



Coordination chemistry of di-2-pyridylketone. Synthesis, spectroscopic investigations, X-ray studies and DFT calculations of Re(III) and Re(V) complexes

B. Machura^{a,*}, J. Mroziński^b, R. Kruszynski^c, J. Kusz^d

^a Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland

^b Faculty of Chemistry, Wrocław University, F. Joliot-Curie 14 St., 50-383 Wrocław, Poland

^c Department of X-ray Crystallography and Crystal Chemistry, Institute of General and Ecological Chemistry, Lodz University of Technology, 116 Żeromski St., 90-924 Łódź, Poland

^d Institute of Physics, University of Silesia, 4th Uniwersytecka St., 40-006 Katowice, Poland

ARTICLE INFO

Article history:

Received 14 May 2009

Accepted 7 June 2009

Keywords:

Rhenium complexes

Di-2-pyridylketone

X-ray

Electronic structure

DFT and TDDFT calculations

Magnetic measurement

ABSTRACT

The paper presents a combined experimental and computational study of Re(III) and Re(V) complexes containing di-2-pyridylketone and its gem-diol form – [ReCl₃(dpk-N,O)(PPh₃)] (**1**), [ReCl₃(dpk-N,N')(OPPh₃)] (**2**) and [ReOBr₃(dpk-OH)]·2(dpKH⁺Br⁻) (**3**). All the complexes have been characterized spectroscopically and structurally (by single-crystal X-ray diffraction). The complex **2** has been additionally studied by magnetic measurement. The magnetic behavior of **2** is characteristic of mononuclear octahedral Re(III) complex with d⁴ low-spin (³T_{1g} ground state) and arise because of the large spin–orbit coupling ($\zeta = 2500 \text{ cm}^{-1}$), which gives diamagnetic ground state. DFT and time-dependent (TD)DFT calculations have been carried out for [ReCl₃(dpk-N,N')(OPPh₃)] and [ReOBr₃(dpk-OH)], and their UV–vis spectra have been discussed on this basis.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The coordination chemistry of rhenium is a field of current growing interest from various viewpoints. The attention of scientists concentrates on synthetic aspects, structural, physicochemical properties and reactivity, as well as on topics with an applied character such as the development of radiotherapeutic cancer agents, nitrogen fixation and catalysis [1].

The ¹⁸⁶Re (1.07 MeV β-emitter, *t*_{1/2} 90 h) and ¹⁸⁸Re (2.12 MeV β-emitter, *t*_{1/2} 17 h) are among the most attractive isotopes for applications in targeted radionuclide therapy [2,3]. The diazenido and dinitrogen rhenium complexes are important in view of their significance in the field of nitrogen fixation [4–6]. Methyltrioxorhenium is one of the most versatile catalysts for olefin oxidation reactions, aldehyde olefination and olefin metathesis [7,8]. The *mer,trans*-[ReOCl₃(PPh₃)₂] and its derivatives catalyze the oxidation of sulfides to sulfoxides, thiols to disulfides and catalyze oxygen-transfer from sulfoxides to phosphines [8]. The [ReOCl₂(O-N)(PPh₃)] chelates with pyridinecarboxylate ligands exhibit a remarkable catalytic activity for the carboxylation of ethane by CO in the presence of K₂S₂O₈ to a mixture of propionic and acetic acids in a single-pot process [9]. The [CH₃ReO(pic)₂] complex is an active precursor in olefin oxidation and forms epoxides in a two-phase H₂O₂–H₂O/CH₂Cl₂ system [10].

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

Here, we present synthesis, spectroscopic investigation, crystal and molecular structure of three rhenium complexes with di-2-pyridylketone (dpk) and its gem-diol. Investigation into the properties of the ligand di-2-pyridyl ketone was first reported in 1967 by Osborne and McWhinnie and numerous reactions of di-2-pyridyl ketone with transition metals have been studied to date. The dpk can act as a bidentate, tridentate or bridging ligand. As a chelate di-2-pyridylketone can bind to the metal center ion *via* one of two modes: either through the two nitrogen atoms located in the pyridine rings or through one pyridyl nitrogen and the carbonyl oxygen [11]. The majority of metal complexes with dpk are coordinated in the N,N-mode. The N,O-coordination mode of dpk has been confirmed in [RuCl₂(DMSO)(dpk-N,O)] [12] and [Ru(Cp)(dpk-N,O)] [13].

