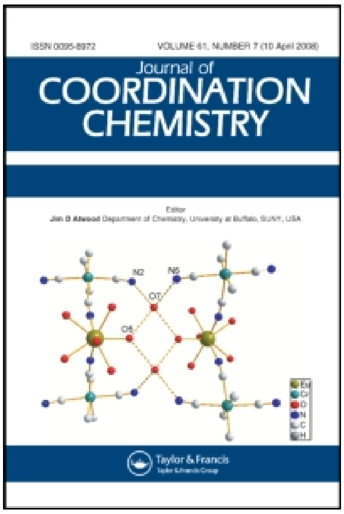

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Nucleophilic addition of water to coordinated dipyridylethylene in rhenium(V) complexes

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Nucleophilic addition of water to coordinated dipyridylethylene in rhenium(V) complexes

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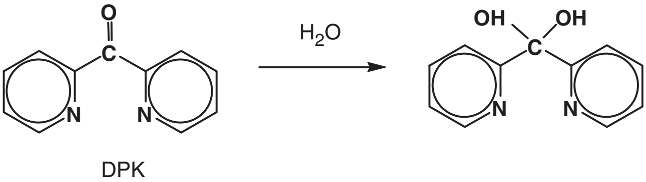
Complexes of general formula $[ReOX_2\{(C_5H_4N)CH(O)CH_2(C_5H_4N)\}]$ $(X = Cl, I)$ were prepared by reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ and *trans*-$[ReOI_2(OEt)(PPh_3)_2]$ with *cis*-1,2-di-(2-pyridyl)ethylene (DPE) in ethanol and benzene in air. The coordinated DPE ligand undergoes addition of water at the ethylenic carbon atoms, and the $(C_5H_4N)CH(O)CH_2(C_5H_4N)$ moiety acts as a uninegative terdentate N,O,N-donor ligand. X-ray crystal structures of both complexes have been determined and show distorted octahedral geometry at the rhenium(V) centre.

Keywords: Rhenium(V); 1,2-Di-(2-pyridyl)ethylene; Addition of water; Crystal structure

1. Introduction

Current interest in the coordination chemistry of rhenium is mainly due to the potential applications of its $^{186/188}$Re isotopes in radiotherapy [1]. One of our focus areas in this field has been the study of oxorhenium(V) complexes with the dipyridyl ligands di-(2-pyridyl)ketone (DPK), 2,3-bis(2-pyridyl)benzoquinoxaline (BBQ) and di-(2-pyridyl)amine (DPA). We have reported earlier on the synthesis and characterization of oxorhenium(V) complexes of DPK, in which the ketone group undergoes metal-promoted nucleophilic addition of water,



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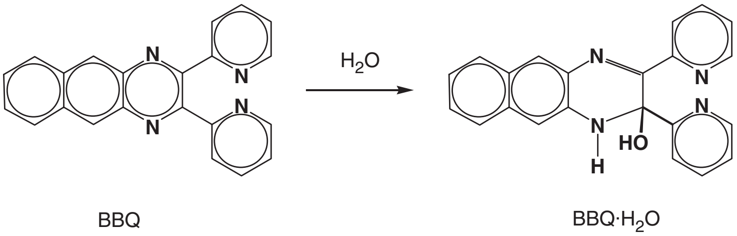
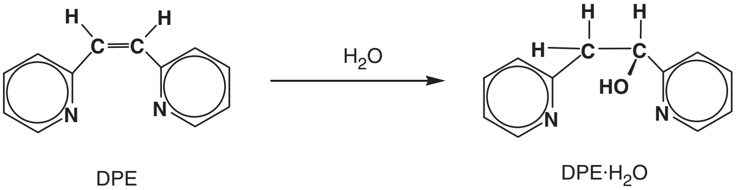
and is coordinated as the uninegative terdentate ligand in [ReOCl$_2${(C$_5$H$_4$N)$_2$ C(O)(OH)}] [2]. Reaction of BBQ with [ReOCl$_4$]$^-$ led to the discovery that BBQ also undergoes addition of water at the imino carbon of the benzoquinoxaline to form 'BBQ · H$_2$O' [3].



