\,cm^{-1}$, but for **3b** only one is observed, at $319\,cm^{-1}$. The lattice DMSO of **3b** gives rise to a strong band at $1025\,cm^{-1}$, which is absent in the spectrum of **3a**.

Complexes **1**–**3** show sharp, well-resolved peaks in their ^1H NMR spectra. The corresponding proton signals of each pyridine ring of the dpa ligand in the complexes are identical, giving the expected doublet–triplet–doublet–triplet set of signals, and implying that the corresponding protons of the two rings of a dpa chelate are magnetically equivalent. Also, the sixteen aromatic protons of the two dpa ligands in **2** give rise to only four signals. Due to the insolubility of **3a** and **3b** in various solvents, their NMR spectra were only recorded in d_6-DMSO, and they were found to be identical.

Structure of *trans*-[$ReO_2(dpa)_2$]Cl·3H_2O

Single crystals of **2**·3H_2O suitable for X-ray analysis were obtained by slow evaporation of the mother liquor from the synthetic solution. An ORTEP plot of the complex is shown in Fig. 1. The rhenium atom resides at the center of an octahedron with the equatorial plane formed by an N_4 pyridinic donor set. The two oxo groups are in *trans* positions relative to each other, with the O(1)–Re–O(2) bond angle close to linearity at 179.2(1)°. The dpa ligands act as neutral bidentate chelates. Selected bond lengths and angles are given in Table II. The Re=O distances [1.762(3) Å average] and the Re–N distances [from 2.137(4) to 2.150(4) Å] lie in the range usually found in other *trans*-dioxo $[ReO_2L_4]^+$ cations (where L = py [25] or imidazole [26]). The rhenium atom is coplanar with the four nitrogen donor atoms [0.0086 Å out of the mean equatorial N_4 plane towards O(1)], with the result that the four O(1)–Re–N angles are all orthogonal [from 90.08(13) to 90.45(13)°]. The average bite angle of the two dpa ligands is 83.80(15)° [N(1)–Re–N(3) = 83.95(15)°; N(4)–Re–N(6) = 83.64(15)°], which is considerably larger than that of 2,2′-bipyridine in rhenium(V) complexes, typically found around 75° [27]. However, it is significantly smaller than the bite angles of dpa in copper(II) and cobalt(II) complexes, which vary from 88.0(2)° to 91.2(2)° [14,28]. The C(5)–N(2)–C(6) and C(15)–N(5)–C(16) angles around the amino nitrogens [126.1(4) and 125.4(4)° respectively] are considerably larger than expected for a trigonal planar nitrogen. C–C–N angles at the ring junctions remain close to 120° (N(1)–C(5)–N(2) = 120.9(4)°; N(3)–C(6)–N(2) = 120.0(4)°), and the metal lies only 2° off the lone-pair direction [C(5)–N(1)–Re = 122.0(3)°; C(6)–N(3)–Re = 122.6(3)°].

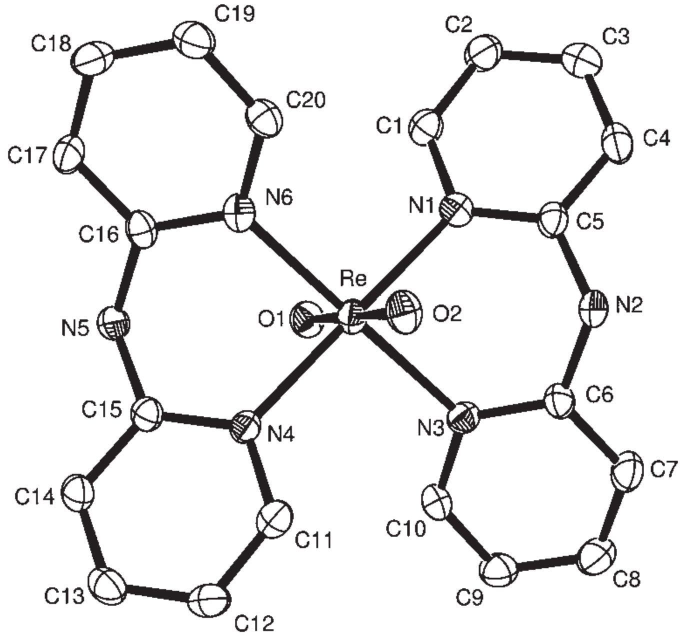

FIGURE 1 ORTEP view of *trans*-[$ReO_2(dpa)_2$]Cl·3H_2O, showing the atom labelling scheme. Atomic displacement ellipsoids are drawn at the 50% probability level (chloride and water molecules have been omitted for clarity).

