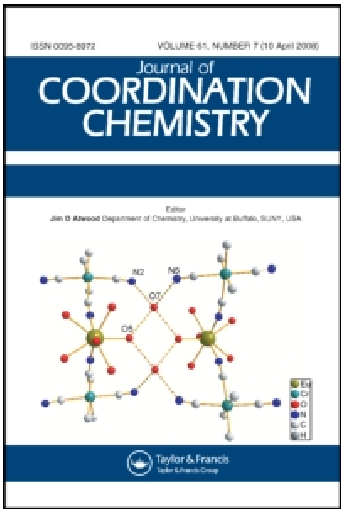


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structure of a '4 + 1' oxorhenium(V) complex containing imidazole derivatives

Thomas I. A. Gerber[a]; Peter Mayer[b]; Zenixole R. Tshentu[a]
[a] Department of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa [b] Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

To cite this Article Gerber, Thomas I. A. , Mayer, Peter and Tshentu, Zenixole R.(2007) 'Synthesis and structure of a '4 + 1' oxorhenium(V) complex containing imidazole derivatives', Journal of Coordination Chemistry, 60: 3, 237 — 242
To link to this Article: DOI: 10.1080/00958970601108323
URL: http://dx.doi.org/10.1080/00958970601108323

Journal of Coordination Chemistry
Vol. 60, No. 3, 10 February 2007, 237–242

Synthesis and structure of a '4 + 1' oxorhenium(V) complex containing imidazole derivatives

THOMAS I. A. GERBER*†, PETER MAYER‡ and
ZENIXOLE R. TSHENTU†

†Department of Chemistry, Nelson Mandela Metropolitan University,
6031 Port Elizabeth, South Africa
‡Department of Chemistry, Ludwig-Maximilians University,
D-81377 München, Germany

(*Received in final form 9 December 2005*)

The '4 + 1' concept was used to prepare the complex salt [ReO(iao)Br]Br (**1**) from the reaction of (n-Bu_4N)[$ReOBr_4(OPPh_3)$] with the ligand *bis*{2′-methyl(1′-methylimidazole)}-2-aminoethanol (Hiao) in methanol. The single-crystal X-ray crystal structure of **1** shows that iao acts as a monoanionic, tetradentate, N_3O-donor chelate. When the reaction was carried out in acetonitrile, the neutral complex [ReO(iao)Br_2] (**2**) was isolated. Elemental analyses and IR data suggest that iao acts as a tridentate, N_2O-donor ligand in **2**.

Keywords: Oxorhenium(V); Tetradentate N_3O ligand; Crystal structure

1. Introduction

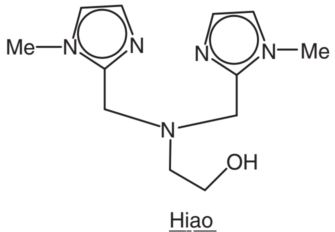
The potential application of complexes of ^{186}Re and ^{188}Re as therapeutic agents in nuclear medicine has necessitated the development of the coordination chemistry of rhenium [1]. One of the approaches to the synthesis of stable rhenium(V) complexes has been the '3 + 2' concept of ligand permutation [2]. This is based on the ligation of a dinegative, tridentate chelate in combination with a bidentate, monoanionic ligand to produce neutral octahedral monooxorhenium(V) complexes. We have become involved in the preparation of rhenium complexes with multidentate ligands containing the imidazole group, and have used the '3 + 2' concept to synthesize the neutral complex [ReO(ox)(ami)] by the reaction of [$ReOBr_2$(ami)] [Hami = 2-(1-ethanolamino-methyl)-1-methylimidazole] with sodium oxalate (Na_2ox) in methanol [3]. The '3 + 2' complex salt [ReO(tmi)(mi)]Cl [Htmi = 2-(1-ethanolthiomethyl)-1-methylimidazole; Hmi = 2-(hydroxymethyl)-1-methylimidazole] was isolated from a one-pot reaction of (n-Bu_4N)[$ReOCl_4$] with Htmi and Hmi in acetonitrile [4]. In this study the '3 + 2'

---

*Corresponding author. Email: thomas.gerber@nmmu.ac.za

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970601108323

concept is extended to '4 + 1', by the synthesis of the complex salt [ReO(iao)Br]Br (**1**) by reaction of (n-Bu_4N)[$ReOBr_4(OPPh_3)$] with the potentially monoanionic, tetradentate N_3O-donor ligand *bis*{2′-methyl(1′-methylimidazole)}-2-aminoethanol(Hiao; below).



