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

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Abstract The aqua rhenium oxocomplex $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ (**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 PPh_3 to OPPh_3 . This proceeds through complex intermediates like $[\text{Re}(\text{PPh}_3)_m]^{3+}$ (**2**), and $[\text{ReO}(\text{PPh}_3)_m]^{3+}$ (**3**). The newly prepared complex (**1**) was also employed as catalyst for catalytic oxidation of cyclohexane. The geometry of $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ has also been optimized in the singlet state by the DFT method with B3LYP level of theory.

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1. Introduction

A major focus of the contemporary interest in the chemistry of the Group VII congener technetium and rhenium reflects the applications of $^{99\text{m}}\text{Tc}$ and ^{186}Re or ^{188}Re in radiodiagnosis and radiotherapy, respectively (Jurisson et al., 1993; Deutsch et al., 1986; Chi et al., 1994). The nuclear properties of $^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6$ h, $\gamma = 140$ keV) are ideal for diagnostic imaging, while the β -emitting isotopes ^{186}Re and ^{188}Re ($t_{1/2} = 90.64$ h, $E_{\text{max}} = 1.1$ MeV, $t_{1/2} = 17$ h, $E_{\text{max}} = 2.1$ MeV, respectively) are promising candidates for therapeutic applica-

tions (Ehrhardt et al., 1990). Rhenium (V) complexes comprise a prominent class of compounds in radiopharmaceutical chemistry. The oxidation state V of rhenium is easily stabilized by a large variety of ligands and it is easily obtained from the reduction of perrhenate (Machura, 2005). A distinctive feature of the most stable Re (V) complexes is the existence of multiple bonds to sulfur, nitrogen and especially oxygen (Davison and Jones, 1982; Blower et al., 1986). There is a considerable interest in the chemistry of inorganic compounds containing an oxygen atom that is multiply bonded to a transition metal in a high oxidation state. These compounds can transfer an oxygen atom to reactants such as phosphines, sulfides and alkenes. For many years they have been the center of interest to those scientists engaged in basic research and to those trying to employ these complexes in catalytic processes. Oxygen atom transfer chemistry has been applied in various reactions of industrial and biological importance, including olefin epoxidation and biomimicking catalysis by cytochrome (Machura and Kusz, 2008). The chemistry of oxorhenium complexes arouses particular interest on these compounds. The oxidation of triphenylphosphine to triphenylphosphine oxide has attracted

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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 $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ (**1**), as well as new Re complex derivatives, $[\text{Re}(\text{PPh}_3)_5]^{3+}$ (**2**) which has been prepared by reduction of **1** with PPh_3 in the ethanolic medium. Further pharmacological and radiochemical studies of these complexes are under investigation.

2. Experimental

2.1. General procedure

All reactions were performed 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 $4000\text{--}400\text{ cm}^{-1}$ with the samples in the form of KBr pellets. Electronic Spectra were measured on a UV-Vis Beckman Du-70 Spectrometer in the range $800\text{--}200\text{ nm}$. ^1H NMR, proton decoupled ^{13}C and ^{31}P NMR spectra were obtained at room temperature in DMSO d_6 or CD_3OD using a JEOL Eclipse400 NMR using TMS for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P $\{^1\text{H}\}$ as external standards. Elemental analysis (H) was performed on a Perkin-Elmer CHN-2400 analyzer. The thermal analysis was carried out using a Perkin-Elmer thermogravimetric analyzer TGA7 in nitrogen atmosphere. The % weight loss was measured from the ambient temperature up to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$. X-ray diffraction patterns of the complex were recorded using a X-ray diffractometer system XRD JDX-3530 with Cu-target.

2.2. Synthesis of $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ (**1**)

Aqueous solution of $\text{Na}_2\text{S}_2\text{O}_6$ (250 mg, 1 mmol) was added dropwise to the stirred solution of NH_4ReO_4 (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 $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ were formed overnight. Yield: 77%.

IR of **1** (KBr, cm^{-1}): 996 s (1055) (ν (Re=O)); 3562 s (3793.3) ($\nu_{\text{str.antisym}}$ (OH)); 3474 s ($\nu_{\text{str.sym}}$ (OH)); 722 s (809) (ν (ReO)). The data in parenthesis is obtained by DFT calculations.

