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Studies on Ni (II) Coordination Compound of N-(2-Hydroxyphenyl)-C-(3'-Carboxy-2'-Hydroxyphenyl)Thiazolidin-4-One

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Abstract

A dry benzene solution of the Schiff base, N-(2-hydroxyphenyl)-3'-carboxy-2'-hydroxybenzylideneimine upon reacting with mercaptoacetic acid undergoes cyclization and forms N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, LH₃ (I). A MeOH solution of I reacts with Ni(II) ions and forms the monomeric coordination compound, [Ni(LH)(MeOH)₃]. The coordination compound has been characterized on the basis of elemental analyses, molar conductance, molecular weight, spectral (IR, reflectance) studies and magnetic susceptibility measurements. I behaves as a dibasic tridentate OOS donor ligand in this compound. The compound is non-electrolyte ($\Lambda_M = 4.3 \text{ mho cm}^2 \text{ mol}^{-1}$) in DMF. An octahedral structure for [Ni(LH)(MeOH)₃] is suggested. The ligand (I) and its coordination compound shows antibacterial activities towards bacteria, *E.coli*. (Gram Negative) and *S. aureus* (Gram Positive).

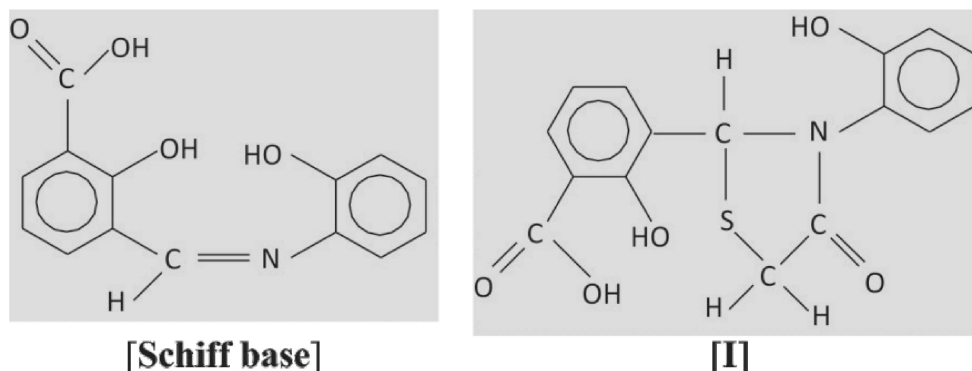
Key words: Thiazolidin-4-one, coordination compounds, magnetic susceptibility, magnetically dilute, strong field and covalent character.

Introduction

Heterocyclic compounds of Schiff bases possessing thiazolidin-4-one skeleton are known for their versatile pharmacological and industrial importance¹. They have been studied extensively because of their ready accessibility, diversified chemical reactivity and broad spectrum of biological activities². Thiazolidinones are also known to exhibit antitubercular, antibacterial³⁻⁵, anticonvulsant⁶⁻⁹, antifungal¹⁰, amoebicidal¹¹, antioxidant¹² and anticancer¹³⁻¹⁵ activities. A perusal of the literature reveals that much has been reported on the syntheses and characterization¹⁶⁻¹⁸ of a variety of thiazolidin-4-ones, very little is known about their coordination compounds^{19,20}. In this manuscript, the synthesis and characterization of N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, LH₃ (I) and its coordination compound with Ni(II) ions is

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discussed.



EXPERIMENTAL

Materials

2-Aminophenol [Loba-Chemie (Mumbai)], mercaptoacetic acid, dry benzene, sodium bicarbonate, nickel (II) acetate tetrahydrate [Ranbaxy] were used as received for the syntheses.

