

# Coordination Compounds of Schiff Base Containing Urea Moiety

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## Abstract

A MeOH solution of salicylaldehyde and *o*-hydroxyphenylurea in 1:1 molar ratio reacts and forms the Schiff base, LH<sub>3</sub> (**1**). A MeOH solution of the latter reacts with Zn(II), Co(II), Ni(II), Fe(III) and Zr(OH)<sub>2</sub>(IV) ions in 1:1 molar ratio and forms the corresponding coordination compounds, [Zn(LH)(MeOH)] (**2**), [M(LH)(MeOH)<sub>2</sub>]<sub>2</sub> (**3**, M = Co, Ni), [FeCl(LH)(MeOH)]<sub>2</sub> (**4**) and [Zr(OH)<sub>2</sub>(LH)(MeOH)<sub>2</sub>] (**5**). The coordination compounds have been characterized on the basis of elemental analyses, molecular weight, molar conductance, spectral (IR, reflectance, NMR) studies, thermo-gravimetric analyses and magnetic susceptibility measurements. **1** acts as a dibasic tridentate ONO donor ligand in **2-5**. The coordination compounds, **3** and **4** are paramagnetic, while **2** and **5** are diamagnetic. A tetrahedral geometry to **2**, an octahedral geometry to **3** and **4** and a pentagonal-bipyramidal geometry to **5** are assigned. The energy optimized structures, **6** and **7** for **1** and **2** respectively are proposed using the semiempirical ZINDO/1 quantum mechanical calculations.

## Introduction

The Schiff bases containing O and N donor atoms are known to play important role in biological systems and represent interesting models<sup>[288]</sup>. The Schiff bases and their coordination compounds have received considerable research interest because of the interaction of donor sites present in these ligands giving the coordination compounds of different geometry and properties<sup>[289]</sup>. The coordination compounds of Schiff bases have also been studied extensively due to their various applications like catalysts, pharmaceutical agents, anti-tumor, antifungal, antibacterial, antiviral, anticonvulsive, antifouling and as corrosion inhibitors<sup>[290]</sup>. The molecular modeling has played an important role in the study of ligands and their coordination compounds<sup>[291]</sup>. The coordination compounds of Cu(II), Zr(IV), Ti(IV) and Sn(IV) ions with the isomeric Schiff base, **56** [R = 2-OH(C<sub>6</sub>H<sub>4</sub>CH), R' = 2-OH(C<sub>6</sub>H<sub>4</sub>)] of **1** have been reported elsewhere<sup>[292]</sup>. In the present Chapter, we have synthesized and characterized the coordination compounds of **1** with Zn(II), Co(II), Ni(II), Fe(III) and Zr(OH)<sub>2</sub>(IV) ions. It is expected that the present coordination compounds may find applications in biochemical, analytical and antimicrobial fields.

## Experimental

### Materials

The various chemicals and solvents obtained from the sources mentioned in Appendix-2 were used as received for the syntheses.

### Analyses and Physical Measurements

The estimation of metal, elemental contents, spectral (IR, reflectance,  $^1\text{H}$  NMR) studies and magnetic susceptibility measurements were carried out by the methods described in Appendix-3.

### Synthesis of *O*-hydroxyphenylurea (ohypu)

*o*-Aminophenol (10.9 g, 100 mmol) was dissolved in 20 mL of 1:1 HCl. To this solution, urea (24.0 g, 400 mmol) in small quantity with constant stirring, distilled water (30 mL), HCl (1 mL) and glacial acetic acid (1 mL) were added. The brown solution obtained was refluxed on a water bath for 2 *h*. The light-brown compound separated out on cooling was suction filtered, washed with distilled water and recrystallised from 50% EtOH and dried *in vacuo* over silica gel. Melting point = 154 °C, yield = 90%; anal. [ $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$ ; found (calcd)%; C = 55.38(55.26), H = 5.32(5.26), N = 18.23(18.42); IR bands (KBr):  $\nu(\text{N—H})$  (3050  $\text{cm}^{-1}$ ),  $\nu(\text{C=O})$ (carbonyl) (1655  $\text{cm}^{-1}$ ),  $\nu(\text{NH}_2)$  (1630  $\text{cm}^{-1}$ ) and  $\nu(\text{C—O})$  (1520  $\text{cm}^{-1}$ ).

