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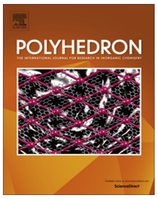

Rhenium(III), (IV) and (V) complexes with 6-hydroxypicolinic acid

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The reaction of *trans*-[$ReOBr_3(PPh_3)_2$] with 6-hydroxypicolinic acid (H_2hpa) in ethanol led to the isolation of the $Re^{IV}\equiv Re^{IV}$ dimer (μ-O)(μ-hpa)$_2$[$Re_2Br(OEt)(PPh_3)_2$] (**1**). Each hpa^{2-} anion acts as a bridging ligand with the coordination of a neutral pyridol oxygen to one rhenium ion, and the coordination of a carboxylate oxygen and a pyridinate nitrogen to the other rhenium ion. By using [$ReOCl_3(PPh_3)_2$] as precursor in ethanol, two products were isolated, i.e. (μ-Cl)(μ-O)(μ-hpa)[$Re^{IV}_2Cl_2(OEt)(PPh_3)_2$] (**2**) and [$Re^{III}Cl_2(Hhpa)(PPh_3)_2$] (**3**). The complexes *cis*-[$ReOX_2(Hhpa)(PPh_3)$] (X = Br (**4**); Cl (**5**)) were the only products formed by the reaction of [$ReOX_3(PPh_3)_2$] with H_2hpa in acetonitrile. The bromide equivalent of **3**, i.e. [$Re^{III}Br_2(Hhpa)(PPh_3)_2$] (**6**), was obtained from the reaction of [$ReOBr_3(PPh_3)_2$] with H_2hpa in 2-propanol. Coordination of $Hhpa^-$ in **3**–**6** occurs through the carboxylate oxygen and neutral pyridyl nitrogen. In addition to the X-ray crystal structures, infra-red, ^1H NMR, electrochemical and electronic properties are also reported.

1. Introduction

There is a renewed interest in the coordination chemistry of rhenium due, not only to the application of its $^{186/188}Re$ isotopes in therapeutic nuclear medicine, but also to its versatility in various catalytic applications [1]. This versatility is enhanced by the large number of stable oxidation states (−I to +VII) and the types of structures that the metal can form, from monomers to ligand-bridged multimers, and even from metal–metal multiply bonded complexes to clusters [2].

In a previous study we have focussed on orotic acid (H_2or) as a ligand for rhenium(V) [3]. Surprisingly, the reaction of H_2or with *trans*-[$ReOBr_3(PPh_3)_2$] in ethanol produced the triply-bridged [Re_2(μ-Br)(μ-O)(μ-or)$Br(OEt)_2(PPh_3)_2$], and in 2-propanol the product [Re_2(μ-Br)(μ-O)(μ-or)$Br_2(OCHMe_2)(PPh_3)_2$] was isolated.

The study has now been extended to the related ligand 6-hydroxypicolinic acid (H_2hpa; Scheme 1). Hydroxypicolinic acids as ligands have attracted attention since they display a variety of bonding modes [4]. Also, with pyridinecarboxylate ligands (HON), the complexes [$ReOCl_2(ON)(PPh_3)$] have shown catalytic activity for the conversion of ethane to propionic/acetic acids [5], and [$ReO(CH_3)(ON)_2$] is active in olefin oxidation [6].

The keto tautomer of 6-hydroxypicolinic acid contains exactly the same donor atoms as orotic acid, and it would be interesting to establish if its coordination behaviour would be similar to that of H_2or. Alternatively, the enol tautomer may display completely different coordination modes to rhenium in the various oxidation states +III, +IV and +V. In this account the products from the reaction of *trans*-[$ReOX_3(PPh_3)_2$] (X = Cl, Br) with H_2hpa in ethanol and acetonitrile (Scheme 2) are reported. Again, as with H_2or as ligand, the dimers (μ-O)(μ-hpa)$_2$[$Re^{IV}_2Br(OEt)(PPh_3)_2$] (**1**) and ($\mu$-Cl)($\mu$-O)($\mu$-hpa)-[$Re^{IV}_2Cl_2(OEt)(PPh_3)_2$] (**2**) were isolated, in addition to [$Re^{III}X_2(Hhpa)(PPh_3)_2$] (X = Cl (**3**), Br (**6**)) and [$ReOX_2(Hhpa)(PPh_3)$] (X = Cl (**4**), Br (**5**)).

2. Experimental

2.1. Materials and instrumentation

(NH_4)[ReO_4], H_2hpa and all other chemicals were obtained from the Aldrich Chemical Co. *trans*-[$ReOX_3(PPh_3)_2$] (X = Cl, Br) was prepared according to a literature procedure [7].

