

Synthesis and Crystal Structure of an Unusual Mixed Crystal Containing an Oxorhenium(V) and Imidorhenium(V) Complex

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An unusual mixed crystal of a square-pyramidal oxorhenium(V), [ReOCl(Hdua)], and an octahedral imidorhenium(V) complex, [Re(dua)Cl₂(PPh₃)], was prepared from the reaction of *trans*-[ReOCl₃(PPh₃)₂] and (6*Z*)-6-(2-aminobenzylideneamino)-5-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (H₃dua) in ethanol. Characterization was performed by single crystal X-ray structure determination and IR spectroscopy. The chelate Hdua is coordinated as a tridentate diamido-imine, and dua is chelated as an imido-imino-amide.

Keywords: Oxorhenium(V), Imido, Mixed crystal, Square-pyramidal

INTRODUCTION

The current interest in the coordination chemistry of rhenium is mainly centred on its +V oxidation state, since it is easily accessible from the reduction of perrhenate, and is stabilized by a large variety of donor atoms. In this oxidation state the complexes are normally octahedral and contain one of the [ReO]³⁺, [ReO₂]⁺, [Re₂O₃]⁴⁺, [ReN]²⁺, [ReS]³⁺ or [Re = NR]³⁺ moieties [1].

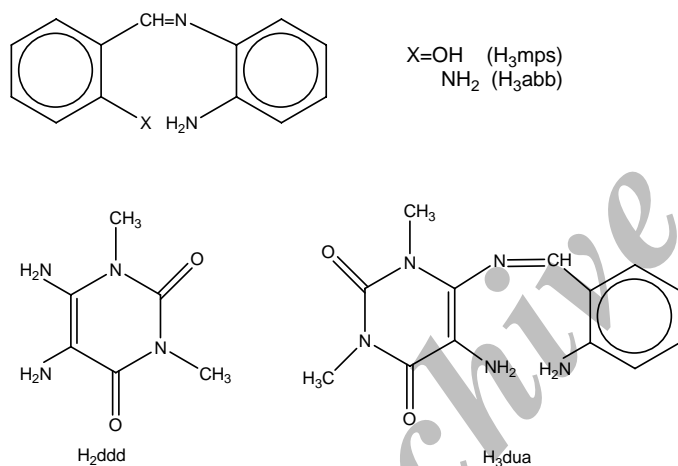
Our current research focus is on oxo-free rhenium(V) compounds with metal-nitrogen multiple bonds, for example, metal-hydrazido and metal-imido complexes [2]. We have shown that the reaction of 1,2-diaminobenzene (H₂dab) with *trans*-[ReOCl₃(PPh₃)₂] (**1**) in ethanol produces *trans*-[Re(dab)Cl₃(PPh₃)₂], in which dab is coordinated as a monodentate imide [3]. With dioxo cores, H₂dab reacts with *trans*-[ReO₂(py)₄]I to form the neutral *cis*-dioxo rhenium(V)

complex [ReO₂(Hdab)(py)₂]I, in which Hdab acts as a bidentate amido-amine [4]. We have extended these studies to multidentate ligands containing an amino group which, on deprotonation, can lead to a coordinated chelate containing the phenylimido core Re = NC₆H₄X. One of the major advantages of the phenylimido moiety is that it can be functionalized and derivatized. The structure of the rhenium(V) complex [Re(amb)(OEt)(PPh₃)₂]I, in which the trianionic bidentate 2-imido-3-methylbenzoate (amb³⁻) chelates *via* the imido nitrogen and acetoxy oxygen, was recently reported [5]. The compound [Re(mps)Cl(PPh₃)₂](ReO₄) was isolated from the reaction of **1** with the tridentate Schiff base *N*-(2-amino-3-methylphenyl) salicylideneimine (H₃mps) in ethanol, with mps³⁻ coordinated as an imido-imino-phenolate [6]. From the reduction of [ReO₄]⁻ with triphenylphosphine in the presence of H₃mps and hydrochloric acid the neutral complex [Re^V(mps)Cl₂(PPh₃)] was isolated [7].

