Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polyhedron 23 (2004) 2013–2020
POLYHEDRON
www.elsevier.com/locate/poly

Heterobimetallic complexes of palladium(II) and platinum(II) bridged by the ligand 5-phenyl-1,3,4-oxadiazole-2-thione

Othman H. Amin [a], Lamaan J. Al-Hayaly [b], Subhi A. Al-Jibori [c], Talal A.K. Al-Allaf [d,*]

[a] Department of Chemistry, College of Science, University of Salahaddin, Erbil, Iraq
[b] Department of Chemistry, College of Education, University of Tikrit, Tikrit, Iraq
[c] Department of Chemistry, College of Science for Women, University of Tikrit, Tikrit, Iraq
[d] Department of Chemistry, College of Basic Sciences, Applied Science University, Shafa Badran, Amman 11931, Jordan

Received 12 May 2004; accepted 18 May 2004

Abstract

The complexes $[ML_2A_2]$ or $[ML_2B]$ where M = Pd or Pt, L = 5-phenyl-1,3,4-oxadiazole-2-thione ion, A = tertiary monophosphines and B = tertiary diphosphines have been used effectively to prepare bimetallic complexes of the type $[A_2M(\mu\text{-}L)_2M'Cl_2]$ or $[BM(\mu\text{-}L)_2M'Cl_2]$, where M′ = Co, Pd or $SnCl_2$. The prepared complexes were characterized by elemental analysis, magnetic susceptibility, IR and UV–Vis spectral data. $^{31}P\text{–}\{^1H\}$ NMR data have been applied to characterize the produced linkage isomers.

Keywords: Palladium; Platinum; Heterobimetallic; Phosphine; Oxadiazole ligand complexes

1. Introduction

The metal complexes of some heterocyclic thiones attract much attention. The interactions of heavy metals such as platinum and gold with N,S-donor atoms have been recognized for their anticancer properties with the potential to develop metal based drugs [1–6]. Recently, some research works involving platinum(II) and palladium(II) ions with 8-thiotheophylline and dppm to give homo- and heterobimetallic complexes have been published [7,8]. Other related works on platinum(II) or (IV) complexes with tertiary phosphines and ligands containing sulfur have been also published recently [9,10]. However, metal complexes containing bis-tertiary phosphines and heterocyclic-2-thiones are rare [11].

In our recent work [12,13], we reported the preparation of some palladium(II) and platinum(II) complexes containing mixed ligands; tertiary monophosphines or diphosphines and 5-phenyl-1,3,4-oxadiazole-2-thione (LH). We found that the tertiary monophosphines or diphosphines reacted with the chelated complexes of the above ligand (L) to give complexes in which L behaves as a monodentate ligand coordinated to the metal centre through either S, N or mixture of both (Fig. 1).

In the present work, we used the uncoordinated end of the ligand (L) in the complexes $[ML_2A_2]$ and $[ML_2B]$ to build up some new types of heterobimetallic complexes bridged by L, i.e., $[A_2M(\mu\text{-}L)_2M'Cl_2]$ and $[BM(\mu\text{-}L)_2M'Cl_2]$, where M = Pt or Pd; M′ = Co, Pd or $SnCl_2$; A = $PMePh_2$; B = $Ph_2P(CH_2)_nPPh_2$ {$n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb} and L = 5-phenyl-1,3,4-oxadiazole-2-thione (–H) (Fig. 1). To the best of our knowledge, this work is novel.

2. Experimental

2.1. General

$^{31}P\text{–}\{^1H\}$ NMR spectra were performed in the laboratories of Prof. Dr. Wilhelm Keim, Insitute for Techische Chemie der RWTH Achen, Worringer Weg 1, D-52074 Achen, Germany. IR spectra were recorded on a PYE-Unicam SP3-300s spectrophotometer in the 200–4000 cm^{-1} range using CsI discs. Electronic spectra were

* Corresponding author. Tel.: +962-6-5609999; fax: +962-6-5232899.
E-mail address: talal_al_allaf@hotmail.com (T.A.K. Al-Allaf).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.05.006

