New aqua rhenium oxocomplex; synthesis, characterization, thermal studies, DFT calculations and catalytic oxidations

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Abstract The aqua rhenium oxocomplex [ReO(OH)(H2O)4]2− (1) has been prepared and characterized by spectroscopy, thermogravimetry, and elemental analysis and its reactivity towards triphenylphosphine has been evaluated. Complex (1) acts as a catalyst precursor in the presence of molecular oxygen for the oxidation of PPh3 to OPPh3. This proceeds through complex intermediates like [Re(PPh3)n]3+ (2), and [ReO(PPh3)n]3+ (3). The newly prepared complex (1) was also employed as catalyst for catalytic oxidation of cyclohexane. The geometry of [ReO(OH)(H2O)4]2− has also been optimized in the singlet state by the DFT method with B3LYP level of theory.

1. Introduction

A major focus of the contemporary interest in the chemistry of the Group VII congener technetium and rhenium reflects the applications of 99mTc and 186Re or 188Re in radiodiagnosis and radiotherapy, respectively (Jurisson et al., 1993; Deutsch et al., 1986; Chi et al., 1994). The nuclear properties of 99mTc (t1/2 = 6 h, γ = 140 keV) are ideal for diagnostic imaging, while the β-emitting isotopes 186Re and 188Re (t1/2 = 90.64 h, Eγ,max = 1.1 MeV, t1/2 = 17 h, Eγ,max = 2.1 MeV, respectively) are promising candidates for therapeutic applica-

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much interest due to its relevance to oxygen atom transfer reaction catalyzed by cytochrome P-450 oxidase (Taqui Khan et al., 1986). The rhenium aqueous compounds are highly important as they are considered as a prerequisite in the design of new compounds by substituting reactions in addition to their catalyzed oxidation.

In the present work, we report the synthesis and characterization of \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) (1), as well as new Re complex derivatives, \([\text{Re} [\text{PPPh}_3]_3]^{3+}\) (2) which has been prepared by reduction of 1 with PPh₃ in the ethanolic medium. Further pharmacological and radiochemical studies of these complexes are under investigation.

2. Experimental

2.1. General procedure

All reactions were carried out in air in reagent-grade solvents, all chemical and solvents were of reagent grade and used without further purification.

FT-IR spectra were recorded on a Perkin–Elmer FT-IR Spectrometer “Spectrum 1000” in the spectra range 4000–400 cm⁻¹ with the samples in the form of KBr pellets. Electronic Spectra were measured on a UV–Vis Beckman Du-70 Spectrometer in the range 800–200 nm. \(^1\)H NMR, proton decoupled \(^1\)C and \(^{31}\)P NMR spectra were obtained at room temperature in DMSO d₆ or CD₃OD using a JEOL Eclipse400 NMR using TMS for \(^1\)H and \(^13\)C and 85% H₃PO₄ for \(^{31}\)P \(^{1}\)H as external standards. Elemental analysis (H) was performed on a Perkin–Elmer C H N-2400 analyzer. The thermal analysis was carried out using a Perkin–Elmer thermogravimetric analyzer TGA7 in nitrogen atmosphere. The % weight loss was carried out using a Perkin–Elmer thermogravimetric analyzer TGA7 in nitrogen atmosphere. The % weight loss.

Aqueous solution of Na₂S₂O₆ (250 mg, 1 mmol) was added dropwise to the stirred solution of NH₄ReO₄ (526 mg, 2 mmol) in water. The reaction was initially refluxed at 70°C for up to 2 h and then stirred for 24 h at room temperature. The solution was concentrated by rotary evaporation. The crystals of \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) were formed overnight. Yield: 77%.

IR of 1 (KBr, cm⁻¹): 996 s (1055) (ν (Re=O)); 3562 s (3793.3) (ν_str,antisym (OH)); 3474 s (3426 s (809) (ν (Re=O)). The data in parenthesis is obtained by DFT calculations.

UV–Vis (H₂O, λ_max, nm (1 g l⁻¹)): 225 (3,2).

\(^1\)H NMR spectra of complex (1) showed a singlet at δ 4.77 ppm assigned to the OH, and another singlet at 4.8 ppm assigned to the coordinated water (Banwell, 1972).