Deprotonation of the hydroxyl oxygen leads to coordination of BBQ · OH as a uninegative terdentate ligand in [ReOCl$_2$(BBQ · OH)]. With DPA as the ligand, the complexes [ReO$_2$(DPA)$_2$]Cl, (μ-O)[{ReOCl$_2$(DPA)}$_2$] and [ReOCl$_2$(OEt)(DPA)] were characterized [4].



This article deals with the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] and *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] with *cis*-1,2-di-(2-pyridyl)ethylene (DPE). It was found that DPE coordinates through the two nitrogens of the two pyridine rings to form a seven-membered metallocycle. In addition, it was discovered that DPE undergoes nucleophilic addition of water at the two ethylene carbons to produce 'DPE · H$_2$O'. A consequence of this process is that the hydroxyl group attached to the sp^3-hybridized carbon atom will necessarily occupy a position close to one of the octahedral coordination sites at right angles to the ReN$_2$ plane and would probably lead to steric interaction with any ligand in that position. Alternatively, it may coordinate to the metal ion, with the ligand now behaving as a terdentate.

2. Experimental

Trans-[ReOCl$_3$(PPh$_3$)$_2$] [5] and *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] [6] were synthesized by literature methods. *cis*-1,2-Di-(2-pyridyl)ethylene (DPE) was obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. Infrared spectra were obtained using KBr discs. The instrumentation used is the same as reported earlier [2].

2.1. *Syntheses*

2.1.1. [ReOCl$_2$(DPE · OH)] (1). A mixture of 100 mg (120 μmol) of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] and 43 mg (235 μmol) of DPE in 15 cm^3 was heated under reflux for 24 h. The colour of the solution gradually turned from green to blue, with continuous precipitation of a blue compound. After cooling to room temperature, the blue precipitate was collected by filtration, washed with ethanol ($2 \times 2\,cm^3$) and dried under vacuum. Yield = 90% (51 mg); m.p. 223°C. Anal. Calcd for $C_{12}H_{11}N_2O_2Cl_2Re$ (%): C, 30.51; H, 2.35; N, 5.93. Found: C, 30.83; H, 2.12; N, 5.96. IR(KBr, cm^{-1}): ν(Re=O) 940; ν(Re–N) 523, 511; ν(Re–O) 441; ν(Re–Cl) 322.

2.1.2. [ReOI$_2$(DPE · OH)] (2). A suspension of DPE (42 mg, 230 µmol) in 5 cm^3 of benzene was added to a benzene solution (7 cm^3) of *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] (115 mg, 112 µmol). The mixture was stirred at room temperature for 24 h, after which an avocado-green solid was removed by filtration, washed with cold benzene ($3 \times 2\,cm^3$) and dried under vacuum. Slow evaporation of the mother liquor at room temperature to a volume of about 2 cm^3 gave another batch of green crystals, which were suitable for X-ray diffraction studies. Yield = 84% (63 mg); m.p. 185°C. Anal. Calcd for $C_{12}H_{11}N_2O_2I_2Re$ (%): C, 22.00; H, 1.69; N, 4.28. Found: C, 22.12; H, 1.91; N, 4.36. IR(KBr, cm^{-1}): ν(Re=O) 922; ν(Re–N) 525, 509; ν(Re–O) 419.

2.2. *X-ray structure determination*

X-ray diffraction studies of crystals (grown from benzene) of **1** and **2** were performed at 200(2) K using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Further details are given in table 1. The structures were solved by direct methods. Nonhydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealized and fixed.