Hiao

2. Experimental

The (n-Bu_4N)[$ReOBr_4(OPPh_3)$] salt was prepared by a literature procedure [5]. Scientific instrumentation used is the same as reported elsewhere [6]. IR spectra were obtained using KBr disks and ^1H NMR spectra were run using d_6-DMSO solutions.

2.1. *Synthesis*

2.1.1. Hiao. A mixture of 2-chloromethyl-1-methylimidazole (5.5 g, 33 mmol) [7] and K_2CO_3 (6.2 g, 45 mmol) was stirred for 20 min in 20 cm^3 of DMF. To this mixture was added dropwise 0.92 g (15 mmol) of ethanolamine dissolved in 10 cm^3 DMF. The reaction mixture was heated at 90°C for 3 h, after which it was cooled to room temperature. The resulting white precipitate (KCl) was filtered off and the solvent removed under reduced pressure. The brown oil which resulted was dissolved in 5 cm^3 of methanol, and dried over anhydrous sodium sulfate. On removal of the methanol by rotary evaporation, a light brown oil, which solidified after standing at room temperature, was obtained. Efforts to determine its boiling point at 5 mTorr led to decomposition. Yield = 69%, based on ethanolamine. Anal. Calcd for $C_{12}H_{19}N_5O$ (%): C, 57.81; H, 7.68; N, 28.09. Found: C, 58.01; H, 7.78; N, 28.76. ^1H NMR (δ, ppm): 6.91 (s, 2H, H(1), H(10)), 6.76 (s, 2H, H(2), H(11)), 3.81 (s, 4H, H(5), H(8)), 3.68 (s, 2H, H(7)), 3.56(s, 6H, H(4), H(12)), 3.30(br s, 1H, OH), 2.89 (s, 2H, C(6)).

2.1.2. [ReO(iao)Br]Br (1). (n-Bu_4N)[$ReOBr_4(OPPh_3)$] (100 mg, 96 µmol) was dissolved in 5 cm^3 of methanol and an equimolar amount of Hiao (24 mg) in 5 cm^3 of methanol added dropwise with stirring at room temperature. The mixture was heated under reflux for 90 min, and after cooling to room temperature, it was filtered and allowed to evaporate slowly at room temperature. After 3 days, bright blue crystals, suitable for X-ray analysis, were obtained. Yield of **1**. $H_2O = 71\%$; m.p. 295°C (dec). Anal. Calcd for $C_{12}H_{18}N_5O_2Br_2Re \cdot H_2O$ (%): C, 22.94; H, 3.21; N, 11.15. Found: C, 23.02; H, 3.31; N, 11.22. IR: ν(Re=O) 941 vs; $\delta(OCH_2)$ 912 vs; ν(Re–N) 555m, 520m; ν(Re–O) 476w. ^1H NMR (δ, ppm): 7.72 (d, 2H, H(1), H(10)), 7.40 (d, 2H, H(2), H(11)),

Table 1. Crystallographic data and structure refinement details for **1**.

Chemical formula	$C_{12}H_{20}N_5O_3Br_2Re$
Formula weight	628.33
Temperature (K)	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.3495(4)
b (Å)	20.860(1)
c (Å)	11.6458(7)
β (°)	97.346(7)
V (Å^3)	1770.8(2)
Z	4
Density (Calcd) (Mg m^{-3})	2.357
Absorption coefficient (mm^{-1})	11.395
F(000)	1184
Crystal size (mm^3)	$0.04 \times 0.10 \times 0.15$
θ range for data collection (°)	2.0–27.9
Index ranges	$-9 \le h \le 9$; $-27 \le k \le 27$; $-15 \le l \le 15$
Reflections measured	15120
Independent/observed reflections	4226/3223
Data/restraints/parameters	3223/2/214
Goodness-of-fit on F^2	0.89
Final R indices [$I > 2\sigma(I)$]	0.0236, $wR_2 = 0.0479$
Largest diff. peak and hole (e Å^{-3})	0.99/−1.04

3.90 (s, 4H, H(5), H(8)), 3.77 (s, 2H, H(7)), 3.71 (s, 6H, H(4), H(12)), 3.56 (s, 2H, H(6)). Conductivity (DMF, 10^{-3} M): 68 ohm^{-1} cm^2 mol^{-1}.