UV-Vis (H_2O , λ_{max} , nm (1 g ϵ)) 225 (3.2).

^1H NMR (DMSO d_6 , δ ppm) OH (s, 4.7), H_2O (4.8).

Anal. Calc. for $\text{ReH}_6\text{O}_{14}\text{S}_2$ (**1**): Re, 38.5; S, 13.2; H, 1.8. Found: *Re, 36.8; *S, 12.9; H, 1.95%. * Were measured by gravimetric measurement.

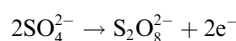
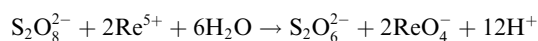
2.3. Computational details

The Gaussian-98 suite of programs (Frisch et al., 2003) was used for the calculations. The geometry optimization of $[\text{Re}(\text{O})(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ in a singlet state was carried out with

the DFT method. The level of theory used to compute the structure was B3LYP/LANL2DZ (Lee et al., 1993). No negative frequency for the optimized structure was revealed from the analysis of hessian, which indicates that the structure was fully optimized. The calculated vibrational frequencies for $[\text{Re}(\text{O})(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ in the infra red spectral range of $200\text{--}4000\text{ cm}^{-1}$ are presented above, together with the experimentally recorded data. The results indicate that the used DFT method and basis set for $[\text{Re}(\text{O})(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ are suitable for obtaining results with satisfactory agreement with the experiment. It should be mentioned that the theoretical values are usually higher than the experimental data. One has to scale the theoretical data by an optimal scaling factor. In our case a good agreement between the theoretical and experimental data was observed. Molecular drawings were obtained using the gaussview98 software package.

3. Results and discussion

The $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ complexes were prepared in good yields by direct reaction between metal salt NH_4ReO_4 and the ligand in the presence of a reducing agent. The complexation reactions were carried out according to the following equations:



The IR spectra $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ displays a strong band assigned to ν (Re=O) at 996 cm^{-1} which are in the range reported for similar mono-oxorhenium complexes ($945\text{--}1067\text{ cm}^{-1}$) Silverstein and Webster, 1996 and the band due to ν (ReO) was recorded at 722 cm^{-1} . A sharp split band in the range $3238\text{--}3562\text{ cm}^{-1}$ 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 $3.2\text{ M}^{-1}\text{ cm}^{-1}$, which is similar to the one reported earlier (Nakamoto, 1970).

^1H 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 $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ 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 H_2O is relatively longer than the expected length found in other rhenium complexes. This indicates that rhenium is weakly bonded to H_2O groups and therefore is labile and may be replaced easily by other ligands.

The calculated charge on the rhenium atom in $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ is considerably lower than the formal charge +5, corresponding to a d^2 configuration of the central ion.

Table 1 The optimized bond lengths (Å) and angles (°) for $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$.

Bond lengths	(Å)	Bond angles	(°)
R(1, 2)	1.702	A(2, 1, 5)	90.102
R(1, 3)	1.861	A(2, 1, 7)	91.091
R(1, 5)	2.155	A(2, 1, 9)	91.097
R(1, 7)	2.095	A(2, 1, 11)	90.187
R(1, 9)	2.095		
R(1, 11)	2.155		

Table 2 Showing atomic charges from the natural population analysis (NPA) for $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$.

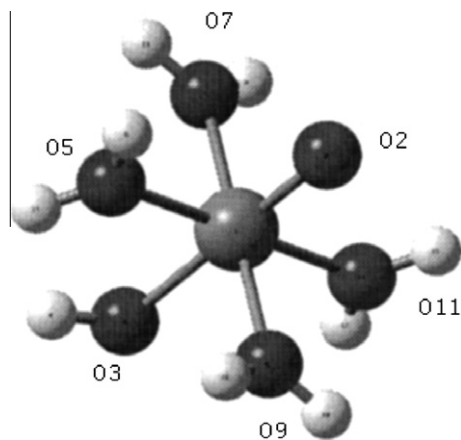
Atom	Charge
Re(1)	1.6737
O(2)	-0.8527
O(3)	-0.9546
O(5)	-0.2154
O(7)	-0.9473

This results from charge donation of H_2O 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 $\text{O}_{\text{H}_2\text{O}(5)}$. Table 2 shows atomic charges for $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$. The charges for O9 and O11 are similar to O7 and O5, respectively.