### Synthesis of 1

An EtOH solution (20 mL) of salicylaldehyde (12.2 g, 100 mmol) and an EtOH solution (100 mL) of *o*-hydroxyphenylurea (15.2 g, 100 mmol) were refluxed on a water bath for 1 *h*. The excess of solvent was evaporated and the mixture was allowed to stand at room temperature. The brown compound separated out was suction filtered, washed with and recrystallized from EtOH and then dried as mentioned above. Melting point = 162 °C, yield = 70%; anal. [ $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ ; found (calcd.)%; C = 65.48(65.63), H = 4.85(4.69), N = 10.78(10.94); IR bands (KBr):  $\nu(\text{C=O})$ (carbonyl) (1665  $\text{cm}^{-1}$ ),  $\nu(\text{C=N})$ (azomethine) (1620  $\text{cm}^{-1}$ ) and  $\nu(\text{C—O})$  (1526  $\text{cm}^{-1}$ ).

### Synthesis of 2, 3 (M = Co, Ni)

A MeOH solution (30 mL) of appropriate metal acetate (5 mmol) was added while constant stirring to a MeOH solution (100 mL) of **1** (1.28 g, 5 mmol). The solution was refluxed on a water bath for 2-3 *h*. In order to stop the oxidation of Co(II) to Co(III), the whole operation was carried out in  $\text{N}_2$  atmosphere. The solid residue obtained was suction filtered, washed with MeOH and dried as mentioned above. Yield = 50–70%.

### Synthesis of 4

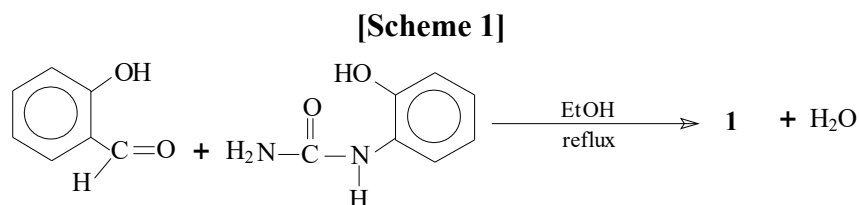
A MeOH solution (30 mL) of iron(III) chloride (anhydrous) (0.81 g, 5 mmol) was added while constant stirring to a MeOH solution (100 mL) of **1** (1.28 g, 5 mmol). The solution was refluxed for 3 *h* under anhydrous conditions and the brown solid obtained was suction filtered, washed with MeOH and dried as mentioned above. Yield = 53%.

### Synthesis of 5

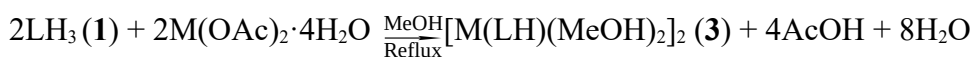
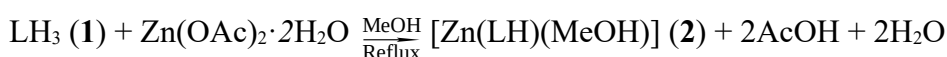
A MeOH solution (50 mL) of freshly prepared HDAOHTZAc (5 mmol) was added to a MeOH solution (50 mL) of **1** (1.28 g, 5 mmol). The mixture was refluxed for 3 *h*. A MeOH solution (50 mL) of MeONa (0.54 g, 10 mmol) was added to the above mixture. The yellow solid obtained was suction filtered, washed with MeOH and dried as mentioned above. Yield = 70%.

## Results and Discussion

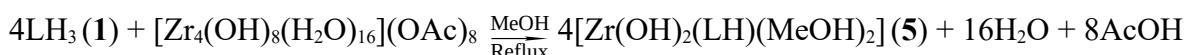
The nucleophilic addition reaction between salicylaldehyde and *o*-hydroxyphenylurea in EtOH in equimolar ratio followed by the elimination of one water molecule results in the formation of LH<sub>3</sub> (**1**) (**Scheme 1**). A MeOH solution of **1** reacts with a MeOH solution Zn(II), Co(II), Ni(II), Fe(III) and Zr(OH)<sub>2</sub>(IV) ions in equimolar ratio and forms **2-5** respectively. The formation of **2-5** takes place according to the **Scheme 2**.



