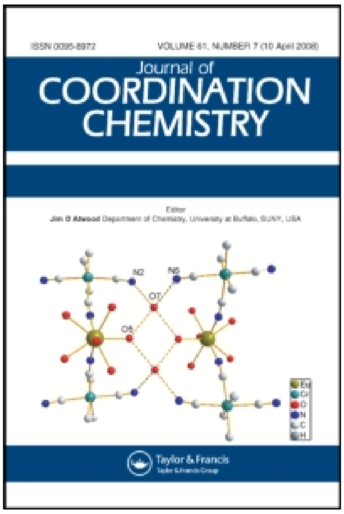

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A trigonal-bipyramidal oxorhenium(V) complex with a bidentate nitrogen-donor ligand

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The oxorhenium(V) complex [ReO(Hapb)(apb)] (**1**) (H_2apb = 2-(2-aminophenyl)-1-benzimidazole) was prepared by reaction of *trans*-[$ReO_2(py)_4$]Cl with a twofold molar amount of H_2apb. The complex was characterized by spectroscopy and X-ray crystallography. The results show that the rhenium atom lies in a distorted trigonal-bipyramidal environment, with the two imidazole nitrogen atoms in apical positions, and the oxo and two amido nitrogens in the trigonal plane.

Keywords: Rhenium(V); Trigonal-bipyramidal; Amide; Crystal structure

1. Introduction

Since the first arylimido rhenium(V) complex, [Re(NPh)$Cl_3(PEt_2Ph)_2$], was synthesized using aniline as the source of the imido ligand [1], many analogous complexes have been reported [2]. In complexes with such monodentate arylimido ligands, the coordinated nitrogen atom is fully deprotonated and very short Re-N(imido) distances are observed. On the other hand, rhenium(V) complexes with polydentate arylimido ligands are still rare. The potentially bidentate ligand 2,3-diaminophenol (H_2dap) reacts with *trans*-[$ReOCl_3(PPh_3)_2$] in ethanol to form the rhenium(V)-imido complex *trans*-[Re(dap)$Cl_3(PPh_3)_2$], in which dap is monodentate *via* the doubly deprotonated nitrogen in the 2-position [3]. However, 2-aminophenol (H_2ap) acts as a monoanionic bidentate N,O-donor in [$ReOCl_2$(Hap)(PPh_3)] [4]. With 2-amino-3-methylphenol (H_2amp), the complex [Re(amp)(Hamp)I$(PPh_3)_2$]I was isolated with amp coordinated through the deprotonated nitrogen only, while Hamp is a monoanionic N,O-donor [5]. However, the reaction of the potential N,O-donor ligand 2-amino-3-methylbenzoic acid (H_3amb) with *cis*-[$ReO_2I(PPh_3)_2$] in ethanol led to isolation of the six-coordinate [Re(amb)(OEt)I$(PPh_3)_2$], in which the trianionic amb is a bidentate chelate *via* the doubly deprotonated amino nitrogen and the deprotonated acetoxy oxygen [6]. This product was therefore an example of a bidentate imido ligand. Another such example is [Re(imq)$Cl_3(PPh_3)$], which was formed by reaction of [$ReOCl_3(PPh_3)_2$] with

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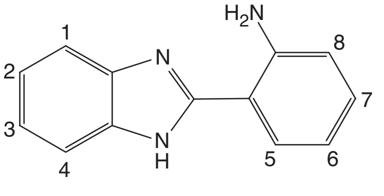
2-methyl-8-aminoquinoline (H_2imq), and in which imq is a bidentate ligand *via* the imido and pyridyl nitrogens [7]. However, if the metal:ligand molar ratio is increased to above two in the latter reaction, the complex [$ReOCl_2$(Himq)(PPh_3)] was isolated, in which Himq is a bidentate monoanionic chelating ligand *via* an amido nitrogen and the neutral pyridyl nitrogens [8].

To synthesize a rhenium(V) complex containing two bidentate imido-coordinated ligands, the reaction of *trans*-[$ReO_2(py)_4$]Cl with 2-(2-aminophenyl)-1-benzimidazole (H_2apb) was investigated.