Analyses and Physical measurements

The organic skeleton of the respective coordination compound was decomposed by the slow heating of ~ 0.1 g of the latter, with conc. HNO_3 . The residue was dissolved in minimum amount of conc. HCl and the corresponding metal ion was estimated as follows: Ni(II) contents of the coordination compound was estimated by complexometric titration method against standardized EDTA solution using murexide indicator. The C, H and N contents of LH_3 and its coordination compound were determined by CHN Eager analyzer model-300. The S and Cl contents were estimated gravimetrically as BaSO_4 and AgCl respectively. The molecular weight measurements were carried out by the Rast method using diphenyl as the solvent. The molar conductance (Λ_m) of the coordination compound was measured in DMF with the help of a Toshniwal conductivity bridge (CL01-02A) and a dip type cell calibrated with KCl solutions. The IR spectra were recorded in KBr pellets ($4000\text{--}400\text{ cm}^{-1}$) on a Beckman-20 spectrophotometer. The reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. The magnetic susceptibility measurements were carried out at room temperature, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the standard. The diamagnetic corrections were computed using Pascal's constants. The magnetic susceptibilities were corrected for temperature independent paramagnetism term (TIP) using value of 200×10^{-6} cgs units for Ni(II) ions.

Synthesis of the Schiff base

A MeOH solution (30 mL) of 2-aminophenol (1.09 g, 10 mmol) was added to a MeOH solution (30 mL) of 3-formylsalicylic acid (1.66 g, 10 mmol) and the mixture was then refluxed for 2 h. The precipitates formed were suction filtered, washed with MeOH and dried *in vacuo* at room temperature over silica gel for 24 h. Yield = 87%. The elemental analyses of the compound gave the satisfactory results.

Synthesis of I

A dry benzene solution of the Schiff base (2.57 g, 10 mmol) and mercaptoacetic acid (0.92 g, 10

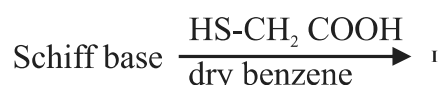
mmol) were refluxed for 12 h on a water bath. The mixture was cooled to room temperature and then was washed with 10% sodium bicarbonate solution. The benzene layer was separated using a separating funnel. The partial evaporation of the benzene layer gave a solid product, which was filtered, washed with and recrystallized from petroleum ether. Yield = 25%. *Anal:* (**I**, C₁₆H₁₃NO₅S) (obsd: C, 57.80%; H, 3.75%; N, 4.10%; S, 9.50%. calc.: C, 58.01%; H, 3.93%; N, 4.23%; S, 9.67%); IR bands (KBr): 2860 cm⁻¹ [ν (O–H) (intramolecular H-bonding)], 1700 cm⁻¹ [ν (C=O)(thiazolidinone ring)], 1670 cm⁻¹ [ν (C=O) (carboxylic)], 1575 cm⁻¹ [ν (C–N)(thiazolidinone ring)], 1525 cm⁻¹ [ν (C–O)(phenolic)] and 835 cm⁻¹ [ν (C–S)(thiazolidinone ring)].

Synthesis of [Ni(LH)(MeOH)₃]

A MeOH solution (30-50 mL) of the appropriate metal salt (10 mmol) was added to a MeOH solution (50 mL) of **I** (3.31 g, 10 mmol) and the mixture was then refluxed for 3-4 h. The solid products formed were suction filtered, washed with and recrystallized from MeOH and were then dried as mentioned above. Yield = 60%.

RESULTS AND DISCUSSION

A dry benzene solution of the Schiff base reacts with mercaptoacetic acid and forms N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, LH₃ (**I**). The reaction of **I** with appropriate metal salt in 1:1 molar ratio in MeOH produces the coordination compound, [Ni(LH)(MeOH)₃]. The formations of **I** from the Schiff base and its coordination compound take place according to the Schemes **I** and **II**.



Scheme I: Preparative scheme of LH₃(I)



Scheme II: Preparative scheme of coordination compounds of LH₃ (I)

Scheme II: Preparative scheme of coordination compounds of LH₃ (I)

The coordination compound is stable at room temperature. It is insoluble in H₂O, partially soluble in MeOH, EtOH and completely soluble in DMSO and DMF. Its molar conductance measurement ($\Lambda_m = 4.3 \text{ mho cm}^2 \text{ mol}^{-1}$) in DMF indicate its non-electrolytic nature. The analytical data of **I** and its coordination compound is presented in **Table 1**.

