

# Oxorhenium(V) complexes with quinoline-2-carboxylate ligand. X-ray structure of $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$ and $[\text{ReOBr}_2(\text{quin-2-c})(\text{AsPh}_3)]$ complexes: DFT and TD-DFT calculations for $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$

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## Abstract

Novel  $[\text{ReOX}_2(\text{quin-2-c})(\text{EPh}_3)]$  complexes ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{E} = \text{As}, \text{P}$ ;  $\text{quin-2-c} = \text{quinoline-2-carboxylate ion}$ ) have been prepared by treatment of  $[\text{ReOX}_3(\text{EPh}_3)_2]$  with quinoline-2-carboxylic acid in acetone at room temperature. All the complexes were characterised by IR, UV–Vis spectroscopy and elemental analysis. The crystal and molecular structures have been determined for  $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$  (**1**) and  $[\text{ReOBr}_2(\text{quin-2-c})(\text{AsPh}_3)]$  (**4**). The electronic structure of **1** has been calculated with the density functional theory (DFT) method. The spin-allowed electronic transitions of **1** have been calculated with the time-dependent DFT method.

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**Keywords:** Rhenium oxo complexes; Quinoline-2-carboxylate ligand; X-ray and electronic structure; DFT calculations; NBO analysis

## 1. Introduction

For many years inorganic compounds containing an oxygen atom multiply bonding to a transition metal have been in the centre 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 implicated in various reactions of industrial and biological importance, including olefin epoxidation and catalysis by cytochrome P-450 [1–3].

The chemistry of oxo rhenium complexes arouses particular interest among these compounds. Methyltrioxorhenium and its derivatives are among the most versatile oxidation catalysts known to date [4]. The oxorhenium(V)

chelates  $[\text{ReOCl}_2(\text{O-N})(\text{PPh}_3)]$  with pyridinecarboxylate ligands exhibit a remarkable catalytic activity for the conversion of ethane, under relatively mild conditions, to a mixture of propionic and acetic acids in a single-pot process with various advantages over the industrial ones [5].

Furthermore, the favourable nuclear properties of  $^{186}\text{Re}$  and  $^{188}\text{Re}$  nuclides make the compounds with these radioisotopes useful for applications in radioimmunotherapy [6,7].

In this context, the design, synthesis and reactivity of novel rhenium oxocomplexes has become the aim of several laboratories, including ours.

Previously, we investigated the reactivity of oxorhenium(V) species –  $[\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2]$ ,  $[\text{ReOX}_3(\text{PPh}_3)_2]$  and  $[\text{ReOX}_3(\text{AsPh}_3)(\text{OAsPh}_3)]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) – towards pyrazole, 3,5-dimethylpyrazole, benzotriazole and pyrazine [8]. In this report, we focus on the examinations of the reactions of  $[\text{ReOX}_3(\text{AsPh}_3)_2]$  and  $[\text{ReOX}_3(\text{PPh}_3)_2]$

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with quinoline-2-carboxylic acid. Quinoline-2-carboxylic acid is the biological compound involved in the metabolism of tryptophan. It is a strong chelator providing the donor set similar to that responsible for binding metal ion in PQQ (pyrroloquinilnequinone) cofactor of quinoprotein family [9].

Here, we present synthesis and spectroscopic data for  $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$  (**1**),  $[\text{ReOBr}_2(\text{quin-2-c})(\text{PPh}_3)]$  (**2**),  $[\text{ReOCl}_2(\text{quin-2-c})(\text{AsPh}_3)]$  (**3**) and  $[\text{ReOBr}_2(\text{quin-2-c})(\text{AsPh}_3)]$  (**4**) complexes. X-ray studies have been performed for **1** and **4**, and electronic structure of **1** has been calculated with the density functional theory (DFT). The singlet–singlet electronic transitions of **1** have been calculated with the time-dependent DFT method (TD-DFT method), and the UV–Vis spectra of these complexes have been discussed on this basis.

Currently, density functional theory (DFT) is commonly used to examine the electronic structure of transition metal complexes. It meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes [10]. Recent calculations with TD-DFT method for open- and closed-shell of 5d-metal complexes (including rhenium complexes) have also supported the TD-DFT method to be applicable for such systems giving good assignment of experimental spectra [11,12].

