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Synthesis and structural characterization of zwitterionic oxorhenium(V) complexes with 2-hydroxypyridine

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Abstract

 $[\text{ReOX}_3(\text{PPh}_3)_2]$ complexes (X = Cl and Br) react with equivalent amounts of 2-hydroxypyridine (Hhp) under formation of the monosubstituted, zwitterionic complexes *mer*- $[\text{ReOCl}_3(\text{Hhp})(\text{PPh}_3)]$ (1) and *mer*- $[\text{ReOBr}_3(\text{Hhp})(\text{PPh}_3)]$ (2). Crystal structure determinations of 1 · CH₂Cl₂ and 2 revealed the Cl and Br ligands adopt a *mer* arrangement. The Hhp ligands coordinate neutral and monodentate via their exocyclic oxygen atoms in axial positions, *trans* to the oxo groups. The distorted octahedral coordination sphere of the rhenium(V) complexes is completed by the phosphorus atom of the remaining PPh₃ ligand. © 2005 Elsevier B.V. All rights reserved.

Keywords: Rhenium zwitterionic complexes; 2-Hydroxypyridine; X-ray crystal structures

1. Introduction

2-Hydroxypyridine (Hhp) has interesting ligand properties, being able to act as a mono-, bi- or tri-nucleating agent, with different possible coordination modes [1]. The known examples of rhenium coordination compounds with Hhp involve mainly a series of Re_2^{6+} compounds and mononuclear complexes prepared from the polyhydride complex $[\text{ReH}_7(\text{PPh}_3)_2]$. In these compounds, 2-hydroxypyridine is singly deprotonated and coordinates N,Obidentate as 2-pyridonate, hp⁻, bridging two transition element centers, or forms a four-membered chelate ring bonded to only one metal ion [1]. More recently, the complex $[\text{Re}_2(\eta^2-\text{hp})\text{Cl}_3(\mu-\text{dppm})_2]$ was prepared from $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2]$ (dppm = Ph₂PCH₂PPh₂). Its X-ray crystal structure was determined and confirmed the 2pyridonate ligand to act as a chelating agent, being coordinated to only one Re^{II} center in a Re_2^{4+} core [2]. The same N,O-chelating coordination mode of 2-hydroxypyridine and related ligands has been found in some other rhenium complexes involving the oxidation states of the metal from "+2" to "+4" [1–9]. Complexes with the composition $\text{Re}_2(\text{hp})_2X_4 \cdot \text{Hhp} \cdot \text{solvent}$ (X = Cl, Br) are supposed to be intermediates in some reactions during the preparation of [Re₂(hp)₂X₄]. The isolation of a complex with the stoichiometry Re₂(hp)₂Cl₄ · Hhp · THF is described [10].

This work describes the preparation and structural characterization of new oxorhenium(V) complexes containing Hhp ligands in a zwitterionic form. The complexes *mer*- $[ReOCl_3(Hhp)(PPh_3)]$ (1) and *mer*- $[ReOBr_3(Hhp)(PPh_3)]$ (2) contain monodentate Hhp ligands in their protonated neutral form, which is novel for rhenium coordination compounds with this type of ligand.



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2. Experimental

2.1. Materials and methods

The starting complexes $[\text{ReOX}_3(\text{PPh}_3)_2]$ (X = Cl, Br) were prepared as previously described [11]. All other reagents were of analytical grade and were used as purchased, without further purification. NMR spectra were recorded on a Varian Mercury Plus spectrometer, 7.05 T, operating at 300.07 MHz for ¹H and 121.47 MHz for ³¹P. They were run at room temperature in solutions of degassed CD₂Cl₂ by purging it with argon for about 15 min. The ¹H spectra were internally referenced to TMS and ³¹P{¹H} spectra were externally referenced to H₃PO₄ (85%, δ 0) with positive chemical shifts downfield the standard. The IR spectra (KBr pellets, 4000– 200 cm⁻¹) were obtained on a Bomem Michelson FT model MB 102 spectrometer. A Carlo Erba 1104 elemental analyzer was used for the microanalyses.

