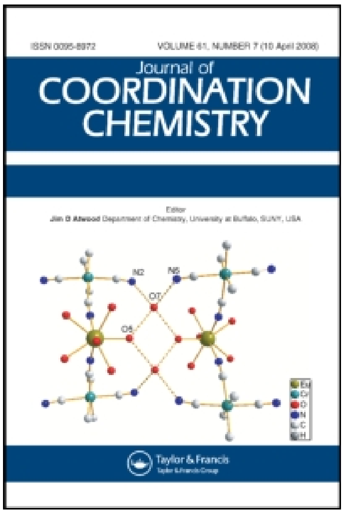

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A rhenium(V) complex containing a terdentate chelate with an imido donor atom: synthesis and structure of [Re(aps)I(PPh$_3$)$_2$]I (H$_3$aps = *N*-(2-aminophenyl)-salicylideneimine)

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A rhenium(V) complex containing a terdentate chelate with an imido donor atom: synthesis and structure of $[Re(aps)I(PPh_3)_2]I$ (H_3aps = *N*-(2-aminophenyl)-salicylideneimine)

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The complex salt *trans*-$[Re(aps)I(PPh_3)_2]I$ (**1**) (H_3aps = *N*-(2-aminophenyl)-salicylideneimine) was prepared by the reaction of *trans*-$[ReO(OEt)I_2(PPh_3)_2]$ in ethanol. The compound was characterized by vibrational and ^1H NMR spectrometry, and by X-ray crystallography. The trianionic ligand aps acts as a terdentate chelate *via* the doubly deprotonated amino nitrogen (which is present in **1** as an imide), the imino nitrogen and the deprotonated phenolic oxygen atoms. The imido nitrogen and phenolate oxygen atoms coordinate *trans* to one another to give distorted octahedral geometry around the rhenium(V) centre.

Keywords: Synthesis; Terdentate imido ligand; Rhenium(V); Crystal structure

1. Introduction

The coordination chemistry of rhenium(V) is dominated by the presence of the oxo group, which limits the variety of different rhenium(V) cores and complexes by influencing their structure, geometry and reactivity [1–3]. As a result, there are numerous attempts to replace the oxo group, for example with the imido entity [4–6]. The introduction of substituents on the imido moiety may lead to a greater variety of rhenium(V) complexes, which may 'fine-tune' the biodistribution of these compounds in therapeutic applications of their $^{186/188}Re$ isotopes [7].

Imidorhenium(V) complexes can easily be prepared by a variety of methods, one of which is the reaction of an oxorhenium(V) complex with an aniline derivative [8].

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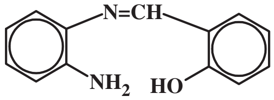
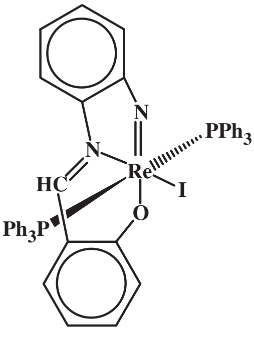
For example, the simple reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with aniline in ethanol leads to the imido compound *trans*-[Re(=NPh)$Cl_3(PPh_3)_2$] and water [9]. We have recently shown that even 1,2-diaminobenzene and its derivatives lead to the isolation of imido complexes from their reactions with oxorhenium(V) compounds [6]. For example, the reaction of 3-hydroxy-1,2-diaminobenzene with *trans*-[$ReOCl_3(PPh_3)_2$] leads to the imidorhenium(V) complex *trans*-[Re{$=NC_6H_3(1\text{-}NH_2)(3\text{-}OH)$}$Cl_3(PPh_3)_2$]. We have extended this project by producing bidentate imidoligands to a rhenium(V) centre [4]. For example, the reaction of 2-amino-3-methyl-benzoic acid(H_3amb) with *cis*-[$ReO_2I(PPh_3)_2$] led to the isolation of [Re(amb)(OEt)I$(PPh_3)_2$], in which the trianionic bidentate amb chelates *via* the imido nitrogen and deprotonated acetoxy oxygen atoms.



H_3aps



[Re(aps)I$(PPh_3)_2$]$^+$

We have now extended this project to the synthesis of the first rhenium(V) complex which contains a terdendate ligand with a coordinated imido nitrogen atom. The reaction of the potentially terdentate Schiff base ligand *N*-(2-aminophenyl) salicylideneimine (H_3aps) with *trans*-[ReO(OEt)$I_2(PPh_3)_2$] leads to the product *trans*-[Re(aps)I$(PPh_3)_2$]I (**1**). It was shown previously that terdentate Schiff-base ligands containing the *ONN* donor atom set like *N*-(8′-quinolyl)salicylideneimine (Hqse) gave complexes of the type [$ReOCl_2$(qse)], with the ON_2 ligand atom set and the oxo oxygen atom occupying the equatorial plane and the two chlorides in *trans* axial positions in a distorted octahedral structure [10].