### [Scheme 2]



(M = Co, Ni)



The complexes are insoluble in H<sub>2</sub>O, MeOH and EtOH but soluble in DMF and DMSO. The experimental molar conductance values (4.5–8.2 mho cm<sup>2</sup> mol<sup>-1</sup> in 10<sup>-3</sup> M DMF solution) reveal their non-electrolytic nature (Table 1.1). The molecular weight measurements indicate a dimeric nature of **3** and **4**, while a monomeric nature of **2** and **5**. The coordination compounds, **2-5** do not lose weight on keeping in open air for hours indicating that MeOH molecules are coordinated to metal ions. The coordinated MeOH molecules are lost completely by heating **2-5** up to 120 °C.

### Infrared Spectral Studies

The IR spectra of **1-5** were recorded in KBr (Table 1.2). **1** exhibits a strong band at 2700 cm<sup>-1</sup> due to the intramolecular H-bonded phenolic OH group<sup>[293]</sup>. The coordination compounds exhibit a broad band at ~3400 cm<sup>-1</sup>. This band may be due to (i) coordinated MeOH molecule(s) in **2-5** and/or (ii) due to the enolization of LH<sub>2</sub> during complexation<sup>[193]</sup>. **1** occurs in keto form as evident by the presence of a band at 1665 cm<sup>-1</sup>. The absence of this band and appearance of a new band at ~1240 cm<sup>-1</sup> in **2-5** are indicative of enolisation during complexation and non-involvement of enolic O atom towards coordination. The ν(C=N)(azomethine) stretch<sup>[294]</sup> of **1** occurs at 1620 cm<sup>-1</sup>. On complex formation, this band shifts to lower energy by 13-22 cm<sup>-1</sup> indicating coordination<sup>[21]</sup> through azomethine N atom of **1**. The ν(C—O)φ stretch of **1** occurring at 1526 cm<sup>-1</sup> shifts to higher energy by 6 and 7 cm<sup>-1</sup> (<10 cm<sup>-1</sup>) in **2** and **5** respectively and by 20-35 cm<sup>-1</sup> in **3** and **4** supporting the involvement of phenolic O atom towards coordination<sup>[295]</sup>. The magnitude of the above shift of the ν(C—O)φ stretch indicates a monomeric structure for **2** and **5**, and a dimeric structure for **3** and **4** as in the event of dimeric structure, the ν(C—O)φ stretch is known to shift to higher energy by >10 cm<sup>-1</sup>. The involvement of phenolic O and azomethine N atoms towards coordination is further supported by the appearance of new non-ligand bands between 540-570 and 420-450 cm<sup>-1</sup> due to the ν(M—O) and ν(M—N) vibrations in **2-5**. These

bands are in the expected order of increasing energy:  $\nu(\text{M—N}) < \nu(\text{M—O})$ <sup>[296]</sup> as expected due to the greater dipole moment change in the M—O vibration, greater electronegativity of the O atom than N atom and shorter M—O bond length than the M—N bond length<sup>[297]</sup>. Thus, **1** behaves as a dibasic tridentate ONO donor ligand in **2-5**. The presence of a new band at 832  $\text{cm}^{-1}$  in **4** due to the  $\nu_{\text{as}}(\text{Fe—O—Fe})$  stretch supports the presence of an oxo-bridged structure in it<sup>[298]</sup>. MeOH exhibits the  $\nu(\text{C—O})$  (alcoholic) stretch<sup>[193]</sup> at 1034  $\text{cm}^{-1}$ . This band shifts to lower energy by 50-70  $\text{cm}^{-1}$  in **2-5** confirming the presence of coordinated MeOH<sup>[193]</sup>. The absence of a new band between 825-960  $\text{cm}^{-1}$  in **5** rules out the presence of the  $\nu(\text{Zr=O})$  stretch as well as the formulation of the compound as  $[\text{ZrO}(\text{H}_2\text{O})(\text{LH})(\text{MeOH})_2]$ . The presence of a new band at 1149  $\text{cm}^{-1}$  in the present compound indicates the presence of the  $\delta(\text{Zr—OH})$  bending mode<sup>[262]</sup> and this supports the formulation of this compound as  $[\text{Zr}(\text{OH})_2(\text{LH})(\text{MeOH})_2]$  and not as  $[\text{ZrO}(\text{LH})(\text{H}_2\text{O})(\text{MeOH})_2]$ . Syamal and Kumar<sup>[200]</sup> have developed a non-aqueous titration method for distinguishing the compounds possessing  $[\text{ZrO}]^{2+}$  or  $[\text{Zr}(\text{OH})_2]^{2+}$  moiety. Oxozirconium(IV) compounds react with 3*N* HCl in MeOH and as a result the oxo group gets protonated, while the zirconium(IV) compounds containing  $[\text{Zr}(\text{OH})_2]^{2+}$  moiety do not add up HCl at all.  $[\text{Zr}(\text{OH})_2(\text{LH})(\text{MeOH})_2]$  does not react with 3*N* HCl in MeOH and this conclusively proves the absence of Zr=O bond in it.

