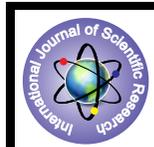


# Physico-Chemical Studies on the Coordination Compounds of N-(2-Carbamoyl-Furanyl)-C-(3'-Carboxy-2'-Hydroxyphenyl) Thiazolidin-4-One



## Chemistry

**KEYWORDS :** Coordination compounds, 3-formylsalicylic acid, furoic acid hydrazide, schiff base, spectral studies, thiazolidin-4-One

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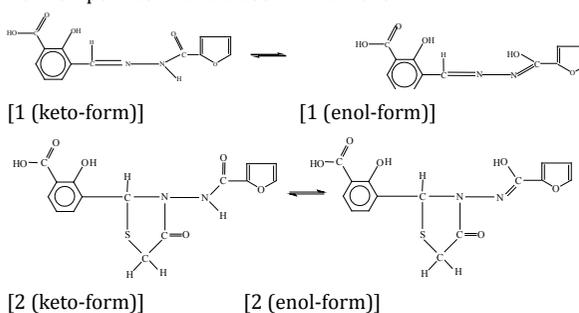
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### ABSTRACT

An equimolar mixture of 3-formylsalicylic acid and furoic acid hydrazide upon refluxing in MeOH forms the Schiff base (1). The latter upon reacting with mercaptoacetic acid in dry benzene, undergoes cyclization and forms N-(2-carbamoylfuranyl)-C-(3'-carboxy-2'-hydroxyphenyl)thiazolidin-4-one, LH3 (2). A MeOH solution of 2 reacts with Mn(II), Cu(II), Cd(II), Zr(OH)<sub>2</sub>(IV) and UO<sub>2</sub>(VI) ions and forms the coordination compounds, [Mn(LH)(MeOH)<sub>2</sub>] (3), [Cu(LH)]<sub>2</sub> (4), [Cd(LH)] (5), [Zr(OH)<sub>2</sub>(OAc)<sub>2</sub>(LH<sub>3</sub>)] (6) and [UO<sub>2</sub>(NO<sub>3</sub>)(LH<sub>2</sub>)(MeOH)] (7) respectively. The coordination compounds have been characterized on the basis of elemental analyses, molar conductance, molecular weight, spectral (IR, reflectance and ESR) studies and magnetic susceptibility measurements. 2 behaves as a neutral tridentate ONO donor ligand in 6, monobasic tridentate ONO donor ligand in 7, dibasic tridentate OOS donor ligand in 4 and dibasic tetradentate OONO donor ligand in 3 and 5. The coordination compound 4 is a dimer, while all other coordination compounds are monomers in diphenyl. The absolute coordination number each of Cu(II) and Cd(II) ions is 4 in 4 and 5 respectively and that of Mn(II) is 6 in 3. The Zr(OH)<sub>2</sub>(IV) and UO<sub>2</sub>(VI) ions have the coordination numbers 7 and 8 in 6 and 7 respectively. A square-planar structure for 4, a tetrahedral structure for 5, an octahedral structure for 3, a pentagonal-bipyramidal structure for 6 and a square-antiprism structure for 7 are proposed.

### 1. INTRODUCTION:

Thiazolidin-4-ones, the derivatives of thiazolidine, belong to an important group of heterocyclic compounds containing S and N in a five membered ring. Due to their pharmaceutical importance, thiazolidin-4-ones have played important roles in medicinal chemistry [1]. They have been studied extensively because of their biological activities like antimicrobial, antibacterial, anticonvulsant, antifungal, anti-HIV, antiproliferative, anti-inflammatory and antithyroid [2] etc. A perusal of the literature indicates that relatively little work has been carried out on the coordination compounds of the thiazolidinones [3] and there is no report on the coordination compounds of Mn(II), Cu(II), Cd(II), Zr(OH)<sub>2</sub>(IV) and UO<sub>2</sub>(VI) ions with 2. In this paper, we describe the syntheses and characterization of 2 and its coordination compounds with the above metal ions.