2.1.3. [ReO(iao)Br$_2$] (2). A mixture of equimolar quantities of (n-Bu$_4$N)-[ReOBr$_4$(OPPh$_3$)] (100 mg, 96 µmol) and Hiao (24 mg) in 20 cm^3 of acetonitrile was stirred overnight at room temperature. After stirring was stopped, a mauve-coloured precipitate was removed by filtration, washed with acetonitrile (3×2 cm^3) and diethylether (3×2 cm^3), and dried under vacuum. Yield = 68%; m.p. 279°C. Anal. Calcd for $C_{12}H_{18}N_5O_2Br_2Re$ (%): C, 23.62; H, 2.97; N, 11.48. Found: C, 23.83; H, 3.02; N, 11.72. IR: ν(Re=O) 953 vs; δ(OCH$_2$) 916 vs; ν(Re–N) 569 m, 527 m; ν(Re–O) 459w. Recrystallization attempts with a variety of solvents led to the decomposition of 2 to a mixture of products, one of which is **1**. ^{1}H NMR spectra of pure **2** could not be obtained.

2.2. *X-ray crystallography*

X-ray diffraction studies on crystals of **1**.H$_2$O were performed with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Further details are given in table 1, with selected bond lengths and angles given in table 2. The structure was solved by direct methods. Non-hydrogen atoms were refined with anisotropic displacement parameters. Refinements were performed using full-matrix least-squares methods on F^2 using SHELXL-97 [7].

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

Re–O(1)	1.912(3)	Re–O(2)	1.704(3)
Re–N(1)	2.116(3)	Re–N(4)	2.082(3)
Re–N(3)	2.166(3)	Re–Br(1)	2.4914(6)
O(1)–C(7)	1.423(5)	C(6)–C(7)	1.509(6)
N(3)–C(5)	1.498(5)	N(3)–C(8)	1.497(5)
N(1)–C(3)	1.348(5)	N(1)–C(1)	1.374(5)
O(1)–Re–O(2)	163.9(1)	O(2)–Re–Br(1)	102.5(1)
O(2)–Re–N(1)	89.0(1)	O(2)–Re–N(3)	87.0(1)
O(2)–Re–N(4)	91.9(2)	Re–O(1)–C(7)	122.1(2)
N(1)–Re–N(3)	80.4(1)	N(3)–Re–N(4)	79.7(1)
N(1)–Re–N(4)	160.1(1)	N(3)–Re–Br(1)	170.6(1)
C(3)–C(5)–N(3)	108.0(3)	C(5)–N(3)–C(8)	113.8(3)
Re–N(3)–C(6)	110.5(2)	C(1)–N(1)–C(3)	107.1(3)
Re–N(1)–C(3)	110.3(3)	Re–N(4)–C(9)	111.5(3)

3. Results and discussion

3.1. *Synthesis*

(n-Bu_4N)[$ReOBr_4(OPPh_3)$] was used as starting material in the synthesis of [ReO(iao)Br]Br (**1**), because of its stability towards moisture and reduction, and the ease of substitution of its bromide and $OPPh_3$ ligands. The commonly used starting materials (n-Bu_4N)[$ReOCl_4$] and *trans*-[$ReOCl_3(PPh_3)_2$] complicate synthetic procedures due to their moisture sensitivity and ease of reduction to Re(III) by free PPh_3 [3]. Methanol was chosen as solvent since the reactants are very soluble in it. Reaction of equimolar amounts of $[ReOBr_4(OPPh_3)]^-$ and Hiao under reflux conditions gave a dark blue solution, from which blue crystals of **1** were obtained by slow evaporation of solvent. The reaction of equimolar quantities in acetonitrile at room temperature, however, gave a mauve-coloured precipitate which analysed for [$ReO(iao)Br_2$] (**2**), in which iao acts as a monoanionic, tridentate chelate. Heating **2** in methanol leads to the formation of **1**. Both **1** and **2** are diamagnetic, and **1** is a 1 : 1 electrolyte in DMF.

