

# Ligational Behavior of the Azetidin-2-One Derived From Salicylaldehyde and O-Hydroxyphenylurea towards Some Di-, Tri- and Hexavalent Metal Ions

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**Abstract** – The cyclo-addition reaction of  $LH_3$  (**1**) with chloroacetyl chloride in the presence of  $Et_3N$  in dioxane affords the corresponding azetidin-2-one,  $L'H_3$  (**8**). The reaction of **8** with  $Cu(II)$ ,  $Cd(II)$ ,  $Mn(II)$ ,  $Fe(III)$  and  $MoO_2(VI)$  ions in MeOH results in the formation of corresponding coordination compounds,  $[Cu(OAc)(L'H_2)]$  (**9**),  $[Cd(OAc)(L'H_2)]$  (**10**),  $[Mn(OAc)(L'H_2)(MeOH)_2]$  (**11**),  $[FeCl_2(L'H_2)(MeOH)]$  (**12**) and  $[MoO_2(acac)(L'H_2)(MeOH)]$  (**13**). The compounds have been characterized on the basis of elemental analyses, molecular weight, molar conductance, spectral (IR, reflectance, ESR) and magnetic susceptibility measurements. **8** acts as a monobasic tridentate ONO donor ligand in these monomeric compounds. A square-planar structure for **9**, a tetrahedral structure for **10** and an octahedral structure for **11** and **12** have been proposed. **13** affords an eight-coordinate structure.

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## INTRODUCTION

The 2-carbonyl derivatives of azetidine containing a four-membered heterocyclic ring with N as heteroatom, are known as azetidin-2-one or  $\beta$ -lactam. They are most widely used antibiotic, antimicrobial, anti-inflammatory, anticonvulsant and antitubercular substances<sup>[308]</sup>. They also act as enzyme inhibitors and are effective on central nervous system<sup>[309]</sup>. In view of the above importance of azetidin-2-one and in continuation of our earlier work on the metal complexes of azetidin-2-one<sup>[310]</sup>, the syntheses and characterization of the coordination compounds of **8** with  $Cu(II)$ ,  $Cd(II)$ ,  $Mn(II)$ ,  $Fe(III)$  and  $MoO_2(VI)$  ions are presented in this Chapter.

## 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, molar conductivity measurements, spectral (IR, reflectance, ESR) studies and magnetic susceptibility

measurements were carried out by the methods described in Appendix-3.

### Synthesis of **8**

Chloroacetyl chloride (2.26 g, 20 mmol) was added drop wise during a period of 2 h to a continuously stirred dioxane solution (50 mL) of **1** (2.56 g, 10 mmol) in the presence of  $Et_3N$  (3.03 g, 30 mmol). Triethylamine hydrochloride formed was filtered off and the volume of the filtrate was reduced to 50%. The solution was kept aside for 24 h and the solid product formed was suction filtered, washed with dioxane, recrystallized from  $CHCl_3$  and then dried as mentioned elsewhere. Yield = 30%; anal.  $[C_{16}H_{13}N_2O_4Cl]$ ; found(calcd)%; C = 57.44(57.74), H = 3.82(3.91), N = 8.45(8.42), Cl = 10.43(10.68); IR bands (KBr):  $\nu(O-H)$  (intramolecular H-bonding) (2765  $cm^{-1}$ ),  $\nu(C=O)(\beta\text{-lactam})$  (1728  $cm^{-1}$ ),  $\nu(C=O)(\text{amide})$  (1670  $cm^{-1}$ ),  $\nu(C-O)\phi$  (1510  $cm^{-1}$ ),  $\nu(C-N)(\beta\text{-lactam})$  (1410  $cm^{-1}$ ) and  $\nu(C-Cl)(\beta\text{-lactam})$  (780  $cm^{-1}$ ).