H_2apb

The expectation was that H_2apb would behave as a ligand to rhenium(V) very similar to 8-aminoquinoline, and that the two *trans* oxo groups would be replaced by two *trans* imido nitrogens. However, its behavior was very different, and [ReO(Hapb)(apb)] (**1**) was produced, in which the metal is coordinated to two bidentate chelating ligands supplying 1½ negative changes each. The complex also has the unusual (for Re(V)) trigonal-bipyramidal geometry. Five-coordinate oxorhenium(V) complexes are usually square pyramidal.

2. Experimental

Trans-[$ReO_2(py)_4$]Cl was prepared by a literature procedure [9]. Scientific instrumentation is the same as reported elsewhere [10]. All solvents were purified and dried by standard methods. All other chemicals were obtained commercially and used without further purification. IR data were obtained using KBr disks and ^{1}H NMR spectra were run in d_6-DMSO.

2.1. *Synthesis*

2.1.1. 2-(2-Aminophenyl)-1-benzimidazole (H_2apb). A mixture of 2.00 g of 2-aminobenzoic acid and 1.58 g of 1,2-diaminobenzene was dissolved in 100 cm^3 of 6M HCl. The resultant solution was then refluxed for 24 h, after which it was placed in a cold room at 10°C. After three days crude brown crystals were obtained, which were filtered off and dried. The crystals were redissolved in ethanol and decolorizing charcoal was added. The resultant mixture was refluxed for 24 h and then allowed to cool to room temperature, after which it was filtered *via* Kieselguhr. The filtrate was then left to stand in the cold room at 10°C, and light brown crystals obtained after two days were collected and dried under vacuum. Yield = 85%, m.p. 211–215°C. Anal. Calcd for $C_{13}H_{11}N_3$ (%): C, 74.62; H, 5.30; N, 20.08. Found: C, 74.60; H, 5.28; N, 19.97. IR (cm^{-1}): ν(C=N) 1614, ν(N–H) 3120, 3061. ^{1}H NMR (295K, ppm): 12.89 (br s, 1H, N*H*); 7.85 (d, 1H, *H*(1)); 7.61 (s, 2H, NH_2); 7.18–7.27 (m, 2H, *H*(2), *H*(3)); 7.15 (t, 2H, *H*(7), *H*(6)); 6.85 (d, 1H, *H*(8)); 6.68 (t, 2H, *H*(5), *H*(4)).

2.1.2. Synthesis of [ReO(Hapb)(apb)] (1). *Trans*-[$ReO_2(py)_4$]Cl (0.100 g, 0.175 mmol) and H_2apb (0.073 g, 0.350 mmol) were added to ethanol (20 cm^3), and the mixture was heated under reflux. After 10 min, the solution changed from yellow to green. Heating was continued for another 50 min, and then the mixture was cooled to room temperature. The green precipitate that formed was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Recrystallization was from a 2 : 1 (v/v) mixture of tetrahydrofuran : ethanol. Yield = 0.079 g (73%), m.p. > 340°C. Anal. Calcd for $C_{26}H_{19}N_6ORe$ (%): C, 25.28; H, 3.10; N, 13.61. Found: C, 25.42; H, 3.11; N, 13.89. IR(cm^{-1}): ν(Re=O) 970; ν(N–H) 3106, 3049; ν(Re–N) 475, 418. ^{1}H NMR (ppm): 14.89 (br s, 1H, N(3)*H*); 11.56 (s, 2H, N(1)*H*); 8.42 (d, 2H, *H*(2)); 7.94 (d, 4H, *H*(13), *H*(10)); 7.70 (t, 2H, *H*(4)); 7.58 (t, 2H, *H*(11)); 7.47 (t, 2H, *H*(3)); 7.21–7.17 (m, 4H, *H*(5), *H*(12)).

2.2. *X-ray crystallography*

A single crystal of **1** was used for data collection on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The unit-cell dimensions were determined by a least-squares refinement of 25 reflections. The intensity data were collected by the ω–2θ scan technique. The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of ψ scans was applied. The crystal data and experimental parameters are listed in table 1. The positions of the non-hydrogen atoms were determined by a direct method (SIR 92) [11]. The structure was refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were included in the refinement but restrained to ride on the atoms (C–H = N–H = 0.95 Å, *U*(H) = 1.2*U*(C, N)). All calculations were performed using SHELX-97 [12].