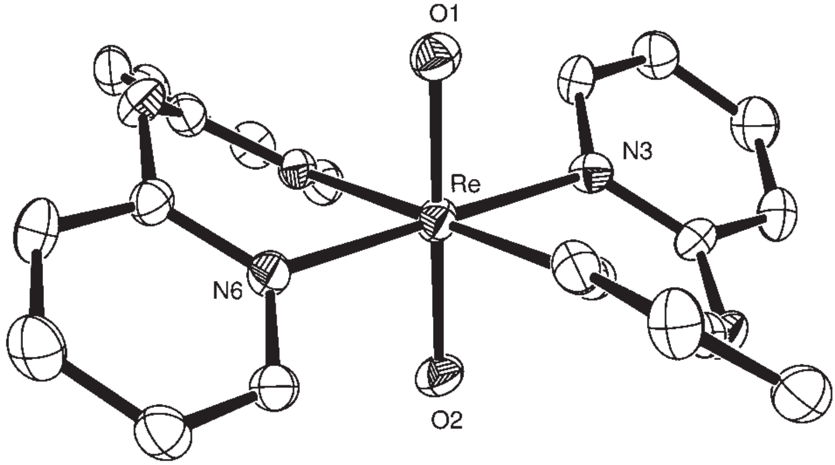

FIGURE 2 ORTEP plot of *trans*-[$ReO_2(dpa)_2$]Cl, showing the folding of the dpa ligands and co-planarity of the *trans* pyridine rings.

The four pyridine rings are folded slightly around the amino nitrogen atoms: rings N(1)–C(5) (ring 2) and N(3)–C(10) (ring 3) towards O(1), and N(4)–C(15) (ring 4) and N(6)–C(20) (ring 5) towards O(2) (Fig. 2). These four rings also make dihedral angles from 35.16 to 36.15° with the mean equatorial N_4 plane. The *trans* pyridine rings are nearly coplanar, with dihedral angles of 1.60° (rings 2 and 4) and 1.13° (rings 3 an 5). Also, the dihedral angle between rings 2 and 3 is 40.83°, and that between 4 and 5 is 42.79°.

The three water molecules of solvation are all involved in hydrogen bonds: $N(5)H\cdots O(91) = 2.818(6)$; $O(91){-}H\cdots O(92) = 2.776(6)$; $O(92){-}H\cdots O(1) = 2.779(5)$; $O(93){-}H\cdots O(2) = 2.788(6)$ Å. Non-bonded contacts for the rest of the atoms are greater than 3.22 Å. The corresponding 2,2′-bipyridine (bpy) complex to **2**, *trans*-[$ReO_2(bpy)_2$]Cl, has been reported in the literature [29], but its crystal structure has never been published. Our efforts to synthesise it were unsuccessful.

Structures of (μ-O)[{$ReOCl_2$(dpa)}$_2$] (3a) and (μ-O)[{$ReOCl_2$(dpa)}$_2$]·2DMSO (3b·2DMSO)

Green crystals of **3a** were grown from acetonitrile, and dark green crystals with the formulation **3b**·2DMSO, suitable for X-ray analysis, were obtained from a dimethyl sulfoxide (DMSO) solution of **3b**. The molecular structures are illustrated in Figs. 3 (**3a**) and 4 (**3b**), and bond lengths and angles are listed in Tables III (**3a**) and IV (**3b**).

Complexes **3a** and **3b** each consist of two independent [$ReOCl_2$(dpa)] units bridged by an oxygen atom. In **3a**, the O=Re–O–Re=O backbone shows considerable deviation from linearity [O(2)–Re–O(1) = 169.5(1)°; Re–O(1)–Re = 172.3(2)°], with bending of the Re_2O_3 axis towards the two π-stacked pyridine rings coordinated via N(3). In **3b**, the bridging O(2) lies on a crystallographic inversion center, making the Re–O–Re angle exactly 180°. The two O(1)=Re–O(2) angles are also equal at 171.1(1)°.