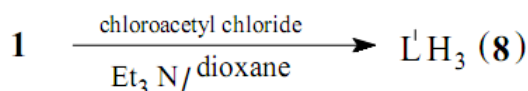
### Syntheses of **9-13**

A MeOH solution (30-50 mL) of appropriate metal acetate/chloride/complex (10 mmol) was added to a MeOH solution (50 mL) of **8** (3.32 g, 10 mmol). The solution was refluxed for ~ 4 h on a water bath and

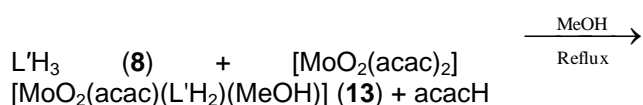
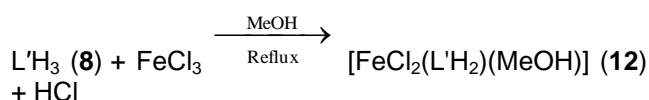
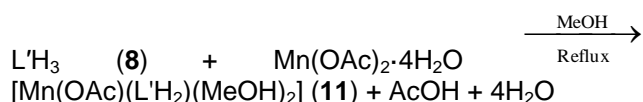
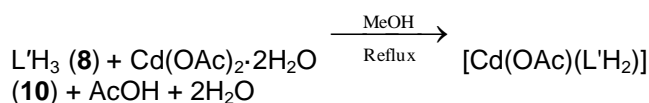
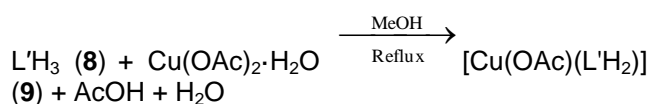
the solid products obtained were suction filtered, washed with MeOH and dried as mentioned above. Yield = 50-60%.

## RESULTS AND DISCUSSION

The Schiff base, sal-o-hydroxyphenylurea (**1**) undergoes cyclo-condensation reaction with chloroacetyl chloride in dioxane in the presence of  $\text{Et}_3\text{N}$  and forms **8** (Scheme 3). The reaction of the latter with appropriate metal ions in 1:1 molar ratio produces the monomeric coordination compounds of the types,  $[\text{Cu}(\text{OAc})(\text{L}'\text{H}_2)]$  (**9**),  $[\text{Cd}(\text{OAc})(\text{L}'\text{H}_2)]$  (**10**),  $[\text{Mn}(\text{OAc})(\text{L}'\text{H}_2)(\text{MeOH})_2]$  (**11**),  $[\text{FeCl}_2(\text{L}'\text{H}_2)(\text{MeOH})]$  (**12**) and  $[\text{MoO}_2(\text{acac})(\text{L}'\text{H}_2)(\text{MeOH})]$  (**13**). The formations of **9-13** takes place according to the Scheme 4.



[Scheme 3]



[Scheme 4]

The coordination compounds are insoluble in common solvents such as  $\text{H}_2\text{O}$ , MeOH, EtOH but are soluble in DMF and DMSO. The experimental molar conductance values ( $5.3\text{--}8.3 \text{ mho cm}^2 \text{ mol}^{-1}$  in  $10^{-3} \text{ M}$  DMF solution) of these compounds are indicative of their non-electrolytic nature. The analytical data of **8** and its coordination compounds are presented in Table 2.1.

