



# Copper(II) and palladium(II) complexes with tridentate NSO donor Schiff base ligand: Synthesis, characterization and structures



Sujit Baran Kumar <sup>a,\*</sup>, Ankita Solanki <sup>a</sup>, Suman Kundu <sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, 390002, Gujarat, India

<sup>b</sup> Dept. of Chemistry, R.K.M. Residential College, Narendrapur, Kolkata, 700103, India

## ARTICLE INFO

### Article history:

Received 6 February 2017

Received in revised form

18 April 2017

Accepted 20 April 2017

Available online 21 April 2017

### Keywords:

Mononuclear

Copper(II)

Palladium (II)

NSO donor ligand

Spectra

Structures

## ABSTRACT

Mononuclear copper(II) complex [CuL<sub>2</sub>] and palladium(II) complexes [Pd(X)L] where X = benzoate(bz) or salicylate(sal) and HL = 2-(methylthio)phenylimino)methyl)phenol, a Schiff base ligand with NSO coordination sites have been synthesized and characterized by microanalyses, IR, UV–Visible spectra, conductivity measurement and magnetic studies. Crystal structures of all the complexes have been solved by single crystal X-ray diffraction studies and showed that there are two molecules in a unit cell in the [CuL<sub>2</sub>] complex - one molecule has square planar geometry whereas second molecule has distorted square pyramidal geometry and palladium(II) complexes have distorted square planar geometry.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Schiff bases have been used as versatile chelating ligand in the synthesis of transition metal complexes because of their ease of preparation and structural variation. Schiff base containing transition metal complexes have been investigated extensively because they have wide application in the fields of biology and catalysis [1–10]. Metal complexes with Schiff base containing N and O donor atoms derived from aromatic amine and salicylaldehyde have been studied extensively and there are many compounds reported in the literature. Transition metal complexes with Schiff base chelating ligand containing hetero N, S and O donor atoms are very interesting because compounds with NSO donor atoms have biological and catalytic activity and there are many reports on the catalytic and bioactivity of metal complexes with NSO coordinate ligand [11–17]. There has been considerable interest in palladium complexes with Schiff base ligand because of their potential catalytic and biological activity [18–23]. As properties of the metal complexes depend on the coordination environment around the metal centre, we are interested to see the coordination behaviour of NSO donor ligand in the copper(II) and palladium(II) complexes.

In this paper, we report on the synthesis, characterization and

structures of mononuclear copper(II) complex [CuL<sub>2</sub>] and palladium(II) complexes of the type [Pd(X)L] where HL = 2-(methylthio)phenylimino)methyl)phenol, a tridentate N, S and O donor atoms containing ligand and X = benzoate or salicylate.

## 2. Experimental

### 2.1. Materials

All chemicals and solvents used were analytical grade reagents. 2-Methylthioaniline, Pd(CH<sub>3</sub>COO)<sub>2</sub> (Aldrich) and salicylaldehyde (Loba) were reagent grade and used as received. 2-(methylthio)phenylimino)methyl)phenol (HL) was synthesized by refluxing the mixture of 2-methylthioaniline and salicylaldehyde in ethanol. Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was prepared by reaction of cupric carbonate with dilute HClO<sub>4</sub> acid, followed by slow evaporation of the solution.

### 2.2. Instruments

The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer. The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. UV–Vis spectra (1200–190 nm) were recorded on a Shimadzu 3600 in CH<sub>3</sub>CN solution. Solution conductivity were measured in CH<sub>3</sub>CN solution using Equip-Tronics conductivity

\* Corresponding author.

E-mail addresses: [sujit\\_baran@yahoo.com](mailto:sujit_baran@yahoo.com), [sujit.kumar-chem@msubaroda.ac.in](mailto:sujit.kumar-chem@msubaroda.ac.in) (S.B. Kumar).

meter (model no. EQ-660A). Room temperature magnetic susceptibility of powder sample was measured by Guoy balance.