Table 1. Crystal data and refinement parameters for **1**.

Chemical formula	$C_{26}H_{19}N_6ORe$
Formula weight	617.68
Temperature (K)	200(2)
Crystal system	Trigonal
Space group	$P3_12_1$
Unit cell dimensions (Å, °)	
a	8.6618(2)
c	24.3675(3)
Crystal size (mm^3)	0.03 × 0.06 × 0.20
V (Å^3)	1583.28(6)
Z	3
Density (Calcd) (Mg m^{-3})	1.944
Absorption coefficient (mm^{-1})	5.791
F(000)	900
θ range for data collection (°)	3.2–27.5
Index ranges	$-11 \le h \le 11$; $-9 \le k < 9$; $-31 \le l \le 31$
Reflections measured	4784
Data/parameters	2417/161
Goodness-of-fit on F^2	1.08
R, wR_2	0.0223, 0.0494
Largest diff. peak and hole (e Å^{-3})	2.19, −0.79

3. Results and discussion

3.1. *Synthesis*

The ligand H_2apb was synthesized by condensation of 2-aminobenzoic acid and 1,2-diaminobenzene in 6M hydrochloric acid. The ligand offers interesting possibilities as a chelate; the amino group can remain as a neutral group, as a mono-deprotonated amide or as a doubly deprotonated imide in a metal complex, whereas the imidazole group can coordinate *via* the neutral imine or deprotonated azole nitrogen.

The reaction of a twofold molar amount of H_2apb with *trans*-[$ReO_2(py)_4$]Cl in ethanol gave the green product [ReO(Hapb)(apb)] (**1**) in good yield. The reaction is given by the equation

$$[ReO_2(py)_4]Cl + 2H_2apb \rightarrow \mathbf{1} + 4py + H_2O + HCl$$

Attempts were also made to prepare other rhenium(V) complexes with H_2apb as ligand, by using the complex *trans*-[$ReOCl_3(PPh_3)_2$] as starting material in ethanol. However, only [$ReOCl_2(OEt)(PPh_3)_2$] was isolated.

Complex **1** is soluble in a wide variety of solvents, including acetone, acetonitrile, dichloromethane, DMF and DMSO, but is insoluble in water, alcohols and benzene. It is stable for months in the solid state, and for days in solution.

3.2. *Spectral characterization*

The dominant feature of the infrared spectrum of **1** is the presence of an intense absorption at 970 cm^{-1}, ascribed to the Re=O stretching mode. Distorted octahedral monooxorhenium(V) complexes [4, 8, 13–18] typically have the ν(Re=O) in the range 945–965 cm^{-1}. The ν(C=N) of the imidazole rings occurs at 1609 cm^{-1}, and N–H stretches are indicated by medium intensity peaks at 3049 and 3106 cm^{-1}. Two medium intensity absorptions at 418 and 475 cm^{-1} are indicative of ν(Re–N).

The ^1H NMR spectrum of **1** in DMSO-d_6 shows sharp and clear peaks and is typical of the diamagnetic nature of the d^2 system. The peak furthest downfield at 14.89 ppm is assigned to the proton on N(3) that is involved in hydrogen-bonding (see paragraph 3.3), and the sharp two-proton singlet at 11.56 ppm is ascribed to the protons on the amide nitrogens N(1) and N(1a). The aromatic region integrates for 16 protons, as required for the phenyl protons of the Hapb and apb chelates (see assignments in paragraph 2.1.2).

3.3. *Structure of [ReO(Hapb)(apb)] (1)*

A representation of the X-ray crystal structure of **1** is shown in figure 1. The rhenium atom lies in a distorted trigonal-bipyramidal environment. The two imidazole N(2) atoms lie in the apical positions *trans* to each other, with the oxo oxygen and two amido N(1) atoms in the trigonal plane. The complex has C_2-symmetry. The two amino groups are singly deprotonated and provide a negative charge each, coordinated as amides. The oxo group provides two negative charges. In order to obtain electroneutrality for the rhenium(V) complex, one more negative charge is needed in the molecule.