Some theoretical investigations have been carried out on rhenium compounds. The electronic structures of nitrido, oxo, carbonyl, nitrosyl and nitrile rhenium complexes, as well as their spectroscopic properties, bonding and reactivity have been theoretically studied at the HF, MP2, EHT and DFT levels of theory using various basis sets [13–22]. Gancheff and co-workers [15] have performed extended tests of the ability of the B3LYP method in LANL2DZ basis set for rhenium compounds in a geometry optimization and calculation of spectral properties. Although this is not a very extended basis set, its use with DFT has shown to be sufficient for the geometry optimization and calculation of spectral properties. It gives good agreement with the experimental data and its use is justified in the case of large molecules.

## 2. Experimental

### 2.1. General procedure

The reagents used to the synthesis were commercially available and were used without further purification. The  $[\text{ReOX}_3(\text{AsPh}_3)_2]$  and  $[\text{ReOX}_3(\text{PPh}_3)_2]$  complexes were prepared according to the literature methods [23].

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400  $\text{cm}^{-1}$  with the samples in the form of KBr pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–VIS 8500 in the range 1000–180 nm in chloroform solution. Elemental analyses (C,H,N) were performed on a Perkin-Elmer CHN-2400 analyzer.

### 2.2. Preparation of $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$ (**1**)

A mixture of  $[\text{ReOCl}_3(\text{PPh}_3)_2]$  (0.50 g, 0.6 mmol), quinoline-2-carboxylic acid (0.12 g, 0.69 mmol) and acetone (50 ml) was stirred at room temperature for 3 h. Half of the solvent was removed and diethyl ether (50 ml) was added to precipitate the product as a green solid, which was filtered off and dried. Yield: 85%. Crystals suitable for X-ray investigation were obtained by recrystallization from acetonitrile.

*Anal. Calc.* for  $\text{C}_{28}\text{H}_{21}\text{Cl}_2\text{NO}_3\text{PRe}$ : C, 47.53; H, 2.99; N, 1.98. *Found*: C, 47.70; H, 3.06; N, 2.05%.

### 2.3. Preparation of $[\text{ReOBr}_2(\text{quin-2-c})(\text{PPh}_3)]$ (**2**)

A procedure similar to that for  $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$  was used with  $[\text{ReOBr}_3(\text{PPh}_3)_2]$  (0.50 g, 0.52 mmol) and quinoline-2-carboxylic acid (0.10 g, 0.58 mmol). Crystalline precipitate of  $[\text{ReOBr}_2(\text{quin-2-c})(\text{PPh}_3)]$  was collected in 80% yield.

*Anal. Calc.* for  $\text{C}_{28}\text{H}_{21}\text{Br}_2\text{NO}_3\text{PRe}$ : C, 42.22; H, 2.66; N, 1.76. *Found*: C, 42.35; H, 2.72; N, 1.84%.

### 2.4. Preparation of $[\text{ReOCl}_2(\text{quin-2-c})(\text{AsPh}_3)]$ (**3**)

A procedure similar to that for  $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$  was used with  $[\text{ReOCl}_3(\text{AsPh}_3)_2]$  (0.50 g, 0.54 mmol) and quinoline-2-carboxylic acid (0.11 g, 0.64 mmol). Crystalline precipitate of  $[\text{ReOCl}_2(\text{quin-2-c})(\text{AsPh}_3)]$  was collected in 80% yield.

*Anal. Calc.* for  $\text{C}_{28}\text{H}_{21}\text{Cl}_2\text{NO}_3\text{AsRe}$ : C, 44.75; H, 2.82; N, 1.86. *Found*: C, 44.68; H, 2.92; N, 1.85%.

### 2.5. Preparation of $[\text{ReOBr}_2(\text{quin-2-c})(\text{AsPh}_3)]$ (**4**)

A procedure similar to that for  $[\text{ReOCl}_2(\text{quin-2-c})(\text{PPh}_3)]$  was used with  $[\text{ReOBr}_3(\text{AsPh}_3)_2]$  (0.50 g, 0.47 mmol) and quinoline-2-carboxylic acid (0.10 g, 0.58 mmol). Yield: 85%. Crystals suitable for X-ray investigation were obtained by recrystallization from acetonitrile.

*Anal. Calc.* for  $\text{C}_{28}\text{H}_{21}\text{Br}_2\text{NO}_3\text{AsRe}$ : C, 40.02; H, 2.52; N, 1.67. *Found*: C, 40.22; H, 2.63; N, 1.69%.

### 2.6. Crystal structures determination and refinement

The X-ray intensity data of **1** and **4** were collected on a KM-4-CCD automatic diffractometer equipped with CCD detector and graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and absorption correction [24] were applied. The structures were solved by the Patterson method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as “riding” on their parent carbon atoms and assigned isotropic temperature factors equal

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