Table 1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Chemical formula	$C_{12}H_{11}N_2O_2Cl_2Re$	$C_{12}H_{11}N_2O_2I_2Re$
Formula weight	472.34	655.24
Temperature (K)	200	200
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
Unit cell dimensions (Å)		
a	11.3582(9)	16.2948(14)
b	14.9274(12)	16.1399(10)
c	16.1135(13)	11.6319(10)
Volume (Å^3)	2732.0(4)	3059.1(4)
Z	8	8
Density (calc., Mg/m^3)	2.297	2.845
Absorption coefficient (mm^{-1})	9.284	11.980
F(000)	1776	2352
Crystal size (mm)	$0.03 \times 0.18 \times 0.26$	$0.02 \times 0.09 \times 0.13$
θ range for data collection (deg.)	2.5–24.0	2.5–26.1
Index ranges	$-12 \le h \le 12$	$-19 \le h \le 19$
	$-17 \le k \le 17$	$-19 \le k \le 19$
	$-18 \le \ell \le 18$	$-14 \le l \le 14$
Reflections measured	14669	19913
Independent/observed reflections	2138/1312	2952/1929
Data/restraints/parameters	2138/0/92	2952/0/172
Goodness of fit on F^2	0.83	0.85
R, wR_2	0.0285, 0.0528	0.0315, 0.0650
Largest diff. peak/hole (e Å^{-3})	1.36/−0.72	1.08/−1.32

Structural refinements were carried out by the full-matrix least-squares method on F^2 using the program SHELXL-97 [7].

3. Results and discussion

The rhenium(V) complex [ReOCl$_2$(DPE · OH)] (**1**) was synthesized by the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with a twofold molar excess of DPE in refluxing ethanol, in air. Reaction of equimolar quantities of starting materials led only to *trans*-[ReOCl$_2$(OEt)(PPh$_3$)$_2$]. [ReOI$_2$(DPE · OH)] (**2**) was prepared by reacting *trans*-[ReOI$_2$(OEt)(PPh$_3$)$_2$] with two equivalents of DPE in benzene at room temperature in air. Complexes **1** and **2** are stable in air. They are highly insoluble in all common solvents, to such a degree that meaningful ^{1}H NMR and electronic spectra could not be recorded. Very intense bands in the solid state infrared spectra of **1** and **2** at 940 and 922 cm^{-1}, respectively, are attributed to Re=O stretching. Deformation vibrations of pyridine rings occur at 1611 and 1613 cm^{-1}, respectively. Two medium intensity bands around 510 and 525 cm^{-1} in each complex are assigned to ν(Re–N). Only one band (322 cm^{-1}) was observed for ν(Re–Cl) in the spectrum of **1**.

The structures of [ReOX$_2$(DPE · OH)] (X = Cl (**1**), I (**2**)) contain discrete, monomeric, neutral monooxorhenium(V) units (figures 1 and 2) and crystal packing is governed by van der Waals contacts. No intermolecular hydrogen bonds exist, and weak intramolecular hydrogen bonds are observed between C(1)H(1) ··· O(2) (2.947(9) Å) and C(12)H(12) ··· O(2) (2.85(1) Å) in **1**, and between C(12)H(12) ··· O(2) (2.86(1) Å) in **2**. Donor atoms surrounding rhenium are at the apices of a distorted octahedron, in which the equatorial plane is occupied by the two *cis* halides and by the two terminal pyridyl nitrogen atoms of the bidentate ligand, with the O(2) oxo ligand *trans* to the O(1) alcoholate atom. The DPE · OH moiety acts as a uninegative, terdentate N,O,N-donor ligand to the rhenium atom. Severe distortions from ideal octahedral configuration are as follows. Re lies out of the equatorial

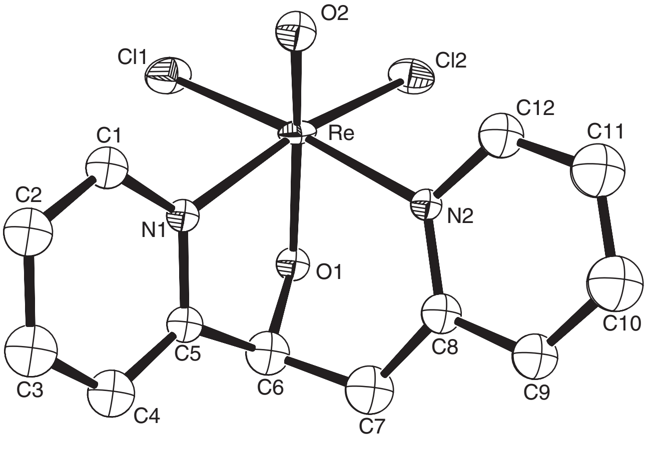


Figure 1. An ORTEP view of the structure of **1**, showing the atom labelling scheme with thermal ellipsoids drawn at the 40% probability level.