2. Experimental

Trans-[ReO(OEt)$I_2(PPh_3)_2$] was synthesized by a literature procedure [11]. Salicylaldehyde and 1,2-diaminobenzene were obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques. IR spectra were obtained using KBr discs and ^{1}H NMR spectra (300 MHz) were run at room temperature in d_6-DMSO. The instrumentation used is the same as reported earlier [12].

2.1. *Synthesis of H_3aps*

Equimolar quantities (0.02 mol) of salicylaldehyde and 1,2-diaminobenzene were heated under reflux for 90 min in 30 cm^3 of a 1 : 1 benzene/ethanol solvent mixture. After heating was stopped, the brown solution was filtered and cooled to room temperature. Orange crystals formed by the slow evaporation of the solvent overnight. The crystals were filtered off, washed with ethanol and diethylether and dried under vacuum. Yield = 3.52 g (83%), m.p. 176°C. Anal. Calcd (%): C, 73.58; H, 5.66; N, 13.21. Found: C, 73.40; H, 5.70; N, 13.36. IR (cm^{-1}): ν(O–H) 3436; ν(N–H) 3207, 3179; ν(C=N) 1628. ^{1}H NMR (ppm): 13.08 (s, 1H, *H*(7)), 8.56 (s, 2H, NH_2), 7.41 (d, 1H, *H*(12)), 7.38 (d, 1H, *H*(2)), 7.36 (t, 1H, *H*(10)), 7.32 (d, 1H, *H*(9)), 7.25 (t, 1H, *H*(4)), 7.22 (t, 1H, *H*(11)), 7.11 (d, 1H, *H*(5)), 6.94 (t, H, *H*(3)).

2.2. *Synthesis of* trans-*[Re(aps)I(PPh_3)$_2$]I (1)*

To a suspension of 0.100 g (98 µmol) of *trans*-[ReO(OEt)I_2(PPh_3)$_2$] in 20 cm^3 of ethanol was added 0.413 g (195 µmol) of H_3aps. The mixture was heated under reflux for approximately 90 min, and then cooled to room temperature to give a brown precipitate, which was filtered off, washed with toluene, ethanol and diethylether, and dried under vacuum. The solid was then dissolved in 15 cm^3 of a 2 : 1 acetonitrile/ethanol mixture, the slow evaporation of which over 3 days gave brown crystals of X-ray quality. Yield = 0.817 g (71%), m.p. 218°C. Anal. Calcd (%): C, 50.14; H, 3.35; N, 2.39. Found: C, 50.11; H, 3.11; N, 2.42. IR (cm^{-1}): ν(Re=N) 1096; ν(C=N) 1597; ν(Re–N) 521; ν(Re–O) 440; ν(C–O) 1277. ^{1}H NMR (ppm): 7.99 (s, 1H, *H*(7)), 7.36–7.68 (m, 36H), 7.36 (d, 1H, *H*(5)), 7.20 (t, 1H, *H*(3)).

2.3. *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 using SIR97 [13] and refined by least-squares procedures using SHELXL97 [14]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [15] after optimising the crystal shape with XShape [16]. There are two molecules of **1** in the asymmetric unit. Crystal and structure refinement data are given in table 1 and selected bond lengths and angles in table 2.

3. Results and discussion

The complex *trans*-[Re(aps)I(PPh_3)$_2$]I (**1**) was synthesized by the reaction of *trans*-[ReO(OEt)I_2(PPh_3)$_2$] with two mol equivalents of H_3aps in ethanol, heated at reflux under nitrogen. Complex **1** could also be prepared by the reaction of $[ReO_4]^-$ with a threefold molar excess of PPh_3 and a twofold excess of H_3aps in the presence of hydroiodic acid in ethanol. These preparative routes are given by the equations below,

$$[ReO(OEt)I_2(PPh_3)_2] + H_3aps \rightarrow \mathbf{1} + H_2O + EtOH$$

$$(n\text{-}Bu_4N)[ReO_4] + 3PPh_3 + H_3aps + 3HI \rightarrow \mathbf{1} + OPPh_3 + 3H_2O + [n\text{-}Bu_4N]I$$