2.2. Preparation of $[ReOCl_3 (Hhp)(PPh_3)]$ (1)

About 0.024 g (0.25 mmol) 2-hydroxypyridine (Hhp) was added to a suspension of 0.208 g (0.25 mmol) [ReO-Cl₃(PPh₃)₂] in 15 mL of degassed dichloromethane. The mixture was refluxed for 3 h and after cooling to room temperature, 10 mL of hexane was added to the resulting green solution. A green precipitate was formed after storing at -15 °C for 24 h. The product was filtered off, washed with cold dichloromethane and hexane and dried in vacuum. Yield: 80% (0.134 g). *Anal.* Calc. for C₂₃H₂₀Cl₃NO₂-PRe: C, 41.50; H, 3.03; N, 2.11. Found: C, 41.22; H, 3.06; N, 1.96%.

IR $(cm^{-1}, KBr pellet)$: 3253(m), 3052(m-w), 1634(s), 1588(vs), 1538(s), 1481(m), 1433(m), 1388(s), 1262(m-w), 1213(w), 1160(w), 1093(m), 995(s, Re=O), 886(m), 772(m-s), 759(w), 751(m), 707(w-m), 693(m), 626(w), 611(w-m), 591(w-m), 527(m), 508(w-m), 495(w), 474(w), 452(w), 333(vw), 307(w), 280(vw).

¹H NMR (ppm, CD₂Cl₂) 5.350 (Hhp, overlapped with the triplet of residual CDHCl₂), 6.755 (dd, J = 6.7 Hz, 1H, Hhp), 7.030–8.025 (m, 17H, Hhp and Ph of PPh₃), 11.712 (br, 1H, NH).

 ${}^{31}P{}^{1}H$ NMR (ppm, CD₂Cl₂): -18.35 (s, Re–PPh₃).

2.3. Preparation of $[ReOBr_3 (Hhp)(PPh_3)]$ (2)

A mixture of 0.242 g (0.25 mmol) [ReOBr₃(PPh₃)₂] and 0.024 g (0.25 mmol) Hhp in 15 mL of degassed dichloromethane was heated under reflux for 10 h. After cooling to room temperature, 10 mL hexane was added and the mixture was left at -15 °C for 24 h to complete the precipitation. The green solid was isolated by filtration, washed with dichloromethane and hexane and dried in vacuum. Yield: 60% (0.127 g). *Anal.* Calc. for C₂₃H₂₀Br₃NO₂PRe: C, 34.64; H, 2.53; N, 1.76. Found: C, 34.36; H, 2.36; N, 1.73%. IR (cm⁻¹, KBr pellet): 3231(m-s), 3158(m), 3091(m-w), 3051(w), 1637(m-s), 1629(m-s), 1587(vs), 1538(vs), 1471(m), 1456(m), 1431(m), 1387(vs), 1274(m), 1213(m), 1160(m-w), 1093(ms), 995(vs, Re=O), 888(s), 867(m-w), 771(s), 760(m-s), 747(m-s), 707(m-s), 693(m-s), 612(s), 526(m), 508(w-m), 494(w-m), 450(m), 279(w).

¹H NMR (ppm, CD₂Cl₂) 5.216 (d, J = 9 Hz, 1H, Hhp), 6.763 (dd, J = 6.8 Hz, 1H, Hhp), 7.350–7.910 (m, 17H, Hhp and Ph of PPh₃), 11,470 (br, 1H, NH).

 ${}^{31}P{}^{1}H{}$ NMR (ppm, CD₂Cl₂): -15.65 (s, Re–PPh₃).

2.4. X-ray structure determinations

Single crystals of the complexes suitable for X-ray diffraction were obtained by slow evaporation of CH_2Cl_2 solutions.

The data collections were performed with Mo K α radiation ($\lambda = 71.073$ pm) on a BRUKER SMART CCD for $1 \cdot CH_2Cl_2$ and on an Enraf-Nonius CAD-4 diffractometer for 2 applying standard procedures.

The structures were solved by the heavy atom method with SHELXS-97 [12] and refined with SHELXL-97 [12]. Hydrogen atom positions were calculated at idealized positions using the riding model option of SHELXL-97 [12]. Additional crystal data and more information about the X-ray structural analyses are shown in Table 1.

