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Note

Synthesis and structure of the first neutral octahedral *cis*-dioxorhenium(V) complex

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Abstract

The complex *cis*-[ReO_2(Hdab)$(py)_2$] (**1**) (H_2dab = 1,2-diaminobenzene) has been prepared by reacting *trans*-[$ReO_2(py)_4$]I with H_2dab in ethanol. This is the first example of a neutral hexacoordinate rhenium(V) complex with a *cis* arrangement of the two oxo groups. The compound also provides the first example of a bidentate monoanionic monoimino coordination mode of H_2dab. Crystal data for **1**·(H_3dab)I·H_2O: $C_{22}H_{26}IN_6O_2Re \cdot H_2O$, triclinic, space group $P\bar{1}$, $a = 9.570(2)$, $b = 12.493(3)$, $c = 12.851(3)$ Å, $\alpha = 61.60(3)$, $\beta = 70.56(3)$, $\gamma = 78.68(4)°$, $V = 1273.1(4)$ Å^3 and $Z = 2$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *cis*-Dioxorhenium(V); Crystal structures; 1,2-Diaminobenzene

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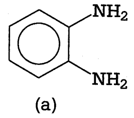
1. Introduction

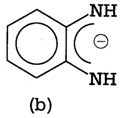
There has recently been a renewed interest in the coordination chemistry of rhenium [1–3]. This is mainly due to the potential application of the radioisotopes ^{186}Re and ^{188}Re in radiotherapy [1]. Rhenium complexes also serve as model compounds for the chemically related technetium compounds which are widely applied in diagnostic medicine [2,3]. Oxorhenium complexes have recently been shown to have applications in many catalytic oxidation processes and to oxygen atom transfer between substrates [4,5].

Our interest is currently focused on the synthesis of rhenium(V) complexes containing the molecule 1,2-diaminobenzene (H_2dab) and its derivatives. The reaction of H_2dab with transition metals has been studied extensively, since it leads to complexes in different oxidation states with reversible oxidation–reduction sequences [6], as well as giving complexes with unusual structural and chemical properties [7].

1,2-Diaminobenzene is a highly delocalised, unsaturated, electron-rich molecule, and the different forms in which it was found in transition metal complexes are



(a)



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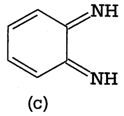

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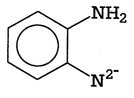

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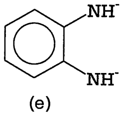
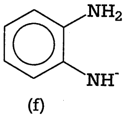


(e)



(f)

The neutral diaminobenzene form (a) has been found in the platinum(II) complex [Pt(H_2dab)I_2] [8]. The 1,2-benzosemiquinone diimine monoanionic form (b) has been isolated in complexes of the type [$M^{II}$$(dab)_2$] (M = Co, Ni, Pd, Pt) [9], while the neutral 1,2-benzoquinone diimine form (c) was found in $[Fe(dab)(CN)_4]^{2-}$ [10]. We have recently discovered the imido form (d) in the complex [Re^V(dab)$Cl_3(PPh_3)_2$] [11] and the diimide form

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(e) in the oxo-free complex [$Re^V(dab)_2Cl(PPh_3)$] [12] and in (n-Bu_4N)[$Tc^VO(dab)_2$] [7].

We have now also discovered the mono-imido form (f) in the complex *cis*-[Re^VO_2(Hdab)$(py)_2$] (**1**), which was prepared from the reaction of *trans*-[$ReO_2(py)_4$]I and H_2dab in ethanol. To our knowledge this is the first example of a neutral hexacoordinate rhenium(V) complex with a *cis*-dioxo structure. The first example of a neutral *cis*-dioxorhenium(V) complex was the trigonal–bipyramidal [$ReO_2I(PPh_3)_2$] [13], and the first example of an octahedral one was the cationic *cis*-[ReO_2(bipy)$(py)_2$](ClO_4) [14].

Table 1
Summary of crystal and refinement data

Empirical formula	$C_{22}H_{26}IN_6O_2Re\cdot H_2O$
Color, habit	dark violet cuboids
Formula weight	737.60
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.570(2)
b (Å)	12.493(3)
c (Å)	12.851(3)
α (°)	61.60(3)
β (°)	70.56(3)
γ (°)	78.68(4)
V (Å^3)	1273.1(4)
Z	2
D_{calc} (mg m^{-3})	1.924
$2\theta_{max}$ (°)	50.0
Independent reflections	4454
Observed reflections ($I>2\sigma(I)$)	3519
R_1 [a]; wR_2 [b]	0.048; 0.129
Goodness-of-fit	1.062

Other details of data collection/refinement: Siemens/Nicolet R3m/V diffractometer; Mo Kα radiation ($\lambda=0.71073$); $T=293$ K; highly oriented graphite monochromator; $\omega-2\theta$ scans; two standard reflections every 150; refinement by full-matrix least-squares method on F_o^2; riding model for H atoms.