We have previously synthesized the compound [Re(ddd)(Hddd)(PPh₃)₂]I(ReO₄) from the reaction of *cis*-

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[ReO₂I(PPh₃)₂] with the uracil derivative 5,6-diamino-1,3-dimethyl-2,4-dioxypyrimidine (H₂ddd) [8]. The X-ray crystal structure shows that ddd is coordinated monodentately as an imide, and Hddd as a bidentate chelate *via* amino and amido nitrogen atoms. In this study H₂ddd is derivatized to form the Schiff base (6*Z*)-6-(2-aminobenzylideneamino)-5-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (H₃dua), the reaction of which with **1** gave crystals which contained both the neutral complexes [ReOCl(Hdua)] and [Re(dua)Cl₂(PPh₃)₂] in a 1:1 ratio in the asymmetric unit. With the very similar ligand *N*-(2-aminobenzylidene)benzene-1,2-diamine (H₃abb), the oxo-free '3+3' complex [Re(Habb)₂](ReO₄) was isolated from its reaction with *trans*-[ReO₂(py)₄]Cl in acetonitrile [9].



EXPERIMENTAL

Reactants and Methods

All chemicals were of reagent grade, and solvents were purified by standard techniques and drying methods [10]. *Trans*-[ReOCl₃(PPh₃)₂] was prepared by a literature method [11]. All reactions and manipulations were carried out under nitrogen. ¹H NMR spectra were recorded in *d*₆-DMSO on a Bruker AX (300 MHz) spectrometer at ambient temperatures, and values are reported relative to TMS. Infrared spectra were obtained with a Digilab FTS 3100 Excalibur HE spectrophotometer with solid samples prepared as KBr disks. Microanalyses were obtained on a Carlo Erba EA 1108

elemental analyzer.

Synthesis

***N*-(2-Aminobenzylidene)-5-amino-1,3-dimethyluracil (H₃dua).** Equimolar amounts of 2-aminobenzaldehyde (1.00 g; 8.3 mmol) and 5,6-diamino-1,3-dimethyluracil (1.41 g) in 50 cm³ anhydrous methanol were refluxed for 2 h under nitrogen. The reaction mixture was cooled to room temperature, and then the solvent was removed under vacuum to yield a yellow precipitate, which was recrystallized from anhydrous methanol to give yellow crystals, which were filtered and dried under vacuum. Yield = 65%, m.p.: 251-254 °C. Anal. Calcd. for C₁₃H₁₅N₅O₂: C, 57.13, H, 5.53; N, 25.63; O, 11.71. Found: C, 57.15; H, 5.55; N, 25.60; O, 11.70. IR: ν(C=N) 1674, ν(N-H) 3448, 3383. ¹H NMR (295K, ppm): 9.64 (s, 1H, CH=N); 7.20 (d, 1H); 7.05 (t, 1H); 6.83 (br, s, NH₂); 6.70 (d, 1H); 6.62 (br, s, NH₂); 6.55 (t, 1H); 3.79 (s, 6H, 2xCH₃).

[[ReOCl(Hdua)]{Re(dua)Cl₂(PPh₃)₂}] (2). A mixture of *trans*-[ReOCl₃(PPh₃)₂] (100 mg, 120 μmol) and H₃dua (66 mg, 240 μmol) in 20 ml of ethanol was heated under reflux for an hour during which a brown precipitate formed. This was filtered off and washed with acetone and diethyl ether. The product was dissolved in 10 ml of a 1:2 (v/v) mixture of ethanol/dichloromethane and left to evaporate slowly at room temperature. After two days, brown crystals, suitable for X-ray diffraction studies, were collected by filtration. They were washed with ethanol and diethyl ether, and dried under vacuum. Yield 56 mg (72% based on Re). Anal. Calcd. for C₄₄H₄₀N₁₀O₅Cl₃PRe₂: C, 40.7; H, 3.1; N, 10.8%. Found: C, 41.0; H, 3.3; N, 10.5%. FTIR (KBr pellet): ν(NH) 3276, 3356, ν(C=O) 1682, 1713, ν(C=N) 1594, 1602, ν(Re=N) 1056, ν(Re=O) 996, ν(Re-N) 464, 484, 500, 521.

