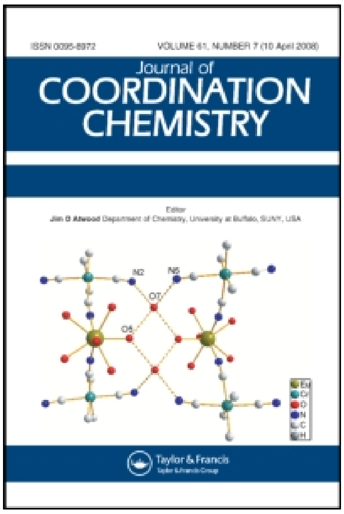

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Coordination of 2,3-diaminopyridine in the diamidopyridinium mode to the ReO^{3+} core

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Coordination of 2,3-diaminopyridine in the diamidopyridinium mode to the ReO^{3+} core

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2,3-Diaminopyridine (H_2dap) reacts with (n-Bu_4N)[$ReOCl_4$] to form an air-stable salt of composition [ReO(Hdap)$_2$]Cl $\cdot$ 2H_2O. Spectroscopic studies and X-ray crystallography show that Hdap is coordinated in the monoanionic diamidopyridinium mode to the oxorhenium(V) center. The protonation of the pyridyl nitrogens and the charge on the complex have no influence on the bond lengths and angles, with the rhenium(V)–oxo and average Re–NH bond lengths equal to 1.688(4) and 1.993(5) Å, respectively.

Keywords: Oxorhenium(V); Cation; Diamidopyridinium; Crystal structure

1. Introduction

In the past few years 1,2-diaminobenzene (H_2dab) and its derivatives have been shown to be versatile ligands for a wide variety of transition metal ions [1]. H_2dab has been found in a number of different forms (**a**–**g**) in metal complexes.

In our work on the coordination chemistry of rhenium, we have shown that the semibenzoquinone diimine form (**b**-sbqdi) exists in the complex [Re^{IV}(sbqdi)$_3$]I [2] and the imido form (**d**) in the complex [Re^{V}(dab)Cl_3(PPh_3)$_2$] [3]. The diamido form (**e**) was found in [Re^{VII}(dab)$_3$]$^+$ and [Re^{V}Cl(PPh_3)(dab)$_2$] [4], and forms (**f**) and (**g**) were discovered in the *cis*-dioxo compound [ReO_2(Hdab)(py)$_2$] $\cdot$ H_3dab $\cdot$ I [5]. Our efforts to isolate rhenium complexes containing forms (**a**) and (**c**) were unsuccessful.

We have now extended our study to investigate 2,3-diaminopyridine (H_2dap) as a ligand for rhenium(V). This article describes the product of the reaction of (n-Bu_4N)[$ReOCl_4$] with a twofold molar excess of H_2dap in benzene/ethanol.

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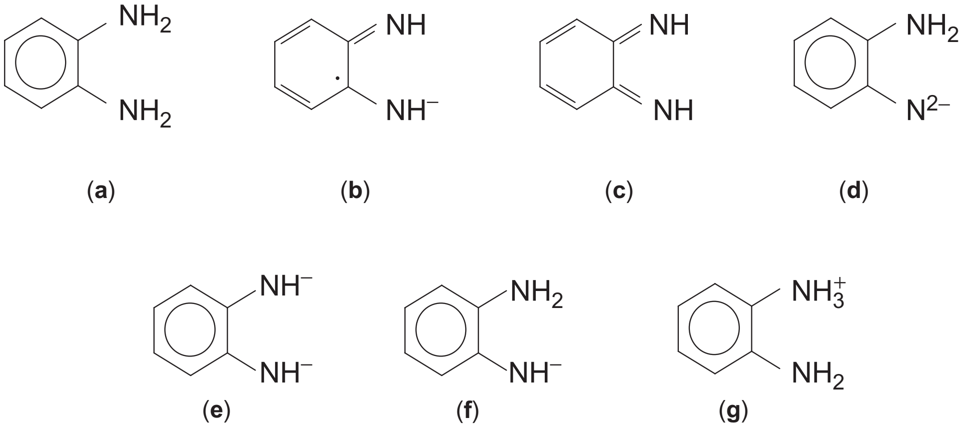


2. Experimental

$(n\text{-}Bu_4N)[ReOCl_4]$ was synthesized using a literature method [6] and H_2dap was obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. IR spectra were obtained using KBr disks and ^1H NMR spectra were run in d_6-DMSO at ambient temperature. The instrumentation used is the same as reported earlier [7].

