

# Syntheses, Magnetic, Spectral and Biological Studies on the Coordination Compounds of N-(2-Hydroxyphenyl)-C-(3'- Carboxy-2'-Hydroxyphenyl) Thiazolidin-4-One

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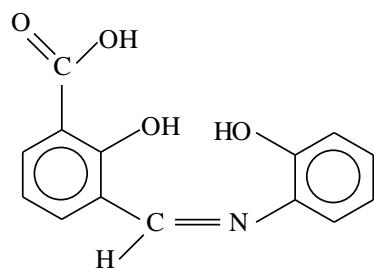
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**Abstract:** A dry benzene solution of the Schiff base, N-(2-hydroxyphenyl)-3'-carboxy-2'-hydroxybenzylideneimine upon reacting with mercaptoacetic acid undergoes cyclization and forms N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, LH<sub>3</sub> (**I**). A MeOH solution of **I** reacts with Ni(II) and UO<sub>2</sub>(VI) ions and forms the monomeric coordination compounds, [Ni(LH)(MeOH)<sub>3</sub>] and [UO<sub>2</sub>(LH)(MeOH)]. The coordination compounds have 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 these compounds. The compounds are non-electrolytes ( $\Lambda_M = 4.3\text{--}6.4 \text{ mho cm}^2 \text{ mol}^{-1}$ ) in DMF. Octahedral structure for Ni(II) and UO<sub>2</sub>(VI) compounds are suggested. LH<sub>3</sub> (**I**) and its complexes while testing with E.Coli. (Gram Negative) and S. Aureus (Gram positive) bacteria show antibacterial activities.

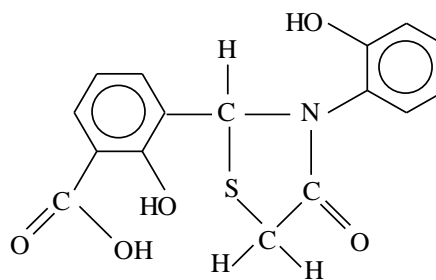
**Key Words:** Thiazolidin-4-one, magnetic susceptibility, magnetically dilute, antibacterial activity

## INTRODUCTION

Heterocyclic compounds of Schiff bases possessing thiazolidin-4-one skeleton are known for their versatile pharmacological and industrial importance<sup>1</sup>. They have been studied extensively because of their ready accessibility, diversified chemical reactivity and broad spectrum of biological activities<sup>2</sup>. Thiazolidinones are also known to exhibit antitubercular, antibacterial<sup>3</sup>, anticonvulsant<sup>4</sup>, antifungal<sup>5</sup>, amoebicidal<sup>6</sup>, antioxidant<sup>7</sup> and anticancer<sup>8</sup> activities. A perusal of the literature reveals that much has been reported on the syntheses and characterization<sup>9</sup> of a variety of thiazolidin-4-ones, very little is known about their coordination compounds<sup>10</sup>. In this manuscript, we describe the syntheses and characterization of N-(2-hydroxyphenyl)-C-(3'-carboxy-2'-hydroxyphenyl) thiazolidin-4-one, LH<sub>3</sub> (**I**) and its coordination compounds with Ni(II) and UO<sub>2</sub>(VI) ions.



[Schiff base]



[I]

## EXPERIMENTAL

### Materials and Methods

2-Aminophenol [Loba-Chemie (Mumbai)], mercaptoacetic acid, dry benzene, sodium bicarbonate [Ranbaxy], nickel (II) acetate tetrahydrate and dioxouranium (VI) acetate tetrahydrate [Sarabhai] were used as received for the syntheses. 3-formylsalicylic acid were synthesized by following the reported procedures<sup>11</sup>. The elemental analyses, IR, reflectance spectral studies and magnetic susceptibility measurements were carried out as described in our previous report<sup>11</sup>.