### 2.3. Syntheses of complexes

#### 2.3.1. Synthesis of complex [CuL<sub>2</sub>] (**1**)

A methanol solution (10 mL) of ligand HL (0.244 g, 1.0 mmol) was added drop wise to a stirring methanol solution (10 mL) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.185 g, 0.5 mmol) and stirring was continued for 3 h. The solution was filtered and the filtrate was kept for slow evaporation. Dark green coloured crystals were obtained from the filtrate after 5 days.

Yield. (0.160 g, 50%). Found. C = 61.68, H = 4.40, N = 5.12%. Anal calc for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>CuO<sub>2</sub>S<sub>2</sub>: C = 61.36, H = 4.38, N = 5.11%. IR (KBr pellet) cm<sup>-1</sup>; ν(C=N) 1604 s. UV–Vis spectra: λ<sub>max</sub>/nm (ε<sub>max</sub>/mol<sup>-1</sup>cm<sup>-1</sup>). 679(127), 398(5969), 231(25563), Λ<sub>M</sub> (Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>) = 14. μ<sub>eff</sub> = 1.80 BM.

#### 2.3.2. Synthesis of complex [Pd(bz)L] (**2**)

A solution of ligand HL (0.061 g, 0.25 mmol) in acetonitrile (10 mL) was added drop by drop to an acetonitrile solution (10 mL) of Pd(CH<sub>3</sub>COO)<sub>2</sub> (0.056 g, 0.25 mmol) with stirring. To this, a solution of benzoic acid (0.25 mmol) in acetonitrile (10 mL) was added and stirring was continued for 3 h. Filtered the solution and the solution was kept for slow evaporation. Orange coloured crystals were obtained from the solution after 5 days. Yield. 0.075 g (63%). Found C = 53.70, H = 3.60, N = 2.90%. Anal calc for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub>PdS; C = 53.68, H = 3.62, N = 2.98%. IR (KBr pellet) cm<sup>-1</sup>; ν(C=N), 1606s; ν((Pd–N), 479. UV–Vis spectra: λ<sub>max</sub>/nm(ε<sub>max</sub>/mol<sup>-1</sup>cm<sup>-1</sup>). 447(7061), 317(14110), 242(35420).

#### 2.3.3. Synthesis of complex [Pd(sal)L] (**3**)

The complex was synthesized by following the similar procedure to that of **2**, but salicylic acid was used in place of benzoic acid. Yield. 0.082 g (67%). Found C = 51.93, H = 3.55, N = 2.78%. Anal calc for C<sub>21</sub>H<sub>18</sub>NO<sub>4</sub>PdS; C = 51.87, H = 3.70, N = 2.88%. IR (KBr pellet) cm<sup>-1</sup>; ν(C=N), 1607s; ν(Pd–N), 479. UV–Vis spectra. λ<sub>max</sub>/nm(ε<sub>max</sub>/mol<sup>-1</sup>cm<sup>-1</sup>). 446 (6077), 318 (11812), 227 (35590).

### 2.4. X-ray crystallography

Crystals for X-ray diffraction of the compounds **1**, **2** and **3** were obtained through slow evaporation of the solution. Single crystal X-ray diffraction intensity measurements were performed on Oxford X-CALIBUR-S diffractometer equipped with CCD detector using Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) for complex **1** and Cu-K<sub>α</sub> radiation (λ = 1.54184 Å) for complexes **2** and **3**. The reflection were measured in the range of 3.71–28.09° for complex **1**, 4.68–88.79° for complex **2** and 4.065–73.03° for complex **3**. Data reduction was carried out using the program CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [24]. An absorption correction based on multi-scan method was applied [25]. The structure was solved by direct methods and refinement was performed by the full-matrix least-square technique on F<sup>2</sup> using the programs SHELXS-97 and SHELXL-97 respectively [26]. All calculations were carried out using WinGX system Ver-1.64 [27]. All hydrogen atoms were located from difference Fourier map and treated as riding. All non-hydrogen atoms were refined with anisotropic displacement coefficients (See Table 1).