3.2. *Spectroscopic analysis*

In the IR, Re=O stretches of **1** and **2** appear as sharp strong bands at 941 and 953 cm^{-1}, respectively, in the region normally observed for six-coordinate rhenium(V) complexes containing N- and O-donor ligands [8]. In the free ligand Hiao the ν(C=N) stretch of the imidazole rings occurs at 1661 cm^{-1}. In **1** a single peak for this mode is observed at 1624 cm^{-1}, indicating coordination of both imidazole nitrogen atoms. However, in the spectrum of **2**, two peaks are observed for ν(C=N) at 1653 and 1631 cm^{-1}, suggesting that of one of the imidazole rings of iao is not coordinated. In **1** the $\delta(OCH_2)$ peak occurs at 912 cm^{-1} (916 cm^{-1} in **2**). In both complexes two peaks are observed (at 555 and 520 cm^{-1} for **1**; 569 and 527 cm^{-1} for **2**) for $\nu(Re–N_{im})$ and ν(Re–N(3)). These data suggest that iao acts as a tetradentate chelate in **1** with coordination *via* the three nitrogen and alcoholate oxygen atoms, but as a tridentate in **2** with a free imidazole group.

^{1}H NMR data support the tetradentate coordination of iao in **1**. Protons of the two imidazole rings are magnetically equivalent and their signals appear furthest downfield

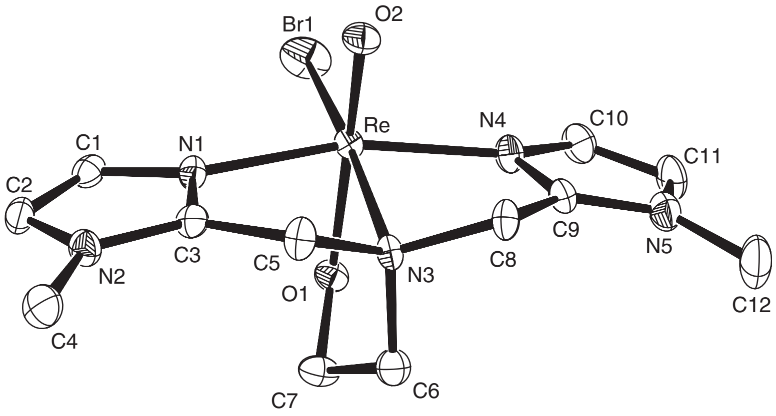


Figure 1. An ORTEP view of the molecular structure of [ReO(iao)Br]Br (**1**), showing the atom labelling scheme and thermal ellipsoids drawn at the 40% probability level.

as doublets at δ 7.72 [H(1), H(10)] and 7.40 ppm [H(2), H(11), see figure 1 for labelling]. Methylene protons attached to C(5) and C(8) are also magnetically equivalent and they appear as a four-proton singlet at δ 3.90 ppm. The spectrum of **2** in d_6-DMSO is inconclusive with respect to the coordination mode of iao. From the signals of the imidazole protons it is clear that two complex species in a 25 : 75 ratio exist in solution. Most of the methylene proton signals are obscured by the solvent peak of d_6-DMSO.