3. Results and discussion

The \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) complexes were prepared in good yields by direct reaction between metal salt NH₄ReO₄ and the ligand in the presence of a reducing agent. The complexation reactions were carried out according to the following equations:

\[
\text{S}_2\text{O}_5^{2-} + 2\text{Re}^{3+} + 6\text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_6^{2-} + 2\text{ReO}^4 + 12\text{H}^+
\]

The IR spectra \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) displays a strong band assigned to ν (Re=O) at 996 cm⁻¹ which is in the range reported for similar mono-oxorhenium complexes (945–1067 cm⁻¹) Silverstein and Webstar, 1996 and the band due to ν (Re=O) was recorded at 722 cm⁻¹. A sharp split band in the range 3238–3562 cm⁻¹ was observed and assigned to coordinated water in the structures of the complex (Nyquist and Kagel, 1971).

The electronic spectrum of the complex shows intensive absorption at 225 nm, attributed to intraligand transition, with a molar extinction coefficient of 3.2 M⁻¹ cm⁻¹, which is similar to the one reported earlier (Nakamoto, 1970).

\(^1\)H NMR spectra of complex (1) show a singlet at δ 4.77 ppm assigned to the OH, and another singlet at 4.8 ppm assigned to the coordinated water (Banwell, 1972).

3.1. Optimized geometry with DFT calculations

The geometry of \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) was optimized in a singlet state by the DFT method with the B3LYP functional. The optimized geometric parameters are presented in Table 1. The calculated Re=O and Re–O bonds are in good agreement with the values reported for other oxo rhenium complexes of related structures (Machura et al., 2007a,b). It should be noted that Re=O bond of H₂O is relatively longer than the expected length found in other rhenium complexes. This indicates that rhenium is weakly bonded to H₂O groups and therefore is labile and may be replaced easily by other ligands.

The calculated charge on the rhenium atom in \([\text{ReO(OH)}(\text{H}_2\text{O})_4]_2\text{S}_2\text{O}_8\) is considerably lower than the formal charge +5, corresponding to a d⁶ configuration of the central ion.
The first decomposition step, in the range of 90–150 °C corresponding to the loss of four water molecules, was attributed to water of coordination. The second decomposition is in the range 200–500 °C. The thermal decomposition ends with the formation of the rhenium oxide Re₂O₇ at 900 °C Table 3. On the basis of the above observations, the following scheme for the thermal decomposition may be proposed. The thermogram is shown in Fig. 2.

ReO(OH)(H₂O)₄ |S₄O₈ (decomposition) [4H₂O (decoordination)] → Intermediate (unstable)

3.3. Determination of reaction order of decomposition

The Horowitz and Metzger equation, \( C_i = (n)^{1−n} \), where \( C_i \) is the weight fraction of the substance present at the DTG peak temperature, \( T_i \) is given as

\[
C_i = \left( W_i - W_f \right) / \left( W_i - W_f \right)
\]

and, was used for the determination of the values of the reaction order (n). Here \( W_i \) stands for the remaining weight of the substance at a given temperature \( T_i \), i.e., the DTG peak temperature, \( W_i \) and \( W_f \) are the initial and final weights of the substance, respectively. The values of \( C_i \) for the thermal decomposition of complexes are not in the range 0.30–0.39 which indicate that the decomposition is not first order kinetics (Horowitz and Metzger, 1963). For a first order process the Horowitz and Metzger equation may be written in the form:

\[
\ln \left[ 1 - (1 - z)^{1−n} \right] = \ln \frac{A R T^2_s}{\phi E_a} - \frac{E_a}{R T} + \frac{E_a \theta}{RT_s}
\]

where \( R \) is the gas constant, \( E_a \) is the activation energy in J mol⁻¹, \( \theta \) is the heating rate. The kinetic parameters were calculated from the plots of the left hand side of Eq. (2) and \( \theta \). The correlation coefficient \( r \) (>0.95) is computed using the least-square method for Eq. (2).

The activation entropy \( \Delta S^* \), the activation enthalpy \( \Delta H^* \) and the free energy of activation \( \Delta G^* \) were calculated using the following equations (Abu-Eittah et al., 2006; Garcia et al., 1986):

\[
\Delta S^* = 2.303 R \left[ \log \frac{h}{kT} \right]
\]

\[
\Delta H^* = E_a - nRT
\]

\[
\Delta G^* = \Delta H^* - T \Delta S^*
\]

where \( K \) and \( h \) are the Boltzman and Plank constants, respectively. The calculated values of \( E_a, A, \Delta S^*, \Delta H^* \) and \( \Delta G^* \) for the two decomposition steps are given in Table 4.

3.4. Applications of aqua rhenium oxocomplex

Use as a catalyst precursor for the catalytic oxidation of PPh₃ and cyclohexane.

