

DFT calculation and X-ray structure of the $[\text{ReCl}_3(\text{pzH})_3]$ complex

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Abstract

The X-ray structure of a new paramagnetic $[\text{ReCl}_3(\text{pzH})_3]$ complex (pzH = pyrazole) has been determined and its geometric parameters have been examined using the density functional theory (DFT) method. The UV–Vis spectrum of the complex has been discussed on the basis of the electronic transitions of $[\text{ReCl}_3(\text{pzH})_3]$ calculated with the time-dependent DFT method (TDDFT). © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Pyrazole and its derivatives possess two adjacent nucleophilic sites and their steric and electronic properties can be modified by the substituents of the heterocyclic ring. They (i) can act as monodentate, *exo*- or even *endo*-bidentate anionic ligands, (ii) can afford oligomers of different nuclearities depending on the used synthesis methods and (iii) have been shown to possess a rather wide conformational variability [1–4].

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 $[\text{ReOX}_3(\text{AsPh}_3)(\text{OAsPh}_3)]$ (X = Cl or Br) – towards pyrazole (pzH) and 3,5-dimethylpyrazole (3,5-Me₂pzH) under different reaction conditions. The products of these syntheses include (i) mononuclear $[\text{ReOX}_2\{\eta^2\text{-N}_2\text{C}_3\text{H}_3\text{C}(\text{CH}_3)_2\text{O}\}(\text{PPh}_3)]$ complexes with the $\text{C}_3\text{H}_3\text{N}_2\text{C}(\text{CH}_3)_2\text{O}^-$ anion obtained in the addition reaction of pyrazole and acetone, and (ii) dinuclear Re(V) compounds of the types $[\{\text{Re}(\text{O})\text{X}(\text{PPh}_3)\}_2(\mu\text{-O})(\mu\text{-pz})_2]$,

$[\{\text{Re}(\text{O})\text{X}_2(3,5\text{-Me}_2\text{pzH})_2\}_2(\mu\text{-O})]$, $[\{\text{Re}(\text{O})\text{Br}(3,5\text{-Me}_2\text{pzH})\}_2(\mu\text{-O})(\mu\text{-3,5-Me}_2\text{pz})_2]$, $[\{\text{Re}(\text{O})\text{X}(\text{PPh}_3)\}_2(\mu\text{-O})(\mu\text{-3,5-Me}_2\text{pz})_2]$ and $[\{\text{Re}(\text{O})\text{X}(\text{PPh}_3)\}(\mu\text{-O})(\mu\text{-3,5-Me}_2\text{pz})_2\{\text{Re}(\text{O})\text{X}(3,5\text{-Me}_2\text{pzH})\}]$ (X = Cl or Br) [5,6].

Here, we report the synthesis and X-ray structure of $[\text{ReCl}_3(\text{pzH})_3]$ complex (**1**) and the results of DFT calculations for **1**, based on B3LYP theory, carried out by using the GAUSSIAN 03 program package. The UV–Vis spectrum of the title complex is discussed based on the electronic transitions of **1**, calculated using the time-dependent DFT method (TDDFT).

Reports of $[\text{ReX}_3\text{L}_3]$ rhenium complexes with monodentate N-donor ligands (L) are restricted, and the only structurally characterized complexes of this type appear to be *mer*- $[\text{ReFI}_2(\text{py})_3]$ [7], *mer*- $[\text{ReCl}_3(\text{py})_3]$, *mer*- $[\text{ReBr}_3(\text{py})_3]$ [8] and *mer*- $[\text{ReCl}_3(3,5\text{-lut})_3]$ [9].

2. Experimental

2.1. General procedure

The reaction was carried out under argon atmosphere. All solvents were of reagent grade and were used as received. Ammonium perrhenate, Ph_3P and pyrazole (pzH) were purchased from Aldrich and used as

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received. The $[\text{ReOCl}_3(\text{PPh}_3)_2]$ complex was prepared according to the literature method [10].

IR spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 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 800–220 nm in deoxygenated dichloromethane solution. Magnetic susceptibilities were measured at 296 K by the Faraday method. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer.

