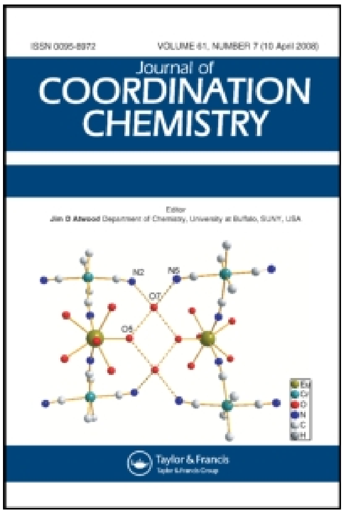

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Irvin Booysen[a]; Thomas I. A. Gerber[a]; Eric Hosten[a]; Dibanisile Luzipo[a]; Peter Mayer[b]
[a] Department of Chemistry, Nelson Mandela Metropolitan University, 6031 Port Elizabeth, South Africa [b] Department of Chemistry, Ludwig-Maximilians University, D-81377 München, Germany

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Synthesis and crystal structure of a rhenium(V) complex containing a tridentate imido-coordinated Schiff base

IRVIN BOOYSEN†, THOMAS I. A. GERBER*†, ERIC HOSTEN†,
DIBANISILE LUZIPO† and PETER MAYER‡

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

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The complex salt *trans*-[Re(mps)Cl(PPh_3)$_2$](ReO_4) (**1**) (H_3mps = *N*-(2-amino-3-methylphenyl)-salicylideneimine) was prepared by reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with a twofold molar excess of H_3mps. The compound was characterized by spectroscopy and X-ray crystallography. The results show that the trianionic ligand mps acts as a tridentate chelate via the doubly deprotonated amino nitrogen (which is present in **1** as an imide), the neutral imino nitrogen and the deprotonated phenolic oxygen atoms. The imido nitrogen and phenolate oxygen atoms coordinate *trans* to each other in a distorted octahedral geometry around the rhenium(V) centre.

Keywords: Rhenium(V); Tridentate *N*,*N*,*O* trianion; Imido group; Crystal structure

1. Introduction

The major reason for the current activity in the coordination chemistry of rhenium(V) is the fact that complexes in this state can easily be prepared from the two-electron reduction of perrhenate (ReO_4^-). These complexes are usually stable and substitutionally inert, which make them ideally suited as building blocks for potential therapeutic radiopharmaceuticals [1]. One of the disadvantages of this approach, however, is that the oxo group dominates the chemistry of rhenium(V) in terms of structures, geometries, reactivity and magnetic properties, which put certain limitations on the further exploration of oxorhenium(V) coordination chemistry. For this reason many current research efforts are concentrated on rhenium(V) moieties with metal-nitrogen multiple bonds, such as metal-nitrido, metal-hydrazido and metal-imido, in order to synthesize substitution inert complexes [2, 3].

We are currently engaged in the synthesis of stable Re(V) complexes with multidentate ligands containing an amino group, which on deprotonation can lead to a coordinated chelate containing the phenylimido core, Re=NC_6H_4-X. One of the

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

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major advantages of the phenylimido moiety is that it can be functionalized and derivatized. For example, the compound [^{188}Re(=NC_6H_4-X)$Cl_3(PPh_3)_2$] contains a *para*-substituted phenylimido group which was functionalized with a carboxylic group conjugated to various cholesterol derivatives [4]. However, it has also been shown that many phenylimidorhenium(V) compounds are hydrolytically unstable, which was ascribed to the presence of monodentate ligands in the coordination sphere [5]. For this reason, the use of multidentate imido-containing ligands in the synthesis of rhenium(V) complexes may be advantageous. We have recently reported the synthesis and structure of the rhenium(V) complex [Re(amb)(OEt)I$(PPh_3)_2$], in which the trianionic bidentate 2-imido-3-methylbenzoate (amb^{3-}) chelates *via* the imido nitrogen and deprotonated acetoxy oxygen [6]. We have now extended this to the synthesis of a rhenium(V) complex containing a tridentate ligand with a coordinated imido nitrogen. The complex salt [Re(mps)Cl$(PPh_3)_2$](ReO_4) was synthesized from the reaction of *trans*-[ReO$Cl_3(PPh_3)_2$] with the Schiff base *N*-(2-amino-3-methylphenyl)salicylideneimine (H_3mps) in ethanol.

2. Experimental

Trans-[ReO$Cl_3(PPh_3)_2$] was prepared by a literature procedure [7]. Scientific instrumentation used is the same as reported elsewhere [8]. Infrared spectra were obtained using KBr discs and ^{1}H NMR spectra were run in d_6-DMSO. Salicylaldehyde and 3-methyl-1,2-diaminobenzene were obtained commercially.

