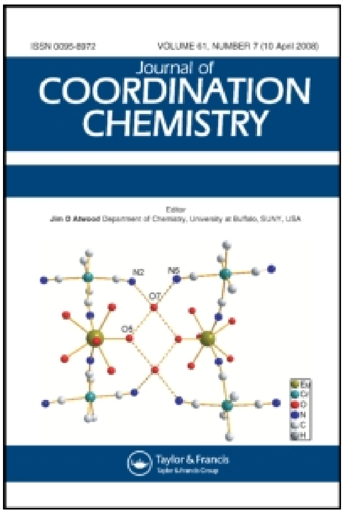

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Coordination of a tridentate imido-amino-phenolate chelate to rhenium(V)

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The complex *cis*-$[Re(apa)Cl_2(PPh_3)]$ (**1**) ($H_3apa = N$-(2-aminophenyl)salicylideneamine) was prepared by reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ with H_3apa in ethanol. Apa acts as a tridentate chelate ligand *via* the doubly deprotonated amino nitrogen (which is coordinated as an imide), the amino nitrogen and the deprotonated phenolic oxygen atoms. The two chlorides lie *cis* to each other in a distorted octahedral geometry around the rhenium(V) centre.

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

1. Introduction

The oxo group (O^{2-}), which is present in the majority of rhenium(V) complexes, dominates the coordination chemistry of the metal in this oxidation state, since it limits the structures, geometries, reactivity and magnetic properties of the complexes [1]. This had a detrimental effect on the development of a greater variety of rhenium(V) cores that may be useful in therapeutic applications of $^{186/188}Re$ isotopes. As a result, there have been numerous attempts to replace the oxo group, for example with the imido entity [2–4]. The introduction of substituents on the imido group may lead to a greater variety of rhenium(V) complexes, which may 'fine-tune' the biodistribution of rhenium in therapeutic applications. All imidorhenium(V) complexes reported in the literature contain the phenylimido unit, which is coordinated as a monodentate through the doubly deprotonated amino nitrogen atom [4, 5]. These complexes are easily prepared by a variety of methods, one of which is the reaction of an oxorhenium(V) complex with an aniline derivative [6].

Our approach is to synthesize complexes containing multidentate ligands, in which one of the donor atoms is an imido nitrogen atom. For example, we have recently reported the reaction of 2-amino-3-methylbenzoic acid (H_3amb) with

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cis-[$ReO_2I(PPh_3)_2$], which led to the isolation of [Re(amb)(OEt)I($(PPh_3)_2$)], in which the trianionic bidentate amb ligand chelates *via* the imido nitrogen and deprotonated acetoxy oxygen atoms [2]. We have now extended this project to the synthesis of a rhenium(V) complex that contains a tridentate ligand with a coordinated imido nitrogen atom. The reaction of the potentially tridentate ligand *N*-(2-aminophenyl)salicylideneamine (H_3apa) with *trans*-[$ReOCl_3(PPh_3)_2$] leads to *cis*-[Re(apa)Cl_2(PPh_3)] (**1**).

2. Experimental

Trans-[$ReOCl_3(PPh_3)_2$] was prepared by a literature procedure [7]. The ligand H_3apa was synthesized by a reported method [8]. Scientific instrumentation used is the same as reported elsewhere [9]. IR spectra were obtained using KBr discs and ^1H NMR spectra were run in d_6-DMSO.

2.1. *Cis-[Re(apa)Cl_2(PPh_3)] (1)*

A mixture of *trans*-[$ReOCl_3(PPh_3)_2$] (150 mg, 180 µmol) and 41 mg of H_3apa (191 µmol) was heated under reflux in 20 cm^3 of ethanol for 1 h. After the solution was cooled to room temperature, a red precipitate was removed by filtration. Recrystallization from 1 : 1 acetonitrile : ethanol gave red crystals. Yield = 74 mg (56%), m.p. 279–281°C. Anal. Calcd (%): C, 50.96; H, 3.59; N, 3.83. Found: C, 51.11; H, 3.68; N, 3.89. IR (cm^{-1}): 3315m, 3061m, 1626m, 1599m, 1435s, 1308s, 1258m, 1160m, 1092s, 744vs, 694vs, 520s, 508s, 430m, 310m, 295m; δ_H(300 MHz): 6.77–7.63 (24H, m), 4.97 (2H, s, C(7)H_2).