2.2. Preparation of $[\text{ReCl}_3(\text{pzH})_3] \cdot \text{H}_2\text{O} \cdot \text{HCl}$ ($1 \cdot \text{H}_2\text{O} \cdot \text{HCl}$)

$[\text{ReOCl}_3(\text{PPh}_3)_2]$ (1 g, 1.20 mmol) and pzH (0.54 g, 8 mmol) in benzene (100 cm^3) were refluxed overnight. The color of the reaction mixture changed quickly from yellow-green to dark brown. The volume was condensed to 10 cm^3 and a reddish-brown microcrystalline solid was formed on addition of 100 cm^3 of diethyl ether. The product was washed with EtOH and cold ether, and dried in vacuo. Crystals of $1 \cdot \text{H}_2\text{O} \cdot \text{HCl}$ suitable for X-ray investigation were obtained by recrystallization from CHCl_3 –EtOH. Yield: 55%.

IR (KBr , cm^{-1}) 3406 (m), 3341 (m), 3142 (s), 1618 (w, br), 1513 (w), 1490 (m), 1470 (m), 1405 (m), 1348 (m), 1327 (m), 1265 (m), 1241 (w), 1125 (s), 1106 (s), 1086 (m), 1052 (vs), 910 (m), 783 (s), 702 (w), 603 (m). Calc. for $\text{C}_9\text{H}_{15}\text{N}_6\text{Cl}_4\text{ORe}$: C, 19.61; H, 2.74; N, 15.24. Found: C, 19.73; H, 2.6; N, 15.30%.

2.3. Crystal structure determination and refinement

The X-ray intensity data of $1 \cdot \text{H}_2\text{O} \cdot \text{HCl}$ were collected on a KM-4-CCD automatic diffractometer equipped with a CCD detector with 21 s exposure time, and a half of the Ewald sphere was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of the 5023 strongest reflections. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and numerical absorption corrections [11] were applied. The structure was solved by means of the Patterson method and subsequently completed by difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using a full-matrix, least-squares technique. The hydrogen atoms of the phenyl rings were treated as “riding” on their parent carbon atoms [$d(\text{C}–\text{H}) = 0.96 \text{ \AA}$] and assigned isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent carbon atom. *SHELXS-97* [12], *SHELXL-97* [13] and *SHELXTL* [14] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

Table 1
Crystal data and structure refinement for $1 \cdot \text{H}_2\text{O} \cdot \text{HCl}$

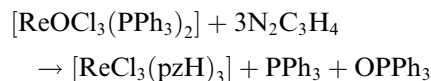
Empirical formula	$\text{C}_9\text{H}_{15}\text{Cl}_4\text{N}_6\text{ORe}$
Formula weight	551.27
Temperature (K)	291(2)
Wavelength (\AA)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (\AA)	7.7451(7)
<i>b</i> (\AA)	8.1581(9)
<i>c</i> (\AA)	14.1257(10)
α ($^\circ$)	75.507(10)
β ($^\circ$)	84.050(8)
γ ($^\circ$)	81.453(9)
Volume (\AA^3)	852.48(14)
<i>Z</i>	2
D_{calc} (Mg/m^3)	2.148
Absorption coefficient (mm^{-1})	7.760
<i>F</i> (000)	524
Crystal size (mm)	0.42 \times 0.21 \times 0.20
θ Range for data collection ($^\circ$)	3.46–25.14
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-15 \leq l \leq 16$
Reflections collected	8672
Independent reflections (R_{int})	3037 (0.0362)
Completeness to 2θ (%)	99.1
Maximum and minimum transmission	0.3046 and 0.1398
Data/restraints/parameters	3037/0/191
Goodness-of-fit on F^2	1.174
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0300$, $wR_2 = 0.0723$,
<i>R</i> indices (all data)	$R_1 = 0.0331$, $wR_2 = 0.0732$
Largest difference peak and hole (e \AA^{-3})	1.508 and -1.387

2.4. Computational details

The GAUSSIAN 03 program [15] was used in the calculations. The geometry optimization was carried out using the DFT method with the use of the B3LYP functional [16,17]. The electronic spectrum was calculated with the TDDFT method [18]. The LANL2DZ basis set [19] was used on the rhenium atom, 6-31G(d) on the chlorine, nitrogen and carbon atoms and 6-31G basis on the hydrogen atoms in the calculations.

3. Results and discussion

Refluxing the $[\text{ReOCl}_3(\text{PPh}_3)_2]$ complex with an excess of pzH in wet benzene under argon atmosphere leads to the isolation of the mononuclear $1 \cdot \text{H}_2\text{O} \cdot \text{HCl}$ complex. The well-known capacity of PPh_3 to interact with the $\text{Re}=\text{O}$ bond in rhenium(V) oxo-complexes explains the course of the reaction between $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and pyrazole:



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