### Reflectance Spectral Studies

The nujol mull electronic spectra of **3** (M = Co, Ni) and **4** could not be recorded as they do not form a good mull and hence their reflectance spectra were recorded (Table-1.2). The coordination compound, **3** (where M = Co) shows three bands at 9210, 13550 and 19760  $\text{cm}^{-1}$  due to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$  transitions respectively, in an octahedral environment<sup>[297,299]</sup>. The spectral parameters calculated by following the standard method<sup>[299,300]</sup> and using the free ion Racah parameter (*B*) value<sup>[107]</sup> of 971  $\text{cm}^{-1}$  are:  $\nu_3:\nu_1$  (2.14),  $10Dq$  (10371  $\text{cm}^{-1}$ ), *B* (780.7),  $\beta$  (0.80),  $B^0$  (19.5%) and CFSE (−99.33  $\text{kJ mol}^{-1}$ ). The coordination compound, **3** (when M = Ni) exhibits three bands at 9720, 16390 and 25540  $\text{cm}^{-1}$  due to the  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_3)$  transitions respectively, indicating an octahedral geometry around Ni(II) ions<sup>[301]</sup>. The spectral parameters calculated by following the standard method<sup>[301,302]</sup> and using the free ion Racah parameter (*B*) value<sup>[107]</sup> of 1030  $\text{cm}^{-1}$  are:  $\nu_2:\nu_1$  (1.69),  $10Dq$  (9720  $\text{cm}^{-1}$ ), *B* (799.8),  $\beta$  (0.77),  $B^0$  (23%) and CSFE (−139.65  $\text{kJ mol}^{-1}$ ). The reduction of Racah parameter [from the free ion values: 971  $\text{cm}^{-1}$  to 780.7  $\text{cm}^{-1}$  for Co(II) and from 1030  $\text{cm}^{-1}$  to 799.8  $\text{cm}^{-1}$  for Ni(II)] and the values of % covalence in **3** [(19.5%, when M = Co(II) and 23.0%, when M = Ni(II)] are indicative of the covalent nature of Co(II) and Ni(II) coordination compounds. The  $10Dq$  value of the Co(II) compound is greater than that of the corresponding Ni(II) compound:  $[\text{Co}(\text{LH})_2(\text{MeOH})_2]_2$ , 10371  $\text{cm}^{-1} > [\text{Ni}(\text{LH})_2(\text{MeOH})_2]_2$ , 9720  $\text{cm}^{-1}$ . This is in line with the spectrochemical series of metal ions for a given ligand, given stoichiometry and a given stereochemistry<sup>[302]</sup>: Co(II) > Ni(II). The  $B^0$  value of the Ni(II) compound is comparable to that of the corresponding Co(II) compound:  $[\text{Co}(\text{LH})_2(\text{MeOH})_2]_2$ , 19.5% ~  $[\text{Ni}(\text{LH})_2(\text{MeOH})_2]_2$ , 23%. This is in line with the nephelauxetic metal ion series in terms of *B* and  $B^0$  for a given ligand, given stoichiometry and a given stereochemistry<sup>[302]</sup>. The higher negative CFSE value in the Co(II) coordination compound in comparison to that of the corresponding Ni(II) coordination compound is as expected. **4** exhibits three bands at 12000, 15650 and 19000  $\text{cm}^{-1}$  corresponding to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$  transitions respectively in an octahedral environment<sup>[25]</sup>.

### NMR Studies

The  $^1\text{H}$  NMR spectra of **1** and **2** have been recorded in  $\text{DMSO-d}_6$ . The chemical shifts ( $\delta$ ) are expressed in ppm downfield from TMS<sup>[303]</sup>. **1** exhibits a multiplet at  $\delta$  6.82-8.00 ppm due to the aromatic protons, a singlet at  $\delta$  7.32 ppm due to the azomethine proton, a broad signal at  $\delta$  10.91 ppm due to the phenolic proton and a singlet at  $\delta$  11.73 ppm due to the N—H proton. MeOH exhibits the alcoholic proton at  $\delta$  4.84 ppm and methyl protons at  $\delta$  3.35 ppm. The appearance of the signals due to the alcoholic proton (singlet, 1H) at  $\delta$  2.74 ppm and methyl protons at  $\delta$  3.58 ppm in **2** confirms the presence of MeOH in **2**. The signal due to the azomethine proton appears at  $\delta$  7.03 ppm. This downward shift is indicative of coordination of N atom of  $>\text{C}=\text{N}$  group<sup>[178]</sup>. The appearance of enolic proton at  $\delta$  13.5 ppm and absence of N—H proton in **2** indicate the enolization of the keto group during complex formation and non-involvement of enolic O towards coordination.