Crystallography

Intensity data collection was performed at 200 K on a Nonius Kappa CCD detector system using the ω scan technique with Mo K α radiation. Intensities were corrected for Lorentz and polarization effects. Data reduction was done with WINGX [12]. The structure was solved by direct methods with SIR97 [13] and refined by full-matrix least-squares procedures with SHELXL-97 [14]. Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen

atoms were placed in idealized positions and allowed to ride on the parent atoms. A summary of the crystal data and refinement details is given in Table 1, and the selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

The reaction of *trans*-[ReOCl₃(PPh₃)₂] (**1**) with two equivalents of H₃dua in ethanol gave a brown precipitate, which was recrystallized from 1:2 ethanol/dichloromethane to yield brown crystals. An X-ray diffraction analysis of this product (**2**) showed that it consisted of an unusual rhenium(V) species including complexes [ReOCl(Hdua)] (**3**) and [Re(dua)Cl₂(PPh₃)] (**4**) in a 1:1 ratio in the asymmetric unit. This result was surprising since in our previous work the reaction of the ligand H₃abb, very similar to H₃dua with the

same donor atoms, with a different starting material, [ReO₂(py)₄]Cl, in a different solvent (acetonitrile) gave the oxo-free '3+3' complex cation [Re(Habb)₂]⁺, with both chelates coordinated as diamido-imines. We found no additional examples of mixed rhenium species of this type in the literature. Although this phenomenon is reasonably common amongst organic molecules, it is rare in transition metal coordination chemistry.

The structure of **3** shows a distorted square-pyramidal geometry around rhenium(V) with the oxo group occupying the apical position. The rhenium atom lies 0.695 Å above the square plane defined by three nitrogen and chlorine atoms, which is the result of the angles O(5)-Re(2)-Cl(3) = 106.8(4)°, O(5)-Re(2)-N(6) = 110.9(6)°, O(5)-Re(2)-N(7) = 103.3(5)° and O(5)-Re(2)-N(8) = 112.5(5)°. The distortion also originates from the geometric constraints imposed by the

Table 1. Crystal and Structure Refinement Data for **2**

Chemical formula	C ₄₄ H ₄₀ N ₁₀ O ₅ Cl ₃ PRE ₂
Formula weight	1298.60
Crystal system	Monoclinic
Space group	<i>Cc</i>
Unit cell dimensions (Å, °)	
<i>a</i>	10.9902(3)
<i>b</i>	20.2787(6)
<i>c</i>	19.7382(5)
β	97.648(2)
Volume (Å ³)	4359.9(2)
<i>Z</i>	4
Density (Calcd.) (mg m ⁻³)	1.978
Absorption coefficient (mm ⁻¹)	5.829
<i>F</i> (000)	2520
θ Range for data collection (°)	3.1-25.4
Index ranges	-13 ≤ <i>h</i> ≤ 13; -24 ≤ <i>k</i> ≤ 24; -23 ≤ <i>l</i> ≤ 23
Reflections measured	28976
Independent/observed reflections	7881/7296
Data/parameters	7881/494
Goodness-of-fit on <i>F</i> ²	1.03
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0759 (<i>wR</i> ₂ = 0.1957)