### 3. EXPERIMENTAL:

#### 2.1 Materials

Cadmium(II) acetate dihydrate [Ranbaxy]; dioxouranium(VI) nitrate hexahydrate, hexadecaquaooctahydroxotetrazirconium (IV) chloride [BDH]; manganese(II) acetate tetrahydrate [Sarabhai]; copper(II) acetate monohydrate [IDPL]; furoic acid hydrazide [Aldrich]; mercaptoacetic acid [s.d.fine]; sodium hydrogen carbonate [Nice] were used as received for the syntheses. 3-Formylsalicylic acid and hexadecaquaooctahydroxotetrazirconium(IV) acetate were prepared by adopting the published procedures [4].

#### 2.2 Analyses and physical measurements

The metal contents of the respective coordination compounds were estimated by following the reported procedures [5]. The elemental analyses (carbon, hydrogen and nitrogen contents) and spectral [IR (in KBr pellets) and reflectance] studies were carried out at the Sophisticated Analytical Instrumentation Centre, Punjab University, Chandigarh. ESR spectrum of 4 was recorded at Sophisticated Analytical Instrumentation Centre,

Indian Institute of Technology, Mumbai at 77 K in DMSO. The magnetic susceptibility measurements of 3 and 4 were carried out by the Gouy method. The molar conductance measurements of the coordination compounds were carried out in DMSO with the help of a Toshniwal conductivity bridge (CL01-02A) and a dip type cell calibrated with KCl solutions. The molecular weights of the coordination compounds were determined by the Rast method using diphenyl as the solvent [6].

#### 2.3.1 Synthesis of 1

The title compound was synthesized by following the published procedure [7].

#### 2.3.2 Synthesis of 2

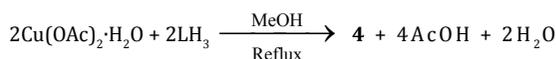
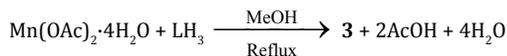
A dry benzene solution of 1 (2.74 g, 10 mmol) and mercaptoacetic acid (0.92 g, 10 mmol) were refluxed on a water bath for 12 h. The mixture was cooled to room temperature and then washed with 10% NaHCO<sub>3</sub> solution. The benzene layer was separated using a separating funnel. The evaporation of the excess of solvent gave the solid product which was recrystallized from petroleum ether. Yield = 45%. Anal: (2, C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>S) (Found (%): C, 51.42; H, 3.38; N, 8.17; S, 9.35. Calcd(%): C, 51.72; H, 3.45; N, 8.05; S, 9.20); IR bands (KBr): 2850 cm<sup>-1</sup> [ν(O--H) (intramolecular H-bonding)], 1695 cm<sup>-1</sup> [ν(C==O) (thiazolidinone ring)], 1670 cm<sup>-1</sup> [ν(C=O) (carboxylic)], 1645 cm<sup>-1</sup> [ν(C=O) (amide)], 1565 cm<sup>-1</sup> [ν(C--N) (thiazolidinone ring)], 1532 cm<sup>-1</sup> [ν(C--O) (phenolic)], 1090 cm<sup>-1</sup> [ν(C--O--C) (furan ring)] and 825 cm<sup>-1</sup> [ν(C--S) (thiazolidinone ring)].

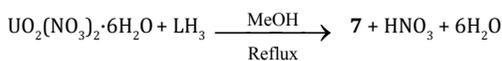
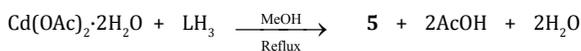
#### 2.3.3 Syntheses of 3-7

A MeOH solution (30-50 mL) of the appropriate metal salt (10 mmol) was added to a MeOH solution (50 mL) of 2 (3.48 g, 10 mmol) and the mixture was then refluxed for 3-4 h. The solid products formed were suction filtered, washed with MeOH and was then dried as mentioned above. Yield = 52-85%.