### Magnetic Measurements

The experimental values (4.3 and 2.5 B.M.) of the magnetic moment for the dimetallic coordination compounds,  $[\text{Co}(\text{LH})(\text{MeOH})_2]_2$  and  $[\text{Ni}(\text{LH})(\text{MeOH})_2]_2$  respectively are lower than the corresponding spin-only values<sup>[304]</sup>. These lower values are due to the presence of an antiferromagnetic exchange between the two metal ions connected by phenoxo bridges. The magnetic moment of **4** is 5.03 B.M. This value is also lower than the expected value for high-spin  $d^5$  state ( $\mu_{\text{eff}} = 5.92$  B. M.) and this indicates the presence of an antiferromagnetic exchange interaction in **4**. The lower value suggests the dimerization through the phenolic O atom of  $\text{LH}_3$ <sup>[107]</sup>. The coordination compounds of Zn(II) and Zr(IV) are diamagnetic as expected.

### Thermo-gravimetric Analyses

The thermo-gravimetric analyses of **2** and **5** indicate that these compounds decompose in two stages. A mass loss of 9.27% (calcd 9.11%) and 14.56% (calcd 14.44%) between 80-120 °C, occurring in the above compounds indicates the loss of one and two coordinated MeOH molecules respectively. A steep decrease in weight (between 250-600 °C) attributes to the decomposition of organic skeleton. The plateau obtained after heating the residue above 600 °C corresponds to the formation of metal oxides [ $\text{ZnO}$  (obsd = 23.48%, calcd = 23.16%) and  $\text{ZrO}_2$  (obsd = 27.52%, calcd = 23.8%)]. These values are in accordance with the proposed formulae for these compounds.

### Molecular Modeling

The 3-D molecular modeling of **1** and **2** have been carried out using hyperchem series of program<sup>[305]</sup>. The structures have been optimized using molecular mechanics and semiempirical ZINDO/1 (Polak-Ribiere, RMS = 0.01 kcal). The energy optimized structures of **1** and **2** are presented in Figures 6 and 7 respectively. The computed structural properties of the above compounds and their selected bond lengths and bond angles are listed in Table 1.3. The model of **1** shows significantly short [ $\text{C}(7)=\text{N}(8)$ , 1.32 Å] bond length indicating the double bond character between C and N atoms. Also, the [ $\text{C}(5)-\text{C}(7)$ , 1.42 Å], [ $\text{C}(13)-\text{O}(21)$ , 1.32 Å] bond lengths are comparable to the reported values<sup>[306]</sup>. The geometry optimized model of **2** possesses bond length [ $\text{Zn}(1)-\text{O}(2)$ , 2.165 Å] and bond angles [ $\text{N}(3)-\text{Zn}(1)-\text{O}(4)$ , 100.3°], [ $\text{O}(2)-\text{Zn}(1)-\text{N}(3)$ , 92.508°] comparable to those reported using X-ray crystallography<sup>[307]</sup>.

## Conclusion

The reaction of the dibasic tridentate ONO donor Schiff base (**1**) with Zn(II), Co(II), Ni(II), Fe(III) and Zr(OH)<sub>2</sub>(IV) ions results in the formation of coordination compounds with different geometries. [M(LH)(MeOH)]<sub>2</sub> (**3**) (where M = Co, Ni) and [FeCl(LH)(MeOH)]<sub>2</sub> (**4**) are dimetallic having an octahedral geometry around the metal ion. [Zn(LH)(MeOH)] (**2**) is monometallic with tetrahedral geometry. [Zr(OH)<sub>2</sub>(LH)(MeOH)<sub>2</sub>] (**5**) is monometallic with trigonal-bipyramidal geometry. The coordination compounds of **1** are quite comparable to those of the isomeric Schiff base derived from the condensation of salicylaldehyde and salicylhydrazide.

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