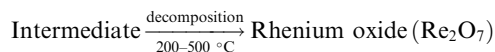
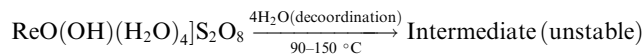
The structure of complex **1** $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ as stabilized by DFT calculations is shown in Fig. 1.

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.

**Figure 1** Molecular structure of $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]^{2-}$ obtained by DFT calculations.

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 Re_2O_7 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.



3.3. Determination of reaction order of decomposition

The Horowitz and Metzger equation, $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature, T_s is given as

$$C_s = (W_s - W_f) / (W_i - W_f) \quad (1)$$

and, was used for the determination of the values of the reaction order (n). Here W_s stands for the remaining weight of the substance at a given temperature T_s , 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_s 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:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{1 - n} \right] = \ln \frac{ART_s^2}{\phi Ea} - \frac{Ea}{RT} + \frac{Ea\theta}{RT_s^2} \quad (2)$$

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

The activation entropy ΔS^* , the activation enthalpy ΔH^* and the free energy of activation ΔG^* were calculated using the following equations (Abu-Eittah et al., 2006; Garcia et al., 1986):

$$\Delta S^* = 2.303R \left[\log \frac{Ah}{KT} \right] \quad (3)$$

$$\Delta H^* = Ea - nRT \quad (4)$$

$$\Delta G^* = \Delta H^* - T_s \Delta S^* \quad (5)$$

where K and h are the Boltzman and Plank constants, respectively. The calculated values of Ea , A , ΔS^* , ΔH^* and ΔG^* for the two decomposition steps are given in Table 4.

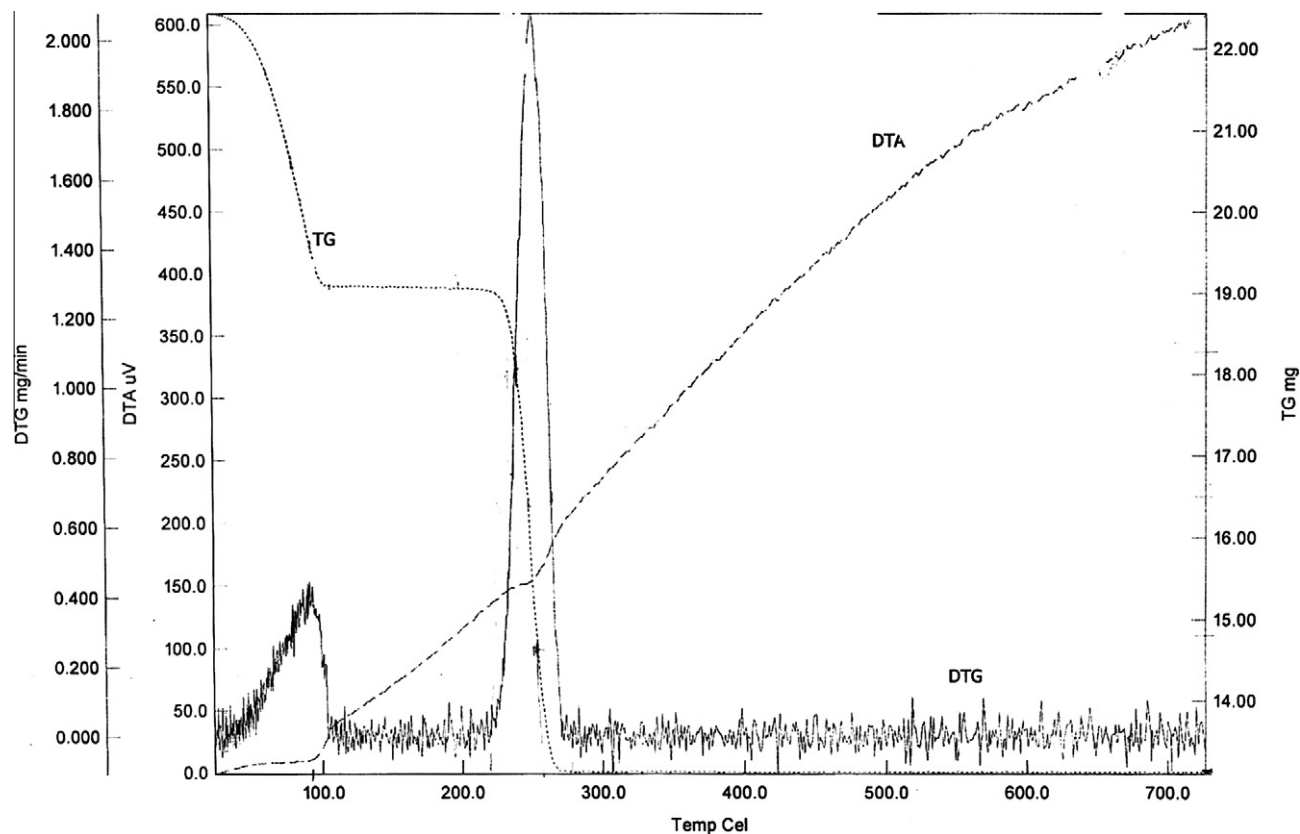
3.4. Applications of aqua rhenium oxocomplex