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

Chemical formula	$C_{49}H_{39}N_2OP_2I_2Re$
Formula weight	1173.81
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 10.7071(2)$
	$b = 20.9116(3)$
	$c = 22.1100(3)$
	$\alpha = 114.633(1)$
	$\beta = 101.652(1)$
	$\gamma = 92.072(1)$
Volume (Å^3)	4366.8(1)
Z	4
Density (Calcd) (Mg m^{-3})	1.785
Absorption coefficient (mm^{-1})	4.309
$F(000)$	2264
Crystal size (mm^3)	0.03 × 0.06 × 0.09
θ range for data collection (°)	3.2–26.0
Index ranges	$-13 \leq h \leq 13$; $-25 \leq k \leq 25$; $-26 \leq l \leq 27$
Reflections measured	55,083
Independent/observed reflections	17,095/12,608
Data/parameters	17,095/1027
Goodness-of-fit on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	0.0418, $wR_2 = 0.0762$
Largest diff. peak and hole (e Å^{-3})	2.09/−2.16

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

	Molecule A	Molecule B
Re–N(1)	1.772(4)	1.771(5)
Re–N(2)	2.185(5)	2.192(6)
Re–O(1)	1.929(4)	1.910(4)
Re–I(1)	2.7045(5)	2.6887(5)
Re–P(1)	2.500(2)	2.506(2)
Re–P(2)	2.504(2)	2.507(2)
C(1)–N(1)	1.395(8)	1.373(9)
C(7)–N(2)	1.270(9)	1.238(9)
N(1)–Re–O(1)	158.8(2)	158.6(2)
P(1)–Re–P(2)	175.53(5)	177.3(6)
N(1)–Re–N(2)	75.1(2)	74.8(2)
N(1)–Re–P(1)	90.8(1)	89.4(2)
N(1)–Re–P(2)	91.4(1)	89.1(2)
N(1)–Re–I(1)	107.2(2)	105.4(2)
Re(1)–N(1)–C(1)	130.3(4)	130.6(4)
C(6)–N(2)–C(7)	120.2(5)	120.1(6)
N(2)–C(7)–C(8)	125.7(6)	125.8(7)

Spectroscopic and X-ray crystallographic results indicate that the ligand aps is present in **1** as a trinegative terdentate ligand, with coordination through the doubly deprotonated amino nitrogen (to give a coordinated imido group), the imino nitrogen and the deprotonated phenolic oxygen atoms. The complex is diamagnetic and a 1 : 1 electrolyte in DMF, and it is only soluble in polar solvents such as acetonitrile, DMF and DMSO.

The IR spectrum of **1** displays the Re = N stretching frequency as a strong band at 1096 cm^{-1}, with no band in the 900–990 cm^{-1} region that can be

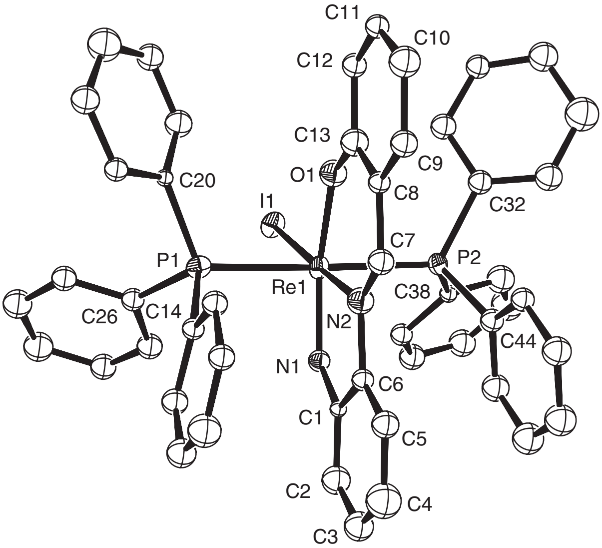


Figure 1. ORTEP drawing of the asymmetric unit in **1** showing the atom labelling scheme; thermal ellipsoids are drawn at the 40% probability level.

ascribed to ν(Re=O). The terdentate coordination of aps is further manifested by the shift of ν(C=N) from $1628\,\mathrm{cm}^{-1}$ in the free ligand to $1597\,\mathrm{cm}^{-1}$ in the complex, and the Re–N and Re–O stretching frequencies at 521 and $440\,\mathrm{cm}^{-1}$, respectively. The ^{1}H NMR spectrum of the complex (which integrates for 39 protons in the range δ 7.20–8.00 ppm) is dominated by signals of triphenylphosphine protons, which obscure most of the protons of the coordinated aps ligand. However, separate signals were observed for protons *H*(3) (at 7.20 ppm) and *H*(5) (at 7.36 ppm), which are shifted downfield from their positions in the spectrum of the free ligand.