Infrared spectral studies

The infrared spectra of the Schiff base, **I** and its coordination compound were recorded in KBr and the prominent peaks (in cm⁻¹) are shown in **Table 2**. The Schiff base exhibits the ν (C=N)(azomethine) stretch at 1630 cm⁻¹. This band disappears in **I** and a new band appears at 1575 cm⁻¹ due to the ν (C–N)(thiazolidinone ring) stretch²¹ indicating the conversion of the Schiff base into **I**. The formation of **I** is further supported by the appearance of a new band at 835 cm⁻¹ due to the

$\nu(\text{C—S})$ (thiazolidinone ring) stretch²² and it shows a negative shift by 35 cm^{-1} in the coordination compound indicating the involvement of the S atom of the thiazolidinone moiety towards coordination²³. **I** shows the $\nu(\text{C=O})$ (thiazolidinone ring) stretch²⁴ at 1700 cm^{-1} . This band remains unchanged in the coordination compound indicating the non-involvement of O atom towards the coordination. **I** exhibits a strong band at 2860 cm^{-1} due to the intramolecular H-bonded OH group of phenolic and/or carboxylic acid moieties²⁵. This band disappears in the coordination compound indicating the breakdown of H-bonding and subsequent deprotonation of the OH group followed by the involvement of phenolic and carboxylic acid O atoms towards coordination. The presence of a broad band at $\sim 3400\text{ cm}^{-1}$ due to $\nu(\text{O—H})$ (MeOH) and the decrease of $\nu(\text{C—O})$ (MeOH) stretch from 1034 cm^{-1} to lower energy by 59 cm^{-1} in its coordination compound indicates the involvement of the O atom of MeOH towards coordination²⁶. The appearance of two new bands between 1570 cm^{-1} , $\nu_{\text{as}}(\text{COO})$ and 1350 cm^{-1} , $\nu_{\text{s}}(\text{COO})$ stretches indicate the presence of the coordinated carboxylate group in the coordination compound. The energy difference ($\Delta\nu = 220\text{ cm}^{-1}$) between these stretches is $> 210\text{ cm}^{-1}$ which indicates the monodentate nature of the carboxylate moiety²⁷. The $\nu(\text{C—O})\phi$ stretch²⁶ of **I** occurs at 1525 cm^{-1} . This band shifts to higher energy by 6 cm^{-1} in the coordination compound indicating the involvement of phenolic O atom of either 3- formylsalicylic acid or 2-aminophenol moieties towards coordination. On the basis of steric grounds, we suggest the non-involvement of phenolic (2-aminophenol moiety) O atom towards coordination. On the basis of analytical data (**Table 1**), valence requirements and the infrared spectral studies, it is proposed that **I** behaves as a dibasic tridentate OOS donor ligand in the coordination compound.

Reflectance spectral studies

$[\text{Ni}(\text{LH})(\text{MeOH})_3]$ exhibits three bands at 9050 , 15250 and 25150 cm^{-1} due to ${}^3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{1g}(\text{F})(\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{1g}(\text{P})(\nu_3)$ transitions, respectively in an octahedral symmetry²⁸. The ν_2/ν_1 value in the present Ni(II) compound is 1.68 and it lies in the usual range (1.60–1.82), reported for the majority of octahedral Ni(II) compounds²⁸. The spectral parameters²⁹ for $[\text{Ni}(\text{LH})(\text{MeOH})_3]$ are: $Dq = 905\text{ cm}^{-1}$, $B' = 854\text{ cm}^{-1}$, $\beta = B'/B = 0.83$, $\beta^0 = 17\%$ and $\text{CFSE} = -129.75\text{ kJ mole}^{-1}$. The reduction of the Racah parameter from the free ion value (1030 cm^{-1}) to 854 cm^{-1} and the β^0 value (17%) are indicative of the presence of covalent nature of the compound and the strong field nature of the tridentate ligand.