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $wR_2=[\Sigma\, w(F_o^2-F_c^2)/^2\Sigma\, w(F_o^2)/^2]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°)

Bond lengths			
Re–O(1)	1.723(7)	Re–O(2)	1.716(6)
Re–N(1)	2.053(8)	Re–N(2)	2.042(9)
Re–N(3)	2.163(9)	Re–N(4)	2.155(9)
N(5)–C(17)	1.41(1)	N(6)–C(22)	1.48(1)
Bond angles			
O(1)–Re–O(2)	118.2(3)	O(1)–Re–N(1)	157.8(3)
O(1)–Re–N(2)	85.2(3)	O(1)–Re–N(3)	88.0(3)
O(1)–Re–N(4)	87.8(3)	O(2)–Re–N(2)	156.6(3)
N(1)–Re–N(2)	72.7(3)	N(3)–Re–N(4)	174.3(3)
Re–N(1)–C(1)	121.2(6)	Re–N(2)–C(6)	121.3(7)

2. Experimental

2.1. Reagents

trans-[$ReO_2(py)_4$]I was synthesized by a published procedure [15]. Solvents were reagent grade, and were purified and dried before use. All other reagents were obtained commercially (Aldrich), and their purity was checked by ^{1}H NMR and melting point.

2.2. Synthesis of cis-[ReO_2(Hdab)$(py)_2$] (1)

A mixture of 100 mg (150 μmol) of *trans*-[$ReO_2(py)_4$]I and 33 mg (305 μmol) of 1,2-diaminobenzene (H_2dab) in 15 cm^3 of ethanol was stirred at room temperature (r.t.) for 30 h. The original red–orange solution gradually turned green, and after the reaction period a fine dark purple precipitate was collected by filtration from the dark green solution. The product **1** was washed with cold ethanol, water and acetone, and dried under vacuum. The slow evaporation of the mother liquor over a period of 3 days at r.t. gave dark violet crystals, suitable for X-ray analysis, with the formulation **1**·(H_3dab)I·H_2O. Yield: 63%, m.p. > 300 °C. *Anal.* Calc. for $C_{16}H_{17}N_4O_2Re$: C, 39.74; H, 3.54; N, 11.59. Found: C, 39.91; H, 3.61; N, 11.34%. IR(KBr): $\nu_s(ReO_2)$ 905; $\nu_a(ReO_2)$ 876; ν(NH) 3236, 3262, 3289 cm^{-1}. ^{1}H NMR (295 K) ppm: 13.63 (br s, 3H, N*H*), 7.36 (s, 8H, py*H*), 6.93 (br s, 6H, py*H*, Hdab). UV–Vis: 668 (9750), 383 (4780).

2.3. X-ray data collection, structure solution and refinement of **1**·(H_3dab)I·H_2O

The most important details of the crystallographic work are reported in Table 1. A crystal of the dimensions 0.20 × 0.20 × 0.20 mm was used for data collection. Cell constants and orientation matrices for the data collection have been obtained from the least-squares refinement of 50 well-centered reflections with $\theta\geq 8.0°$. The intensities were corrected for Lorentz and polarization factors as well as for absorption effects. The latter have been treated empirically (Ψ-scans method).

The structure was solved by heavy-atom methods, completed by difference Fourier syntheses and refined by full-matrix least-squares procedures based on F^2, using the SHELX suite of programs [16,17]. All the atoms have been refined anisotropically with the exception of the hydrogen atoms, which have been described by means of a riding model. The final difference map did not show any relevant feature. The minimum and maximum difference peaks were −1.22 and 1.36 e Å^{-3}, respectively. A collection of selected bond distances and angles for **1** is given in Table 2.

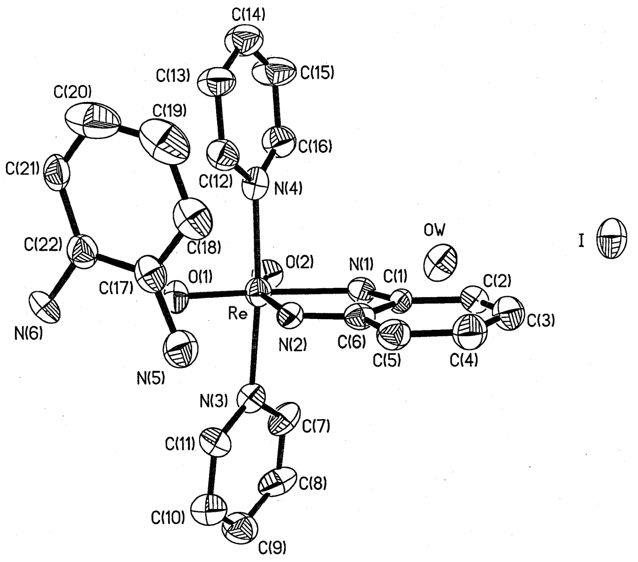

Fig. 1. A perspective view of the asymmetric unit of **1**·(H_3dab)I·H_2O with its numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

