Inorganica Chimica Acta 363 (2010) 1707–1712

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

The syntheses, characterizations, X-ray crystal structures and properties of Cu(I) complexes of a bis-bidentate schiff base ligand

Anindita Mukherjee[a], Rajesh Chakrabarty[b], Seik Weng Ng[c], Goutam Kumar Patra[a,*]

[a] *Department of Chemistry, Vijoygarh Jyotish Ray College, Jadavpur, Kolkata 700 032, India*
[b] *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India*
[c] *Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

ARTICLE INFO

Article history:
Received 7 August 2009
Received in revised form 25 November 2009
Accepted 4 December 2009
Available online 4 January 2010

Keywords:
Schiff bases
Bis-bidentate ligands
N-donor ligands
Copper(I) complex
Crystal structure
Electrochemistry
Photophysics

ABSTRACT

Bis-bidentate Schiff base ligand **L** and its two mononuclear complexes [Cu**L**(CH_3CN)$_2$]ClO_4 (**1**) and [Cu**L**(PPh_3)$_2$]ClO_4 (**2**) have been prepared and thoroughly characterized by elemental analyses, IR, UV–Vis, NMR spectroscopy and X-ray diffraction analysis. In both the complexes the metal ion auxiliaries adopt tetrahedral coordination environment. Their reactivity, electrochemical and photophysical behavior have been studied. Complex **1** shows reversible $Cu^{II/I}$ couple with potential 0.74 V versus Ag/AgCl in CH_2Cl_2. At room temperature **L** is weakly fluorescent in CH_2Cl_2, however in Cu(I) complexes **1** and **2** the emission in quenched.

1. Introduction

Schiff bases are significant class of compounds which can be used in a variety of studies, such as organic synthesis, catalyst and drug design [1–3] and models for active sites of metalloenzymes [4]. They are the most versatile group of chelators for facile preparation of metal–organic hybrid materials [5–10], single molecule based magnets [11–16], highly porous materials [17,18], optoelectronic devices [19–21], and sensors [22–24]. Rational design of organic ligand plays a vital role in assembling diverse architectures in the area of supramolecular chemistry [25–27]. Polydentate diazine ligands containing N–N bridge fragments can produce a variety of structural types, such as helices, polygons, polyhedra and oligomers [28–32,5] due to the free rotation of the metal-coordination planes around the N–N single bond. Polyvinyl chloride membrane electrode based on zinc complex of butane-2,3-dione bis(salicylhydrazone) are widely used as thiocyanate sensor. This can further be used in the titration of thiocyanate in saliva and urine sample [33,34]. The continued interest in coordination chemistry of Cu(I) is due to the fact that copper(I) complexes of polydentate ligands are the model compounds that can mimic or even ideally duplicate some of the important physical and chemical properties of Cu(I) containing proteins and also because of their diverse structural and physicochemical properties [35]. Cu(I) salts catalyses many organic transformations like aryl guanidinylation [36], amination [37], photocycloaddition [38], oxidation of adrenaline [39], ferrocytrochrome *c* oxidation [40] and also olefin cyclopropanation [41].

Herein we report the synthesis of a flexible bis-bidentate ligand butane-2,3-dione bis(salicylhydrazone), **L** along with two of its Cu(I) complexes **1** and **2** (Scheme 1). The complexes have been characterized by various spectroscopic as well as with single crystal X-ray diffraction method. The reactivity, electrochemical and photophysical properties of the complexes **1** and **2** have also been studied.

