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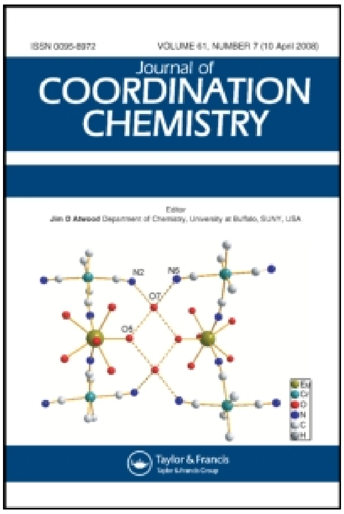

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Imido, amino and amido coordination of diaminouracil to rhenium(V)

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Reaction of equimolar quantities of *cis*-$[ReO_2I(PPh_3)_2]$ with 5,6-diamino-1,3-dimethyl-2,4-dioxopyrimidine (H_2ddd) in acetonitrile led to the formation of $[Re(ddd)(Hddd)I(PPh_3)_2](ReO_4)$ (**1**). A single-crystal X-ray crystal structure shows that ddd is coordinated as a monodentate through the doubly deprotonated amino nitrogen and is therefore present as an imide. The chelate Hddd is coordinated as a bidentate via a neutral amino nitrogen atom, *trans* to the imido nitrogen, and a singly deprotonated amido nitrogen atom, *trans* to the iodide.

Keywords: Rhenium(V); Uracil; Amine; Amide; Imide; Crystal structure

1. 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 rhenium(V) complexes without an oxo group are relatively rare. We have for the last few years explored the reactivity of monooxo- and dioxorhenium(V) cores with the aromatic ligand 1,2-diaminobenzene (H_2dab) and its derivatives. It has been shown [1] that reaction of H_2dab with *trans*-$[ReOCl_3(PPh_3)_2]$ in ethanol produces *trans*-$[Re(dab)Cl_3(PPh_3)_2]$, in which dab is coordinated as a monodentate imide. With dioxo cores, H_2dab reacts with *trans*-$[ReO_2(py)_4]I$ to form the neutral *cis*-dioxo rhenium(V) complex $[ReO_2(Hdab)(py)_2]$, in which Hdab acts as a bidentate amido-amine [2]. With *cis*-$[ReO_2I(PPh_3)_2]$, the product $[Re^{IV}(sbqdi)_3]I$ (sbqdi is the monoanionic oxidized semibenzoquinone diimine of dab^{2-}) was isolated [3].

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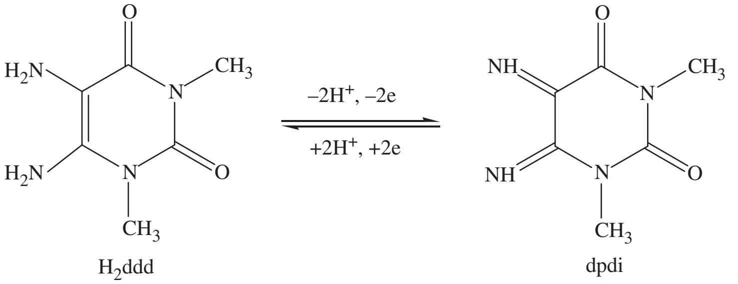
Here we report the product of the reaction of *cis*-$[ReO_2I(PPh_3)_2]$ with the uracil derivative 5,6-diamino-1,3-dimethyl-2,4-dioxopyrimidine (H_2ddd). The pyrimidine ring forms a constituent of nucleic acids, antibiotics, coenzymes and vitamins, and its coordination properties are important in understanding the role of metal ions in biological systems [4]. Interest in uracil (2,4-dioxo-pyrimidine) derivatives arises from their potential biological activity. For example, some derivatives show antitumour [5] and anti-inflammatory action [6]. Uracil and its derivatives are known to bind to metal centres by using various combinations of donor atoms, which make them versatile ligands [7–9]. A crystal structure of H_2ddd has shown that the two amino groups have two different conformations [10]. The amino group in the 5 position seems to be a true primary amino group with a strongly sp^3-hybridized nitrogen, whereas that at the 6 position is nearly coplanar with the uracil ring and displays predominantly sp^2 character. Extrapolating from the properties of H_2dab, it should also be possible for H_2ddd to be oxidized to the diimine form dpdi by metal centres.



2. Experimental

Cis-$[ReO_2I(PPh_3)_2]$ was prepared by a literature method [11] and stored under argon. The ligand H_2ddd hydrate was obtained commercially (Aldrich) and used without further purification. All chemicals were of reagent grade and used as received. Solvents were purified and dried before use. Scientific instrumentation and procedures are the same as reported previously [12]. Infrared spectra were obtained using KBr disks and ^1H NMR spectra were run in d_6-DMSO.

