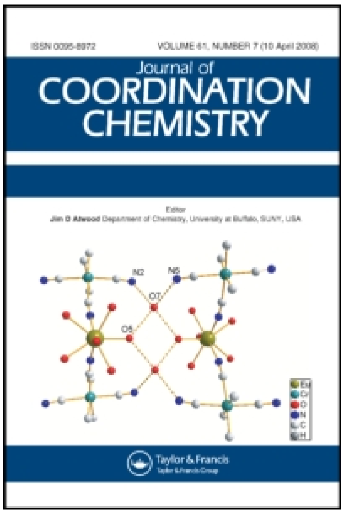

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Synthesis and crystal structure of [ReO(ahp)$_2$(PPh$_3$)]Cl (Hahp=2-amino-3-hydroxypyridine): a novel cationic monooxorhenium(v) complex

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SYNTHESIS AND CRYSTAL STRUCTURE OF [ReO(AHP)$_2$(PPh$_3$)]Cl (HAHP=2-AMINO-3-HYDROXYPYRIDINE): A NOVEL CATIONIC MONOOXORHENIUM(V) COMPLEX

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The cationic complex [ReO(ahp)$_2$(PPh$_3$)]$^+$ was isolated as the chloride salt from the reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] and 2-amino-3-hydroxypyridine (Hahp) in ethanol. Coordination of the chelates only occurs through the amino nitrogen and the phenolate oxygen of ahp$^-$. The X-ray crystal structure shows a distorted octahedral geometry, in which a phenolate oxygen coordinated *trans* to the oxo group and the rhenium atom is displaced by 0.2520(1) Å out of the mean equatorial plane towards the oxo oxygen.

Keywords: Oxorhenium(V); Cationic; 2-Amino-3-hydroxypyridine; X-ray structure

INTRODUCTION

Due to potential applications in radiotherapy, there is currently considerable interest in the coordination chemistry of rhenium, especially in its +V oxidation state, which is dominated by neutral monooxo complexes. Cationic octahedral monooxorhenium(V) complexes, however, are relatively rare.

We have shown previously that reaction of 2-aminophenol (Hap) with *trans*-[ReOCl$_3$(PPh$_3$)$_2$] in ethanol led to the isolation of the neutral rhenium(V) complex [ReOCl$_2$(ap)(PPh$_3$)], where ap coordinates as a bidentate monoanionic chelate *via* the neutral amino and deprotonated phenolate oxygen groups [1]. However, on repeating the reaction with 2,3-diaminophenol (H$_2$dap), the complex [Re(dap)Cl$_3$(PPh$_3$)$_2$] was formed, in which dap coordinates as a monodentate through the doubly deprotonated 2-nitrogen as an imide [2].

Study of rhenium(V) with *N*,*O*-donor chelates has largely been limited to Schiff base ligands containing an imine nitrogen and phenolic oxygen. For example, the reaction

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of *trans*-[$ReOCl_3(PPh_3)_2$] with *N*-methylsalicylideneimine (MesalH) yielded the six-coordinate complexes [$ReOCl_2$(Mesal)(PPh_3)] and [ReOCl(Mesal)$_2$] under various conditions [3]. Oxorhenium(V) complexes with *N*,*O*-donor ligands containing the amino group have not been well studied. In this account, the unusual product of the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] and 2-amino-3-hydroxypyridine (Hahp) in ethanol, i.e., the charged species [ReO(ahp)$_2$(PPh_3)]$^+$, is reported as the chloride salt.

EXPERIMENTAL

Trans-[$ReOCl_3(PPh_3)_2$] was synthesised using a literature method [4], and 2-amino-3-hydroxypyridine (Hahp) was obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. IR spectra were obtained using KBr discs and ^{1}H NMR spectra were run at ambient temperature in d_6-DMSO. The instrumentation used is the same as reported earlier [5].

Synthesis of [ReO(ahp)$_2$(PPh_3)]Cl (1)

Hahp (27 mg, 246 μmol) was added to a stirred suspension of *trans*-[$ReOCl_3(PPh_3)_2$] (100 mg, 120 μmol) in 10 cm^3 of ethanol. After the mixture was heated under reflux for 30 mins, it was cooled to room temperature and a green solid removed by filtration. Recrystallization from dichloromethane/ethanol gave green platelets in 69% yield; mp 195–197°C. *Anal.* Found: C, 46.63; H, 3.43; N, 7.80. $C_{28}H_{25}N_4O_3PClRe$ requires C, 46.83; H, 3.51; N, 7.80%; IR(cm^{-1}): ν(Re=O) 955s; ν(N-H) 3273m, 3241m, 3161m, ν(C=N) 1619vs; ν(C-O) 1258vs, 1281s; ν(Re-N) 510m, 529m. ^{1}H NMR (295K) ppm: 13.63(2H, br s, NH_2), 11.58 (2H, br s, NH_2), 7.72 (15H, m PPh_3), 7.43 (2H, d, *H*(5), *H*(10), *J* 5.8), 7.29 (2H, d, *H*(3), *H*(8), *J* 7.6), 6.70 (2H,t, *H*(4), *H*(9), *J* 7.0).