Infrared spectra were obtained by a Bruker Tensor 27 spectrometer. All NMR spectra were recorded at 298 K using a 300 MHz Bruker AMX-300 spectrometer with chemical shifts relative to $SiMe_4$. A Perkin–Elmer Lamda 35 UV/Vis spectrophotometer was used for absorption spectra, and extinction coefficients are given in the unit M^{-1} cm^{-1}. Melting points were determined using a Lasec Stuart SMP30 melting point apparatus. The cyclic voltammetry studies were carried out with a Bas Epsilon Version 1.30.64 system which consists of a platinum working electrode, a platinum auxiliary electrode and a pseudo silver/silver chloride Re-5 reference electrode. The supporting electrolyte, tetrabutylammonium perchlorate

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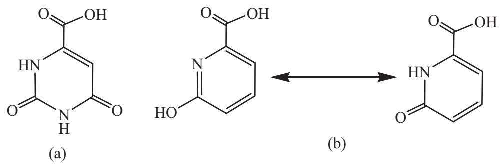
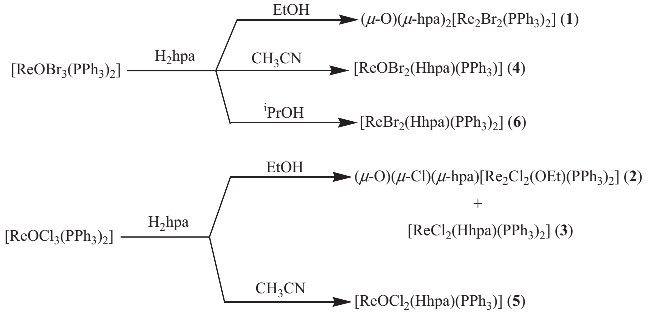


Scheme 1. Line structure of (a) orotic acid, and (b) keto-enol tautomerism of 6-hydroxypicolinic acid (H_2hpa).



Scheme 2. Reaction scheme showing the products formed.

(TBAP), had a concentration of 0.1 M and the respective complex concentrations were 0.001 M. The sample solutions were deoxygenated by nitrogen before runs.

2.2. Synthesis of the complexes

2.2.1. (μ-O)(μ-hpa)$_2$[Re$_2^{IV}$Br(OEt)(PPh$_3$)$_2$] (**1**)

To a solution of H_2hpa (50 mg, 0.36 mmol) in 10 cm^3 of ethanol was added *trans*-[ReOBr$_3$(PPh$_3$)$_2$] (150 mg, 155 μmol) in 10 cm^3 of ethanol. The yellow mixture was heated under reflux for 24 h, resulting in a dark green solution, which was filtered after being cooled to room temperature. No precipitate was obtained. The filtrate was left to evaporate slowly at room temperature, and after three weeks dark green crystals were harvested by filtration. Yield: 41%; m.p. 150 °C. IR (ν_{max}/cm^{-1}): $\nu_s(CO_2)$ 1695; $\nu_a(CO_2)$ 1316; ν(Re—O—Re) 722; ν(Re—N) 509, 519; ν(Re—O) 453br. ^1H NMR (d_6-DMSO, ppm): 1.02 (t, 3H, OCH$_2$*CH*$_3$), 4.01 (q, 2H, O*CH*$_2$), 7.26–7.34 (m, 30H), 7.36 (dd, 2H), 7.76 (d, 2H), 8.20 (d, 2H). Electronic spectrum (acetonitrile, λ_{max} nm (ε)): 335 (4360), 376 (2700), 483 (2750).

2.2.2. (μ-Cl)(μ-O)(μ-hpa)[Re$_2^{IV}$Cl$_2$(OEt)(PPh$_3$)$_2$] (**2**) and [Re^{III}Cl$_2$(Hhpa)(PPh$_3$)$_2$] (**3**)

To *trans*-[ReOCl$_3$(PPh$_3$)$_2$] (180 mg, 216 μmol) in 10 cm^3 of ethanol was added 0.432 μmol of H_2hpa (60 mg) in 10 cm^3 of ethanol. The resulting yellow-green mixture was heated at reflux for 24 h, resulting in a dark green solution. After cooling to room temperature, a red-orange residue was removed by filtration. The recrystallisation of this precipitate in an ethanol/dichloromethane mixture gave red-orange crystals of complex **3**. A volume of 2 cm^3 of acetonitrile was added to the filtrate, and the mixture was left to evaporate slowly at room temperature. After a month dark green crystals of **2** were collected, and they were washed with ethanol and acetone. **2**·3MeCN: Yield = 23%, m.p. = 152 °C. IR (ν_{max}/cm^{-1}): $\nu_s(CO_2)$ 1699; $\nu_a(CO_2)$ 1312; ν(Re—O—Re) 721; ν(Re—N) 522; ν(Re—O) 457. ^1H NMR (d_6-DMSO, ppm): 1.04 (t, 3H, OCH$_2$*CH*$_3$), 4.02 (q, 2H, O*CH*$_2$), 7.26–7.34 (m, 30H), 7.38 (dd, 1H), 7.79 (d, 1H), 8.24 (d, 1H). Electronic spectrum (methanol, λ_{max} nm (ε)): 329 (4200), 468 (3760). **3**: Yield = 29%, m.p. = 286 °C. IR (ν_{max}/cm^{-1}): ν(O—H) 3177; $\nu_s(CO_2)$ 1678; $\nu_a(CO_2)$ 1321; ν(C=N) 1621; ν(Re—N) 496; ν(Re—O) 451. Electronic spectrum (acetonitrile, λ_{max} nm (ε)): 339 (8240), 447 (4020).