2.1. *H_3mps*

A solution of 100 mg of salicylaldehyde (819 μmol) in 15 cm^3 of benzene was added to 100 mg (819 μmol) of 3-methyl-1,2-diaminobenzene in 15 cm^3 of ethanol, and the mixture was heated under reflux for 90 min. The hot solution was filtered and left to cool at room temperature. After 3 h orange crystals were collected by filtration. They were washed with toluene and diethylether, and dried under vacuum. Yield = 176 mg (95%), m.p. 73–76°C. Anal. Calcd (%): C, 74.31; H, 6.24; N, 12.38. Found: C, 74.21; H, 12.43; N, 12.19. IR (cm^{-1}): ν(C=N) 1609; ν(O–H) 3398; ν(N–H) 3168, 3074. ^{1}H NMR (ppm): 13.08 (br s, 1H, H(7)), 8.63 (s, 2H, NH_2), 7.42 (t, 2H, H(4), H(12)), 7.07 (d, 1H, H(2)), 7.03 (d, 1H, H(13)), 6.98 (d, 1H, H(5)), 6.94 (d, 1H, H(11)), 6.77 (t, 1H, H(3)), 2.21 (s, 3H, CH_3).

2.2. *[Re(mps)Cl$(PPh_3)_2$](ReO_4) • H_2O (1 • H_2O)*

A mixture of *trans*-[ReO$Cl_3(PPh_3)_2$] (100 mg, 120 μmol) and 54 mg of H_3mps (239 μmol) was heated under reflux in 20 cm^3 of ethanol for 2 h. After the solution was cooled to room temperature, a maroon-coloured precipitate was removed by filtration. Recrystallization from 1 : 2 ethanol : dichloromethane gave maroon crystals. Yield of **1** · H_2O = 48 mg (65%), m.p. 185–188°C. Anal. Calcd (%): C, 48.52; H, 3.50; N, 2.26. Found: C, 48.66; H, 3.61; N, 2.21. IR (cm^{-1}): ν(Re=N) 1096; ν(C=N) 1597; ν(Re–N) 531; ν(Re–O) 462; ν(Re–Cl) 327. ^{1}H NMR (ppm): 13.59 (s, 1H, H(7)),

Table 1. Crystal data and structure refinement details for $\mathbf{1}\cdot H_2O$.

Chemical formula	$C_{50}H_{41}N_2O_5P_2ClRe_2\cdot H_2O$
Formula weight	1237.70
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.8666(2)
b	14.3542(3)
c	14.7295(3)
α	90.459(1)
β	91.557(1)
γ	95.179(1)
Volume (Å^3)	2287.18(8)
Z	2
Density (Calcd) (Mg m^{-3})	1.797
Absorption coefficient (mm^{-1})	5.468
$F(000)$	1204
Crystal size (mm^3)	$0.03\times0.06\times0.20$
θ range for data collection (°)	3.2–27.5
Index ranges	$-14\le h\le 13$; $-18\le k\le 18$; $-19\le \ell\le 19$
Reflections measured	18982
Independent/observed reflections	10297/8324
Data/parameters	10297/646
Goodness-of-fit on F^2	1.14
Final R indices $[I>2\sigma(I)]$	0.0449, $wR_2=0.0974$
Largest diff. peak and hole (e Å^{-3})	1.49/−2.11

7.80 (t, 2H, H(4), H(12)), 7.61–7.33 (m, 32H), 7.17 (d, 1H, H(5)), 6.93 (t, 1H, H(3)), 6.70 (d, 1H, H(11)), 2.09 (s, 3H, CH_3). Electronic spectrum (DMF), $\lambda(\varepsilon$, $M^{-1}\,cm^{-1})$: 327(7300), 376(3300), 489(800). Conductivity (10^{-3} M, CH_3CN) = 141 ohm^{-1}cm^2 mol^{-1}.

2.3. *X-ray structure*

Data collection was performed on a Nonius Kappa CCD diffractometer at 200K with Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [10] after optimising the crystal shape with XShape [11]. There are two molecules of **1** in the cell. Crystal and refinement data are given in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

The ligand H_3mps was synthesized by the condensation of equimolar quantities of salicylaldehyde and 3-methyl-1,2-diaminobenzene in benzene/ethanol. The compound *trans*-[Re(mps)Cl$(PPh_3)_2$](ReO_4) (**1**) was prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with two mol equivalents of H_3mps in ethanol, heated at reflux,