### 4. RESULTS AND DISCUSSION:

A dry benzene solution of 1 reacts with mercaptoacetic acid and forms 2. The reaction of 2 with Mn(II), Cu(II), Cd(II), Zr(OH)<sub>2</sub>(IV) and UO<sub>2</sub>(VI) ions in MeOH in 1:1 molar ratio produces the coordination compounds 3-7. The formations of these coordination compounds are shown below:





The coordination compounds are air-stable at room temperature. They are insoluble in  $\text{H}_2\text{O}$ , partially soluble in MeOH, EtOH and completely soluble in DMSO and DMF. Their molar conductance values ( $\Lambda_m = 6.6\text{-}9.9 \text{ mho cm}^2 \text{ mol}^{-1}$ ) of  $10^{-3} \text{ M}$  solutions in DMSO indicate their non-electrolytic nature. The analytical data of **2** and its coordination compounds are presented in Table 1.

### 3.1. Spectral discussion

#### 3.1.1. Infrared spectral studies

The infrared spectra of **1-7** were recorded in KBr pellets and the prominent bands (in  $\text{cm}^{-1}$ ) are given in Table 2. The Schiff base **1** exhibits the  $\nu(\text{C}=\text{N})$  (azomethine) stretch at  $1620 \text{ cm}^{-1}$ . This band disappears in **2** and a new band due to the  $\nu(\text{C}=\text{N})$  (thiazolidinone ring) stretch [8] appears at  $1565 \text{ cm}^{-1}$  indicating the conversion of **1** into **2**. The formation of **2** is further supported by the appearance of a new band at  $825 \text{ cm}^{-1}$  due to the  $\nu(\text{C}-\text{S})$  (thiazolidinone ring) stretch [9]. The  $\nu(\text{C}-\text{N})$  (thiazolidinone ring) stretch of **2** shifts from  $1565 \text{ cm}^{-1}$  to lower energy by  $55$  and  $60 \text{ cm}^{-1}$  in **3** and **5** respectively suggesting the involvement of the ring N atom in coordination [9]. However, the existence of this band at the same energy in **4**, **6** and **7** indicates the non-involvement of the ring N atom in coordination. **2** exhibits a band at  $2850 \text{ cm}^{-1}$  due to the intramolecular H-bonded OH groups of phenolic and/or carboxylic acid moieties [10]. The appearance of this band almost at the same energy in **6** and **7** is indicative of the non-involvement of the OH groups of the above moieties in coordination. On the other hand, the coordination compounds **3-5** do not exhibit this band indicating the breakdown of H-bonding and subsequent deprotonation of the OH groups followed by the involvement of phenolic and carboxylic O atoms in coordination. The  $\nu(\text{C}=\text{O})$  (thiazolidinone ring) stretch [11] of **2** occurs at  $1695 \text{ cm}^{-1}$ . This band shifts to  $1650 \text{ cm}^{-1}$  and  $1665 \text{ cm}^{-1}$  in **6** and **7** respectively indicating the coordination of **2** through O atom of the carbonyl group of thiazolidinone moiety. However, the above band remains unchanged in **3-5** suggesting the non-involvement of the above O atom in coordination. The  $\nu(\text{C}=\text{O})$  (carboxylic) stretch [12] of **2** occurs at  $1670 \text{ cm}^{-1}$ . This band remains unchanged in **6** and **7** indicating the non-involvement of the O atom of carboxylic group in coordination. However, the coordination compounds **3-5** exhibit two new bands at  $1555\text{-}1568 \text{ cm}^{-1}$  and  $1345\text{-}1352 \text{ cm}^{-1}$ . These bands are assigned to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  stretches respectively of the coordinated ligand. The energy separation ( $\Delta\nu = 210\text{-}216 \text{ cm}^{-1}$ ) between the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  stretches is indicative of the monodentate behaviour of the carboxylic acid group [13]. The presence of a strong band at  $1645 \text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  (amide) stretch in **2** indicates that it exists in the keto-form. This band shifts to lower energy by  $14$  and  $32 \text{ cm}^{-1}$  in **3** and **5** respectively suggesting the involvement of the keto O atom in coordination. However, the existence of this band at the same energy in **4**, **6** and **7** indicates the non-involvement of the keto O atom in coordination. The  $\nu(\text{C}-\text{O})$  (phenolic) stretch [7] ( $1532 \text{ cm}^{-1}$ ) of **2** undergoes a positive shift by  $\leq 10 \text{ cm}^{-1}$  in **3** and **5**, while it shifts by  $20 \text{ cm}^{-1}$  in **4**. This band remains unchanged in **6** and **7** respectively indicating the non-involvement of the phenolic O atom in coordination. The  $\nu(\text{C}-\text{S})$  (thiazolidinone ring) stretch [8] of **2** shifts from  $825 \text{ cm}^{-1}$  to lower energy by  $35 \text{ cm}^{-1}$  in **4** suggesting the formation of a bond between the copper ion and the S atom. However, it remains unchanged in **3**, **5-7** indicating the non-involvement of S atom in coordination. The  $\nu(\text{C}-\text{O}-\text{C})$  (furan moiety) stretch of **2** occurs at  $1090 \text{ cm}^{-1}$ . The appearance of a band at the same energy in **3-5** indicates the non-involvement of the O atom of furan moiety in coordination. On the other hand, the negative shift of this band by  $75$  and  $65 \text{ cm}^{-1}$  in **6** and **7** respectively indicates the coordination through the O atom of furan moiety to [6]. The presence of a broad band at  $3300\text{-}3400 \text{ cm}^{-1}$  due to the  $\nu(\text{O}-\text{H})$  (MeOH) stretch and the decrease of the  $\nu(\text{C}-$