2. Experimental

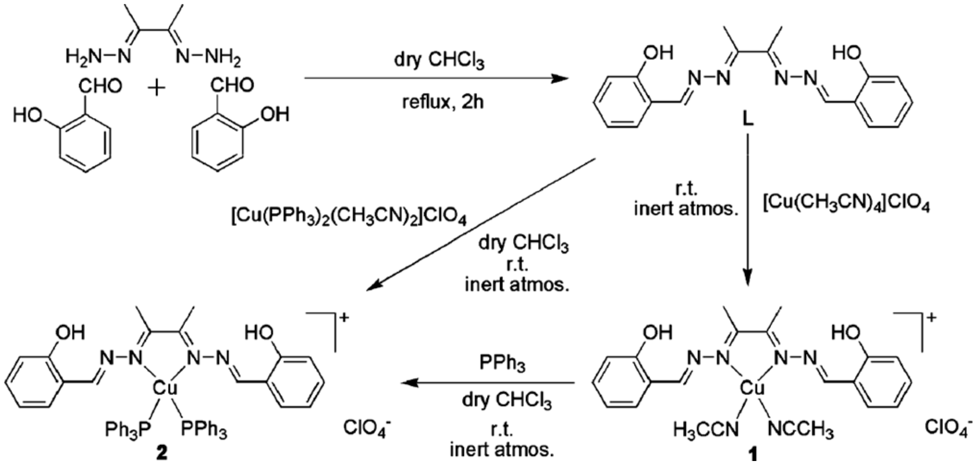
2.1. General procedures

2,3-Butane dihydrazone and [Cu(CH_3CN)$_4$]ClO_4 were synthesized by reported procedures [42,43]. All other reagents were procured commercially and used without further purification. Copper was estimated gravimetrically as CuSCN. Microanalyses were carried out using a Perkin–Elmer 2400II elemental analyzer. The melting point was determined by an Electrothermal IA9000 series digital melting point apparatus and is uncorrected.

---

* Corresponding author. Tel.: +91 33 24124082.
E-mail address: patra29in@yahoo.co.in (G.K. Patra).

0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.12.009



Scheme 1. Synthesis of ligand and copper(I) complexes.

Fourier transform infrared (FTIR) and solution electronic spectra were recorded on Nicolet Magna-IR (Series II) and Shimadzu UV-160A spectrophotometers, respectively. ^{1}H NMR and Electrospray ionization mass (ESI-MS) measurements were made using a Bruker Advance 400 MHz and Finnigan LCQ Decaxp MAX mass spectrometer, respectively. Fluorescence spectra were recorded on a Perkin–Elmer LS50B spectrophotometer. All electrochemical measurements were made in dichloromethane on a BAS (Epsilon model) having a three-electrode setup consisting of a glassy carbon (polished with alumina before measurement) working, platinum wire auxiliary and a Ag/AgCl reference electrodes. Oxygen was rigorously removed from the dichloromethane solutions of the samples by purging with dry argon gas of high purity. Under the experimental conditions employed here, the ferrocene–ferrocenium couple appears at 0.42 V versus Ag/AgCl in 1 M KCl with an ΔE_p of 110 mV at a scan rate of 50 mV s^{-1}.

2.2. Synthesis of butane-2,3-dione bis(salicylhydrazone) (**L**)

2,3-Butane dihydrazone (0.57 g, 5 mmol) was dissolved in 50 mL of anhydrous chloroform. To this solution, 1.22 g (10 mmol) of freshly distilled salicylaldehyde was added. The resulting bright yellowish mixture was refluxed for 2 h, maintaining a dry atmosphere. Within 30 min of reflux orange yellow solid started separating out. After 2 h, the reaction mixture was cooled to room temperature and the product was collected by filtration. Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform solution. Yield, 1.44 (90%); mp > 250 °C. ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 11.81 (s, 2H), 8.68 (s, 2H), 7.39 (m, 4H), 7.10 (d, 2H), 6.90 (t, 2H), 2.43 (s, 6H). FTIR/cm^{-1} (KBr): 506(s), 562(w), 647(m), 713(s), 757(vs), 790(m), 896(w), 981(w), 1019(s), 1040(s), 1123(m), 1160(m), 12099s), 1271(vs), 1361(s), 1406(m), 1447(m), 1497(m), 1547(s), 1581(m), 1612(vs), 1626(vs), 2407(w), 2779(w), 2851(m), 2945(w), 3431(wb). ESI MS: 323.2 (LH$^+$, 100%). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$): 238 (15 080); 307 (21 450); 366 (10 970). *Anal.* Calc. for $C_{18}H_{18}N_4O_2$: C, 67.05; H, 5.63; N, 17.39. Found: C, 67.07; H, 5.69; N, 17.32%.