### 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

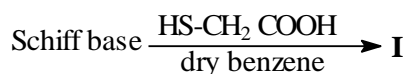
A dry benzene solution of the Schiff base (2.57 g, 10 mmol) and mercaptoacetic acid (0.92 g, 10mmol) were refluxed for 12 h on a water bath. The mixture was cooled to room temperature and then was washed with 10% sodium bicarbonate solution. The benzene layer was separated using a separating funnel. 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, C<sub>16</sub>H<sub>13</sub>NO<sub>5</sub>S) (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<sup>-1</sup> [ν(O—H) (intramolecular H-bonding)], 1700 cm<sup>-1</sup> [ν(C=O)(thiazolidinone ring)], 1670 cm<sup>-1</sup> [ν(C=O) (carboxylic)], 1575 cm<sup>-1</sup> [ν(C—N) (thiazolidinone ring)], 1525 cm<sup>-1</sup> [ν(C—O)(phenolic)] and 835 cm<sup>-1</sup> [ν(C—S)(thiazolidinone ring)].

### Syntheses of coordination compounds of I

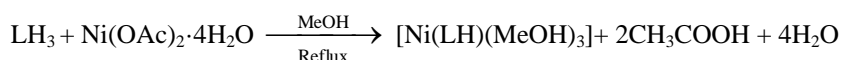
A MeOH solution (30-50 mL) of the appropriate metal salt (10 mmol) was added to a MeOH solution (50 mL) of I (3.31 g, 10 mmol) and the mixture was then refluxed for 3-4 h. The solid products formed were suction filtered, washed with and recrystallized from MeOH and were then dried as mentioned above. Yield = 50–80%.

## 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, LH<sub>3</sub> (**I**). The reaction of **I** with appropriate metal salt in 1:1 molar ratio in MeOH produces the coordination compounds, [Ni(LH)(MeOH)<sub>3</sub>] and [UO<sub>2</sub>(LH)(MeOH)]. The formations of **I** from the Schiff base and the coordination compounds of the latter take place according to the Schemes **I** and **II**.



**Scheme I: Preparative scheme of LH<sub>3</sub> (I)**



**Scheme II: Preparative scheme of coordination compounds of LH<sub>3</sub> (I)**

The coordination compounds are stable at room temperature. They are insoluble in H<sub>2</sub>O, partially soluble in MeOH, EtOH and completely soluble in DMSO and DMF. Their molar conductance measurements ( $\Lambda_M = 4.3\text{--}6.4 \text{ mho cm}^2 \text{ mol}^{-1}$ ) in DMF indicate their non-electrolytic nature. The analytical data of **I** and its coordination compounds are presented in **Table 1**.

**Table 1**

**Analytical, molar conductance ( $\Lambda_M$ ) and molecular weight data of I and its coordination compounds**

Compound	Mol. Formula	$\Lambda_M$ (mho cm <sup>2</sup> mol <sup>-1</sup> )	Mol. wt obsd (calcd)	Obsd (Calcd)%				
				M	C	H	N	S
LH <sub>3</sub> ( <b>I</b> )	C <sub>16</sub> H <sub>13</sub> NO <sub>5</sub> S	—	331 <sup>a</sup> (331.0)	—	57.80 (58.01)	3.75 (3.93)	4.10 (4.23)	9.50 (9.67)
[Ni(LH)(MeOH) <sub>3</sub> ]	NiC <sub>19</sub> H <sub>23</sub> NO <sub>8</sub> S	4.3	467.2 <sup>b</sup> (483.7)	11.98 (12.14)	47.00 (47.14)	4.89 (4.76)	2.98 (2.89)	6.48 (6.62)
[UO <sub>2</sub> (LH)(MeOH)]	UC <sub>17</sub> H <sub>15</sub> NO <sub>8</sub> S	6.4	645.6 <sup>b</sup> (631.0)	37.50 (37.72)	32.10 (32.33)	2.20 (2.38)	2.10 (2.22)	5.18 (5.07)