Use as a catalyst precursor for the catalytic oxidation of PPh_3 and cyclohexane.

Due to the weak nature of the Re-OH_2 bond, aqua complexes are very good starting materials in coordination chemistry. Reaction of (1) with excess PPh_3 in the presence of

Table 3 Thermal data of aqua oxorhenium complex.

Complex	Decomposition behavior		Percent decomp.		Assignment
	Steps	Temp. range (°C)	Calc%	Found%	
[ReO(OH)(H ₂ O) ₄] ₂ S ₂ O ₈	First	90–150	14.9	15.3	Loss of 4H ₂ O
	Second	200–500	30	31.5	Loss of violate

**Figure 2** TG/DTA of complex 1 [ReO(OH)(H₂O)₄]₂S₂O₈ showing the weight loss steps.**Table 4** Kinetic and equilibrium parameters of the thermal decomposition of aqua oxorhenium complex.

Complex	Decomposition step (°C)	<i>E_a</i> (kJ mol ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	ΔH^* (kJ·mol ⁻¹)	ΔG^* (kJ·mol ⁻¹)	ln <i>A</i> (min ⁻¹)
[ReO(OH)(H ₂ O) ₄] ₂ S ₂ O ₈	90–150	116	–165.3	96.5	156	1.4
	200–500	359.4	–205.8	348.2	458	5.8

molecular oxygen was studied by in situ ³¹P{¹H} NMR spectroscopy. In the proposed mechanism the aqua rhenium oxocomplex (1) reacts with triphenylphosphine to form [Re(PPh₃)_{*n*}]³⁺ (2). The formation of complex (2) has been confirmed by spectroscopic studies. Complex (2) reacts with O₂ to form complex (3). The formation of complex [ReO(PPh₃)_{*n*}]³⁺ (3) and OPPh₃ has also been confirmed by spectroscopic studies. The oxygen atom transfer from complex (3) to PPh₃ may be a concerted process with the slow release of the product OPPh₃ as rate determining.

A ³¹P NMR spectrum of complex (3) shows three peaks initially at –18, –4 and 32 ppm, corresponding to PPh₃-complex, PPh₃-free and OPPh₃, respectively, as shown in Fig. 3.

