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Synthesis and Spectral Aspects of Mixed Ligand Cadmium (II) Chelates of an ONS Donor Thiosemicarbazone

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Abstract

Cadmium(II) complexes have been synthesized by the reaction of cadmium(II) acetate with an ONS donor thiosemicarbazone and heterocyclic bases like 1,10-phenanthroline, 2,2'-bipyridine as coligands. They were physico-chemically characterized by CHNS analyses, conductivity measurements, infrared and electronic spectral studies.

Keywords: Cd^{II} complexes; thiosemicarbazone.

Introduction

Thiosemicarbazones with potential donor atoms in their structural skeleton fascinate coordination chemists with their versatile chelating behavior. The coordinating ability of thiosemicarbazones to both transition and main group metallic cations is attributed to the extended delocalization of electron density over -NH-C(S)-NH-N= system which is enhanced by substitution at the N(4)

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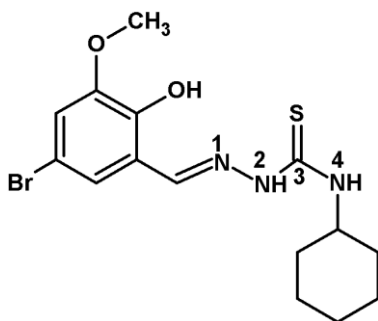
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position. They have been studied for a considerable period of time for their biological properties.

Cadmium is a soft, malleable, ductile, bluish-white divalent metal and it prefers +2 oxidation state in most of its compounds. Although cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms. Cadmium is used as a barrier to control neutrons in nuclear fission [1]. In molecular biology, cadmium is used to block voltage-dependent calcium channels from fluxing calcium ions, as well as in hypoxia research to stimulate proteasome-dependent degradation of Hif-1 α [2]. There is substantial interest in the coordination chemistry of cadmium complexes because of the toxic environmental impact of cadmium. The mobilization and immobilization of cadmium in the environment, in organisms and in some technical processes (such as in ligand exchange chromatography) have been shown to depend significantly on the complexation of the metal center by chelating nitrogen donor ligands [3]. Complexes of Cd(II) with different molecular architectures with the same trimesate ligands showing strong fluorescence have been reported [4]. The cadmium(II) ion has recently been found to serve as the catalytic center in a newly discovered carbonic anhydrase [5].

Thiosemicarbazones and their complexes have been subject of interest in numerous studies because of their chemical and biological activities and they possess a wide range of beneficial medicinal properties that are often attributed to their chelating ability with metal ions. Complexes of Group 12 metals, zinc and cadmium, can provide an interesting range of stoichiometries depending on the preparative salts [6].

In this work we report the syntheses and spectral characterization of cadmium(II) chelates of 5-bromo-3-methoxysalicylaldehyde-N(4)-cyclohexylthiosemicarbazone (H₂L). Structure of the thiosemicarbazone (H₂L) which has been reported [7] is shown below.



5-Bromo-3-methoxysalicylaldehyde-N(4)-cyclohexylthiosemicarbazone (H₂L)

Experimental

Materials

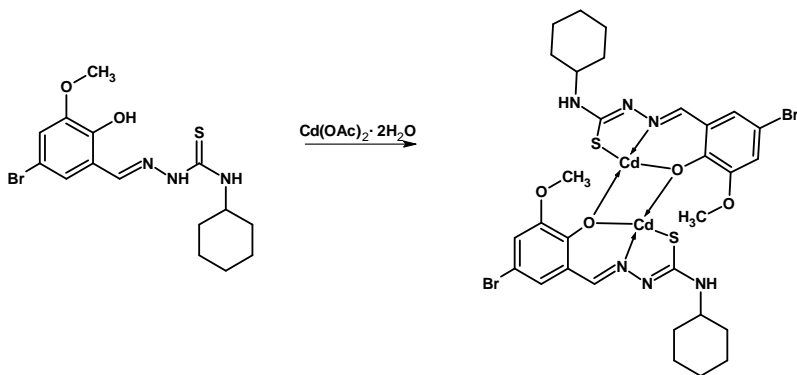
Cadmium(II) acetate dihydrate (E-Merck), 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) were used as received.