Abbreviations: <sup>a</sup>Mass spectral data, <sup>b</sup>Rast method data

### Infrared spectral studies

The infrared spectra of the Schiff base, **I** and the coordination compounds of the latter were recorded in KBr and the prominent peaks (in  $\text{cm}^{-1}$ ) are shown in **Table 2**. The Schiff base exhibits the  $\nu(\text{C}=\text{N})$  (azomethine) stretch at  $1630\text{ cm}^{-1}$ . This band disappears in **I** and a new band appears at  $1575\text{ cm}^{-1}$  due to the  $\nu(\text{C}-\text{N})$ (thiazolidinone ring) stretch<sup>12</sup> indicating the conversion of the Schiff base into **I**. The formation of **I** is further supported by the appearance of a new band at  $835\text{ cm}^{-1}$  due to the  $\nu(\text{C}-\text{S})$ (thiazolidinone ring) stretch<sup>13</sup> and it shows a negative shift by  $20\text{-}35\text{ cm}^{-1}$  in the coordination compounds indicating the involvement of the S atom of the thiazolidinone moiety towards coordination<sup>14</sup>. **I** shows the  $\nu(\text{C}=\text{O})$ (thiazolidinone ring) stretch<sup>15</sup> at  $1700\text{ cm}^{-1}$ . This band remains unchanged in the coordination compounds indicating the non-involvement of O atom towards the coordination. **I** exhibits a strong band at  $2860\text{ cm}^{-1}$  due to the intramolecular H-bonded OH group of phenolic and/or carboxylic acid moieties<sup>16</sup>. This band disappears in the coordination compounds 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  $\nu(\text{O}-\text{H})$ (MeOH) and the decrease of  $\nu(\text{C}-\text{O})$ (MeOH) stretch from  $1034\text{ cm}^{-1}$  to lower energy by  $50\text{-}59\text{ cm}^{-1}$  in the coordination compounds of **I** indicate the involvement of the O atom of MeOH towards coordination<sup>17</sup>. The  $\nu(\text{C}-\text{O})\phi$  stretch<sup>17</sup> of **I** occurs at  $1525\text{ cm}^{-1}$ . This band shifts to higher energy by  $6\text{-}10\text{ cm}^{-1}$  in the coordination compounds 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.  $[\text{UO}_2(\text{LH})(\text{MeOH})]$  exhibits the  $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$  stretch at  $895\text{ cm}^{-1}$  and this band occurs in the usual range ( $870\text{-}950\text{ cm}^{-1}$ ) observed for the majority of *trans*- $\text{UO}_2(\text{VI})$  compounds<sup>18</sup>. The force constant ( $f_{\text{U}-\text{O}}$ ) and U—O bond length in the present dioxouranium (VI) compound are  $6.66\text{ mdyn/\AA}$  and  $1.74\text{ \AA}$  respectively. These values are in the expected range ( $6.58\text{--}7.03\text{ mdyn/\AA}$  and  $1.60\text{--}1.92\text{ \AA}$ ) reported for the majority of  $\text{UO}_2(\text{VI})$  compounds<sup>18</sup>. The new non-ligand bands in the present coordination compounds in the low frequency region are assigned to the  $\nu(\text{M}-\text{O})$ ( $550\text{-}570\text{ cm}^{-1}$ ) and the  $\nu(\text{M}-\text{S})$ ( $345\text{-}370\text{ cm}^{-1}$ ) and these bands<sup>19</sup> are in the expected order of increasing energy:  $\nu(\text{M}-\text{S}) < \nu(\text{M}-\text{O})$ . 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 compounds.