Crystallography

Intensity data were collected on a Nonius Kappa CCD diffractometer at 200(2) K with Mo Kα radiation ($\lambda = 0.71073$ Å). Further details are given in Table I. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [6]. All non-hydrogen atoms were refined anisotropically. Selected bond lengths and angles are given in Table II.

RESULTS AND DISCUSSION

The new cationic rhenium(V) complex [ReO(ahp)$_2$(PPh_3)]Cl (**1**) was synthesized by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with two mol equivalents of 2-amino-3-hydroxypryidine (Hahp) in ethanol, heated at reflux in air. The lime-green color of the starting material was replaced by a dark green color after 15 mins heating, and when heating was stopped after 30 min and the solution cooled to room temperature, a green precipitate was collected in good yield. With equimolar quantities of reactants in ethanol [ReO(OEt)$Cl_2(PPh_3)_2$] was obtained as the only product. A rhenium(V) complex with the formulation [$ReOCl_2$(ahp)(PPh_3)], as was isolated for 2-aminophenol [1], could

TABLE I Crystal data and structure refinement data for **1**

Chemical formula	$C_{28}H_{25}N_4O_3ClPRe$
Formula weight	718.16
Temperature (K)	200(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	$a = 9.9815$ (2) $b = 18.1324$ (4) $c = 15.3406$ (4) $\beta = 95.522$ (1)
Volume (Å^3)	2763.6(1)
Z	4
Density (calc.) (Mg/m^3)	1.726
Absorption coefficient (mm^{-1})	4.588
θ range for data collection	3.2–25.0
Index ranges	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-18 \leq l \leq 18$
Reflections measured	33627
Independent/observed reflections	4858/3609
Data/restraints/parameters	4858/1/343
Goodness of fit on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	0.0398, $wR_2 = 0.0954$
Largest diff. peak and hole (e/Å^3)	0.86,−1.33

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Re–O(3)	1.697(4)	Re–P	2.462(2)
Re–N(1)	2.015(6)	Re–N(3)	2.110(6)
Re–O(1)	2.043(5)	Re–O(2)	2.039(5)
C(2)–O(1)	1.318(9)	C(1)–N(1)	1.347(9)
C(1)–N(2)	1.346(9)	C(5)–N(2)	1.389(11)
C(6)–N(3)	1.325(10)	C(6)–N(4)	1.377(10)
C(7)–O(2)	1.341(8)	C(10)–N(4)	1.394 (12)
O(2)–Re–O(3)	166.5(2)	O(3)–Re–O(1)	99.9(2)
O(3)–Re–N(1)	104.5(2)	O(3)–Re–N(3)	95.5(2)
O(3)–Re–P	88.4(2)	O(1)–Re–N(1)	79.5(2)
Re–O(1)–C(2)	114.5(5)	O(2)–Re–N(3)	75.1(2)
Re–N(1)–C(1)	114.1(4)	P–Re–O(1)	171.5(2)
N(1)–Re–N(3)	157.4(2)	C(7)–O(2)–Re	119.2(4)

not be isolated. Complex **1** is diamagnetic and a 1:1 electrolyte in DMF, and it is soluble in acetonitrile, dichloromethane, DMSO and DMF.

The infrared spectrum of **1** displays the Re=O stretching frequency as an intense band at 955 cm^{-1}. Bands of medium intensity at 3273, 3241 and 3161 cm^{-1} are indicative of the presence of coordinated neutral amino groups. Re–N stretches are assigned to bands of medium intensity at 510 and 529 cm^{-1}. In the ^{1}H NMR spectrum the broad singlets at δ13.63 and 11.58 ppm are attributed to protons of coordinated amino groups. A fifteen proton multiplet around δ7.72 ppm illustrates the presence of PPh_3, while the corresponding protons on the two pyridyl rings are magnetically equivalent, giving rise to only one set of doublet-doublet-triplet signals.

An ORTEP perspective view of the asymmetric unit of **1** is shown in Fig. 1. The rhenium atom is at the centre of a distorted octahedron. The basal plane is defined

