

## ORIGINAL PAPER

# Synthesis of $[\text{Re}_2\text{Cl}_4(\text{O})_2(\mu\text{-O})(3,5\text{-lut})_4]$ and investigation of its structure via X-ray and spectroscopic measurements and DFT calculations

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A combined experimental and computational study of the dinuclear rhenium(V) complex containing  $(\text{ReO})_2(\mu\text{-O})$  core is presented in this article. The solid-state  $[\text{Re}_2\text{Cl}_4(\text{O})_2(\mu\text{-O})(3,5\text{-lut})_4]$  ( $3,5\text{-lut} = 3,5\text{-dimethylpyridine}$ ) complex was characterised structurally (by single crystal X-ray diffraction) and spectroscopically (by IR, NMR, UV-VIS). The electronic structure was examined using the density functional theory (DFT) method. The spin-allowed electronic transitions were calculated using the time-dependent DFT method, and the UV-VIS spectrum was discussed.

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## Introduction

The coordination chemistry of rhenium is currently attracting interest from various perspectives. Rhenium(V) complexes comprise a prominent class of compounds in radiopharmaceutical chemistry. They have a wide range of applications because  $^{186}\text{Re}$  and  $^{188}\text{Re}$  emit  $\beta$  particles which have therapeutically useful energies (Sagnou et al., 2011; Aufort et al., 2011; Zhu et al., 2012; Chiotellis et al., 2012). Rhenium complexes are also structural models of their less easily-handled technetium analogues, which are useful in nuclear medicine (Sagnou et al., 2011; Chiotellis et al., 2012). In addition, many rhenium compounds catalyse oxygen atom transfer reactions (Espenson, 2005), synthesise mixed acetals from carbonyl compounds and diols (Krompiec et al., 2012) and deoxygenate epoxides to alkenes (Sousa & Fernandes, 2011). Most of these rhenium complexes contain a  $\text{Re(V)O}$  core. Other investigations of rhenium compounds are associated with their unique electrochemical (Schrebler et al., 2001), photophysical and photochemical properties (Liu et al., 2013), crucial for a number of potential

applications, as well as some already introduced into practice.

This paper investigates the reaction of  $[\text{ReCl}_2(\eta^2\text{-N}_2\text{COPh-N',O})(\text{PPh}_3)_2]$  with 3,5-dimethylpyridine (3,5-lut) and presents a new method of synthesis and the spectroscopic data for the complex  $[\text{Re}_2\text{Cl}_4(\text{O})_2(\mu\text{-O})(3,5\text{-lut})_4]$  with the chloride ions and 3,5-lut molecules in the cis geometry. The experimental studies were accompanied computationally by density functional theory (DFT) calculations. Currently, DFT is commonly used to examine the electronic structure of transition metal complexes. It meets the requirements of being accurate, easy to use and sufficiently rapid to allow the study of relatively large molecules of transition metal complexes. Finally, the time-dependent density functional theory (TD-DFT) was used to calculate the electronic absorption spectra. Based on a molecular orbital scheme, these results made possible interpretation of the UV-VIS spectra obtained at the experimental level. Additional information on bonding between the rhenium atom and oxo ligand and 3,5-lut was obtained by natural bond orbital (NBO) analysis.

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