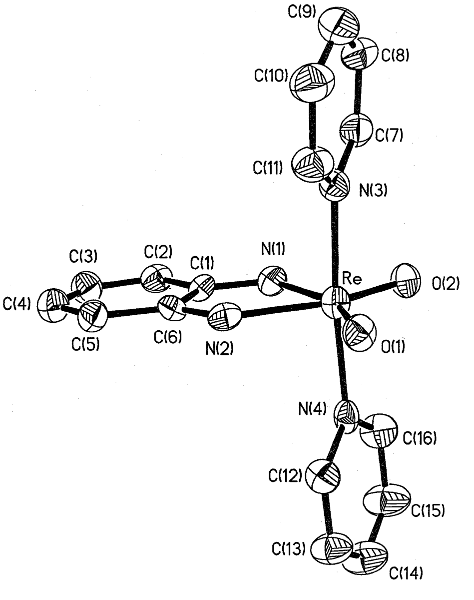

Fig. 2. The *cis*-[ReO_2(Hpda)(py)$_2$] neutral complex.

2.4. Physical measurements

The instrumentation used in this study is the same as reported elsewhere [18]. IR spectra were obtained in KBr discs and ^{1}H NMR spectra were run in d_6-DMSO. Electronic spectra were all obtained in acetonitrile, and data are given as λ_{max} with extinction coefficients (in units M^{-1} cm^{-1}) in parentheses. Elemental analyses for carbon, hydrogen and nitrogen were carried out by the Department of Chemistry at the University of the Western Cape in Cape Town.

3. Results and discussion

The reaction of *trans*-[ReO_2(py)$_4$]I with 1,2-diaminobenzene (H_2dab) at room temperature in ethanol did not result in the expected *trans*-dioxo complex [ReO_2(H_2dab)$_2$]I, but rather yielded the novel neutral complex *cis*-[ReO_2(Hdab)(py)$_2$] (**1**). The best yield was obtained with a 1:2 metal–ligand molar ratio, and the slow evaporation of the mother liquor of the synthetic solution led to the crystallization of a compound with the formulation **1**·(H_3dab)I·H_2O. Heating of the reaction mixture under reflux conditions for 2 h gave a mixture of products, one of which was **1**. Complex **1** is air stable in the solid state for weeks, and in solution for at least 8 h. It is soluble in a variety of solvents such as acetonitrile, acetone, chloroform, water and Me_2SO. It is also diamagnetic; diamagnetism for *cis*-dioxo d^2 species has been explained earlier on the basis of spin–orbit coupling energetics [19].

The presence of the *cis*-dioxo bonds is confirmed by two strong peaks at 905 and 876 cm^{-1} in the infrared spectrum; the former the symmetric and the latter the asymmetric stretch. The IR spectrum in acetonitrile was identical with that obtained in a KBr pellet. In the NMR spectrum a convergence of the proton resonances of the aromatic rings is observed, as a consequence of the delocalization of the π-electron density in the rings.

Single crystals of **1**·(H_3dab)I·H_2O of X-ray quality were obtained from the slow evaporation of the ethanolic mother liquor of the synthetic solution. An ORTEP [20] perspective view of the asymmetric unit, along with the atom numbering scheme, is given in Figs. 1 and 2 shows the neutral complex **1**. In the asymmetric unit, together with the monomeric complex, there is an unbound molecule of the ligand in its protonated form H_3dab^+, which is neutralized by an iodide ion. The rhenium atom is at the center of a distorted octahedral environment. The equatorial positions are held by the nitrogen atoms of the monoanionic $Hdab^-$ ligand and two *cis*-oxo atoms. The apical positions are occupied by the nitrogen atoms of the two pyridine ligands. The data in Table 2 indicate that the largest deviations from ideality in the equatorial plane are due to the restrictions imposed on the ligand Hdab by the formation of a five-membered ring with the metal; in fact, the N(1)–Re–N(2) angle is only 72.7°. The strain originating from such a distortion may be responsible for the *cis* orientation of the two oxygen atoms, which have a O(1)–Re–O(2) angle of 118.2°. The Re, N(1), N(2), O(1) and O(2) atoms are nearly coplanar within 0.03 Å. The monoanionic $Hdab^-$ ligand is also planar within the equatorial plane and is nearly orthogonal in respect of the two pyridine synthons. The mean planes of the pyridines bound to rhenium through the N(3) and N(4) atoms define, respectively, angles of 97.1 and 87.5° with the $Hdab^-$ plane. Also, the mean planes passing