3.3. *Crystal structure of 1*

The structure (figure 1) consists of discrete, monomeric oxorhenium(V) $[ReO(iao)Br]^+$ ions packed with no intermolecular contacts shorter than the sum of van der Waals radii. The coordination geometry around rhenium is highly distorted octahedral; the three nitrogen atoms of the tetradentate, uninegative iao ligand lie on the equatorial plane, along with the bromide ion, while the alcoholate O(1) atom lies *trans* to the O(2) oxo atom. The rhenium atom is displaced by 0.13 Å towards O(2). This leads to the non-orthogonal angles O(2)–Re–Br(1) = 102.5(1)°, O(2)–Re–N(1) = 89.0(1)°, O(2)–Re–N(3) = 87.0(1)° and O(2)–Re–N(4) = 91.9(2)°. Distortion results in a nonlinear O(1)–Re–O(2) axis of 163.9(1)°, accomplished by Br(1)–Re–N(3) and N(1)–Re–N(4) angles of 170.6(1) and 160.1(1)°, respectively. The three bite angles of iao, N(1)–Re–N(3) = 80.4(1)°, N(3)–Re–N(4) = 79.7(1)° and N(3)–Re–O(1) = 77.9(1)°, contribute considerably to this distortion. Interestingly, the two bite angles of the very similar tridentate ligand ami in the complex $[ReOBr_2(ami)]$ are N–Re–N = 79.1(3)° and N–Re–O = 75.7(3)° [3]. The imidazole rings are planar, as expected for aromatic systems, with torsion angles C(3)N(1)C(1)C(2) = 1.5(5)°, C(2)N(2)C(3)N(1) = 1.1(5)°, C(10)N(4)C(9)N(5) = −0.1(5)° and C(9)N(4)C(10)C(11) = 0.2(5)°. There are delocalized double bonds over the N(1)–C(3)–N(2) and N(4)–C(9)–N(5) fragments of the imidazole rings, with the bonds N(1)–C(3) = 1.348(5), C(3)–N(2) = 1.338(5), N(4)–C(9) = 1.339(6) and C(9)–N(5) = 1.333(6) Å. Bond angles around C(5) and C(8) are 108.0(3) and 106.2(3)°, respectively. The axial Re–O(1) bond [1.912(3) Å] is longer than Re–O (ethoxide) bonds, and indicates significant double bond character [6], with the Re–O(1)–C(7) bond splayed to 122.1(2)°. The average Re–N(imidazole) bond [2.099(3) Å] is markedly shorter that the Re–N(3) bond [2.166(3) Å], showing the effects of π-acidity of the imidazole rings. The Re–Br(1) bond distance of 2.4914(6) Å is very similar to that [2.503(1) Å] found in complexes with a bromide *trans* to a tertiary amino nitrogen in oxorhenium(V) complexes [3]. Recent work on oxorhenium(V) complexes containing tetradentate ligands include the compounds *trans*-[ReOCl(acac$_2$pn)] (acac$_2$pn = *N*,*N*′-propylenebis(acetylacetone)diimine) [9], [ReO(H$_2$O) (dioxo-tetH$_4$)]Cl (dioxo-tetH$_6$ = 1,4,8,11-tetraazaundecane-5,7-dione) [10] and [ReO(cyclen-H)Cl]Cl (cyclen-H$_2$ = 1,4,7,10-tetraazacyclododecane) [11].

Supplementary data

CCDC 287382 contains the crystallographic data for complex **1**. 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].

References

[1] J.R. Dilworth, S.J. Parrott. *Chem. Soc. Rev.*, **27**, 43 (1998).

[2] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta. *Inorg. Chim. Acta*, **307**, 149 (2000).

[3] T.I.A. Gerber, P. Mayer, Z.R. Tshentu. *J. Coord. Chem.*, **58**, 947 (2005).

[4] T.I.A. Gerber, P. Mayer, Z.R. Tshentu. *J. Coord. Chem.*, **58**, 1589 (2005).

[5] K.P. Maresca, F.J. Femia, G.H. Bonavia, J.W. Babich, J. Zubieta. *Inorg. Chim. Acta*, **297**, 98 (2000).

[6] T.I.A. Gerber, P. Mayer, Z.R. Tshentu. *J. Coord. Chem.*, **56**, 1357 (2003).

[7] G.M. Sheldrick. *SHELXL-97, Program for Structure Refinement*, University of Göttingen, Germany (1997).

[8] A. Abrahams, G. Bandoli, S. Gatto, T.I.A. Gerber, J.G.H. du Preez. *J. Coord. Chem.*, **42**, 303 (1997).

[9] P.D. Benny, J.L. Green, H.P. Engelbrecht, C.L. Barnes, S.S. Jurisson. *Inorg. Chem.*, **44**, 2381 (2005).

[10] L. Hansen, Y.D. Lampeka, S.P. Gavrish, X. Xu, A.T. Taylor, L.G. Marzilli. *Inorg. Chem.*, **39**, 5859 (2000).

[11] C. Xavier, A. Paulo, A. Domingos, I. Santos. *Eur. J. Inorg. Chem.*, **243** (2004).