2.2.3. cis-[ReOX$_2$(Hhpa)(PPh$_3$)] (X = Br (**4**); Cl (**5**))

To *trans*-[ReOX$_3$(PPh$_3$)$_2$] (155 μmol) in 10 cm^3 of acetonitrile was added 380 μmol of H_2hpa (53 mg) in 10 cm^3 of acetonitrile. The resulting mixture was heated at reflux for 4 h, resulting in a dark green solution, which was filtered after being cooled to room temperature. No precipitate was obtained. Dark green crystals were grown in one week from the slow evaporation of the mother liquor at room temperature. **4**: Yield = 57%, m.p. = 191 °C. IR (ν_{max}/cm^{-1}): ν(Re=O) 974; $\nu_s(CO_2)$ 1693; $\nu_a(CO_2)$ 1322; ν(C=N) 1620; ν(Re—N) 496; ν(Re—O) 442. ^1H NMR (d_6-DMSO, ppm): 5.08 (s, O*H*), 7.38–7.60 (m, 15H), 7.30 (dd, 1H), 7.43 (d, 1H), 7.65 (d, 1H). Electronic spectrum (acetonitrile, λ_{max} nm (ε)): 339 (6200), 358 (5460), 391 (2420). **5**·OPPh$_3$·H$_2$O: Yield = 66%, m.p. = 183 °C. IR (ν_{max}/cm^{-1}): ν(Re=O) 974; $\nu_s(CO_2)$ 1691; $\nu_a(CO_2)$ 1352; ν(Re—N) 497; ν(Re—O) 435. Electronic spectrum (acetonitrile, λ_{max} nm (ε)): 338 (6730), 375 (4760).

2.2.4. [Re^{III}Br$_2$(Hhpa)(PPh$_3$)$_2$] (**6**)

To *trans*-[ReOBr$_3$(PPh$_3$)$_2$] (213 mg, 220 μmol) in 10 cm^3 of 2-propanol was added 432 μmol of H_2hpa (60 mg) in 10 cm^3 of 2-propanol. The resulting mixture was heated at reflux for 24 h, resulting in a dark orange solution. After cooling to room temperature an orange precipitate was removed by filtration. The recrystallization of the solid from an ethanol/dichloromethane mixture produced orange crystals. X-ray crystallographic analysis of these crystals confirmed the formulation of the complex as **6**.[1] Yield = 39%, m.p. = 225 °C. IR (ν_{max}/cm^{-1}): ν(O—H) 3194; $\nu_s(CO_2)$ 1677; $\nu_a(CO_2)$ 1325; ν(Re—N) 499; ν(Re—O) 451. Electronic spectrum (acetonitrile, λ_{max} nm (ε)): 311 (8240), 361 (3660).

2.3. X-ray crystallography

X-ray diffraction studies of complexes **1**–**3** and **5** were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). APEX-II was used for data collection and SAINT for cell refinement and data reduction [8]. The structures were solved by direct methods using SHELXT-2014 [9] and refined by least-squares procedures using SHELXL-2014 [9] with SHELXLE [10] as a graphical interface. Data were corrected for absorption effects using the numerical method implemented in SADABS [9]. Selected crystal and data collection details are given in Table 2, and selected bond lengths and angles for the complexes are shown in Table 3.

All non-hydrogen atoms were refined anisotropically. Carbon-bound H atoms were placed in calculated positions (C—H bond lengths: aromatic CH 0.95 Å, methine CH 1.00 Å, methylene CH$_2$ 0.99 Å and methyl CH$_3$ 0.98 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 Ueq(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [9]), with U_{iso}(H) set to 1.5 Ueq(C). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C—O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [9]), with U_{iso}(H) set to 1.5 Ueq(O). Hydrogen atoms of the solvent water molecules were located on a difference Fourier map and refined with the O—H bond lengths and the H—O—H bond angles

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[1] Crystallographic data for $C_{42}H_{34}Br_2NO_3P_2Re$: triclinic; space group $P\bar{1}$; $a = 9.2814(5)$, $b = 12.6715(7)$, $c = 16.4316(9)$ Å; $\alpha = 83.851(2)$, $\beta = 84.809(2)$, $\gamma = 73.960(2)°$; $V = 1842.8(2)$ Å^3; $Z = 2$; $D_c = 1.818$ g cm^{-3}; $\mu = 5.594$ mm^{-1}; data/parameters: 9203/461; $S = 1.08$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0152$, $wR_2 = 0.0375$.