$\text{O})$  (MeOH) stretch [14] from  $1034 \text{ cm}^{-1}$  to lower energy by  $34$  and  $46 \text{ cm}^{-1}$  in **3** and **7** indicate the involvement of the O atom of MeOH in coordination [15]. The absence of a band at  $835\text{-}955 \text{ cm}^{-1}$  due to the  $\nu(\text{Zr}=\text{O})$  stretch in **6** suggests its formulation as  $[\text{Zr}(\text{OH})_2(\text{OAc})_2(\text{LH}_3)]$  and not as  $[\text{Zr}(\text{O}(\text{H}_2\text{O})(\text{OAc})_2(\text{LH}_3)]$  [12]. The presence of a broad band at  $3440 \text{ cm}^{-1}$  due to the coordinated OH group and the appearance of a new medium intense band at  $1125 \text{ cm}^{-1}$  due to the  $\delta(\text{Zr}-\text{OH})$  bending mode [12] also support the formulation of the present coordination compound as  $[\text{Zr}(\text{OH})_2(\text{OAc})_2(\text{LH}_3)]$ . Syamal *et al.* [16] have developed a non-aqueous titrimetric method to distinguish the Zr(IV) compounds possessing the  $[\text{ZrO}]^{2+}$  or  $[\text{Zr}(\text{OH})_2]^{2+}$  moiety. Oxozirconium(IV) compounds react with  $3\text{N HCl}$  and as a result, the oxo group gets protonated, while the zirconium(IV) compounds containing the  $[\text{Zr}(\text{OH})_2]^{2+}$  moiety do not add up HCl at all. Our newly synthesized coordination compound  $[\text{Zr}(\text{OH})_2(\text{OAc})_2(\text{LH}_3)]$  does not react with  $3\text{N HCl}$  in MeOH and this indicates the absence of  $\text{Zr}=\text{O}$  bond in the present case. The acetato group is coordinated to the  $\text{Zr}(\text{OH})_2(\text{IV})$  ion in a monodentate fashion [17] as is evident from the appearance of two new bands, one at  $1575 \text{ cm}^{-1}$  and another at  $1360 \text{ cm}^{-1}$  due to the  $\nu_{\text{as}}(\text{OAc})$  and  $\nu_{\text{s}}(\text{OAc})$  stretches respectively in **6**. The  $\text{UO}_2(\text{VI})$  coordination compound (**7**) exhibits the  $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$  stretch [18] at  $914 \text{ cm}^{-1}$ . The force constant ( $f_{\text{U}-\text{O}}$ ) and  $\text{U}-\text{O}$  bond length are  $6.94 \text{ mdyne/\AA}$  and  $1.74 \text{ \AA}$  respectively [12] and these are in the usual ranges observed in the majority of dioxouranium(VI) coordination compounds. The nitrate entity is associated with  $D_{3h}$  symmetry in the free ion and exhibits three IR active vibrations:  $\nu_2$  ( $\sim 820 \text{ cm}^{-1}$ ),  $\nu_3$  ( $\sim 1380 \text{ cm}^{-1}$ ),  $\nu_4$  ( $\sim 700 \text{ cm}^{-1}$ ). The  $D_{3h}$  symmetry of the free nitrate ion is lowered to the  $C_{2v}$  symmetry on coordination compound formation and six normal modes are expected to be IR active [19]. The present  $\text{UO}_2(\text{VI})$  coordination compound does not exhibit any strong band at  $\sim 1380 \text{ cm}^{-1}$  but displays two bands, one at  $1503 \text{ cm}^{-1}$  and another at  $1305 \text{ cm}^{-1}$  characteristic of  $\nu_1(\text{NO})$  and  $\nu_4(\text{NO}_2)_{\text{as}}$  stretches respectively of the  $C_{2v}$  nitrate group [20] indicating that the nitrate group is not present in the free ion form but is coordinated [21] to the  $\text{UO}_2(\text{VI})$  ion in this coordination compound. The molar conductance data ( $9.9 \text{ mho cm}^2 \text{ mol}^{-1}$ ) also support this. The bidentate nature of the nitrate group is indicated from the presence of six bands at  $1048 \text{ cm}^{-1}$  ( $\nu_2$ ),  $768 \text{ cm}^{-1}$  ( $\nu_6$ ),  $743 \text{ cm}^{-1}$  ( $\nu_3$ ),  $682 \text{ cm}^{-1}$  ( $\nu_5$ ) and the combination bands ( $\nu_2 + \nu_3$ ) and ( $\nu_2 + \nu_5$ ) at  $1791 \text{ cm}^{-1}$  and  $1730 \text{ cm}^{-1}$  respectively. For bidentate coordination of the nitrate group [22], the values of energy separation ( $\nu_3 - \nu_5$ ) and ( $\nu_1 - \nu_4$ ) are usually  $\sim 38\text{-}71 \text{ cm}^{-1}$  and  $\sim 185\text{-}235 \text{ cm}^{-1}$  respectively. These energy separations are usually  $\sim 13\text{-}20 \text{ cm}^{-1}$  and  $\sim 105\text{-}115 \text{ cm}^{-1}$  in monodentate coordination of the nitrate group [23]. We have observed the energy separations of these bands as  $61$  and  $198 \text{ cm}^{-1}$  respectively, indicating the bidentate coordination of the nitrate group in the present coordination compound. The new non-ligand bands in **3-7** in the low frequency region are assigned to the  $\nu(\text{M}-\text{O})$  ( $538\text{-}563 \text{ cm}^{-1}$ ), the  $\nu(\text{M}-\text{N})$  ( $418\text{-}456 \text{ cm}^{-1}$ ) and the  $\nu(\text{Cu}-\text{S})$  ( $342 \text{ cm}^{-1}$ ) vibrations [24]. The increasing order of the  $\nu(\text{M}-\text{N}) < \nu(\text{M}-\text{O})$  is as expected according to the greater dipole moment change in the  $\text{M}-\text{O}$  vibration than the  $\text{M}-\text{N}$  vibration, greater electronegativity of the oxygen atom than the nitrogen atom and shorter bond length of the  $\text{M}-\text{O}$  bond than the  $\text{M}-\text{N}$  bond length [25].