2.1. *Synthesis of $[ReO(Hdap)_2]Cl \cdot 2H_2O$ (1)*

$(n\text{-}Bu_4N)[ReOCl_4]$ (100 mg, 170 µmol) and H_2dap (38 mg, 348 µmol) were dissolved in $20\,cm^3$ of a 10 : 1 benzene/ethanol solvent mixture and heated under reflux for 90 min. The color of the mixture gradually changed to dark red. After cooling to room temperature, the solution was filtered and left to evaporate slowly at room temperature. After 2 days, maroon crystals suitable for X-ray studies were collected. Yield: 54 mg (65%); m.p. 138°C. Anal. Calc. for $C_{10}H_{16}N_6O_3ReCl$(%): C, 24.5; H, 3.3; N, 17.2. Found: C, 24.6; H, 3.5; N, 17.1. IR(cm^{-1}): ν(NH) 3272, 3169, 3132; ν(ReO) 956; ν(ReN) 469. ^1H NMR (295 K, ppm): 14.19 (2H, br s, $N_{pyr}H$), 10.44 (1H, s, NH), 10.32(1H, s, NH), 10.16 (1H, s, NH), 10.13 (1H, s, NH), 7.11 (4H, m), 6.18 (2H, m).

2.2. *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 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELXL-97 [8]. All nonhydrogen atoms were refined anisotropically. Selected bond lengths and angles are given in table 2.

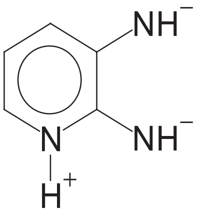
3. Results and discussion

Reaction of $(n\text{-}Bu_4N)[ReOCl_4]$ with a twofold molar excess of H_2dap under reflux led to the formation of a dark red solution from which a stable maroon-colored

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

Chemical formula	$C_{10}H_{14}N_6O_3ClRe$
Formula weight	489.93
Crystal system	Triclinic
Temperature (K)	200(2)
Space group	$P\bar{1}$
Unit cell dimensions (Å,°)	$a = 7.1477(2)$ $b = 9.2464(4)$ $c = 12.1316(5)$ $\alpha = 73.838(1)$ $\beta = 78.658(2)$ $\gamma = 73.786(1)$
Volume (Å^3)	733.29(5)
Z	2
Density (Calc.) (Mg/m^3)	2.219
Absorption coefficient (mm^{-1})	8.487
F(000)	468
Crystal size (mm)	0.04 × 0.07 × 0.12
θ range for data collection (°)	3.3–27.5
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 12$, $-15 \le l \le 15$
Reflections measured	10 120
Independent/observed reflections	3273/3004
Data/restraints/parameters	3273/0/227
Goodness-of-fit on F^2	1.08
Final R indices [$I > 2\sigma(I)$]	0.0299, $wR2 = 0.0723$
Largest diff. peak and hole (e/Å^3)	1.11, −2.21

crystalline solid was isolated. This proved to be the rhenium(V) complex salt $[ReO(Hdap)_2]Cl \cdot 2H_2O$ (**1**). In this complex the two bidentate chelates Hdap exist in the monoanionic diamidopyridinium form, that is both amino groups of each ligand are singly deprotonated and the pyridyl nitrogen protonated. With H_2dab as ligand, the same reaction led to the isolation of orange (n-Bu_4N)$[ReO(dab)_2]$ as the only product [9].



Complex **1** is diamagnetic and a 1 : 1 electrolyte in acetonitrile and DMF. It is soluble in a wide variety of polar solvents, including water, chloroform, acetone and ethanol. It is stable in solution and in the solid state, at least for a period of weeks.

IR spectra display a very intense band at 956 cm^{-1}, which we attribute to the Re=O stretching frequency. Medium-intensity bands at 3272, 3169 and 3132 cm^{-1} are indicative of the different N–H bonds. Only one band (at 469 cm^{-1}) was observed for the four Re–N stretching frequencies. In the ^{1}H NMR spectrum a broad singlet at δ 14.19 ppm, which integrates for two protons, is assigned to the two pyridinium protons.

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

Re–O(1)	1.688(4)	C(1)–N(1)	1.346(7)
Re–N(2)	2.002(4)	C(6)–N(4)	1.355(7)
Re–N(3)	1.995(4)	C(2)–N(3)	1.371(6)
Re–N(5)	1.994(4)	C(1)–N(2)	1.347(6)
Re–N(6)	1.982(5)	C(7)–N(6)	1.419(7)
C(1)–C(2)	1.428(6)	C(6)–N(5)	1.349(6)
O(1)–Re–N(2)	108.7(2)	N(2)–Re–N(6)	141.4(2)
O(1)–Re–N(3)	110.1(2)	N(3)–Re–N(5)	139.0(2)
O(1)–Re–N(5)	110.9(2)	N(2)–Re–N(3)	77.6(2)
O(1)–Re–N(6)	109.9(2)	N(5)–Re–N(6)	77.2(2)
Re–N(3)–C(2)	117.6(3)	Re–N(5)–C(6)	117.9(3)
Re–N(2)–C(1)	116.8(3)	Re–N(6)–C(7)	117.7(3)
N(2)–C(1)–N(1)	125.8(4)	N(6)–C(7)–C(6)	112.9(4)