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

Re–O(1)	1.85(2)	Re–N(2)	1.82(2)
Re–Cl	2.371(1)	Re–N(1)	2.211(9)
Re–P(1)	2.497(2)	Re–P(2)	2.499(2)
C(1)–O(1)	1.31(3)	C(7)–N(1)	1.30(2)
N(1)–C(8)	1.44(2)	N(2)–C(9)	1.41(2)
P(1)–Re–P(2)	179.46(5)	Cl–Re–N(1)	176.1(3)
O(1)–Re–N(2)	152.1(6)	Cl–Re–P(1)	89.44(5)
Cl–Re–O(1)	101.5(5)	Cl–Re–P(2)	90.93(5)
Cl–Re–N(2)	106.4(4)	C(1)–O(1)–Re	138(2)
Re–N(2)–C(9)	135(1)	C(7)–N(1)–C(8)	117.4(9)
N(1)–Re–N(2)	69.9(5)	C(6)–C(7)–N(1)	125(1)
N(1)–Re–O(1)	82.2(5)	N(1)–Re–P(1)	89.3(2)

$[ReOCl_3(PPh_3)_2] + H_3mps \rightarrow [Re(mps)Cl(PPh_3)_2]^+ + H_2O + Cl^- + 2HCl$. Spectroscopic and X-ray crystallographic results indicate that the chelate mps is present in **1** as a trinegative tridentate ligand, with coordination through the doubly deprotonated amino nitrogen (to form a coordinated imido group), the amine nitrogen and the deprotonated phenolic oxygen atoms. Due to the propensity of rhenium(V) to form neutral complexes, the formation of the cation $[Re(mps)Cl(PPh_3)_2]^+$ is quite surprising, since neutrality could easily have been obtained by substitution of a PPh_3 ligand to form $[Re(mps)Cl_2(PPh_3)]$. The formation of the $[ReO_4]^-$ counterion is also surprising, and it intimates that complex redox processes are operative in this reaction system.

Complex **1** is diamagnetic and a 1 : 1 electrolyte in acetonitrile, and it is only soluble in the polar solvents DMF, DMSO and acetonitrile. The IR spectrum of **1** displays the Re=N stretching frequency as a medium-intensity band at $1096\,cm^{-1}$, with no band in the $920–990\,cm^{-1}$ region that can be ascribed to ν(Re=O). The presence of the perrhenate is indicated by the very strong peak centred at $885\,cm^{-1}$ [$\nu(Re^{VII}{=}O)$]. Re–N and Re–O stretches occur at 531 and $462\,cm^{-1}$, respectively, and a medium intensity band at $327\,cm^{-1}$ is typical of ν(Re–Cl). The ^1H NMR spectrum of the complex is dominated by signals of the phosphine protons, and is not informative on the coordination mode of the mps ligand. The electronic spectrum of **1** in DMF shows two intense absorptions at 327 and 376 nm, with a weaker one at 489 nm. With reference to previous spectroscopic studies [12], the intense band at 327 nm, with an extinction coefficient of $7300\,M^{-1}\,cm^{-1}$, is tentatively assigned to a ligand-to-metal charge transfer transition $[p_\pi(N^{2-}) \rightarrow d_\pi^*(Re)]$, and the one at 376 nm to the $p_\pi(Cl^-) \rightarrow d_\pi^*(Re)$, $(d_\pi^* = d_{xz}, d_{yz})$. The weak absorption at 489 nm is probably due to a $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi^*)^1$ transition.

X-ray crystallographic analysis of $\mathbf{1} \cdot H_2O$ shows that the rhenium(V) ion is centred in an octahedral environment with the equatorial plane formed by the $P_2ClN(1)$ donor set (figure 1). The octahedron is severely distorted, with the Cl–Re–P(1) and Cl–Re–P(2) bond angles close to orthogonality [89.44(5) and 90.93(5)° respectively], but with large deviations from orthogonality for Cl–Re–O(1) [101.5(5)°], Cl–Re–N(1) [176.1(3)°] and Cl–Re–N(2) [106.4(4)°]. The N(2)–Re–O(1) angle is also non-linear [152.1(6)°]. The two phenyl rings of mps make a dihedral angle of 12.10° with one another, and the P(1)–Re–P(2) angle is nearly linear at 179.46(5)°. The two bite angles of mps are N(1)–Re–O(1) = 82.2(5) and N(1)–Re–N(2) = 69.9(5)°. The mps ligand acts as a terdentate trianionic moiety, with N(2) coordinated to Re as a dinegative imido nitrogen atom. The Re–N(2) bond length of 1.82(2) Å is longer than normally observed