Syntheses of the complexes

[(CdL)₂] (1)

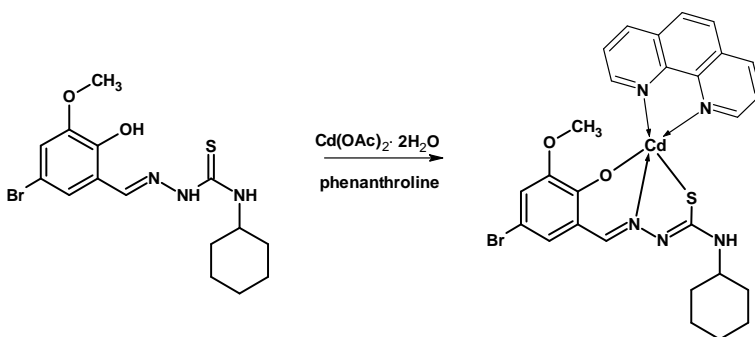
This complex was synthesized by refluxing a solution of H₂L (0.193 g, 0.5 mmol) in 1:1 (v/v) mixture of DMF and methanol with a methanolic solution of Cd(OAc)₂·2H₂O (0.133 g, 0.5 mmol) for 3 hours. The complex formed was filtered, washed with methanol and dried *in vacuo*.

Colour: Light yellow, m.p. 260°C, yield: 60%



[CdL(phen)] (2) and [CdL(bipy)] (3)

Methanolic solution of cadmium(II) acetate dihydrate (0.133 g, 0.5 mmol) was added to a stirred mixture of H₂L (0.193 g, 0.5 mmol) in DMF and methanol (1:1 v/v) and the respective heterocyclic base (phenanthroline/bipyridine) in methanol. The resultant homogenous yellow solution was refluxed for three hours. The yellow product obtained was filtered, washed with methanol and dried *in vacuo*. The scheme for the synthesis of [CdL(phen)] (2) is shown below.



[CdL(phen)] (2) Colour: Yellow, m.p. 212°C, yield: 67%

[CdL(bipy)] (3) Colour: Light yellow, m.p. 246°C, yield: 69%

Results and Discussion

We synthesized and characterized three cadmium(II) complexes which are found to be stable. The complexes are soluble in organic solvents like DMF and DMSO. The thiosemicarbazones coordinate to the central metal ion in the thioiminolate form in all the complexes as evidenced by the IR spectral data. The compound [(CdL)₂] (1) is dimeric in nature while others are monomeric mixed ligand metal chelates. The isolation of X-ray quality single crystals of the Cd(II) complexes had not been successful. The synthesized complexes are characterized by the following physico-chemical methods.

Elemental analyses

Elemental analyses data of complex **1** reveal that metal and thiosemicarbazone are in the ratio 1:1 and in the other two complexes the metal, thiosemicarbazone and the respective heterocyclic bases are in the ratio 1:1:1 (Table 1).

Molar conductivity

The molar conductivities of the complexes in DMF (10^{-3} M) were measured at 298 K with a Systronic model 303 direct reading conductivity bridge, which suggest that these complexes are non-electrolytic in nature [8].

Table 1. Elemental analyses data and molar conductivity of Cd(II) complexes

Compound	Elemental Anal. Found (Calcd) %				λ_m^a
	C	H	N	S	
[(CdL) ₂] (1)	36.59 (36.27)	3.82 (3.65)	8.55 (8.46)	6.47 (6.46)	3.5
[CdL(phen)] (2)	47.64 (47.91)	3.61 (3.87)	10.44 (10.35)	4.56 (4.74)	4.0
[CdL(bipy)] (3)	45.78 (45.99)	4.14 (4.01)	10.58 (10.73)	4.78 (4.91)	3.3

^a mho cm² mol⁻¹

Infrared spectra

The IR spectra of the thiosemicarbazone when compared with the Cd(II) complexes confirm the coordination of the thiosemicarbazone to the metal. The significant bands observed in the IR spectra of the thiosemicarbazone and its complexes are summarized in Table 2.