Table 2

IR, reflectance spectral data ( $\text{cm}^{-1}$ ) and magnetic moments of coordination compounds of **I**

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\nu(\text{C-O})$ (phenolic)	$\nu(\text{C-S})$	$\nu(\text{C-O})$ (MeOH)	$\nu_{\text{max}}$	Mag. moment (B. M.)
LH <sub>3</sub> ( <b>I</b> )	—		1525	835	—	—	Diamagnetic
[Ni(LH)(MeOH) <sub>3</sub> ]	1570	1350	1531	800	975	9050, 15250, 25150	3.19
[UO <sub>2</sub> (LH)(MeOH)]	1565	1355	1535	815	984	—	Diamagnetic

### Reflectance spectral studies

[Ni(LH)(MeOH)<sub>3</sub>] exhibits three bands at 9050, 15250 and 25150  $\text{cm}^{-1}$  due to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$  transitions, respectively in an octahedral symmetry<sup>20</sup>. The  $\nu_2/\nu_1$  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) compounds<sup>21</sup>. The spectral parameters<sup>22</sup> for [Ni(LH)(MeOH)<sub>3</sub>] 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  $\text{cm}^{-1}$ ) to 854  $\text{cm}^{-1}$  and the  $\beta^0$  value (17%) are indicative of the presence of covalent nature of the compound and the strong field nature of the tridentate ligand<sup>23</sup>.

### Magnetic measurements

The room temperature magnetic moments of the coordination compounds of **I** are presented in **Table 2**. The magnetic moment of [Ni(LH)(MeOH)<sub>3</sub>] is 3.19 B.M. The value indicates magnetically dilute high-spin octahedral coordination compound of Ni(II) ions<sup>24</sup>.

### Antibacterial Studies

The antibacterial activity of ligand (**I**) and its complexes 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. The results are in accordance with our published paper<sup>25</sup>.

**Determination of Minimum Inhibitory Concentration (MIC)**

The stock solution of compounds were prepared using distilled water as diluent. In a set of test tubes having 2 mL of Mueller Hinton Broth, compounds were serially diluted. 2 mL of the test culture was added to all tubes and tubes were incubated at 37°C for 24 hr. Lack of turbidity was noted for the determination of MIC (**Table 4**). The results are in accordance with our published paper<sup>26</sup>.

**Table 3**  
**Antibacterial activity of I and its Coordination compounds**  
**(Zone of Inhibition in mm)**

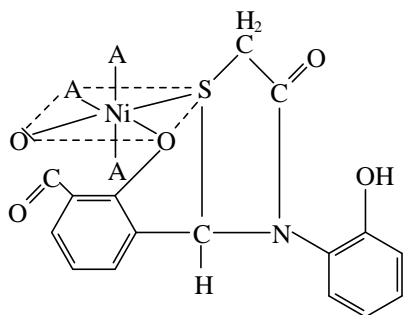
<b>Compound</b>	<b>E.Coli (Gram negative)</b>	<b>S. Aureus (Gram positive)</b>
LH <sub>3</sub> ( <b>I</b> )	8	7
[Ni(LH)(MeOH) <sub>3</sub> ]	9	9
[UO <sub>2</sub> (LH)(MeOH)]	9	8

**Table 4**  
**Minimum inhibitory concentration (MIC) of I and its Coordination compounds ((μg/ml)**

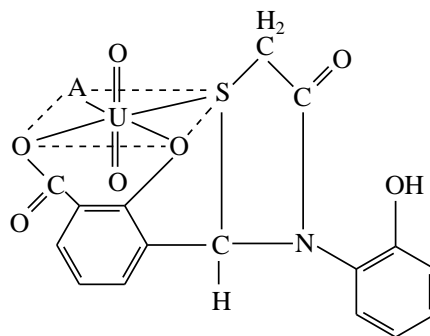
<b>Compound</b>	<b><i>E.Coli</i> (Gram negative)</b>	<b>S. Aureus (Gram positive)</b>
LH <sub>3</sub> ( <b>I</b> )	30	28
[Ni(LH)(MeOH) <sub>3</sub> ]	34	56
[UO <sub>2</sub> (LH)(MeOH)]	61	60

## CONCLUSIONS

Thus, on the basis of analytical, molecular weight, spectral and magnetic studies, we suggest octahedral structure, **II** for  $[\text{Ni}(\text{LH})(\text{MeOH})_3]$  and **III** for  $[\text{UO}_2(\text{LH})(\text{MeOH})]$ .



[II, A = MeOH]



[III, A = MeOH]

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