## 3. Results and discussion

### 3.1. Synthesis

Mononuclear copper(II) complex [CuL<sub>2</sub>] was readily obtained

with good yield (~50%) by the reaction of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with the ligand HL in 1:2 mol ratio in methanol at room temperature [Scheme 1]. The molecular composition of the complex was supported by micro analyses, IR and solution conductivity measurement. Molar conductivity measurement of the complex in CH<sub>3</sub>CN solution (~10<sup>-3</sup>M) shows that the complex has very low molar conductivity (Λ<sub>M</sub> ~10 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>), indicating the complex is neutral and no counter anion is present. Infrared spectrum of the complex also indicate the absence of ClO<sub>4</sub><sup>-</sup> ion in the complex. Single crystal X-ray diffraction study of the copper(II) complex shows there are two molecules in the unit cell—one molecule has square planar geometry where the ligand acts as bidentate and another molecule has distorted square pyramidal geometry where one ligand acts as bidentate ligand with N,O coordination mode but another ligand acts as tridentate with N, S and O coordination mode. The structure and bioactivities of the ternary five coordinated copper(II) complexes with this NSO donor ligand and nitrogen containing heterocycle ligand is reported in the literature [11,28,29]. The complex is moderately soluble in organic solvents such as acetonitrile, methanol, ethanol, dichloromethane, acetone etc.

Mononuclear palladium(II) complexes of the type [Pd(X)L] were readily obtained in good yield (65%) by the reaction of Pd(CH<sub>3</sub>COO)<sub>2</sub>, ligand HL and HX (where HX = salicylic acid/benzoic acid) in 1:1:1 mol ratio in acetonitrile at room temperature. Orange coloured crystals of [Pd(X)L] were obtained by slow evaporation of acetonitrile solution of the complexes. Both the complexes have slightly distorted square planar geometry. The Schiff base ligand L acts as tridentate monoprotic NSO coordinate ligand in both the complexes. The microanalysis data of the two complexes are found to be consistent with their molecular compositions. There is no change in composition even after adding excess benzoic/salicylic acid. Molar conductivity measurements in CH<sub>3</sub>CN solution show the complexes are neutral. The complexes are soluble in common organic solvents like dichloromethane, methanol, acetonitrile etc.

### 3.2. IR data

The IR spectra of the complexes were assigned by comparing the IR spectra of the ligand HL. The IR spectrum of all the complexes exhibit one strong band at 1604 cm<sup>-1</sup> correspond to ν(C=N) of imine and the absence of ligand's phenolic –OH band in the region of 3320 cm<sup>-1</sup> in the compounds confirming the coordination of phenolic-OH with metal centre in the complexes. Infrared spectra of both complexes **2** and **3** are nearly identical. For both the compounds, one weak band exhibited at 479 cm<sup>-1</sup> due to ν(Pd–N) [30] and one strong absorption band exhibited at 1376 and 1335 cm<sup>-1</sup> for the complexes **2** and **3** respectively, due to asymmetric stretching vibration of monodentate –COO<sup>-</sup> group confirming the coordination of acid ligand with palladium(II) ions. For [Pd(sal)L], the phenolic-OH is not coordinated to the palladium centre and therefore, salicylic acid acts as monodentate ligand and coordinate only through oxygen atom of carboxylate ion. This was confirmed by single crystal X-ray diffraction study of the complex **3**. This type of non-coordination of phenolic-OH group in the complexes was reported in the literature [31]. Finally, coordination of ligand with metal atoms were confirmed by single crystal X-ray diffraction studies.

### 3.3. UV–vis spectra

The UV–Vis spectra of both the complexes were recorded in the range of 200–1100 nm in CH<sub>3</sub>CN. A broad absorption band observed at 679 nm with ε = ~131 mol<sup>-1</sup> cm<sup>-1</sup> for complex **1** which is attributed to d-d transition. For palladium(II) complexes, both the

Download English Version:

<https://daneshyari.com/en/article/5160796>

Download Persian Version:

<https://daneshyari.com/article/5160796>

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