After the initial coordination with the metal ion, the carbonyl oxygen atom of the dpk ligand can become subject to nucleophilic attack by water or alcohols, and the formation of (2-py)₂C(OH)₂ or (2-py)₂C(OR)(OH) has been frequently observed. The deprotonated gem-diol or hemiacetal form of (2-py)₂CO coordinates to the metal centers as N,N',O chelates or as bridging ligands. The monoanionic form usually bridge two or three metal ions, while the dianionic form can bridge as many as five metal sites [11].

The rhenium complexes with di-2-pyridylketone have been studied relatively little [14,15]. It prompts us to explore the

* Corresponding author.

E-mail addresses: basia@ich.us.edu.pl (B. Machura), jmroz@wchuwr.chem.uni.wroc.pl (J. Mroziński), rafal.kruszynski@p.lodz.pl (R. Kruszynski).

reactivity of $[\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2]$ towards the dpk ligand. The $[\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2]$ complex has proven to be useful precursor in the synthesis of Re(III) compounds [16–18]. The $[\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2]$ also easily reacts with di-2-pyridylketone to give $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ (**1**) with rarer N,O-coordination of dpk ligand. The solid $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ can be handled in air without significant degradation, but rapid isomerisation with oxidation of coordinated PPh_3 occurs in organic solvents at room temperature in the presence of atmospheric oxygen. In fact, the starting purple solution of $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ in chloroform turns to dark red and crystals of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ (**2**) with N,N'-coordination of dpk ligand are deposited.

N,N',O coordination mode of monoanionic form of $(2\text{-py})_2\text{CO}$ has been confirmed in the $[\text{ReOBr}_3(\text{dpk-OH})]\cdot 2(\text{dpkH}^+\text{Br}^-)$ (**3**), isolated from the reaction of $[\text{ReOBr}_3(\text{PPh}_3)_2]$ with excess of di-2-pyridylketone in acetone in air.

The structures of all the complexes $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ (**1**), $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ (**2**) and $[\text{ReOBr}_3(\text{dpk-OH})]\cdot 2(\text{dpkH}^+\text{Br}^-)$ (**3**) have been proven by X-ray diffraction. The complexes $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ and $[\text{ReOBr}_3(\text{dpk-OH})]$, which are stable in solution, have been also studied by UV–vis spectroscopy. The electronic spectra of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ and $[\text{ReOBr}_3(\text{dpk-OH})]$ have been discussed in detail using the density functional theory (DFT) and time-dependent DFT (TDDFT) calculations.

Currently the 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 [19]. Recent studies have also supported the TDDFT method to be applicable for open- and closed-shell of 5d-metal complexes giving good assignment of experimental spectra [20–22].

2. Experimental

2.1. General procedure

The reagents used to the synthesis were commercially available and were used without further purification. The $[\text{Re}(\text{MeCN})\text{Cl}_3(\text{PPh}_3)_2]$ [16] and $[\text{ReOBr}_3(\text{PPh}_3)_2]$ [23] complexes were prepared according to the literature methods.

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

2.2. Preparation of $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ (**1**)

$[\text{Re}(\text{MeCN})\text{Cl}_3(\text{PPh}_3)_2]$ (0.5 g, 0.58 mmol) and di-2-pyridylketone (0.11 g, 0.60 mmol) in CH_2Cl_2 (80 cm^3) were heated under argon atmosphere for 5 h. The starting material gradually dissolved and the color of the reaction solution became blue-purple. The volume of the reaction solution was condensed to 10 cm^3 and allowed to cool to room temperature. Dark pink microcrystalline precipitate was formed and filtered off.

IR (KBr; ν/cm^{-1}): 1646(s) $\nu_{\text{C=O}}$; 1608(w), 1590(m), 1572(m) and 1538(w) ν_{CN} and $\nu_{\text{C=C}}$.

Anal. Calc. for $\text{C}_{29}\text{H}_{23}\text{Cl}_3\text{N}_2\text{OPRe}$: C, 47.13; H, 3.14; N, 3.79. Found: C, 47.61; H, 3.42; N, 3.62%.