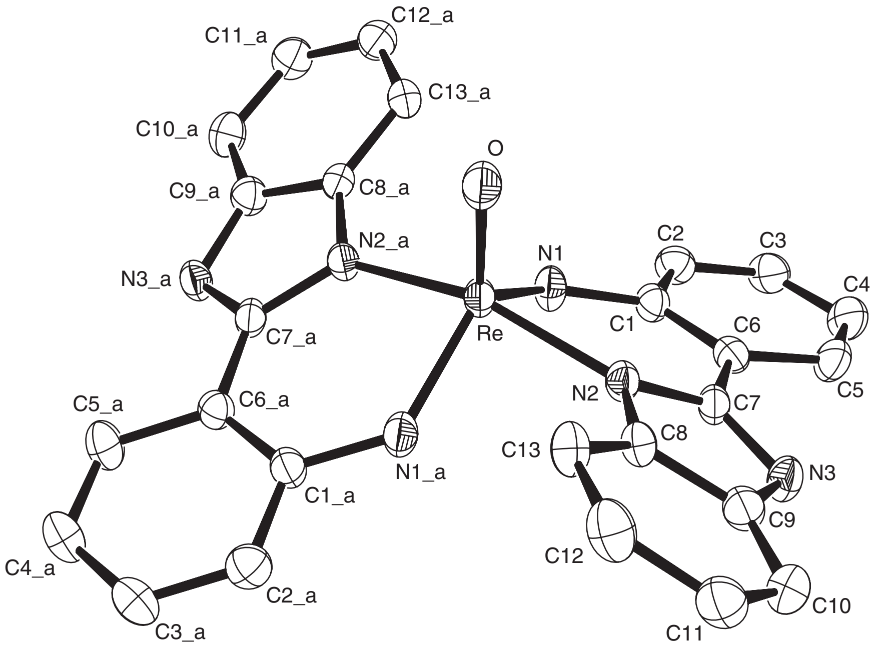


Figure 1. ORTEP view of **1**, showing 40% probability displacement ellipsoids and the atom labeling. Hydrogen atoms have been omitted for clarity.

Nitrogen N(3) makes an intermolecular hydrogen bond to N(3) of another molecule of **1** [2.814(5) Å] (see figure 2), which means that the hydrogen site bound to N(3) cannot have the site occupation factor 1, but the factor must be 0.5. So formally there are two N(3) half negative charges in **1**. In practice, however, one H$_2$apb is doubly deprotonated at N(1) and N(3) and the other is singly deprotonated at N(1). Distortions from an ideal rhenium-centered trigonal-pyramid mainly results in a non-linear N(2)–Re–N(2a) axis of 160.7(1)°. The trigonal plane angles are O–Re–N(1) = 119.7(2)°, O–Re–N(1a) = 119.7(2)° and N(1)–Re–N(1a) = 120.6(2)°. Furthermore, the angles N(2)–Re–O [99.6(2)°], N(2)–Re–N(1) [85.6(2)°] and N(2)–Re–N(1a) [84.9(2)°] deviate considerably from 90°. The bite angle [N(1)–Re–N(2)] of the chelates is 85.6(2)°. The C(1)–C(6) phenyl and imidazole rings are not coplanar, with a dihedral angle of 16.37° between their least-squares planes. Both the imidazole and phenyl rings are planar, as expected. The C–C–N angles at the ring junctions deviate considerably from 120° [C(1)–C(6)–C(7)=122.5(3)°, N(2)–C(7)–C(6) = 123.3(4)°], and the rhenium atom lies about 10° off the lone-pair direction on N(2)[Re–N(2)–C(7) = 129.6(3)°].

The Re–O bond distance of 1.663(4)Å table 2 is shorter than those observed in octahedral monooxorhenium(V) complexes, which normally occur in the range 1.68–1.72 Å, and can be considered as a formal ReηO triple bond. In rhenium-oxo complexes the idealized ReηO and Re=O bond distances are estimated to be 1.60 and 1.75Å, respectively [13–15]. The Re–N(1) length of 1.947(4) Å confirms that the N(1) atoms are present as amides, since Re(V)–NH$_2$ bond distances fall in the range 2.10–2.22 Å [4, 16]. The Re–N(2) bond [2.060(4) Å] is slightly shorter than those of neutral imidazole-ring nitrogen-to-rhenium(V) bonds [2.081(4)–2.122(5) Å range] [17, 18]. However, in benzimidazole rhenium(V) complexes, the Re–N (neutral imidazole) bond distance