#### 3.1.2. Reflectance spectral studies

The ground state term of Mn(II) ion is sextet. The only sextet term of the  $d^5$  configuration in octahedral stereochemistry is the  ${}^6A_{1g}$ . The reflectance spectral bands of Mn(II) coordination compounds are assigned to the transitions from the  ${}^6A_{1g}$  ground term to the quartet excited terms [26]. The coordination compound **3** exhibits three electronic spectral bands at  $18150$ ,  $23190$  and  $25300 \text{ cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)(\nu_1)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)(\nu_2)$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)(\nu_3)$  transitions, respectively in an octahedral environment [27]. The coordination compound **4** exhibits a broad band at  $12700 \text{ cm}^{-1}$  due to the  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  transition in a distorted square-planar arrangement around the Cu(II) ion [28]. This energy value is much less than those usually found in monomeric square-planar Cu(II) coordination compounds and this is indicative of the presence of distortion from square-planar structure due to dimerization [28]. The absence of any spectral band below  $10000 \text{ cm}^{-1}$  rules out the possibility of its having a tetrahedral structure [29].

### 3.1.3. EPR spectral studies

The X-band EPR spectrum of **4** in DMSO at 77 K has been recorded in frozen solution, using 100 kHz field modulation and the  $g$  values are relative to the standard marker tetracyanoethylene (TCNE) ( $g = 2.0028$ ). Since  $g_{\parallel}$  (2.25)  $>$   $g_{\perp}$  (2.07)  $>$  2, it suggests a square-planar geometry for  $[\text{Cu}(\text{LH})_2]$  with unpaired electron lying in the  $d_{x^2-y^2}$  orbital ( ${}^2B_{1g}$  as the ground state) [30]. The coordination compound **4** exhibits an additional weak half-field signal at  $\sim 1600$  G typical of Cu—Cu interaction corresponding to the  $\Delta M_s = 2$  forbidden transition indicating its dimeric nature and its involvement in magnetic exchange interaction. The value of spin Hamiltonian parameters  $g_{\parallel}$  (2.25),  $g_{\perp}$  (2.07),  $G = 3.6$  and  $A_{\parallel} = (1.50 \times 10^{-2} \text{ cm}^{-1})$  are comparable with those of other dimetallic Cu(II) coordination compounds [31]. The observed molecular weight (803.2) for this compound is very close to the theoretical value (819.0) confirming its dimeric nature. The covalent nature of metal-ligand bonding is indicated by  $g$  and  $a_{\text{Cu}}^2$  values. The value of  $g_{\parallel} < 2.3$  indicates a significant covalent character in M—L bonding. The covalence parameter  $a_{\text{Cu}}^2$  (a measure of covalence in the in-plane  $\sigma$ -bonding) was calculated using the relation:

$$a_{\text{Cu}}^2 = - (A_{\parallel} / 0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

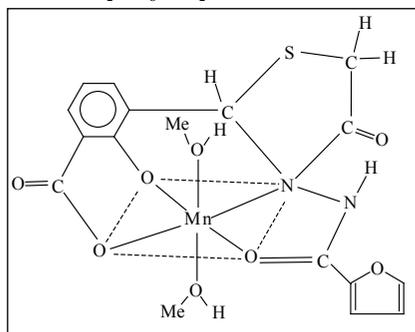
A value of  $a_{\text{Cu}}^2 = 0.5$  indicates the complete covalent bonding, while the value of  $a_{\text{Cu}}^2 = 1.0$  suggests complete ionic bonding [32]. The observed value of  $a_{\text{Cu}}^2 = 0.72$  of the present Cu(II) coordination compound is less than unity and this indicates that this coordination compound possesses a significant covalent character in the M—L bonding [33].