2.1. *$[Re(ddd)(Hddd)I(PPh_3)_2](ReO_4)\cdot 2H_2O$ (1)*

Equimolar quantities of *cis*-$[ReO_2I(PPh_3)_2]$ (100 mg, 115 µmol) and H_2ddd (20 mg) were added to acetonitrile (20 cm^3) and the mixture refluxed for 3 h under nitrogen. After cooling to room temperature, the solution was filtered (no precipitate formed) and left to evaporate slowly at room temperature. After four days dark brown crystals were collected by filtration, washed with acetone and dried under vacuum. Yield 47 mg (56% based on Re), m.p. 131°C. Anal. Calcd (%): C, 39.45; H, 3.52; N, 7.67. Found: C, 39.68; H, 3.68; N, 7.97. IR (cm^{-1}): ν(N–H) 3257, 3332, 3432; ν(C=O) 1717, 1700, 1685; ν(C–N) 1363; ν(Re=N) 1119; ν(Re–N) 542. ^1H NMR (295 K; ppm): 14.12 (1H, s, N(1)H), 11.74(1H, s, N(1)H), 10.54 (1H, s, N(2)H), 9.32 (1H, s, N(5)H), 9.08(1H, s, N(5)H), 7.41–7.69(20H, m, 2 × PPh_3), 3.25 (3H, s, CH_3), 3.19(3H, s, CH_3), 3.13 (3H, s, CH_3), 3.10(3H, s, CH_3). Conductivity ($ohm^{-1} cm^2 mol^{-1}$, DMF): 74.

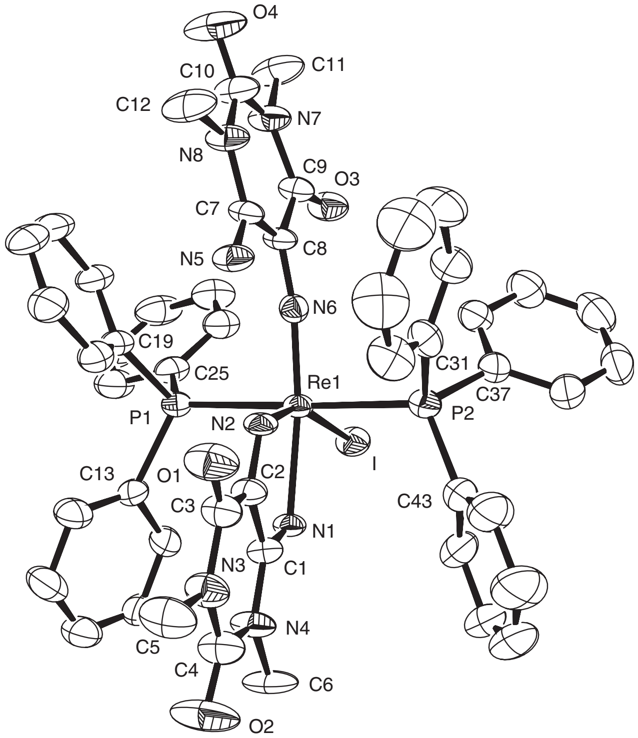


Figure 1. Structure of [Re(ddd)(Hddd)I(PPh_3)$_2$]$^+$ with the atom numbering scheme and thermal ellipsoids drawn at 40% probability. Hydrogen atoms are omitted for clarity.

2.2. *X-ray crystallography*

Intensity data for **1** were collected at 200(2) K on a Nonius Kappa CCD single-crystal diffractometer, using Mo-Kα radiation. Unit cell and space group determinations were carried out in the usual manner [13]. The structure was solved by direct methods and refined by full-matrix least-squares procedures using SHELX-97 [14]. All non-hydrogen atoms were geometrically constrained. An ORTEP view of [Re(ddd)(Hddd)I(PPh_3)$_2$]$^+$ along with the atom numbering scheme is given in figure 1. A summary of crystal data and refinement details is given in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

Reaction of *cis*-[$ReO_2I(PPh_3)_2$] with 5,6-diamino-1,3-dimethyluracil (H_2ddd) with heating for 3 h in acetonitrile gave the product [Re(ddd)(Hddd)I(PPh_3)$_2$](ReO_4) · 2H_2O (**1**). Complex **1** could only be isolated in pure form by using equimolar amounts of reactants. With a twofold molar excess of H_2ddd, or using solvents other than acetonitrile (ethanol and chloroform), mixtures of products were formed. The formation of the perrhenate counterion is surprising, despite the use of the Re(V)

Table 1. Crystal data and structure refinement for $\mathbf{1}\cdot 2H_2O$.