Each rhenium is centered in a distorted octahedron with the equatorial plane formed by a N_2Cl_2 donor set. The **3a** molecule adopts a conformation in which the ReN_2Cl_2 planes are mutually rotated by 61.42° about the Re_2O_3 axis, which, together with the

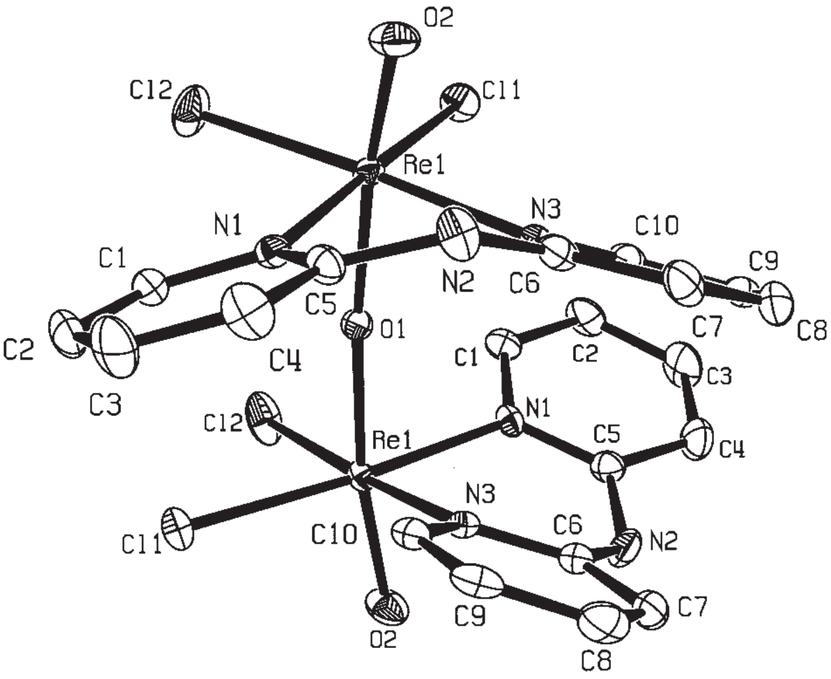

FIGURE 3 ORTEP drawing (50% probability for thermal ellipsoids) of (μ-O)[{ReOCl$_2$(dpa)}$_2$] (**3a**).

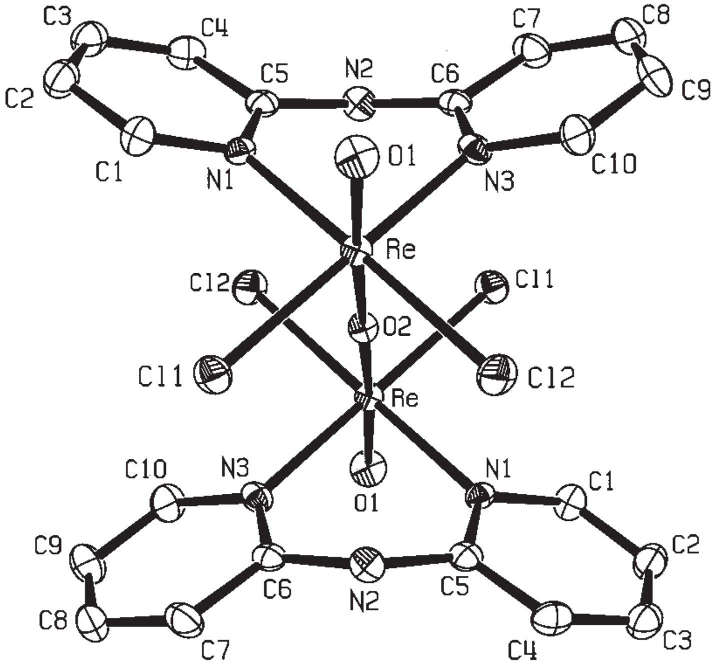

FIGURE 4 ORTEP drawing of the (μ-O)[{ReOCl$_2$(dpa)}$_2$] unit of **3b** · 2DMSO. The bridging O(2) lies on a crystallographic inversion center. DMSO molecules are not shown. Ellipsoids correspond to 50% probability.

