Synthesis, structure, spectroscopic properties, electrochemistry, and DFT correlative studies of trans-[Ru(P-P)Cl₂] complexes

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ABSTRACT
Five trans-[Ru(P-P)Cl₂] complexes were prepared by reacting RuCl₃(PPh₃)₃ with P-P ligands (P-P = 3-benzyl-1,3-bis(diphenyolphosphino)propane (hppp); (1); 1,3-bis(diphenyolphosphino)propane (dppp); (2); 1,2-bis(diphenyolphosphino)ethane (dpe); (3); 1,1-bis(diphenyolphosphino)ethane (dpeppp); (4); 1,2-bis(diphenyolphosphino)ethylene (depe); (5)). The complexes were characterized by elemental analysis, IR, 1H, 13C and 31P{1H}NMR, FAB-MS and TG/DTA. These Ru(II) complexes showed Ru(III)/Ru(II) quasi-reversible redox couple. The molecular structures of the complexes 1 and 3 were determined by X-ray crystallography, and their spectroscopic properties were studied. Another polymorph of 3 was reported in literature. the reported polymorph of 3 in this work crystallizes in P1 space group, whereas, the previously reported polymorphs crystals in C2/c space group. The two complexes adopt a distorted trans octahedral coordination and ruthenium(II) ions are located on a crystallographic centre of symmetry. Based on the optimized structures, computational investigations were carried out in order to determine the electronic structures of the complexes. The electronic spectra of 1 and 1* in dichloromethane were calculated with the use of time-dependent DFT methods, and the electronic spectra of the transitions were correlated with the molecular orbitals of the complexes.

1. Introduction

Ruthenium(II) complexes with polynodentate phosphines ligands have received much attention in the last decades due to their application in the field of homogenous catalysis [1,2]. Several complexes of the general formula cis- and trans-[M(P-P)X₂] (X = Cl, I; M = Ru, Os) were prepared by Chitt and Hayter [3,4]. These complexes, trans-[Ru(P-P)Cl₂] could be used as starting materials to prepare bi- and pronuclear complexes [5,6]. Classical procedures for the syntheses of these complexes require the reflux conditions in acidic media [7] or the aqueous solution of K[RuCl₃(H₂O)] [8]. Poor yields of complexes are obtained by these preparation procedures. For this reason, a study of the electronic structures of such complexes is valuable as a mean to predict their properties [9-11].

In this paper, we present the synthesis, crystal, molecular, the electronic structures, and the spectroscopic characterization of five ruthenium(II) complexes with diphosphine ligands. The trans-[Ru(P-P)Cl₂] complexes, (P-P = (hppp); 3-benzyl-1,3-bis(diphenyolphosphino)propane (1); (dppp) = 1,3-bis(diphenyolphosphino)propane (2); (dpe) = 1,2-bis(diphenyolphosphino)ethane (3); (dpeppp); 1,1-bis(diphenyolphosphino)ethane (dpeppp); (4); 1,2-bis(diphenyolphosphino)ethylene (depe); (5)), were prepared from the reaction RuCl₃(PPh₃)₃, and the corresponding P-P ligand. These trans complexes have a poor solubility in many organic solvents. The solubility can be improved by modification of the diphosphine backbone chelating ligand with alkyl group. Hcpp is a newly prepared diphosphine ligand to improve the solubility of the trans-[Ru(P-P)Cl₂] complexes. To probe the effect of the size of chelating ring of P-P on the electronic behavior trans-[RuCl₃(P-P)₃] complexes. In this work, we present and discuss the spectroscopic (IR, UV-Vis, 1H NMR and 31P{1H}NMR) and electrochemical (cyclic voltammetry) behavior of 1-5, and report the X-ray structures for 1 and 3. The absorption spectrum of complex 1 and 1* in dichloromethane have been modeled by time-dependent density functional theory (TD-DFT) using a mixed basis set, M06-2X/6-31+G(d,p) to correlate experimental findings with theoretical predictions.

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