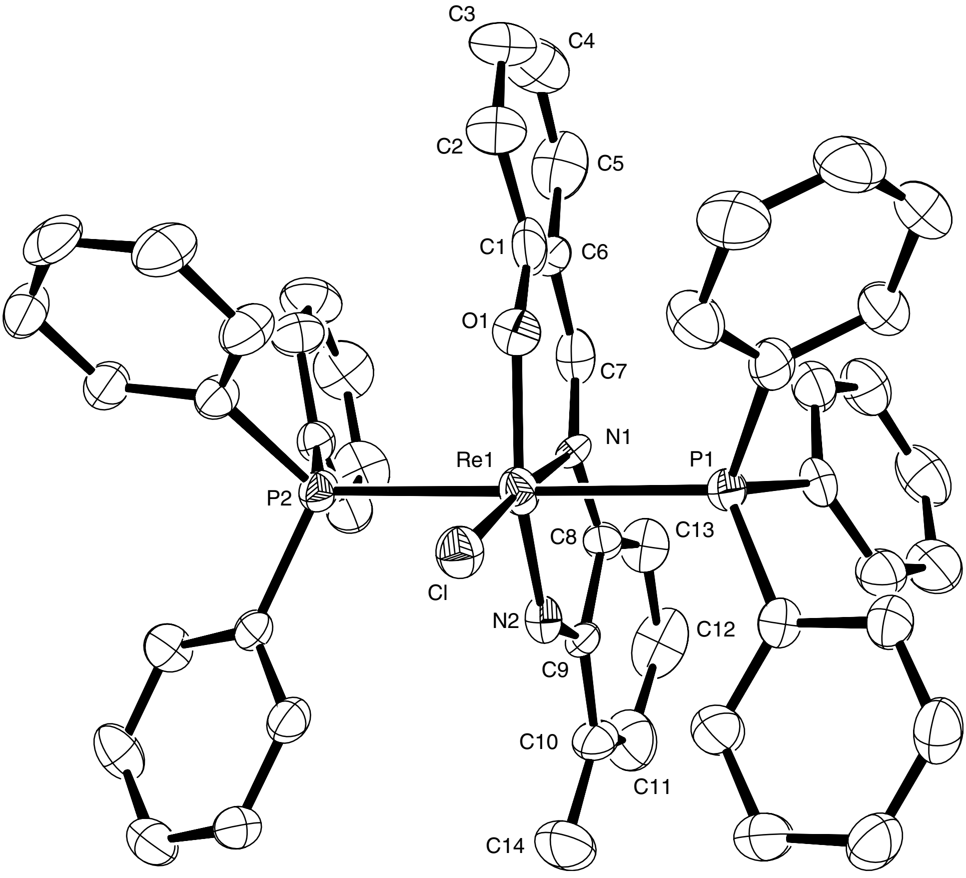

Figure 1. ORTEP drawing of the molecular structure of $[Re(mps)Cl(PPh_3)_2]^+$ showing the atom labelling scheme; thermal ellipsoids are drawn at the 40% probability level.

for the phenylimido unit [1.726–1.740 Å] [3, 13], but is considerably shorter than the values usually found for Re^V–NH and Re^V–NH_2 bonds [1.98–2.05 Å and 2.15–2.23 Å, respectively] [14]. The Re–N(2)–C(9) bond angle of 135(1)° indicates significant deviation from linearity of the coordination mode of the phenylimido unit, with a reduction in bond order. These data intimate that the imido nitrogen is doubly, rather than triply, bonded to the rhenium, thereby making the complex a sixteen-electron species. The Re–N(1) bond length of 2.211(9) Å is typical of Re^V–N(imine) bonds [14], and the Re–O(1) bond length of 1.85(2) Å falls at the lower end of the range normally observed for Re–O (phenolate) bonds [15]. The C(7)–N(1)–C(8) bond angle of 117.4(9)° is close to the ideal of 120° for a sp^2 hybridized nitrogen atom. The C(7)–N(1) bond length of 1.30(2) Å is typical for a carbon–nitrogen double bond of this type. The Re–Cl bond length [2.371(1) Å] is within the range [2.34(2)–2.44(2) Å] found normally for Re(V) complexes containing phosphine ligands [16].

$[ReO_4]^-$ has approximately regular tetrahedral geometry, with the average Re(2)–O distance equalling 1.707(8) Å. The closest contact that this counterion has with the complex is 3.176(9) Å, between the perrhenyl oxygen O(2) and H(38) attached to C(38) of one of the P(2) phenyl rings. Two significant hydrogen bonds are formed between two of the perrhenyl oxygens and the water of crystallization, (O(6)–H(6A)H(6B)): O(6)–H(6A) $\cdots$ O(4) = 2.87(1) Å and (O(6)–H(6B) $\cdots$ O(5) = 2.83(1) Å.

We have recently reported the reaction between *trans*-[$ReOCl_3(PPh_3)_2$] and *N*-(2-aminophenyl)salicylideneamine (H_3apa), which gave *cis*-[Re(apa)$Cl_2(PPh_3)$] as product [17]. The chelate apa acts as a tridentate ligand via the doubly deprotonated amino nitrogen (which is coordinated as an imide), the neutral secondary amino nitrogen and the deprotonated phenolic oxygen. This result is in contrast to the cationic complex **1** reported here.

Supplementary data

File CCDC-298179 contains crystallographic data for the complex. 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).

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