3. Results and discussion

3.1. Synthesis of the complexes

The complexes 1 and 2 were prepared in satisfactory yields by ligand exchange reactions starting from $[ReOX_3(PPh_3)_2]$ complexes (X = Cl in 1 and Br in 2) and 2-hydroxypyridine in dichloromethane (Eq. (1)). The chloro derivative is rapidly formed, while the synthesis of 2 requires prolonged heating on reflux.

$$[\operatorname{ReOX}_{3}(\operatorname{PPh}_{3})_{2}] + \operatorname{Hhp} \to [\operatorname{ReOX}_{3}(\operatorname{Hhp})(\operatorname{PPh}_{3})] + \operatorname{PPh}_{3}$$
$$(X = \operatorname{Cl}, \operatorname{Br})$$
(1)

Both complexes precipitate as green solids upon addition of *n*-hexane to the reaction solutions and by keeping them at a low temperature. The solids are nearly insoluble in MeOH, toluene and hydrocarbons. They are sparingly soluble in CHCl₃ and moderately soluble in CH₂Cl₂ or CH₃CN. The compounds are air-stable as solids. In solution, however, oxidation of the PPh₃ ligand to OPPh₃ takes place which can be seen in the ³¹P NMR spectra as small signals at 30.9 ppm (free OPPh₃) and 49.8 ppm (coordinated OPPh₃) [13]. This process could be efficiently eliminated if degassed solvents were employed in ³¹P NMR measurements. After becoming conscious of that, all preparations were conducted on previously degassed solvents in order to avoid the formation of side products. The new complexes were characterized by IR and NMR spectroscopy, elemental analysis and X-ray structure deter-

Table 1 Crystal data and structure refinement parameters for $1 \cdot CH_2Cl_2$ and 2

| Complex | $1\cdot CH_2Cl_2$ | 2 |
|---|-------------------------------|--------------------------------|
| Empirical formula | C24H22Cl5NO2PRe | C23H20Br3NO2PRe |
| Formula weight | 750.85 | 799.30 |
| Temperature (K) | 173(2) | 293(2) |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| a (pm) | 918.2(1) | 945.0(3) |
| <i>b</i> (pm) | 1103.3(1) | 1903.9(3) |
| <i>c</i> (pm) | 1345.0(2) | 1413.3(2) |
| α (°) | 91.61(1) | 90 |
| β (°) | 98.62(1) | 107.61(1) |
| γ (°) | 98.94(1) | 90 |
| $V (pm^3)$ | $1.3290(3) \times 10^{6}$ | $2.4234(8) \times 10^{6}$ |
| Ζ | 2 | 4 |
| Absorption coefficient (mm^{-1}) | 5.158 | 10.047 |
| Absorption correction | empirical | empirical |
| $T_{\rm max}/T_{\rm min}$ | 1.000/0.593 | 0.4332/0.1077 |
| Crystal size (mm) | $0.4 \times 0.04 \times 0.02$ | $0.40 \times 0.30 \times 0.10$ |
| Crystal shape and color | green needle | green plate |
| Collected reflections | 18324 | 6212 |
| Unique reflections/R _{int} | 9189/0.0194 | 5252/0.0424 |
| Observed data $[I \ge 2 \sigma(I)]$ | 8600 | 3281 |
| Refined parameters | 307 | 280 |
| Structure factors $[I \ge 2 \sigma(I)]$ | $R_1^{a} = 0.0174,$ | $R_1^{a} = 0.0495,$ |
| | $wR_2^{b} = 0.0415$ | $wR_2^{b} = 0.0884$ |
| Goodness-of-fit, S ^c | 0.970 | 1.003 |
| CCDC reference No. | CCDC 283846 | CCDC 283847 |

^a
$$R_1 = \frac{\sum \|F_o| - |F_o\|}{\sum |F_o|}$$
.
^b $wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}}$.
^c $S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)}}$.

mination. All results agree with the zwitterionic structures of **1** and **2**, in which the Hhp ligand remains protonated in the complexes.

3.2. Crystal and molecular structures of $1 \cdot CH_2Cl_2$ and 2

Both complexes show distorted octahedral coordination spheres for the Re(V) central atoms, composed by the oxo ligand, the phosphorus atom of PPh₃, the three halogeno ligands in a *mer* arrangement and the oxygen atom of Hhp. The latter one is coordinated in *trans* position to the oxo oxygen, as is shown in Figs. 1 and 2. Selected bond lengths and angles for $1 \cdot CH_2Cl_2$ and 2 are given in Table 2.

In both complexes, the Hhp ligands coordinate monodentate and are neutral via the exocyclic oxygen atoms. The protonation of the pyridine nitrogen atoms is supported by N-H···X (X = Cl, Br) hydrogen bonds, which are established between the pyridine rings and halogeno ligands. These hydrogen bonds are intramolecular in $1 \cdot CH_2Cl_2$ and intermolecular in 2, as is indicated in the Figs. 1 and 3, respectively.