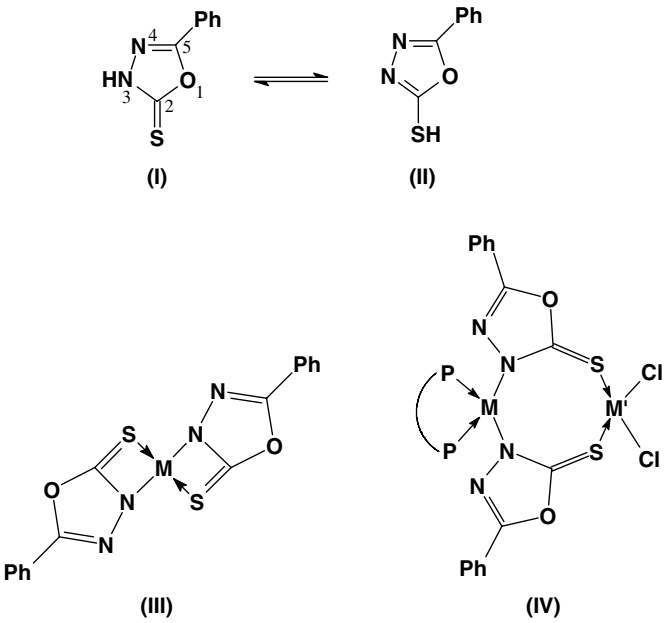

Fig. 1. The ligand 5-phenyl-1,3,4-oxidiazole-2-thione (LH), its tautomeric forms (I) and (II) and the suggested structure of its bis(chelated) complexes (III) and the bridging bimetallic complexes (IV), M = Pd or Pt, M′ = Co, Pd or $SnCl_2$, P···P = 2PMePh$_2$, dppm, dppe, dppp or dppb.

obtained using a Perkin–Elmer lambda 9 spectrophotometer. Elemental analyses were carried out on a CHN Analyzer, type 1106 (Carlo Erba). Magnetic measurements were recorded on a Bruker BH6 instrument at room temperature following the Faraday method. Conductivity measurements were made on a conductivity meter type CDM 83 70. Melting points were measured on an Electrothermal 9300 melting point apparatus.

2.2. Starting materials

The compounds K_2PtCl_4, $Na_2PdCl_4 \cdot 3H_2O$, $PdCl_2$, $CoCl_2$, $SnCl_4 \cdot 5H_2O$, $PMePh_2$, dppm, dppe, dppp and dppb were commercial products and used as supplied. The ligand 5-phenyl-1,3,4-oxadiazole-2-thione (LH) its potassium salt (LK) [14], *trans*-[$PdCl_2$ $(DMSO)_2$], *cis*-[$PtCl_2(DMSO)_2$] [15], [PdL_2]$\cdot H_2O$, [PtL_2], [PdL_2 (dppm)]$\cdot H_2O$, [PtL_2(dppm)], [PdL_2(dppe)], [PtL_2(dppe)] [12], [$PdL_2(PMePh_2)_2$] and [$PtL_2(PMePh_2)_2$] [13] were prepared according to the literature.

2.3. [PdL_2(dppp)] (**4**) and [PdL_2(dppb)] (**5**)

These complexes were prepared by a method similar to that reported for the preparation of [PdL_2-(dppm)]$\cdot H_2O$ [12].

2.4. [PtL_2(dppp)] (**9**) and [PtL_2(dppb)] (**10**)

These complexes were prepared by a method similar to that reported for the preparation of [PtL_2(dppm)] [12].

2.5. [$(PMePh_2)_2Pd(\mu$- L)$_2CoCl_2$]$\cdot 2H_2O$ (**11**)

Solid $CoCl_2$ (0.05 g, 0.38 mmol) was added to a solution of [$PdL_2(PMePh_2)_2$] (0.15 g, 0.17 mmol) in chloroform (15 ml). The yellow solution turned green. The mixture was stirred at room temperature for ca. 10 h. The unreacted $CoCl_2$ was removed by filtration and the green filtrate was evaporated to dryness. Diethylether was added and the green solid was filtered off and dried under vacuum (yield, 0.13 g, 75%).

The following complexes were prepared and isolated by a similar method: **13**, **17**, **20**, **23**, **25**, **28** and **31**.

2.6. [$(PMePh_2)_2Pd(\mu$-L)$_2PdCl_2$] (**12**)

Solid *trans*-[$PdCl_2(DMSO)_2$] (0.13 g, 0.38 mmol) was added with stirring to a solution of [$PdL_2(PMePh_2)_2$] (0.2 g, 0.23 mmol) in chloroform (15 ml). The mixture was stirred at room temperature for ca. 8 h, then filtered. The filtrate was evaporated to dryness and diethylether was added. The orange–brown solid thus formed was filtered off and dried in vacuum (yield, 0.23 g, 95%).

The following complexes were prepared and isolated by a similar method: **15**, **18**, **21**, **24**, **26**, **29** and **32**.

2.7. [$(PMePh_2)_2Pd(\mu$-L)$_2SnCl_4$] (**13**)

Solid $SnCl_4 \cdot 5H_2O$ (0.07 g, 0.22 mmol) was added with stirring to a clear yellow solution of [$PdL_2(PMePh_2)_2$] (0.14 g, 0.16 mmol) in chloroform (12 ml). The mixture was stirred at room temperature for ca. 10 h, then filtered. The filtrate was evaporated to dryness