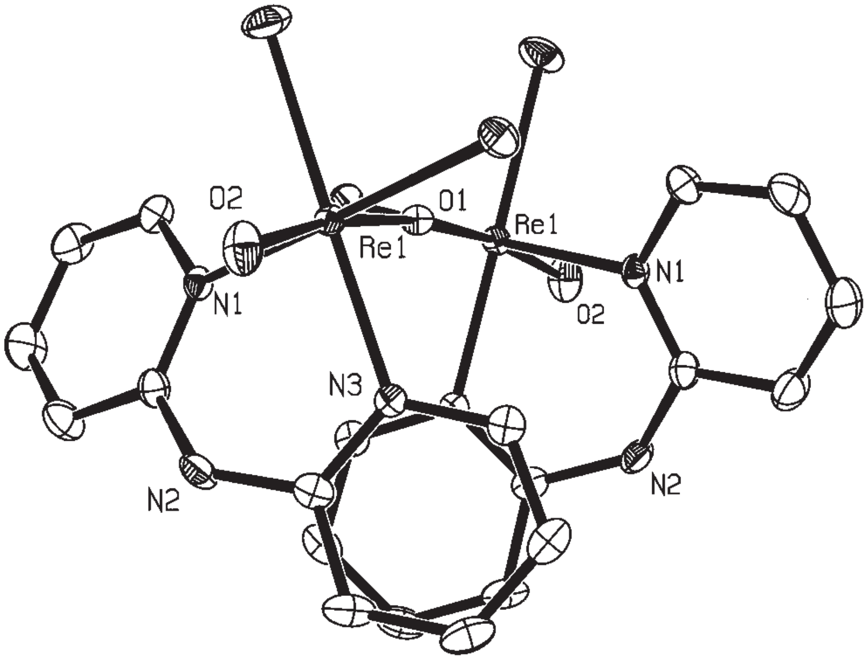

FIGURE 5 ORTEP view of the orientation of the π-stacked pyridine rings in **3a**.

bond along the Re–O–Re axis, allows the symmetry-related pyridine rings coordinated through N(3) on opposite sides of the molecule to interact at an average contact distance of 3.27 Å (Fig. 5). The dihedral angle between the least-squares planes through these two stacked pyridine rings is 6.24°. In **3b** the ReN_2Cl_2 planes are mutually rotated by 180.0°, so that the chlorines of one $ReON_2Cl_2$ unit almost eclipse the nitrogen atoms of the other part of the molecule. The distances of the chlorine atoms of one unit to the pyridine planes in the other unit are on average 3.080 Å, that is, roughly equal to the sum of the van der Waals radii.

In **3a**, the pyridine rings of each dpa ligand are folded towards the bridging oxygen O(1). In contrast, the pyridine rings in **3b** are folded towards the terminal oxo groups. In **3a** these four rings make dihedral angles of 26.80 and 27.75° with the mean equatorial plane, and 31.58° with each other in each dpa ligand. The corresponding values for **3b** are 32.12 and 30.83° with the mean equatorial plane, and 36.93° with each other. As expected, the dihedral angle between the two equatorial N_2Cl_2 planes is 0° in **3b**, but 16.81° in **3a**.

The chloride ligands are displaced away from the terminal Re=O bonds [average O=Re–Cl = 95.34(9) in **3a**; 95.0(1)° in **3b**], while the opposite is true for the pyridine nitrogen donor atoms [average O=Re–N in **3a** equals 88.1(3); 88.3(2)° in **3b**]. These distortions, typical of such systems, are due to the relatively high double bond character of the terminal bonds [Re=O(2)=1.692(3) in **3a**; Re=O(1) = 1.6959(5) Å in **3b**] compared to the bridging Re–O single bonds [1.9151(3) in **3a**; 1.9258(4) Å in **3b**]. The result of these distortions is that the rhenium atoms are displaced from the mean equatorial planes by 0.0670 in **3a** and by 0.0651 Å in **3b** towards the terminal oxo oxygen. The average Re–N [2.137(3) in **3a**; 2.130(5) Å in **3b**] and Re–Cl bond distances [2.387(1) in **3a**; 2.393(2) Å in **3b**] differ very little from these average values in the *cis,cis* [25] and *trans*,*trans* dimers [$Re_2O_3Cl_4(py)_4$] [30]. The bite angles of the dpa ligands in **3a** and **3b** are 87.6(1) and 86.7(2)° respectively, which are significantly different from that in **2** [83.8(1)°].

The C(5)–N(2)–C(6) angles of 129.7(3)° in **3a** and 129.6(5) in **3b** are significantly larger than in **2**. C–C–N angles at the ring junctions deviate little from 120° [N(1)–C(5)–N(2) = 120.9(3) and N(3)–C(6)–N(2) = 121.3(3)° in **3a**; 121.8(5) and 121.6(5)°, respectively, in **3b**], and the rhenium atoms lie just about on the lone-pair directions [C(5)–N(1)–Re = 121.6(2) and C(6)–N(3)–Re = 120.6(2)° in **3a**; 122.7(4) and 122.8(4)°, respectively, in **3b**]. The oxygen atoms of the DMSO solvents of crystallisation in **3b** · 2DMSO are hydrogen bonded to the aminic hydrogens, with $N(2)-H \cdots O(3)$ distances equal to 2.814(7) Å. Non-bonded contacts for the rest of the atoms are greater than 3.23 Å.