Due to the weak nature of the Re–OH₂ bond, aqua complexes are very good starting materials in coordination chemistry. Reaction of (1) with excess PPh₃ in the presence of

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The optimized bond lengths (Å) and angles (°) for [ReO(OH)(H₂O)₄]²⁻.</th>
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</thead>
<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td>Bond angles (°)</td>
</tr>
<tr>
<td>R(1, 2)</td>
<td>1.702</td>
</tr>
<tr>
<td>R(1, 3)</td>
<td>1.861</td>
</tr>
<tr>
<td>R(1, 5)</td>
<td>2.155</td>
</tr>
<tr>
<td>R(1, 7)</td>
<td>2.095</td>
</tr>
<tr>
<td>R(1, 9)</td>
<td>2.095</td>
</tr>
<tr>
<td>R(1, 11)</td>
<td>2.155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Showing atomic charges from the natural population analysis (NPA) for [ReO(OH)(H₂O)₄]²⁻.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>Charge</td>
</tr>
<tr>
<td>Re(1)</td>
<td>1.6737</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.8527</td>
</tr>
<tr>
<td>O(3)</td>
<td>-0.9546</td>
</tr>
<tr>
<td>O(5)</td>
<td>-0.2154</td>
</tr>
<tr>
<td>O(7)</td>
<td>-0.9473</td>
</tr>
</tbody>
</table>

This results from charge donation of H₂O ligands. There is unequal occupancy of degenerate orbitals in this system – admittedly they are \( t_2g \) and so Jahn–Teller distortion effects will be more minor than in the case of unequal \( e_g \) occupancy. The terminal oxo ion is less negative in comparison with the oxygen atom of the hydroxy group in the trans position. It indicates higher electron density delocalization from the \( O_t \) ligand towards the central ion and corresponding to the differences in the Re–OH and Re=O bond lengths. Much less negative charge is reported for \( O_{9} \) and \( O_{11} \) as similar to \( O_{7} \) and \( O_{5} \), respectively.

The structure of complex 1 [ReO(OH)(H₂O)₄]²⁻ as stabilized by DFT calculations is shown in Fig. 1.

3.2. Thermogravimetric analysis

Thermal decomposition behavior of the investigated complexes was followed using thermogravimetric (TG) and differential thermogravimetric (DTG) techniques. The complex under investigation has two decomposition steps.
molecular oxygen was studied by in situ $^{31}$P{1H} NMR spectroscopy. In the proposed mechanism the aqua rhenium oxocomplex (1) reacts with triphenylphosphine to form $[\text{Re}(\text{PPh}_3)_n]^{3+}$ (2). The formation of complex (2) has been confirmed by spectroscopic studies. Complex (2) reacts with O$_2$ to form complex (3). The formation of complex $[\text{ReO(PPh}_3)_n]^{3+}$ (3) and OPPh$_3$ has also been confirmed by spectroscopic studies. The oxygen atom transfer from complex (3) to PPh$_3$ may be a concerted process with the slow release of the product OPPh$_3$ as rate determining.

A $^{31}$P NMR spectrum of complex (3) shows three peaks initially at $-18$, $-4$ and $32$ ppm, corresponding to PPh$_3$-complex, PPh$_3$-free and OPPh$_3$, respectively, as shown in Fig. 3.

The peak at $-18$ ppm is due to the Re complex formation with PPh$_3$. The peak at $-4$ ppm is due to excess free un-oxidised ligand and the peak at $32$ ppm is due to the catalytic oxidation of PPh$_3$ with molecular oxygen resulting in the formation of OPPh$_3$. The downfield shift for the complex formation at $-18$ ppm clearly shows that there is more back donation of electrons from the metal Re to the ligand PPh$_3$ compared to the electron donation of PPh$_3$ to the metal in the complex formation.

Complex (1) was also used as a catalyst for the oxidation of cyclohexane with molecular oxygen as oxidant. The results as confirmed by gas chromatography indicate the formation of cyclohexanol and cyclohexanone in trace amounts. Further
studies are being made for the oxidation of cyclohexane using other oxidants.

According to our studies we can say that the complex (1) is a catalyst or precursor for preparing a new class of rhenium oxo complexes which can be used in catalytic oxidations.

4. Conclusions

The aqua complex \([\text{ReO(OH)}(\text{H}_2\text{O})_3]\text{S}_2\text{O}_8\) has been shown to be a good precursor for preparing a new class of rhenium oxo complexes which can be used in catalytic oxidations. In this respect, the \([\text{ReO(PPh}_3)_n]\text{S}_2\text{O}_8\) can be prepared by an exchange reaction between the aqua complex and free PPh3. Either this complex or the aquo complex 1 can be used as a catalyst for the oxidation of PPh3 to OPPh3 using molecular oxygen as an oxidant.

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