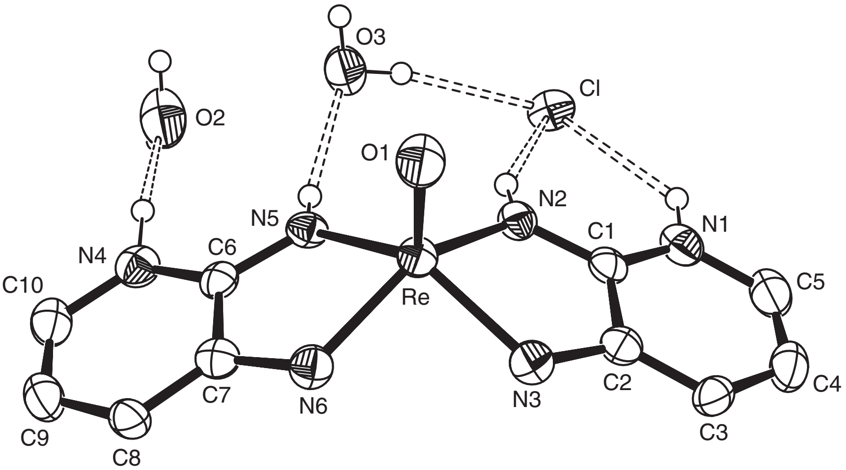


Figure 1. The molecular structure of [ReO(Hdap)$_2$]Cl · 2H$_2$O showing the atom numbering scheme and thermal ellipsoids drawn at the 50% probability level. Hydrogen bonds are indicated by broken lines.

The four amide protons give rise to two pairs of singlets at δ 10.44, 10.32, 10.16 and 10.13 ppm.

X-ray analysis of **1** (figure 1) shows it to be five-coordinate and to have square-pyramidal geometry with the oxo group occupying the apical position; the Re atom lies 0.679 Å above the plane defined by the four amido nitrogen atoms. The dihedral angle between the least-squares planes containing the two Hdap ligands is 34.8°. The Re=O distance of 1.688(4) Å is typical of monooxorhenium(V) complexes [10], and the Re–N distances [mean = 1.993(5) Å] are similar to those found for rhenium–amide bonds (average = 1.989 Å) in a large variety of complexes [4, 5]. The bite angles of the two chelates are nearly identical [N(2)–Re–N(3) = 77.6(2)°, N(5)–Re–N(6) = 77.2(2)°] and close to that of diamidobenzene in rhenium(V) complexes (average = 78°) [4, 5]. Angles about the amido nitrogens [Re–N–C] are of the order of 118°, consistent with sp^2-hybridization.

Protonation of the pyridyl nitrogen atoms has a minor effect on the aromaticity of the rings. There is a slight deviation from planarity in both rings. In the N(1) ring the torsion angles vary from 1.9(7)° [N(1)–C(1)–C(2)–C(3)] to −1.6(8)° [C(1)–C(2)–C(3)–C(4)], and in the N(4) ring these angles vary from 1.3(9)° [C(7)–C(8)–C(9)–C(10)] to –1.6(8)° [C(6)–C(7)–C(8)–C(9)].

Packing of the molecules in the crystal is essentially achieved by hydrogen bonds between N–H, Cl^- and H_2O. The Cl^- counterion hydrogen bonds to the protons on the pyridyl nitrogen N(1) [N(1)–H···Cl = 3.380(5) Å] and N(2) [N(2)–H···Cl = 3.379(5) Å]. The proton on the pyridyl nitrogen N(4) is hydrogen bonded to O(2) of a water molecule [2.982(7) Å, N(4)–H–O(2) angle = 175(5)°], and the O(3) oxygen of the other water molecule hydrogen bonds with N(5)H [3.134(6) Å]. Additional hydrogen bonds are O(2)–H···O(3) = 2.829(7), O(2)–H···Cl = 3.118(5), O(3)–H···Cl = 3.141(5) and O(3)–H···O(2) = 2.829(7) Å.

This report again highlights the versatility of aromatic diamines as ligands for a wide variety of metal ions. We could not find a similar coordinated pyridinium example in the literature. We are currently focusing our efforts on the possible isolation of the neutral species [ReO(Hdap)(dap)], in which dap is in the dianionic diamide form, and exploring the possibility that the same phenomenon would occur with 3,4-diaminopyridine as ligand.

Supplementary material

CCDC-250096 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].

Acknowledgements

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