To our knowledge, there is only one other reported example of a zwitterionic oxorhenium(V) complex of the ReO_2Cl_3P type, the structure of which was determined crystallographically, namely



Fig. 1. Ellipsoid representation [19] of the complex molecule in $1 \cdot CH_2Cl_2$ with the thermal ellipsoids representing 50% probability. The dashed lines indicate the N–H···Cl hydrogen bonds, with the following distances and angles: N–H(6) = 86 pm, H(6)···Cl(2) = 261 pm, N···Cl(2) = 319.0(2) pm, N–H(6)···Cl(2) = 126.2°, H(6)···Cl(3) = 267 pm, N···Cl(3) = 324.8(2) pm, and N–H(6)···Cl(3) = 125.7°.



mer-[ReOCl₃(L)(PPh₃)] with L = 2-(diethylaminomethyl)-4-methylphenol (3) [14]. Complex **2** is the first zwitterionic complex of the type ReO₂Br₃P, which was structurally analyzed, and the only other example of a structurally characterized Re(V) complex of this donor atom constellation is [ReOBr₃(OPEt₂Ph)(PEt₂Ph)] (4) [15].

The Re–O1 distances of 166.4(1) in $1 \cdot CH_2Cl_2$ and 165.9(6) pm in **2** are in the expected range for rhenium(V) monooxo complexes [16], and can easily be explained by the multiple bond character of these bonds. The interatomic distances between the rhenium atoms and the 2(1H)-pyridinonate oxygen atoms coordinated in the axial position *trans* to the oxo groups ($1 \cdot CH_2Cl_2$: Re-O(2) = 206.8(1) pm; **2**: Re–O(2) = 203.7(6)) are considerably longer than the corresponding bond to the phenoxy oxygen atom in **3** (191.5(3) pm [14]) and all examples where alkoxy donor sites are bonded *trans* to oxo ligands in [ReO(OR)Cl₂(PPh₃)₂ complexes (R = Et, iso-Prop), show Re–O(alkoxy) bond lengths between 188.8 and 192.8 pm



Fig. 2. Ellipsoid representation [19] of 2 with the thermal ellipsoids representing 50% probability.

[17]. The comparably short Re–O bond length in the latter compounds is discussed to be a result of delocalization of π -electron density from the oxo bonds to the *trans*-situated ones and has also been found for some chelating ligands with phenoxy or alkoxy functionalities, which direct their oxygen donor atoms to the trans-positions of the oxo ligands [16,18]. Despite the fact that the oxygen atoms of the Hhp ligands in 1 and 2 are also situated in *trans* positions to an oxo group, such a delocalization of electron density seems not to play a significant role in the rhenium complexes under study.

The bonding situation in the equatorial coordination spheres of 1 and 2 is very similar (except the different

Table 2

Re-X bond lengths). A good similarity is also found between the bond lengths in complexes 2 and 4.

The bond lengths within the ring of the coordinated Hhp in 1 and 2 (see Table 2) show considerable double bond character. The ligand can be best described by the three resonance structures $\mathbf{a}-\mathbf{c}$ shown below, in which the negative charge located at the donor oxygen atom, in a and **b**, is formally transferred to the rhenium(V) center via the O-Re bond.



3.3. Spectroscopic characterization

Strong absorptions at 995 cm⁻¹ in the IR spectra of the products 1 and 2 are assigned to v(Re=O). The presence of the 2-hydroxypyridine ligand coordinated in the protonated form is confirmed by the characteristic v(N-H) bands at 3253 and 3231 cm⁻¹. Its coordination via the oxygen atom in the products results in a shift of the v(CO) band from 1653 cm⁻¹ in the uncoordinated Hhp to 1634 and 1637 cm^{-1} in 1 and 2, respectively. The coordination of triphenylphosphine in 1 and 2, is confirmed by its typical absorptions v(P-C) at 1093 cm⁻¹, γ (out of plane CH in PPh₃) at 751 cm⁻¹ and δ (phenyl ring deformation) at 693 cm⁻¹, without significant changing when compared to the starting complexes. A band attributable to v(Re-Cl) in 1 was found at 307 cm⁻¹. The corresponding v(Re-Br) band in 2 could not be clearly identified in its spectrum.