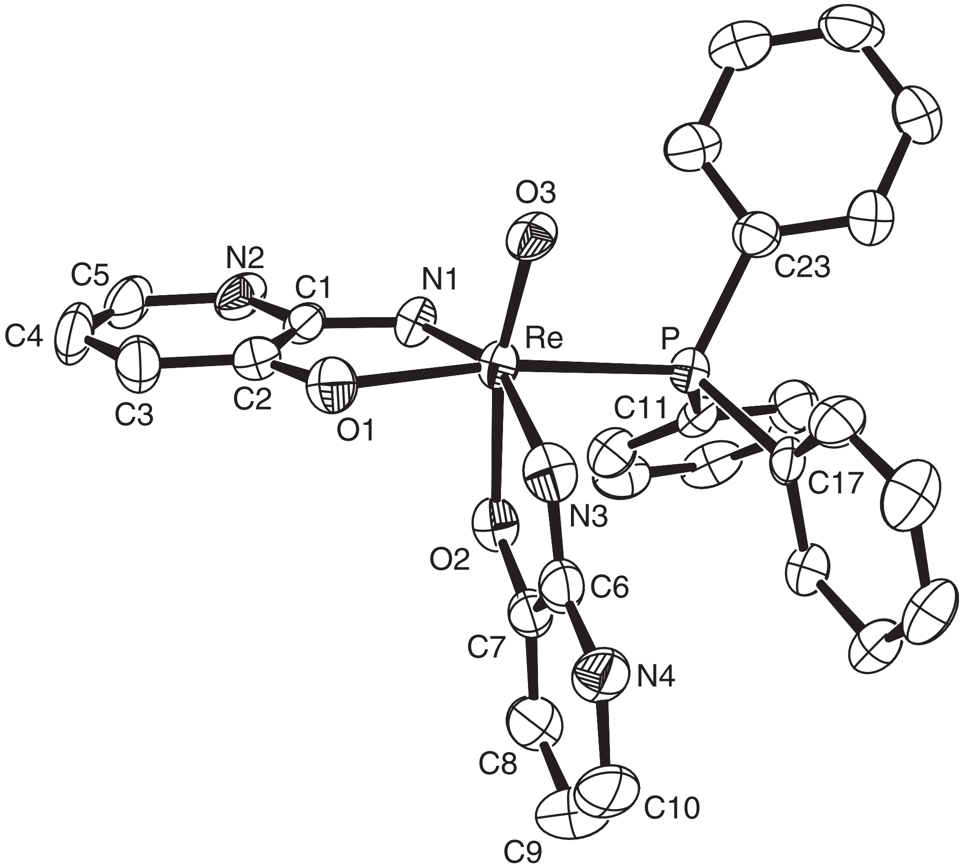

FIGURE 1 An ORTEP view of the molecular structure of $[ReO(ahp)_2(PPh_3)]^+$, showing the atom labeling scheme and thermal ellipsoids drawn at the 40% probability level.

by a N_2OP donor set. The phenolate oxygen and the oxo group lie in *trans* axial positions. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(3)=Re-O(2) axis of 166.5(2)°, accomplished by N(1)-Re-N(3) and O(1)-Re-P angles of 157.4(2)° and 171.5(2)°, respectively. N(3)-Re-P and O(2)-Re-O(1) angles are nearly orthogonal at 90.5(2)° and 89.3(2)°, respectively. The rhenium ion is lifted out of the mean equatorial plane by 0.2520(1)Å towards O(3), which is the result of the non-orthogonal angles O(3)-Re-O(1) = 99.9(2)°, O(3)-Re-N(1) = 104.5(2)°, O(3)-Re-N(3) = 95.5(2)° and O(3)-Re-P = 88.4(2)°. The bite angles of the two ahp ligands differ significantly: O(1)-Re-N(1) = 79.5(2)° and O(2)-Re-N(3) = 75.1(2)°. In the N_2O_3P polyhedron the rhenium ion is 0.973Å from the O(3)-P-N(1) plane, and 1.30 Å from the O(2)-N(3)-O(1), the dihedral angle being 13.4°.

The Re = O(3) distance if 1.697(4) Å implies some triple bond character and is typical of complexes of this kind [1–3]. The difference between the bond distances Re-O(1) (2.043(5)Å) and Re-O(2) (2.039(5)Å), *trans* to the oxo group, is insignificant, and these lengths fall within the observed range 2.015(2)-2.097(5) Å for Re-O (phenolate) bonds [7]. The Re-N distances are unequal (Re-N(1) = 2.015(6); Re-N(3) = 2.110(6)Å) and typical of Re(V)-NH_2 bonds, which vary in the range 2.10–2.22Å [1,8]. All other bond distances and angles are normal. The two pyridine rings are planar with a dihedral angle of 88.42°. For example, the ReN(1)C(1)N(2) and N(2)C(1)C(2)O(1) torsion angles are 178.6(5)° and 179.9(6)°, respectively.

Compound **1** is unusual since it is a six-coordinate cationic complex of monooxorhenium(V) containing two monoanionic bidentate *N,O*(phenolate)-donor ligands. Neutral complexes of general formulae [$ReOCl_2(L)(PPh_3)$] and [$ReOCl(L)_2$] (HL = 8-hydroxyquinoline, *N*-methyl- and *N*-phenylsalicylideneimine) were previously prepared by the reaction of *trans*-[$ReOCl_3(PPh_3)_2$] with the ligands HL, their lithium salts or in the presence of triethylamine [3,9].

Supplementary Material

CCDC-225320 contains crystallographic data for this paper. 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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