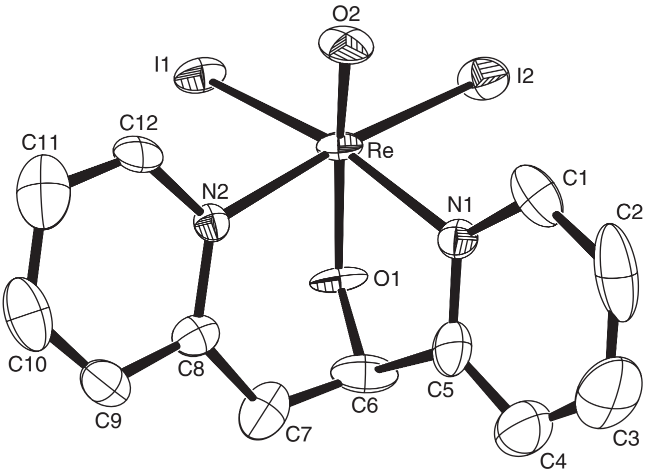


Figure 2. An ORTEP view of **2**, showing the atom labelling scheme with thermal ellipsoids drawn at the 40% probability level.

mean plane by 0.15 Å in **1** (0.17 Å in **2**) toward the oxo ligand and the nonlinear O(1)–Re–O(2) axis of 160.1(2)° in **1** (160.7(3)° in **2**) is accomplished by Cl(1)–Re–N(2) and Cl(2)–Re–N(1) angles of 174.4(2)° and 170.0(2)°, respectively (in **2**, I(1)–Re–N(1) = 169.4(2)°, I(2)–Re–N(2) = 174.3(2)°). Edge distances lie in a rather narrow range (from 3.01 Å for N(1) ⋯ N(2) to 3.33 Å for Cl(1) ⋯ Cl(2) in **1**, but in a larger range for **2** (from 2.98 Å for N(1) ⋯ N(2) to 3.82 Å for I(1) ⋯ I(2)), and inter-ligand angles in the equatorial plane are from 86.5 to 93.4° in **1** and from 82.3° to 97.0° in **2**. In the $X_2N_2O_2$ coordination polyhedron, the Re atom lies 1.02 Å away from the Cl(1)Cl(2)O(2) plane (1.09 Å in **2**), and 1.35 Å from the N(1)N(2)O(1) plane (1.37 Å in **2**), the angle between the two triangles being 12.1° in **1** (14.4° in **2**). These structural properties are a common feature of numerous octahedral monooxo complexes of Re(V) [8–12]. In particular, the present complexes closely resemble [$ReOCl_2$(DPK · OH)] and [$ReOCl_2$(BBQ · H)] [2, 3]. For example, the two pyridine rings make a dihedral angle of 81.3° in **1** (84.6° in **2**), as compared with values of 65.9° and 69.2°, respectively, in the abovementioned complexes (table 2).

In addition, the Re–O(1)–C(6) plane is virtually normal (dihedral angle of 91.0°(**1**) and 91.3° (**2**)) to the equatorial mean plane, as found in the above two complexes (91.5° and 90.6°, respectively). On the other hand, the most significant feature of the structure is that it unambiguously establishes the tetrahedral environment around the C(6) atom, as confirmed by the bond angle pattern. Bond lengths and angles in the complexes **1** and **2** show no unusual features, being within the ranges expected by comparison to other six-coordinate monooxo complexes of Re(V) [2, 3, 8–12].

The driving force for the nucleophilic addition of water to the ethylenic carbon C(6) after coordination of DPE to rhenium(V) was interpreted earlier as being the result of angular strain caused in DPE by the formation of a seven-membered metallocycle [3]. The formation of a planar seven-membered ring between rhenium and DPE will be difficult, leading to severe strain in the chelate. Nucleophilic attack by water and rehybridization of C(6) and C(7) to sp^3 will relieve this strain. In this case, the coplanarity of the ligand and the conjugation over the ethylene group will be destroyed. An additional driving force is the coordination of the deprotonated

Table 2. Relevant bond lengths (Å) and angles (°) for **1** and **2**.