Magnetic measurements

The room temperature magnetic moment of $[\text{Ni}(\text{LH})(\text{MeOH})_3]$ is presented in the table. The magnetic moment of $[\text{Ni}(\text{LH})(\text{MeOH})_3]$ is 3.19 B.M. The value is indicative of magnetically dilute high-spin octahedral coordination compounds of Ni(II) ions³⁰.

Thus, on the basis of analytical, molecular weight, spectral and magnetic studies, we suggest an octahedral structure for $[\text{Ni}(\text{LH})(\text{MeOH})_3]$.

Antibacterial Studies

The antibacterial activity of ligand (**I**) and $[\text{Ni}(\text{LH})(\text{MeOH})_3]$ were tested against bacteria, *E. coli* (Gram negative) and *S. aureus* (Gram positive) by using disc diffusion method (**Table 3**). Stock solution were prepared by dissolving compounds in DMSO. Under aseptic conditions, plain sterilised discs were soaked in solution of compounds for overnight. Test culture was spread over the plates containing Mueller Hinton Agar (MHA) by using sterile swab. Inoculated plates were dried for

30 minutes and discs were placed on inoculated plates. The plates were left for 30 minutes at room temperature to allow diffusion. The plates were then incubated at 37 °C for 24 hours for *E. Coli* and *S. aureus*. After incubation, diameter of zone of inhibition were noted for each disc.

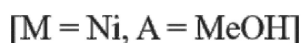
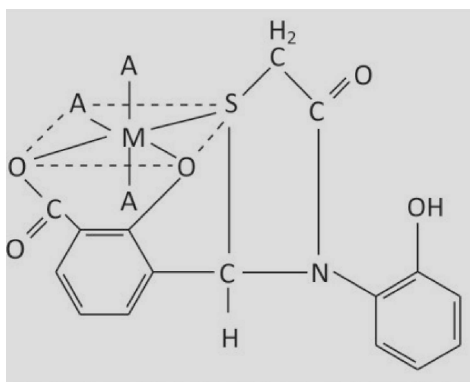


Table 1: Analytical, molar conductance (ΔM) and molecular weight data of I and its coordination compound

Compound	Mol. Formula	ΔM (mho cm ² mol ⁻¹)	Mol. wt obsd (calcd)	obsd (calcd) %				
				M	C	H	N	S
LH ₃ (I)	C ₁₆ H ₁₃ NO ₅ S	–	331 ^a (331.0)	–	57.80 (58.01)	3.75 (3.93)	4.10 (4.23)	9.50 (9.61)
[Ni(LH)(MeOH) ₃]	NiC ₁₉ H ₂₃ NO ₈ S	4.3	467.2 ^b (483.7)	11.98 (12.14)	47.00 (47.14)	4.89 (4.76)	2.98 (2.89)	6.41 (6.61)

Abbreviations: ^aMass spectral data, ^bRast method data

Table 2: IR, reflectance spectral data (cm⁻¹) and magnetic moments of coordination compound of I

Compound	$\nu_{as}(\text{COO})$	$\nu_s(\text{COO})$	$\nu(\text{C-O})$ (phenolic)	$\nu(\text{C-S})$	$\nu(\text{C-O})$ (MeOH)	ν_{max}	Mag. moment (B. M.)
LH ₃ (I)	–	–	1525	835	–	–	Diamagnetic
[Ni(LH)(MeOH) ₃]	1570	1350	1531	800	975	9050, 15250, 25150	3.19

Table 3: Antibacterial activity of I and its Coordination compound (Zone of Inhibition in mm)

Compound	E.Coli	S. Aureus
	(Gram negative)	(Gram positive)
LH ₃ (I)	7	6
[Ni(LH)(MeOH) ₃]	7	8

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