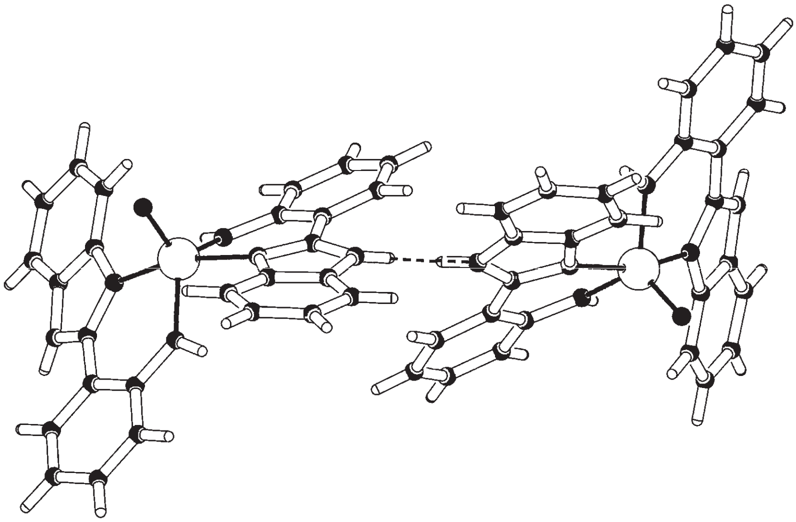


Figure 2. View of **1**, showing the intermolecular hydrogen-bond.

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

Re–O	1.663(4)	Re–N(1)	1.947(4)
Re–N(2)	2.060(4)	N(1)–C(1)	1.399(5)
C(1)–C(6)	1.395(6)	C(6)–C(7)	1.450(7)
N(2)–C(7)	1.369(5)	N(3)–C(7)	1.332(6)
N(2)–C(8)	1.403(6)	N(3)–C(9)	1.385(6)
C(8)–C(9)	1.399(6)	C(8)–C(13)	1.394(6)
O–Re–N(1)	119.7(2)	N(1)–Re–N(1a)	120.6(2)
O–Re–N(2)	99.6(2)	Re–N(1)–C(1)	133.5(4)
N(1)–Re–N(2)	85.6(2)	C(6)–C(7)–N(2)	123.3(4)
N(2)–Re–N(2a)	160.7(1)	C(7)–N(2)–C(8)	104.9(3)
C(1)–C(6)–C(7)	122.5(3)	C(7)–N(3)–C(9)	107.1(3)
N(2)–C(7)–N(3)	112.6(4)		
N(2)–C(8)–C(13)	130.9(4)		

varies around 2.14 Å, but the Re–N$^-$ (imidazole) length equals 2.072(4) Å [19]. This result intimates that the imidazole N(2) nitrogens supply some negative charge to the rhenium(V) center.

The average C–C bond length [1.389(8) Å] in the C(1)–C(6) phenyl ring is identical to that of the C(8)–C(13) ring [1.388(8) Å]. In the imidazole ring, the N(2)–C(7) [1.369(5) Å] and N(3)–C(7) [1.332(6) Å] bonds are localized single and double bonds, respectively, again implying a negative charge located on N(2).

Trigonal-bipyramidal complexes of monoxorhenium(V) are rare in the literature, while they are more common for rhenium(III) [20]. The complexes [ReO {EtN($CH_2CH_2S)_2$}{*o*-MeOC_6H_4N($CH_2CH_2)_2NCH_2CH_2S$}] and [Re{*o*-MeOC_6H_4N ($CH_2CH_2)_2N(CH_2)_3N(CH_2CH_2S)_2$}{Ph$CH_2CH_2S$}], which contain the "3 + 1" ligand system [SN(R)S/S combination] have distorted trigonal-bipyramidal geometries [21].

Trigonal-bipyramidal oxorhenium(V) complexes were also prepared with tetradentate NS_3-donor ligands [22].

Supplementary material

CCDC-643783 contains the crystallographic data for **1**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html

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