2.2. *X-ray structure*

Data collection was performed on a Nonius Kappa CCD diffractometer at 200 K with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods applying SIR97 [10] and refined by least-squares procedures using SHELXL-97 [11]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [12] after optimizing the crystal shape with XShape [13]. There are two molecules of **1** in the cell. Crystal and structure refinement data are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

The ligand H_3apa was prepared by reduction of the Schiff base *N*-(2-aminophenyl) salicylideneimine (which was synthesized by the condensation of equimolar quantities of salicylaldehyde and 1,2-diaminobenzene) with sodium borohydride in ethanol/water. The complex *cis*-[Re(apa)Cl_2(PPh_3)] (**1**) was made by the reaction of

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

Chemical formula	$C_{31}H_{26}N_2Cl_2PORe$
Formula weight	730.64
Temperature (K)	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	$a = 10.2232(2)$ $b = 21.3566(5)$; $\beta = 91.673(1)$ $c = 13.2560(3)$
Crystal size (mm^3)	$0.02 \times 0.04 \times 0.19$
Volume ($Å^3$)	2893.0(1)
Z	4
D_{Calcd} ($Mg\,m^{-3}$)	1.678
Absorption coefficient (mm^{-1})	4.467
Absorption correction	Numerical [12]
θ range for data collection (°)	3.2–27.5
Reflections measured	30185
Independent/observed reflections	6422 ($R_{int} = 0.081$)/4513
Data/restraints/parameters	6422/0/361
Goodness-of-fit on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0461$, $wR_2 = 0.1103$

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

Re–N(1)	1.802(5)	Re–O(1)	1.866(4)
Re–Cl(1)	2.435(2)	Re–Cl(2)	2.342(2)
Re–P	2.429(2)	Re–N(2)	2.18(1)
N(1)–C(9)	1.362(8)	N(2)–C(7)	1.39(2)
N(1)–Re–O(1)	157.5(2)	N(1)–Re–N(2)	70.1(3)
N(1)–Re–Cl(1)	95.3(1)	N(1)–Re–Cl(2)	102.0(2)
N(1)–Re–P	91.0(1)	N(2)–Re–O(1)	87.7(3)
Cl(1)–Re–Cl(2)	89.11(5)	Re–N(1)–C(9)	133.4(4)
P(1)–Re–Cl(1)	173.36(5)	N(2)–Re–Cl(2)	171.5(3)

trans-[$ReOCl_3(PPh_3)_2$] with an equimolar quantity of H_3apa in ethanol, according to the equation $ReOCl_3(PPh_3)_2 + H_3apa \rightarrow \mathbf{1} + H_2O + HCl + PPh_3$. Spectroscopic and X-ray crystallographic results indicate that the ligand apa is present in **1** as a trinegative tridentate ligand, with coordination through the doubly deprotonated amino nitrogen (to give a coordinated imido group), the amine nitrogen and the deprotonated phenolic oxygen atoms.

The complex is diamagnetic and a non-electrolyte in DMF, and is only soluble in the polar solvents acetonitrile, DMF and DMSO. The IR spectrum of **1** displays the Re=N stretching frequency as a strong band at 1092 cm^{-1}, with no band in the 900–990 cm^{-1} region that can be ascribed to ν(Re=O). Re–N and Re–O stretches occur at 520 and 430 cm^{-1}, respectively, and a medium intensity band at 3315 cm^{-1} is assigned to the N(2)–H stretch. A band of medium intensity at 310 cm^{-1} with a shoulder at 322 cm^{-1} is typical of ν(Re–Cl), indicating that the two chlorides are coordinated in the equatorial plane *cis* to each other [4, 6, 8]. 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 apa ligand.