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Re(1)-Cl(1)	2.406(4)	Re(1)-Cl(2)	2.339(4)
Re(1)-P(1)	2.464(4)	Re(1)-N(1)	1.75(2)
Re(1)-N(2)	2.14(1)	Re(1)-N(3)	2.04(1)
C(7)-N(2)	1.32(3)	C(38)-N(7)	1.30(2)
Re(2)-Cl(3)	2.328(6)	Re(2)-N(6)	1.95(2)
Re(2)-N(7)	2.07(1)	Re(2)-N(8)	1.98(1)
Re(2)-O(5)	1.74(1)		
Cl(1)-Re(1)-P(1)	175.1(2)	Cl(2)-Re(1)-N(2)	168.0(4)
N(1)-Re(1)-N(3)	158.3(6)	N(1)-Re(1)-N(2)	83.4(6)
N(2)-Re(1)-N(3)	75.6(5)	N(1)-Re(1)-Cl(1)	96.3(4)
N(1)-Re(1)-P(1)	88.6(4)	C(7)-Re(2)-C(8)	122(1)
O(5)-Re(2)-Cl(3)	106.8(4)	O(5)-Re(2)-N(6)	110.9(6)
O(5)-Re(2)-N(7)	103.3(5)	O(5)-Re(2)-N(8)	112.5(5)
N(6)-Re(2)-N(7)	85.6(6)	N(7)-Re(2)-N(8)	77.7(6)
N(6)-Re(2)-N(8)	135.9(6)	N(7)-Re(2)-Cl(3)	149.9(4)

chelating ligand. The N(6)-Re(2)-N(7) and N(7)-Re(2)-N(8) bond angles are different at 85.6(6)° and 77.7(6)°, respectively, which is the result of the six- and five-membered rings formed by complexation of the tridentate ligand. The Re(2)-N(7) bond distance [2.07(1) Å] and the similar Re(2)-N(6) and Re(2)-N(8) lengths of average 1.96(2) Å, are consistent with those found in the literature for Re-N(imino) and Re-N(amido) bonds, respectively [15,16]. The N(7)-C(38) is a double bond [1.30(2) Å], with the C(38)-N(7)-C(39) bond angle equal to 122(2)°. There is nothing unusual about the other intraligand bond lengths and angles.

The infrared spectrum of **2** shows a medium intensity absorption at 996 cm⁻¹, which is ascribed to $\nu(\text{Re}=\text{O})$ of complex **3**. It also illustrates peaks at 3276 and 3356 cm⁻¹, consistent with $\nu(\text{NH})$, and a strong absorption at 1056 cm⁻¹, which is ascribed to $\nu(\text{Re}=\text{N})$ of complex **4**. The proton NMR spectrum of **2** is complex, with an eight-proton multiplet in the region 7.39-7.67 ppm being flanked by the proton signals of triphenylphosphine centred at 7.35 ppm (nine protons) and 7.74 ppm (six protons).

The structure of **4** shows that the rhenium(V) ion is in an octahedral environment with the equatorial plane formed by

the PCl₂N(2) donor set (Fig. 1). The octahedron is severely distorted with large deviations from orthogonality for N(1)-Re(1)-Cl(1) = 96.3(4)°, N(1)-Re(1)-Cl(2) = 108.3(5)°, N(1)-Re(1)-N(2) = 83.4(6)° and N(1)-Re(1)-P(1) = 88.6(4)°. The outcome is that the rhenium atom is lifted out of the mean equatorial plane by 0.162 Å towards N(1). The N(1)-Re(1)-N(3) bond angle deviates considerably from linearity at 158.3(6)°, with the other *trans* angles Cl(1)-Re(1)-P(1) = 175.1(2)° and Cl(2)-Re(1)-N(2) = 168.0(4)°. The dihedral angle between the uracil ring and imidophenyl ring is 7.77°, and the two bite angles of *dua* are N(1)-Re(1)-N(2) = 83.4(6)° and N(2)-Re(1)-N(3) = 75.6(5)°, which are about 2° smaller than the corresponding angles in **3**.