X-ray crystallographic analysis of complex **1** shows that two molecules of the complex (**A** and **B**) exist in the asymmetric unit. These have different orientations in the lattice, and their equatorial coordination planes (P_2IN) make a dihedral angle of 71.7° with each other. They have comparable bond distances and angles. The molecular structure of the complex is illustrated in figure 1 and selected bond lengths and angles are listed in table 2. The rhenium ion is centred in an octahedron with the equatorial plane formed by the P_2IN donor set. The octahedron is severely distorted, with N(1)–Re–P bond angles close to 90° [N(1)–Re–P(1) = 90.8(1)°, N(1)–Re–P(2) = 91.4(1)°], but with large deviations from orthogonality for N(1)–Re–I(1) [107.2(2)°] and N(1)–Re–N(4) [75.1(2)°] (corresponding values for molecule B are 89.1(2), 89.4(2), 105.4(2) and 74.8(2)°). The result of this distortion is that the Re ion is shifted out of the mean equatorial plane by 0.057 Å towards N(1) in molecule A, but is shifted by 0.013 Å towards O(1) in molecule B. In addition, the N(1)–Re–O(1) angle is nonlinear at 158.8(2) (A) and 158.6(2)° (B). In the P_2ION_2 coordination polyhedra, the Re ion is 1.30 Å from the P(1)I(1)O(1) and 1.32 from the N(1)N(2)P(2) plane, with the dihedral angle between these planes being 11.9° (corresponding values in molecule B are 1.26, 1.33 Å and 9.4°). The coordinated aps ligand is extremely planar in A, with the largest deviation form the mean plane through all ligand atoms being for N(2) at 0.041 Å. In molecule B, atom C(11) shows the largest deviation from the aps plane at 0.12 Å. The two phenyl rings of aps make a dihedral angle of 1.7° with one another in A, and 6.9° in B. P–Re–P bond angles in A and B are 175.53(5) and 177.34(6)°, respectively. The two bite angles of aps are N(1)–Re–N(2) = 75.1(2)° and N(2)–Re–O(1) = 83.8(2)° (in B, 74.8(2) and 83.8(2)°, respectively).

The aps ligand acts as a terdentate trianionic moiety, with N(1) coordinated to Re as a dinegative imido nitrogen atom. The Re–N(1) bond length of 1.772(4) Å (1.771(5) Å in B) is slightly longer than is normally observed for the phenylimido unit (1.726–1.740 Å) [5, 17], but considerably shorter than the values of 1.98–2.05 Å and 2.15–2.23 Å usually found for Re^V–NH and Re^V–NH_2 bond lengths, respectively [18]. The Re–N(1)–C(1) bond angle of 130.3(4)° [130.6(4)° in B] is rather acute, and illustrates an unusual deviation from linearity of the coordination mode of the triply bonded phenylimido unit. This contributes to lengthening of the Re=N in **1**. These data intimate that the imido nitrogen atom is doubly, rather than triply, bonded to the rhenium. The Re–N(2) bond length of 2.185(5) Å (2.192(6) Å in B) is typical of Re(V)–N(imine) bonds [19]. The Re–O(1) bond length of 1.929(4) Å (1.910(4) Å in B) falls within the range normally observed for Re(V)–O (phenolic) bonds [19].

Iodide is rarely found as a ligand in rhenium(V) complexes, and the Re–I distances of 2.7045(5) and 2.6887(5) Å in A and B fall in the observed range of 2.664(2)–2.789(3) Å [11, 20]. PPh_3 ligands are coordinated to the metal centre *trans* to each other with an average Re–P distance of 2.504(2) Å in A (2.506(2) Å in B). The C(6)–N(2)–C(7) bond angle of 120.2(5)° in A illustrates sp^2 hybridization of the imine nitrogen (120.1(6)° in B). Similarly, the N(2)–C(7)–C(8) angle equals 125.7(6)° in A.

Rhenium(V) complexes containing chelating imido ligands are not common, the first example being the bidentate *N*,*O* coordination of 2-imido-3-benzoate (ana^{3-}) in $[Re(ana)Cl(OEt)(PPh_3)_2]$ [21]. Another example is $[Re(dpa)Cl_2(Hdpa)]$, prepared from *trans*-$[ReOCl_3(PPh_3)_2]$ and 2-diphenylphosphinoaniline (H_2dpa), and which contains the *N*,*P*-chelated imido ligand dpa [22]. Complex **1** represents the first example of a rhenium(V) complex containing a terdentate chelate with an imido nitrogen as one of the donor atoms.

Supplementary data

CCDC-279062 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; e-mail: deposit@ccdc.cam.ac.uk].

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