The peak at –18 ppm is due to the Re complex formation with PPh₃. 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 PPh₃ with molecular oxygen resulting in the formation of OPPh₃. 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 PPh₃ compared to the electron donation of PPh₃ 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

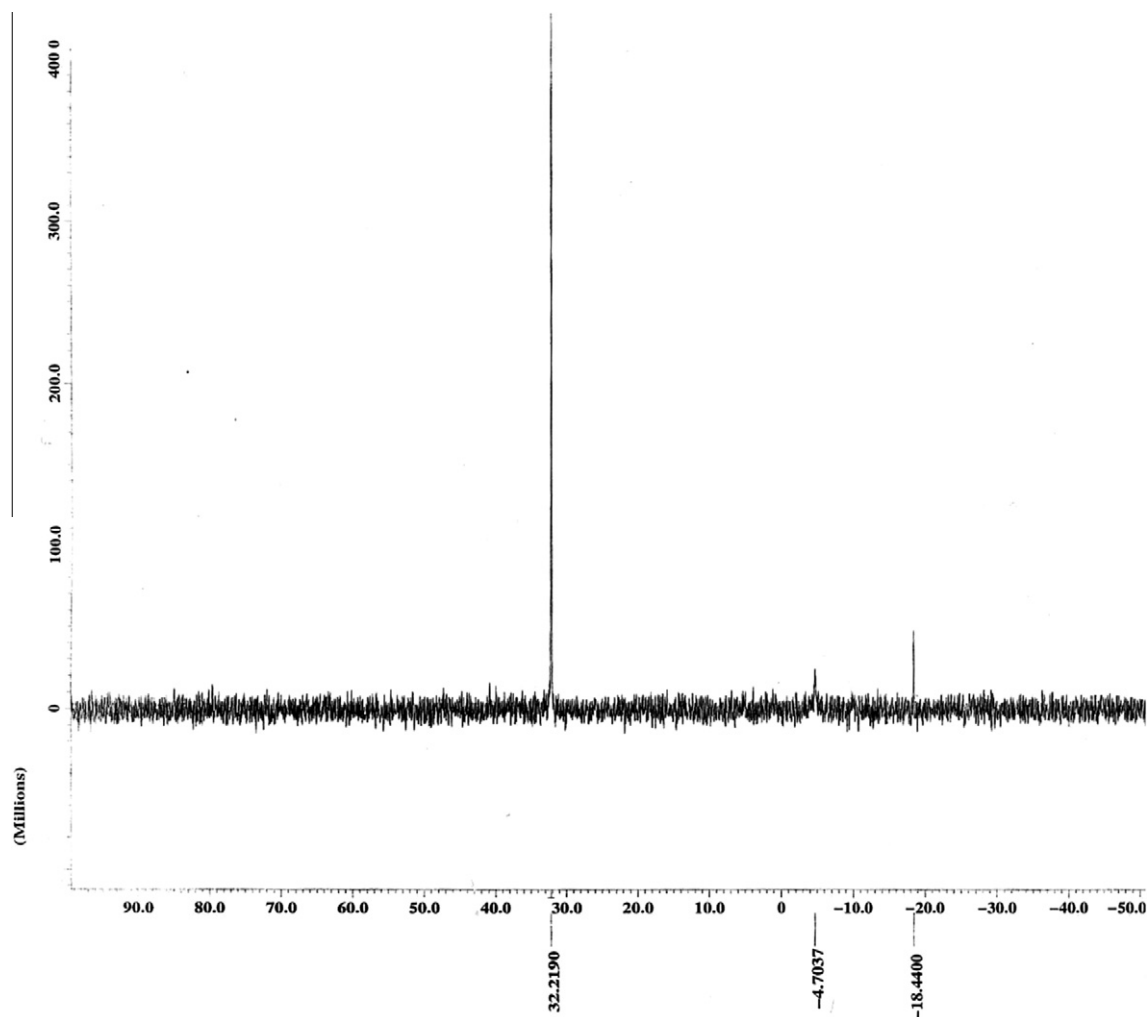


Figure 3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **1** in the presence of excess PPh_3 .

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 $[\text{ReO}(\text{OH})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_8$ 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 $[\text{ReO}(\text{PPh}_3)_n]^{3+}$ can be prepared by an exchange reaction between the aqua complex and free PPh_3 . Either this complex or the aquo complex **1** can be used as a catalyst for the oxidation of PPh_3 to OPPh_3 using molecular oxygen as an oxidant.

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