The disappearance of the band at 3454 cm⁻¹ corresponding to phenolic group of H₂L in all complexes indicate the coordination of H₂L as phenoxide ion. The band corresponding to azomethine bond, $\nu(\text{C}=\text{N})$, shifts to higher energy on complexation due to the combination of $\nu(\text{C}=\text{N})$ with the newly formed C=N bond which results from the loss of the thioamide hydrogen from the thiosemicarbazone moiety [9-13]. Strong band found at 1067 cm⁻¹ in the thiosemicarbazone is assigned to the $\nu(\text{N}-\text{N})$ band. The increase in frequency of this band in the spectra of complexes is due to the increase in the bond strength, again confirming the coordination *via* the azomethine nitrogen. Coordination *via*

thioiminolate sulfur is indicated by the downward shift of frequencies of δ/ν C=S bands in the complexes [14,15].

Table 2. IR spectral assignments (cm^{-1}) of thiosemicarbazone and its Cd (II) complexes

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{N=C})^a$	$\nu(\text{N-N})$	$\nu(\text{C=S})/\nu(\text{C-S}), \delta(\text{C=S})/\delta(\text{C-S})$	$\nu(\text{C-O})$	$\nu(\text{Cd-O})$	$\nu(\text{Cd-N})$
H ₂ L	3454	1539	----	1067	1342, 851	1257		----
[(CdL) ₂] (1)	----	1597	1556	1101	1328, 811	1225	472	459
[CdL(phen)] (2)	----	1590	1560	1090	1330, 840	1230	466	446
[CdL(bipy)] (3)	----	1586	1558	1092	1325, 833	1228	475	442

Electronic spectra

The electronic spectral assignments for the thiosemicarbazone and its Cd(II) complexes recorded in DMF are summarized in Table 3. The electronic spectra of the thiosemicarbazone showed bands at 29300 and 30490 cm^{-1} which are assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine and the thiosemicarbazone moieties [16]. These bands are slightly shifted on complexation. In addition to these bands due to intraligand transitions, new bands in the 25550-26050 cm^{-1} range are observed in the spectra of complexes. These bands can be assigned to metal to ligand charge transfer transitions. No appreciable absorptions occurred below 20000 cm^{-1} , indicating the absence of $d-d$ bands, which is in accordance with the d^{10} configuration of Cd(II) ion [17].

Table 3. Electronic spectral assignments (cm^{-1}) and molar extinction coefficients ($\log \epsilon$) of thiosemicarbazone and its Cd(II) complexes

Compound	$n \rightarrow \pi^* / \pi \rightarrow \pi^*$	MLCT
H ₂ L	29300 (4.45), 30490 (4.48)	----
[(CdL) ₂] (1)	29590 (4.49), 30890 (4.43)	26050 (4.56)
[CdL(phen)] (2)	29520 (4.28), 30820 (4.35)	25550 (4.33)
[CdL(bipy)] (3)	29520 (4.30), 30700 (4.19)	25740 (4.38)

Analytical Method

Elemental analyses of complexes were performed on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The molar conductances of the complexes in DMF (10^{-3} M) solution were measured at 298 K with a Systronic model 303 direct-reading conductivity bridge. IR spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer using KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$. Electronic spectra were recorded in DMF on a Spectro UV-vis Double Beam UVD-3500 spectrometer in the 200-900 nm range.

Conclusion

The molar conductivity measurements in DMF (10^{-3} M) indicate that all the complexes are non-electrolytes. The IR spectral studies show that the thiosemicarbazone coordinates in the thioiminolate form in all the complexes and acts as a dideprotonated tridentate ligand. The electronic spectra of complexes showed bands corresponding to MLCT transitions.

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