Chemical formula	$C_{48}H_{47}N_8O_8P_2IRe_2\cdot 2H_2O$
Formula weight	1461.23
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.2044(3)
b (Å)	13.1392(2)
c (Å)	17.4866(4)
α (°)	103.030(1)
β (°)	93.661(1)
γ (°)	95.977(1)
Volume ($Å^3$)	2706.0(1)
Z	2
Density (Calcd) ($Mg\,m^{-3}$)	1.788
Absorption coefficient (mm^{-1})	5.160
$F(000)$	1408
Crystal size (mm^3)	$0.03\times 0.06\times 0.14$
θ range or data collection (°)	3.2–27.6
Index ranges	$-15\leq h\leq 15$; $-16\leq k\leq 17$; $-22\leq l\leq 22$
Reflections measured	23575
Independent/observed reflections	12408/9458
Data/parameters	12408/639
Goodness-of-fit on F^2	1.03
Final R indices $[I>2\sigma(I)]$	0.0492; $wR_2=0.1337$
Largest diff. peak and hole ($e\,Å^{-3}$)	2.13; −4.69

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

Re(1)–N(1)	2.184(5)	Re(1)–N(2)	1.914(5)
Re(1)–N(6)	1.779(5)	Re(1)–I	2.7271(4)
Re(1)–P(1)	2.474(2)	Re(1)–P(2)	2.473(2)
N(6)–C(8)	1.305(8)	N(1)–C(1)	1.291(9)
N(5)–C(7)	1.311(9)	N(2)–C(2)	1.294(9)
C(1)–N(4)	1.356(9)	C(3)–N(3)	1.38(1)
C(7)–N(8)	1.360(9)	N(7)–C(9)	1.40(1)
C(3)–O(1)	1.215(9)	C(4)–O(2)	1.21(1)
C(9)–O(3)	1.205(9)	C(10)–O(4)	1.20(1)
C(1)–C(2)	1.43(1)	C(7)–C(8)	1.422(9)
N(1)–Re(1)–N(6)	170.0(2)	P(1)–Re(1)–P(2)	178.22(6)
I–Re(1)–N(2)	155.8(2)	N(6)–Re(1)–P(1)	87.9(2)
N(6)–Re(1)–N(2)	96.7(2)	N(6)–Re(1)–P(2)	90.5(2)
N(6)–Re(1)–I	107.4(2)	Re(1)–N(1)–C(1)	114.8(4)
Re(1)–N(6)–C(8)	168.8(5)	N(1)–Re(1)–N(2)	74.0(2)
N(3)–C(4)–O(2)	121.0(8)	C(3)–N(3)–C(4)	125.5(7)

starting material and the presence of PPh_3, and indicates that the reaction mechanism involves complex redox processes. Other rhenium(V) complex cations with perrhenate as the counterion are known [12, 15, 16]. Complex **1** is air-stable and a 1 : 1 electrolyte in DMF. It dissolves in THF, acetonitrile, DMF and DMSO to give red-brown solutions that are stable for days.

Single crystals of X-ray quality were obtained by slow evaporation of the mother liquor of the synthetic solution. The X-ray study indicates that the rhenium atom lies at the centre of a distorted octahedral environment. The basal plane is defined by the iodide, two phosphorus atoms and the amide nitrogen N(2). The Re atom lies 0.211 Å out of this mean plane towards N(6). The doubly deprotonated imido nitrogen N(6) and neutral amino nitrogen N(1) are in *trans* axial positions, with N(5)H_2 uncoordinated. Bond distances and angles are given in table 2. The two triphenylphosphine ligands are coordinated to the metal centre *trans* to each other, with the P(1)–Re(1)–P(2) angle being practically linear at 178.22(6)°. The average Re–P distance equals 2.473(2) Å, which is significantly shorter than in the *trans*-biphosphine imido complex *trans*-$[Re(map)(Hmap)I(PPh_3)_2]^+$ ($H_2map = $ 3-methyl-2-aminophenol) [17], where the average distance is 2.496(1) Å. Iodide is rarely found as a ligand in rhenium(V) complexes, and the Re–I distance of 2.7271(4) Å falls in the observed range of 2.664(2)–2.789(3) Å [11, 17]. The iodide is coordinated *trans* to the amido nitrogen N(2) of Hddd, with which it makes an angle of 155.8(2)°.

