

Synthesis and spectral studies of cadmium(II) complexes derived from di-2-pyridyl ketone and N^4 -phenylsemicarbazide: First structural report of a cadmium(II) complex of semicarbazone

T.A. Reena, E.B. Seená, M.R. Prathapachandra Kurup*

Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

Received 7 August 2007; accepted 18 February 2008

Available online 26 March 2008

Abstract

A new semicarbazone (HL) based on di-2-pyridyl ketone and its three cadmium(II) complexes $[\text{CdL}(\text{CH}_3\text{COO})]_2 \cdot 2\text{CH}_3\text{OH}$ (**1**), $\text{Cd}(\text{HL})\text{Br}_2$ (**2**) and $[\text{Cd}_2\text{L}_2\text{N}_3]_2 \cdot \text{H}_2\text{O}$ (**3**) were synthesized and characterized by different physicochemical techniques. The complex, $[\text{CdL}(\text{CH}_3\text{COO})]_2 \cdot 2\text{CH}_3\text{OH}$ (**1**) is having a dimeric structure. In complexes **1** and **3**, the ligand moieties are coordinated as monoanionic (L^-) forms and in complex **2**, the ligand is coordinated as neutral (HL) one. The coordination geometry around cadmium(II) in **1** is distorted octahedral, as obtained by X-ray diffraction studies.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Crystal structure; IR spectra; Cadmium(II) complex; Di-2-pyridyl ketone; Semicarbazone

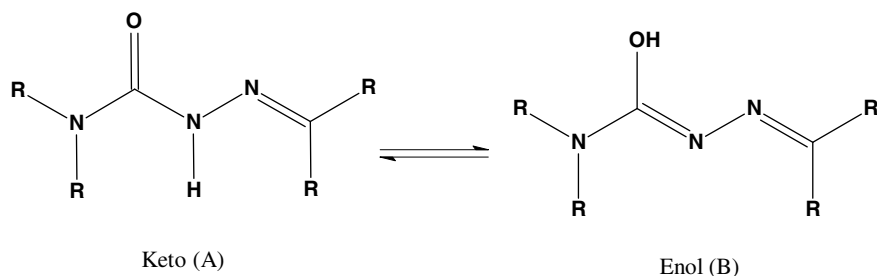
1. Introduction

Semicarbazones are compounds having the formula $\text{R}_2\text{C}=\text{N}-\text{NH}-(\text{CO})-\text{NH}_2$ formally derived by condensation of aldehyde or ketone with semicarbazide. A great number of studies have been devoted to the search for derivatives of semicarbazides. In recent years there has been considerable interest in semicarbazones due to their wide spectrum of biological applications [1]. These materials have been used as drugs whose action is attributed to their ability to form metal complexes [2]. It was reported that many metal complexes of semicarbazones have antimicrobial and antitumor activities [3]. A number of aryl semicarbazones displayed anticonvulsant activity in the maximal estroschock (MES) and subcutaneous pentylenetetrazole (SCPTZ) screens when administered intraperitoneally to mice [4].

Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Semicarbazones exist in two tautomeric forms, keto (A) and enol (B) (Scheme 1). The coordination possibilities in the semicarbazones are increased if the substituents of the aldehyde or ketone include additional donor atoms. The π -delocalization and the configurational flexibility of their molecular chain can give rise to a great variety of coordination modes [5]. In some metal complexes, semicarbazone can act as a tridentate ligand with a donor atom apart from ketone/enol oxygen atom and azomethine nitrogen.

Cadmium is well known to form complexes with acetates and carboxy-ligands to yield both charged and neutral compounds [6]. The possibility of forming structures with higher coordination numbers has resulted in the observation of unusual coordination geometries about the metal atom and formation of polymeric species [7]. Here we report three cadmium(II) complexes of N^4 -substituted semicarbazone ligand derived from di-2-pyridyl ketone and N^4 -phenylsemicarbazide. There are no previous

* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595.
E-mail address: mrp@cusat.ac.in (M.R. Prathapachandra Kurup).



Scheme 1.

structural reports on cadmium(II) complexes of a semicarbazone according to the best of our knowledge [5].