2.3. Synthesis of [CuL(CH$_3$CN)$_2$]ClO$_4$ (**1**)

0.161 g (0.5 mmol) of **L** was dissolved in 75 ml of dry chloroform. Argon was purged through the solution for 15 min and to this orange yellowish solution 0.165 g (0.5 mmol) of [Cu(CH$_3$CN)$_4$]ClO$_4$ was added at a time. The reddish brown reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Then the reddish brown clear solution was cooled under argon. Reddish brown crystals suitable for X-ray analysis separated out, which were filtered out, and dried in *vacuo* over fused CaCl$_2$. Yield, 0.185 g (65%). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 11.1 (s, 2H), 8.74 (s, 2H), 7.40 (m, 6H), 6.95 (d, 2H), 2.43 (s, 6H), 2.18 (s, 6H), 2.04 (s, 6H). FTIR/cm^{-1} (KBr): 636(s), 765(s), 905(m), 1091(vs), 1121(vs), 1160(m), 1209(m), 1227(vs), 1315(s), 1375(m), 1470(vs), 1553(vs), 1608(s), 1642(vs), 2235(s), 2931(w), 3435(wb). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$): 322 (18 050); 432 (7500). Elemental analysis of the powdered material was performed. *Anal.* Calc. for $C_{22}H_{24}N_6CuClO_6$: C, 46.54; H, 4.26; N, 14.81; Cu, 11.20. Found: C, 46.56; H, 4.35; N, 14.88; Cu, 11.27%.

2.4. Synthesis of [CuL(PPh$_3$)$_2$]ClO$_4$ (**2**)

0.161 g (0.5 mmol) of **L** was dissolved in 75 mL of dry chloroform. Argon was purged through the solution for 15 min. Then to this orange yellow solution 0.365 g (0.5 mmol) of [Cu(PPh$_3$)$_2$(CH$_3$CN)$_2$]ClO$_4$ was added with stirring. The color of the reaction mixture gradually changed from yellow to red. The red reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Red solid separated out. It was filtered off, washed with little amount of chloroform and dried in *vacuo* over fused CaCl$_2$. Yield, 0.388 g (76%). Red crystals suitable for X-ray analysis were grown by slow evaporation of its methanol solution. ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 8.72 (s, 2H), 7.49 (m, 4H), 7.44–7.39 (m, 30H) 6.89 (t, 4H), 2.43 (s, 6H). FTIR/cm^{-1} (KBr): 506(s), 518(vs), 526(s), 549(vs), 620(s), 645(s), 667(s), 695(s), 725(s), 744(s), 761(s), 805(s), 890(m), 958(m), 995(vs), 1028(vs), 1070(s), 1089(vs), 1129(vs), 1158(vs), 1125(vs), 1276(s), 1312(m), 1329(m), 1434(vs), 1451(vs), 1461(m), 1478(s), 1508(m), 1564(vs), 1583(m), 1609(vs), 1627(vs), 1649(vs), 2925(m), 3080(s), 3227(w), 3432(wb). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$): 312 (10 500); 443 (8250). *Anal.* Calc. for $C_{54}H_{48}N_4P_2CuClO_6$: C, 64.20; H, 4.79; N, 5.55; Cu, 6.30. Found: C, 64.28; H, 4.88; N, 5.63; Cu, 6.36%.

2.5. X-ray crystallography

X-ray diffraction data for crystalline samples of **1**, **2** and **L** were collected using Mo Kα radiation (0.71073 Å) on a Bruker KAPPA APEX II diffractometer. The SMART [44] program was used for collecting frames of data, indexing the reflections, and determination of lattice parameters; SAINT [44] program for integration of the intensity of reflections and scaling; SADABS [45] program for absorption correction. The structures were solved by direct methods (SHEL-