The ¹H NMR spectra of compounds 1 and 2 in CD_2Cl_2 at room temperature exhibit the expected signals for the

| Selected bond distances (pm) and angles (°) for 1 · CH ₂ Cl ₂ and 2 | | | | | | |
|---|-------------------------------------|----------|------------------------|-------------------------------------|-----------|--|
| | $1\cdot \mathrm{CH}_2\mathrm{Cl}_2$ | 2 | | $1\cdot \mathrm{CH}_2\mathrm{Cl}_2$ | 2 | |
| Re–O(1) | 166.4(1) | 165.9(6) | C(1)–O(2) | 129.1(2) | 128.7(10) | |
| Re-O(2) | 206.8(1) | 203.7(6) | C(1)–N | 135.0(2) | 133.1(11) | |
| Re-X(1)^{a} | 236.07(5) | 254.4(1) | C(5)–N | 136.4(2) | 134.2(12) | |
| $Re-X(2)^{a}$ | 240.06(5) | 253.7(1) | C(1)–C(2) | 140.8(2) | 138.3(13) | |
| Re-X(3)^{a} | 239.87(5) | 252.9(1) | C(2)–C(3) | 137.0(3) | 137.9(15) | |
| Re–P 247 | 247.77(5) | 249.9(3) | C(3)–C(4) | 140.3(3) | 139.5(15) | |
| | | | C(4)-C(5) | 135.5(3) | 133.2(15) | |
| O(1)-Re-O(2) | 172.68(6) | 172.9(3) | $P-Re-X(1)^a$ | 86.68(2) | 90.10(6) | |
| O(1)–Re–P | 90.79(5) | 92.6(2) | $P-Re-X(2)^{a}$ | 170.39(2) | 166.41(6) | |
| $O(1)$ -Re- $X(1)^a$ | 99.37(5) | 93.7(3) | $P-Re-X(3)^{a}$ | 97.59(2) | 95.18(6) | |
| $O(1)$ -Re- $X(2)^a$ | 98.03(5) | 100.6(2) | $X(1)$ -Re- $X(2)^{a}$ | 88.12(2) | 85.72(4) | |
| $O(1)$ -Re- $X(3)^a$ | 92.76(5) | 92.8(3) | $X(1)$ -Re- $X(3)^{a}$ | 167.10(2) | 171.45(4) | |
| O(2)–Re–P | 84.16(4) | 81.1(2) | $X(2)$ -Re- $X(3)^a$ | 85.84(2) | 87.61(4) | |
| $O(2)-Re-X(1)^a$ | 85.65(4) | 89.6(2) | $O(2)$ -Re- $X(3)^a$ | 82.70(4) | 84.6(2) | |
| O(2)-Re-X(2) ^a | 87.40(4) | 85.9(2) | | | | |

^a X = Cl for 1 and Br for 2.



Fig. 3. PLUTON view [20] of the unit cell, showing three units of **2** forming a linear chain of hydrogen bonded molecules, which is oriented perpendicular to the crystallographic *b*-axis, bisecting the β angle. Except H(6), the hydrogen atoms are omitted for clarity. N–H(6) = 84 pm, H(6) ··· Br(2)' = 261 pm, N···Br(2)' = 341.6(8) pm, N–H(6) ··· Br(2)' = 156.3°. Symmetry operation used to generate Br(1)': x - 1/2, -y + 3/2, z - 1/2.

aromatic protons of the PPh₃ and Hhp ligands. In addition, the NH resonance can be seen as broad signals in both compounds. The ${}^{31}P{}^{1}H{}$ NMR spectra of 1 and 2 show sharp singlets at -18.35 (1) and -15.65 ppm (2). The spectroscopic results agree with the coexistence of Hpy and PPh₃ ligands in the complexes and are in accord with the solid-state structures.

4. Conclusion

In contrast to the reactions between Hhp, and Re_2^{6+} and Re_2^{4+} centres, or $[\text{ReH}_7(\text{PPh}_3)_2]$ species, which lead to complexes containing hp⁻ as chelating or bridging ligands [1–9], zwitterionic complexes of the type $[\text{ReOX}_3(\text{Hhp})(\text{PPh}_3)]$ are obtained from reactions of Hhp with $[\text{ReOX}_3(\text{PPh}_3)_2]$ (X = Cl, Br) under mild conditions. The products contain the Hhp ligands in a monodentate, neutral O-bonded coordination mode. The pyridine nitrogen atoms are protonated and form hydrogen bonds.

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