Supplementary Data

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

References

[1] M. Nicolini and U. Mazzi, Technetium, Rhenium and other Metals in Chemistry and Nuclear Medicine 5 (Servizi Grafici Editoriali, Padova, 1999).
[2] G. Bandoli, A. Dolmella, T.I.A. Gerber, J. Perils and J.G.H. du Preez, *Bull. Chem. Soc. Ethiop.* **16**, 149 (2002) and references therein.
[3] T.I.A. Gerber, H.J. Kemp, J.G.H. du Preez and G. Bandoli, *J. Coord. Chem.* **28**, 329 (1993).
[4] G. Bandoli, T.I.A. Gerber, R. Jacobs and J.G.H. du Preez, *Inorg. Chem.* **33**, 178 (1994).
[5] J.G.H. du Preez, T.I.A. Gerber and R. Jacobs, *J. Coord. Chem.* **33**, 147 (1994).
[6] G. Bandoli, T.I.A. Gerber, J. Perils and J.G.H. du Preez, *Inorg. Chem. Acta* **278**, 96 (1998).
[7] G. Bandoli, A. Dolmella, T.I.A. Gerber, J. Perils and J.G.H. du Preez, *Inorg. Chim. Acta* **303**, 24 (2000).
[8] G. Bandoli, A. Dolmella, T.I.A. Gerber, D. Luzipo and J.G.H. du Preez, *Inorg. Chim. Acta* **325**, 215 (2001).
[9] W.R. McWhinnie, *Coord. Chem. Rev.* **5**, 293 (1970).
[10] M.P. Suh and Y. Oh, *Bull. Korean Chem. Soc.* **3**, 5 (1982).
[11] E. Freire, S. Baggio, A. Mombru and R. Baggio, *Aust. J. Chem.* **54**, 193 (2001).
[12] T.J. Hurley and M.A. Robinson, *Inorg. Chem.* **7**, 33 (1968).
[13] C.E. Baxter, O.R. Rodig, R.K. Schlatzer and R. Sinn, *Inorg. Chem.* **18**, 1918 (1979).
[14] J.L. Mesa, J.L. Pizarro and M.I. Arriortua, *Cryst. Res. Technol.* **33**, 489 (1998) and references therein.
[15] L.P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B.J. Hathaway, C. Simmons and P. Thornton, *J. Chem. Soc. Dalton Trans.* 3835 (1990).
[16] S. Aduldecha and B.J. Hathaway, *J. Chem. Soc.*, *Dalton Trans.* 993 (1991).
[17] E.C. Yang, M.C. Cheng, M.S. Tsai and S.M. Peng. *J. Chem. Soc.*, *Chem. Commun.* 2377 (1994).
[18] N.P. Johnson, C.J.L. Lock and G. Wilkinson, *Inorg. Synth.* **9**, 145 (1967).
[19] T.I.A. Gerber, A.J. Kemp, G. Bandoli, A. Dolmella and J.G.H. du Preez, *Inorg. Chim. Acta* **202**, 191 (1992).
[20] G.M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures (University of Göttingen, Germany, 1997).
[21] S. Fortin and A.L. Beauchamp, *Inorg. Chem.* **39**, 4886 (2000).
[22] E. Iengo, E. Zangrando, S. Mestroni, G. Fronzoni, M. Stener and R. Alessio, *J. Chem. Soc.*, *Dalton Trans.* 1338 (2001).
[23] G. Backes-Dahmann and J.H. Enemark, *Inorg. Chem.* **26**, 3960 (1987).
[24] E. Alessio, L. Hansen, M. Iwamoto and L.G. Marzilli, *J. Am. Chem. Soc.* **118**, 7593 (1996).
[25] C.J.L. Lock and G. Turner, *Can. J. Chem.* **56**, 179 (1978).
[26] C. Pearson and A.L. Beauchamp, *Acta Crystallogr. Sect. C* **50**, 42 (1994).
[27] M. Bakir, S. Paulson, P. Goodson and B.P. Sullivan, *Inorg. Chem.* **31**, 1129 (1992).
[28] C. Liu, S. Gao, H. Hu and Z. Wang, *Chem. Commun.* 1636 (2001).
[29] M.C. Chakravorti, *J. Indian Chem. Soc.* **44**, 809 (1967).
[30] S. Fortin and A.L. Beauchamp, *Inorg. Chim. Acta* **279**, 159 (1998).