### 3.2. Magnetic measurements

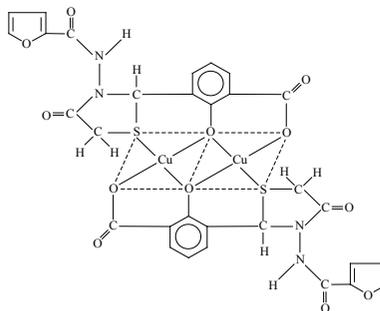
The coordination compound **3** exhibits a magnetic moment of 5.90 B.M. which is consistent with the magnetically dilute octahedral compounds of Mn(II) ion [34]. The coordination compound **4** exhibits a magnetic moment of 1.52 B.M. which is substantially less than the spin-only value of 1.73 B. M. per Cu(II) ion indicating the presence of anti-ferromagnetic type of spin-spin coupling between the unpaired electrons belonging to two different Cu(II) ions in the structural unit [35]. The decrease in magnetic moment occurs due to the antiferromagnetic exchange via the  $\pi$ -pathway  $[\pi(\text{Cu}_{dx^2-y^2} - \text{O}_{px,py} - \text{Cu}_{dx^2-y^2})]$ . The coordination compounds 5-7 containing no unpaired electron are diamagnetic in nature as expected.

### 4. CONCLUSION:

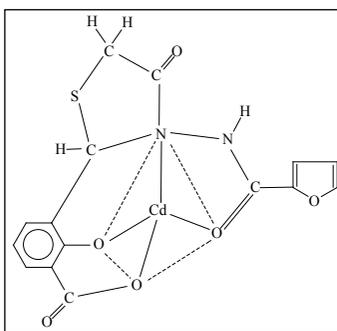
From the above discussion, it is proposed that **2** behaves as a neutral tridentate ONO donor ligand in **6**, monobasic tridentate ONO donor ligand in **7**, dibasic tridentate OOS donor ligand in **4** and dibasic tetradentate OONO donor ligand in **3** and **5**. On the basis of analytical, molecular weight, spectral and magnetic studies, we propose a square-planar structure (**4**) for  $[\text{Cu}(\text{LH})_2]$ , a tetrahedral structure (**5**) for  $[\text{Cd}(\text{LH})]$ , an octahedral structure (**3**) for  $[\text{Mn}(\text{LH})(\text{MeOH})_2]$ , a pentagonal bipyramidal structure (**6**) for  $[\text{Zr}(\text{OH})_2(\text{OAc})_2(\text{LH}_3)]$  and a square-antiprism geometry (**7**) for  $[\text{UO}_2(\text{NO}_3)(\text{LH}_2)(\text{MeOH})]$ .



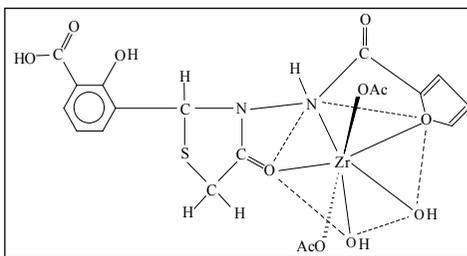
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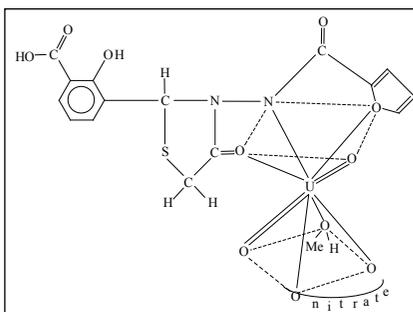
[4]



[5]



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## REFERENCE

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