The *dua* ligand acts as a tridentate trianionic moiety, with N(1) coordinated as a dinegative imido nitrogen, with the Re(1)-N(1) bond length [1.75(1) Å] falling in the range normally observed [1.726(3)-1.768(4) Å] for the phenylimido unit [2-8], but considerably shorter than the values found for Re^V-NH and Re^V-NH₂ bonds [1.94-2.05 Å and 2.15-2.23 Å], respectively [15,16]. The Re(1)-N(2) and Re(1)-N(3)H lengths are 2.14(1) and 2.04(1) Å, respectively, the latter longer than the Re-N (amide) bonds in **3** due to the larger *trans* influence

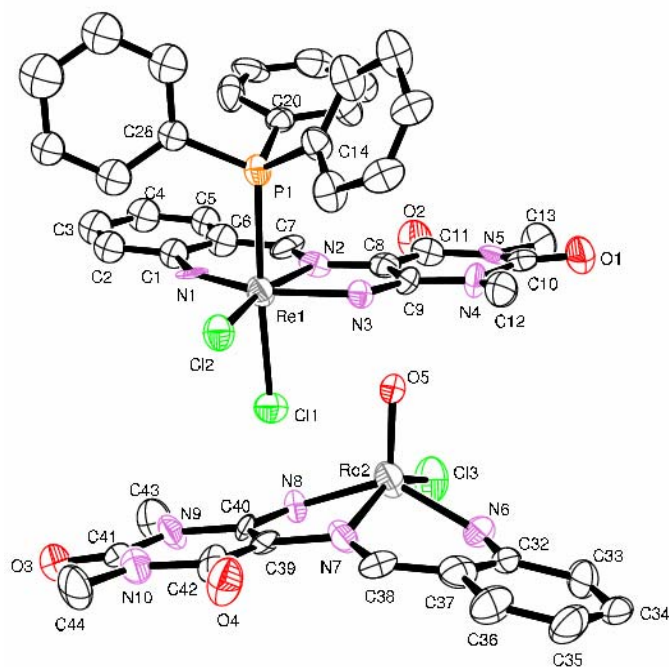


Fig. 1. Molecular diagrams and atom numbering scheme of $[\text{ReOCl}(\text{Hdua})]$ (**3**) and $[\text{Re}(\text{dua})\text{Cl}_2(\text{PPh}_3)]$ (**4**).

of N(1). The *trans* effect of the phosphine is also illustrated in the longer Re(1)-Cl(1) bond length [2.406(4) Å] when compared to Re(1)-Cl(2) [2.339(4) Å]. The Re(1)-N(1)-C(2) bond angle [145(1)°] deviates significantly from 180° and shows that the imido nitrogen is doubly, rather than triply, bonded to the rhenium, making the complex **4** a sixteen-electron species. The C(7)-N(2)-C(8) bond angle [122(1)°] is close to that for a sp^2 -hybridized nitrogen atom.

The packing of the complexes **3** and **4** in the crystal is essentially achieved by intermolecular hydrogen-bonds between N(3)H and O(5) [3.34(2) Å], N(8)H and Cl(1) [3.40(2) Å] and C(36)H and Cl(1) [3.60(2) Å], in addition to intramolecular bonds, mainly between the oxygen atoms on the uracil rings and adjacent methyl protons.

In conclusion, a mixed crystal of a square-pyramidal oxorhenium(V) complex, $[\text{ReOCl}(\text{Hdua})]$ (**3**), and a distorted octahedral imidorhenium(V) complex $[\text{Re}(\text{dua})\text{Cl}_2(\text{PPh}_3)]$ (**4**), was isolated from the reaction of *trans*- $[\text{ReOCl}_3(\text{PPh}_3)]$ in ethanol. The tridentate chelate *dua* in **4** is coordinated as an imido-imino-amide.

SUPPLEMENTARY MATERIAL

CCDC 723161 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk.

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