	1	**2**
Re–O(1)	1.916(5)	1.923(5)
Re–O(2)	1.694(5)	1.681(6)
Re–X(1)	2.363(2)	2.685(1)
Re–X(2)	2.351(2)	2.700(1)
Re–N(1)	2.147(7)	2.162(8)
Re–N(2)	2.168(6)	2.178(6)
O(1)–C(6)	1.454(9)	1.43(1)
C(6)–C(7)	1.48(1)	1.45(2)
C(6)–C(5)	1.52(1)	1.53(2)
O(1)–Re–O(2)	160.1(2)	160.7(3)
O(2)–Re–X(1)	98.7(2)	101.7(2)
O(2)–Re–X(2)	102.9(2)	98.3(2)
O(2)–Re–N(1)	86.9(2)	88.3(3)
O(2)–Re–N(2)	86.8(2)	87.2(3)
X(1)–Re–N(1)	90.5(2)	169.4(2)
X(2)–Re–N(2)	90.2(2)	174.3(2)
N(1)–Re–N(2)	88.5(2)	86.9(3)
X(1)–Re–X(2)	89.88(8)	90.41(2)
Re–O(1)–C(6)	117.1(4)	119.5(5)
C(5)–C(6)–C(7)	113.2(8)	112.1(8)
C(6)–C(7)–C(8)	119.3(8)	119.7(9)
O(1)–C(6)–C(7)	104.9(8)	105.0(8)
C(7)–C(8)–C(9)	117.8(8)	117.0(9)
C(4)–C(5)–C(6)	128.2(8)	124(1)
Re–N(1)–C(1)	124.6(6)	124.7(7)
Re–N(2)–C(12)	116.3(5)	116.9(6)

alcoholate oxygen O(1) of $\mathrm{DPE \cdot OH^-}$ to the metal, as expected for rhenium(V), which has a propensity to form octahedral complexes [8–12]. This unusual example of metal-promoted nucleophilic attack of water at ethylene presents interesting alternatives in the field of reactions of coordinated ligands.

Supplementary material

Files CCDC-263413 (**1**) and CCDC-263414 (**2**) contain 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; Email: deposit@ccdc.cam.ac.uk.

References

[1] M. Nicolini, U. Mazzi. *Technetium, Rhenium and Metals in Chemistry and Nuclear Medicine 5*, Servizi Grafici Editorial, Padova (1999).

[2] T.I.A. Gerber, H.J. Kemp, J.G.H. du Preez, G. Bandoli. *J. Coord. Chem.*, **28**, 329 (1993).

[3] G. Bandoli, T.I.A. Gerber, R. Jacobs, J.G.H. du Preez. *Inorg. Chem.*, **33**, 178 (1994).

[4] T.I.A. Gerber, A. Abrahams, P. Mayer, E. Hosten. *J. Coord. Chem.*, **56**, 1397 (2003).

[5] N.P. Johnson, C.J.L. Lock, G. Wilkinson. *Inorg. Synth.*, **9**, 145 (1967).

[6] G.F. Ciani, G. D'Alfonso, P. Romiti, A. Sironi, M. Freni. *Inorg. Chim. Acta*, **72**, 29 (1983).

[7] G.M. Sheldrick. *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[8] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli, M. Nicolini. *Inorg. Chim. Acta*, **189**, 97 (1991).
[9] T.I.A. Gerber, D. Luzipo, P. Mayer. *J. Coord. Chem.*, **57**, 1345 (2004).
[10] T.I.A. Gerber, D. Luzipo, P. Mayer. *J. Coord. Chem.*, **57**, 1399 (2004).
[11] T.I.A. Gerber, D. Luzipo, P. Mayer. *J. Coord. Chem.*, **57**, 1419 (2004).
[12] T.I.A. Gerber, Z.R. Tshentu, S. Garcia-Granda, P. Mayer. *J. Coord. Chem.*, **56**, 1093 (2003).