2. Experimental

2.1. Materials

Di-2-pyridyl ketone (Aldrich) was used as received. $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O}$ and NaN_3 were commercial products of higher grade (Aldrich) and solvents were purified according to standard procedures. Elemental analyses were carried out using a vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT-IR-5300 spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$ using KBr pellets. Electronic spectra were recorded on a Cary 5000 version 1.09 UV–Vis–NIR spectrophotometer using solutions in DMF. The ^1H and ^{13}C NMR spectra were recorded using Bruker DRX 500, with CDCl_3 as solvent and TMS as standard at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India.

2.2. Synthesis of di-2-pyridyl ketone-*N*⁴-phenyl semicarbazone (HL)

The semicarbazone was synthesized by the following method. A methanolic solution of di-2-pyridyl ketone (0.184 g, 1 mmol) was mixed with *N*⁴-phenylsemicarbazide (0.151 g, 1 mmol) in methanol and three drops of glacial acetic acid. The reaction mixture was refluxed for 2 h. On slow evaporation, colorless crystalline compound formed was filtered, washed with ether and recrystallized from ethanol and dried over P_4O_{10} *in vacuo*. Melting point = $160\text{ }^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz, δ from TMS): 13.37 (s, N^4H , 1H), 8.78 (d, C^1H , 1H, $J = 6.4$ Hz), 8.66 (d, C^{11}H , 1H, $J = 7.2$ Hz), 8.37 (s, N^5H , 1H), 7.87 (t, C^3H , 1H, $J = 7$), 7.79 (t, C^9H , 1H, $J = 6$), 7.56 (d, C^4H , 1H, $J = 8$), 7.51 (d, C^8H , 1H, $J = 8$), 7.34 (m, $\text{C}^{2,10,14,15,17,18}$, 6H), 7.07 (t, C^{16}H , 1H, $J = 7$). ^{13}C NMR (CDCl_3 , δ from TMS): C(1), 148.68, C(2), 123.87, C(3), 136.81, C(4), 126.24, C(5), 151.96, C(6), 152.95, C(7), 148.0; C(8), 128.89, C(9), 137.98, C(10), 123.87, C(11), 140.28, C(12), 156.20, C(13), 137.98, C(14), 123.75, C(15), 123.38, C(16), 119.60, C(17), 123.38, C(18), 123.75 (see Fig. 1).

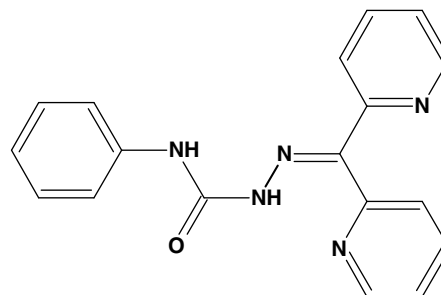


Fig. 1. Molecular structure of HL.

2.3. Synthesis of $[\text{CdL}(\text{CH}_3\text{COO})]_2 \cdot 2\text{CH}_3\text{OH}$ (1)

A methanolic solution of HL (0.317 g, 1 mmol) and $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.266 g, 1 mmol) were mixed and heated under reflux for 5 h. On slow evaporation, yellow crystals were obtained, which were separated, washed with ether and dried over P_4O_{10} *in vacuo*.

2.4. Synthesis of $\text{Cd}(\text{HL})\text{Br}_2$ (2)

A methanolic solution of HL (0.317 g, 1 mmol) and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (0.344 g, 1 mmol) were mixed and heated under reflux for 5 h. On slow evaporation, yellow coloured solid was resulted which were separated, washed with ether and dried over P_4O_{10} *in vacuo*.

2.5. Synthesis of $\text{Cd}_2\text{L}_2(\text{N}_3)_2 \cdot \text{H}_2\text{O}$ (3)

A methanolic solution of HL (0.317 g, 1 mmol) and $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.266 g, 1 mmol) were mixed and heated under reflux for 2 h and then added methanolic solution of NaN_3 (0.065 g, 1 mmol). The resulting mixture was refluxed for 4 h. On slow evaporation yellow colored solid formed was separated, washed with ether and dried over P_4O_{10} *in vacuo*.

2.6. X-ray crystallography

Single crystals of compound **1** suitable for X-ray analysis were obtained from its methanolic solution and were found to be orthorhombic with a space group '*pbca*'. X-ray diffraction measurements were carried out on Crysalis CCD diffractometer with graphite-monochromated

Download English Version:

<https://daneshyari.com/en/article/1340493>

Download Persian Version:

<https://daneshyari.com/article/1340493>

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