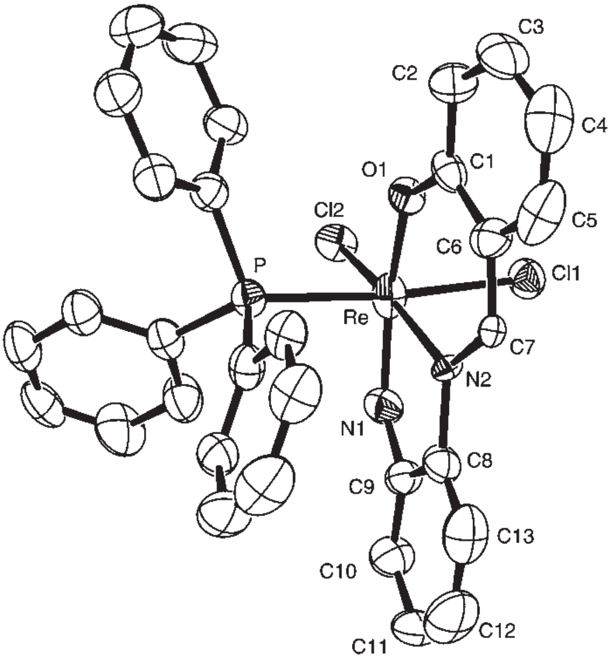

Figure 1. An ORTEP drawing of **1**, showing the atom labelling scheme and 40% probability ellipsoids.

X-ray crystallographic analysis of **1** shows that the structure is disordered, with 50% of the molecules having the N(1) atom below the PCl(1)Cl(2)N(2) plane (as shown in figure 1), and the remainder with O(1) in this position. This made the structure difficult to refine, since it appears that the ring carbon atoms are also disordered. However, attempted modelling of this disorder was unsuccessful. The rhenium(V) ion is centred in an octahedral environment with the equatorial plane formed by the $PCl_2N(2)$ donor set. The octahedron is severely distorted, with the N(1)–Re–P bond angle close to orthogonality [91.0(1)°], but with large deviations from orthogonality for N(1)–Re–Cl(1) [95.3(1)°], N(1)–Re–Cl(2) [102.0(2)°] and N(1)–Re–N(2) [70.1(3)°]. The N(1)–Re–O(1) angle is also non-linear [157.5(2)°]. The two phenyl rings of apa make a dihedral angle of 11.9(1)° with one another and the Cl(1)–Re–Cl(2) bond is nearly orthogonal at 89.11(5)°. The two bite angles of apa are N(1)–Re–N(2) = 70.1(3)° and N(2)–Re–O(1) = 87.7(3)°.

The apa ligand acts as a tridentate trianionic moiety, with N(1) coordinated to Re as a dinegative imido nitrogen atom. The Re–N(1) bond length of 1.802(5) Å is longer than is normally observed for the phenylimido unit (1.726–1.740 Å) [3, 14], but is considerably shorter than 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) [15]. The Re–N(1)–C(9) bond angle of 133.4(4)° 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(2) bond length of 2.18(1) Å is typical of Re(V)–N(amine) bonds [15] and the Re–O(1) bond length of 1.866(4) Å falls at the lower end of the range normally observed for Re–O (phenolate) bonds [16]. The two

Re–Cl bond lengths are unequal, with the Re–Cl(1) bond (*trans* to P) significant longer than Re–Cl(2) (2.44(2) and 2.34(2) Å, respectively).

No examples could be found in the literature of a complex containing a tridentate chelate having an imido nitrogen as a donor atom. In the complex [Re(ana)Cl(OEt)(PPh_3)$_2$] the ana^{3-} (2-imido-3-benzoate) ligand is coordinated as a bidentate *N*,*O*-donor chelate [17]. Also, the *N*,*P*-chelated imido ligand dpa was found in the complex [Re(dpa)Cl_2(Hdpa)] (H_2dpa = 2-diphenylphosphinoaniline) [18].

Supplementary material

File CCDC 284484 contains crystallographic data for this article. 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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