2.3. Preparation of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ (**2**)

A solution of $[\text{ReCl}_3(\text{dpk-N,O})(\text{PPh}_3)]$ in chloroform was stood for several days in air and dark red crystals were deposited.

IR (KBr; ν/cm^{-1}): 1649(vs) $\nu_{\text{C=O}}$; 1609(m), 1591(m), 1575(m) and 1542(w) ν_{CN} and $\nu_{\text{C=C}}$; 1135(vs) and 1119(vs) $\nu_{\text{Re=O}}$.

Anal. Calc. for $\text{C}_{29}\text{H}_{23}\text{Cl}_3\text{N}_2\text{O}_2\text{PRe}$: C, 46.13; H, 3.07; N, 3.71. Found: C, 46.79; H, 3.30; N, 3.45%.

2.4. Preparation of $[\text{ReOBr}_3(\text{dpk-OH})]\cdot 2(\text{dpkH}^+\text{Br}^-)$ (**3**)

A mixture of $[\text{ReOBr}_3(\text{PPh}_3)_2]$ (0.50 g, 0.52 mmol), di-2-pyridylketone (0.28 g, 1.52 mmol) and acetone (100 ml) was stirred at room temperature for 12 h. Half of the solvent was removed and diethyl ether (50 ml) was added to precipitate the product as green solid, which was filtered off and dried. Yield 85%. Crystals suitable for X-ray investigation were obtained by recrystallization from acetonitrile.

IR (KBr; ν/cm^{-1}): 1683(vs) $\nu_{\text{C=O}}$; 1599(s), 1579(s) and 1520(s) ν_{CN} and $\nu_{\text{C=C}}$; 958(s) $\nu_{\text{Re=O}}$.

Anal. Calc. for $\text{C}_{33}\text{H}_{27}\text{Br}_4\text{N}_6\text{O}_5\text{Re}$: C, 36.25; H, 2.49; N, 7.69. Found: C, 36.89; H, 2.37; N, 7.39%.

2.5. Crystal structures determination and refinement

The X-ray intensity data of **1**, **2** and **3** were collected on a KM-4-CCD automatic diffractometer equipped with CCD detector and graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). 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 adjacent atoms and assigned isotropic temperature factors equal 1.2 times the value of equivalent temperature factor of the aromatic parent atoms and equal 1.5 times the value of equivalent temperature factor of the oxygen atom (OH). SHELXS97 [25], SHELXL97 [26] and SHELXTL [27] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

2.6. Computational details

The ground states geometries of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ and $[\text{ReOBr}_3(\text{dpk-OH})]$ were optimized without any symmetry restrictions with the DFT method using the hybrid B3LYP functional of GAUSSIAN-03 [28–30].

The calculations were performed using ECP basis set LANL2DZ [31] with an additional *d* and *f* function with the exponent $\alpha = 0.3811$ and $\alpha = 2.033$ [32] for rhenium and the standard 6-31G basis set for other atoms. For chloride, bromide, oxygen, nitrogen and phosphorous atoms, diffuse and polarization functions were added [33–38]. Vibrational frequencies of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ and $[\text{ReOBr}_3(\text{dpk-OH})]$ were calculated to ensure that optimized geometries represented minima.

The electronic spectra of $[\text{ReCl}_3(\text{dpk-N,N}')(\text{OPPh}_3)]$ and $[\text{ReOBr}_3(\text{dpk-OH})]$ were calculated with the TDDFT method, and the solvent effect (acetonitrile) was simulated using the polarizable continuum model with the integral equation formalism (IEF-PCM) [39–42].

Natural bond orbital (NBO) calculations for $[\text{ReOBr}_3(\text{dpk-OH})]$ were performed with the NBO code [43] included in GAUSSIAN-03.

2.7. Magnetic measurement

Magnetization measurements of polycrystalline samples were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5-type) at a magnetic field of 0.5 T over the temperature range $1.8\text{--}300\text{ K}$. Magnetization measurements versus magnetic field (0–5 T) were made at 2 K.

Download English Version:

<https://daneshyari.com/en/article/1337521>

Download Persian Version:

<https://daneshyari.com/article/1337521>

[Daneshyari.com](https://daneshyari.com)