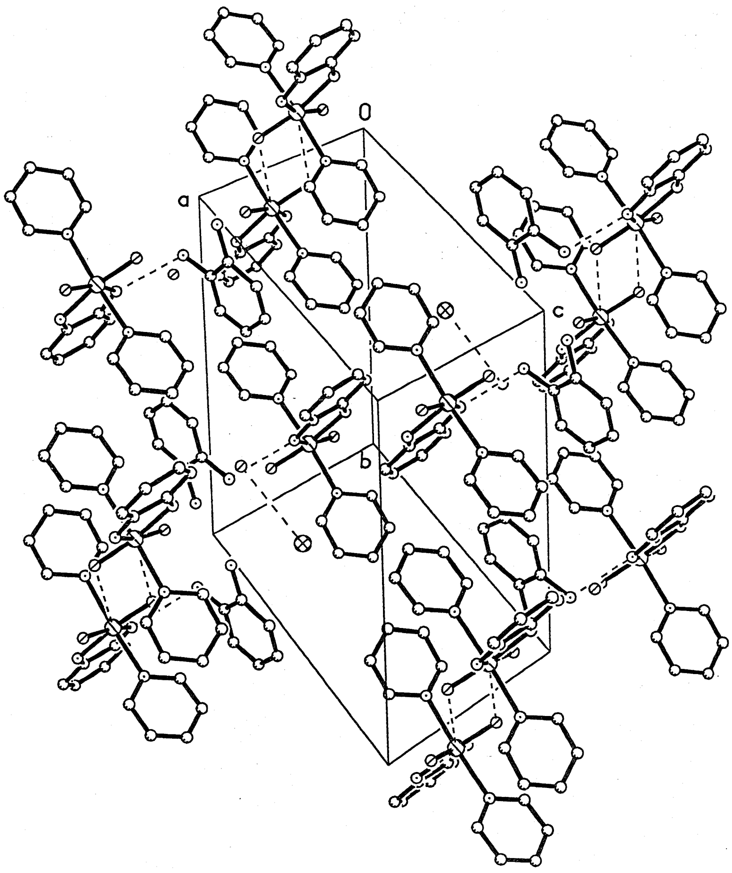

Fig. 3. The crystal lattice showing the shortest intermolecular interactions.

through the pyridines define an angle to each other of only 12.5°, so the two ligands are nearly coplanar. The deviation from ideality can also be measured by the dihedral angle between two opposing triangular faces of the octahedron. The angle between the planes N(1)–N(3)–O(2) and N(2)–N(4)–O(1) is 11.2° (ideally 0°). All the above indicate that the octahedral environment is only moderately distorted. The Re=O_{oxo} (in *cis*-dioxo compounds), Re(V)–N_{py}, and Re(V)–N_{amine} bond lengths have been compared with those reported in the Cambridge Structural Database System [21], and in all cases they fall within the reported limits, close to the average values. So no unexpected features have been found.

With respect to the unbound protonated H_3dab^+ ion, the only feature that deserves mention is that the C(17)–N(5) and the C(22)–N(6) bond distances are different. The former measures 1.414 Å, while the latter is 1.476 Å. This indicates that protonation occurred at the N(6) atom.

With respect to cell packing (Fig. 3), no really strong intermolecular interactions have been found, and only a few contacts are worth mentioning. The iodide anion is involved in two interactions with the water oxygen atom (O_w) at x, y, z and at $-x$, $1-y$, $1-z$. The I–O_w distances are 3.67 and 3.54 Å, respectively. The nitrogen atoms of the bonded ligand molecule also define two contacts. The first is between N(1) and O_w at x, y, z, with a distance of 2.98 Å, and the second is between N(2) and the N(5) again at x, y, z; the bond distance in this case being 2.96 Å.

Complex **1** is a rare sample of a neutral *cis*-dioxo rhenium(V) complex. For Re(V), as well as for other transition metals with a d^2 electron configuration, the *trans*-dioxo arrangement is the most common, and most of the reported *trans*-dioxo Re(V) complexes are positively charged [22]. To the best of our knowledge, **1** is the only known example of a neutral octahedral *cis*-dioxo complex, and it also provides the first example of the bidentate coordination of H_2dab in a monoanionic monoimino form (see structure (f) in Section 1).

4. Supplementary material

All atomic and thermal parameters and all interactive angles are available from the authors upon request.

Acknowledgements

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