The ddd ligand acts as a dianionic monodentate, with coordination through the doubly deprotonated imido nitrogen N(6) only. The Re(1)–N(6)–C(8) bond angle of 168.8(5)° illustrates an unusual significant deviation from linearity of the coordination mode of the triply bonded pyrimidylimido unit, and the Re(1)–N(6) distance of 1.779(5) Å falls well outside the range [1.72(1)–1.74(1) Å] normally found in other octahedral rhenium(V)-phenylimido complexes [16–18]. The pyrimidylimido moiety forms a dihedral angle of 81.2° with the mean equatorial plane. The intraligand ddd bond distances show C(9)–O(3) [1.205(9) Å] and C(10)–O(4) [1.20(1) Å] double bonds, with the C(8)–C(9)–O(3) and N(8)–C(10)–O(4) bond angles equal to 124.2(6)° and 120.2(7)°, respectively. Both C(8)–N(6) and C(7)–N(5) distances are shorter than expected for C–N single bonds [1.305(8) and 1.311(9) Å, respectively]. Coordination of the imido nitrogen decreases the planarity of the ddd ring, with increased torsion angles, for example C(10)–N(7)–C(9)–C(8) = 7(1)° and C(7)–N(8)–C(10)–N(7) = −4(1)°. In contrast, the torsion angles of the PPh_3 phenyl rings are barely larger than 1.5°. All intraligand ring distances imply single bond [C(8)–C(9) = 1.461(9), C(7)–C(8) = 1.422(9), C(7)–N(8) = 1.360(9), N(7)–C(10) = 1.37(1), N(7)–C(9) = 1.40(1) Å].

The Hddd ligand acts as a monoanionic bidentate chelate, with coordination through the neutral amino group N(1)H_2 and the deprotonated amido group N(2)H. The N(1)–Re(1)–N(6) bond deviates from linearity [170.0(2)°], and the bite angle [N(1)–Re(1)–N(2)] equals 74.0(2)°. The Re(1)–N(1) bond length [2.184(5) Å] is typical of rhenium(V)-amino bond distances, which normally occur in the range 2.11(1)–2.23(1) Å [1, 17–20]. The Re(1)–N(2) bond length of 1.914(5) Å falls within the range observed [1.91(1)–2.01(1) Å] for rhenium(V)-amide bonds [17–21]. Hddd is thus present as an aminoamide. This coordination mode has previously been observed in the complex *cis*-$[ReO_2(Hdab)(py)_2]$ [2]. There are also large differences in the Re–N–C bond angles [Re(1)–N(1)–C(1) = 114.8(4), Re(1)–N(2)–C(2) = 123.5(4)°]. C–N bond distances are the same as in the ddd ligand [C(1)–N(1) = 1.29(1), C(2)–N(2) = 1.29(1) Å], and indicate considerable double bond character, with delocalization of nitrogen π-lone pair in the ring.

As shown in table 3, the molecules in the unit cell exhibit an extended network of intermolecular and non-classical hydrogen bonds (N–H ⋯ N, N–H ⋯ O, C–H ⋯ O, C–H ⋯ N, C–H ⋯ I). The two water molecules of crystallization O(9) and O(10) are hydrogen bonded to the free N(5)H_2 group [N(5)–H(5A) ⋯ O(9) = 2.86(1) Å] and to C(22)–H(22) [3.30(1) Å], respectively.

There are no peaks in the 890–1020 cm^{-1} region of the IR spectrum of **1**, and the medium intensity band at 1119 cm^{-1} is assigned to $\nu(Re{=}N)$. Bands of medium

Table 3. Hydrogen-bonding geometry (Å, °).

D	H	A	D–H	H···A	D···A	D–H···A
N2	H2	N5	0.88	2.23	3.02(1)	149.0
N5	H5A	$O9H_2$	0.88	2.00	2.86(1)	164.8
N5	H5B	N2	0.88	2.16	3.03(1)	168.5
N5	H5B	N6	0.88	2.44	2.75(1)	100.8
C5	H5A	O2	0.98	2.22	2.69(1)	107.8
C6	H6A	N1	0.98	2.45	2.88(1)	106.5
C6	H6A	I	0.98	2.96	3.87(1)	154.8
C11	H11A	O3	0.98	2.26	2.72(1)	107.2
C12	H12C	O4	0.98	2.25	2.70(1)	106.7
C22	H22	$O10H_2$	0.95	2.39	3.30(1)	160.1
C23	H23	O4	0.95	2.35	3.22(1)	151.4
C26	H26	I	0.95	3.03	3.48(1)	110.4
C26	H26	O3	0.95	2.52	3.30(1)	139.8

intensity in the range 3250–3450 cm^{-1} [ν(N–H)] are indicative of the presence of amino and amido groups of ddd and Hddd. Only a single absorption at 542 cm^{-1} could be ascribed to ν(Re–N). The ^{1}H NMR spectrum of **1** not only clearly establishes the presence of the ddd and Hddd ligands, but also shows their inequivalence. Five one-proton signals are observed in the 9.00–14.20 ppm region, indicative of the NH protons, and also showing the involvement of the amino groups in hydrogen bonding. The signals of the two phosphine ligands appear as a multiplet in the region 7.40–7.70 ppm, and integrate for 30 protons. The four methyl groups of the two uracil derivatives give rise to four three-proton singlets around 3.20 ppm.

Supplementary material

CCDC-615853 contains crystallographic data for complex **1**. 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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