## INFRARED SPECTRAL STUDIES

The IR spectra of **8-13** were recorded in KBr and the prominent peaks are presented in Table 2.2. The Schiff base (**1**) exhibits the  $\nu(\text{C}=\text{O})$ (carbonyl),  $\nu(\text{C}=\text{N})$ (azomethine) and  $\nu(\text{C}-\text{O})\phi$  stretches at  $1665$ ,  $1620$  and  $1526 \text{ cm}^{-1}$  respectively. The  $\nu(\text{C}=\text{N})$ (azomethine) stretch of **1** disappears in **8** and a new band due to the  $\nu(\text{C}-\text{N})$ ( $\beta$ -lactam) stretch appears at  $1410 \text{ cm}^{-1}$  supporting the formation of the corresponding azetidin-2-one<sup>[31]</sup>. The formation of **8** is further supported by the appearance of a new band at  $1728 \text{ cm}^{-1}$  and other at  $780 \text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$ ( $\beta$ -lactam) and the  $\nu(\text{C}-\text{Cl})$ ( $\beta$ -lactam) stretches respectively<sup>[312]</sup>. The  $\nu(\text{C}-\text{O})\phi$  stretch of **8** occurring at  $1510 \text{ cm}^{-1}$  shifts to higher energy by  $\leq 10 \text{ cm}^{-1}$  in **9-13** indicating the involvement of phenolic O atom towards coordination. The magnitude of above shift of the  $\nu(\text{C}-\text{O})\phi$  stretch indicates the monomeric nature of the present coordination compounds. The molecular weight data also suggest their monomeric nature. **8** occurs in keto form as evident by the presence of a band at  $1670 \text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$ (amide) stretch<sup>[91]</sup>. The persistence of this band at the same energy in **8** as well as in **9-13** indicates the non-involvement of amide O atom towards coordination. The  $\nu(\text{C}=\text{O})$ ( $\beta$ -lactam) stretch of **8** occurring at  $1728 \text{ cm}^{-1}$  shifts to lower energy by  $12\text{--}30 \text{ cm}^{-1}$  indicating the involvement of O atom of  $\beta$ -lactam moiety towards coordination<sup>[313]</sup>. The Cl atom of the  $\beta$ -lactam ring does not participate in coordination as evident by the presence of the  $\nu(\text{C}-\text{Cl})$ ( $\beta$ -lactam) stretch at the same energy in **8** and **9-13**. The appearance of a broad band between  $3360\text{--}3440 \text{ cm}^{-1}$  due to the  $\nu(\text{O}-\text{H})(\text{MeOH})$  stretch and the decrease of the  $\nu(\text{C}-\text{O})(\text{MeOH})$  stretch from  $1034 \text{ cm}^{-1}$  to lower energy by  $40\text{--}60 \text{ cm}^{-1}$  in **11-13** indicates the presence of coordinated MeOH molecule(s)<sup>[314]</sup>. The  $\nu_{\text{as}}(\text{OAc})$  and  $\nu_{\text{s}}(\text{OAc})$  stretches of free acetate ions occur at  $1560$  and  $1416 \text{ cm}^{-1}$  respectively<sup>[25]</sup>. These bands occur between  $1586\text{--}1595$  and  $1372\text{--}1380 \text{ cm}^{-1}$  respectively in **9-11**. The magnitude of energy separation ( $\Delta\nu = 211\text{--}223$ ) between  $\nu_{\text{as}}(\text{OAc})$  and  $\nu_{\text{s}}(\text{OAc})$  stretches is  $>144 \text{ cm}^{-1}$  which indicates the monodentate nature<sup>[315]</sup> of acetate group in **9-11**. The occurrence of two bands, one at  $940 \text{ cm}^{-1}$  and other at  $880 \text{ cm}^{-1}$  in **13**, due to the  $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$  stretches respectively, indicates the presence of a *cis*- $\text{MoO}_2$  configuration in it<sup>[208]</sup>. Acetylacetone is coordinated here as a monobasic bidentate OO donor ligand as evident by the presence of a band at  $1695 \text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  stretch<sup>[316]</sup>. The new non-ligand bands in the present coordination compounds in the low frequency region are assigned as  $\nu(\text{M}-\text{O})(550\text{--}575 \text{ cm}^{-1})$  and  $\nu(\text{M}-\text{N})(430\text{--}465 \text{ cm}^{-1})$  and these bands are in the expected order of increasing energy:  $\nu(\text{M}-\text{N}) < \nu(\text{M}-\text{O})$ <sup>[297]</sup>.

## REFLECTANCE SPECTRAL STUDIES

The appearance of an asymmetric band at  $17450 \text{ cm}^{-1}$  due to the  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{2g}$  and  ${}^2E_g$  transitions in **9** is consistent with the Cu(II) ion in a square-planar environment<sup>[30]</sup>. **11** exhibits three bands at  $16236$ ,

23400 and 25570  $\text{cm}^{-1}$  due to the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)(v_1)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)(v_2)$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)(v_3)$  transitions respectively in an octahedral symmetry<sup>[300]</sup>. **12** exhibits three bands at 12450, 15000 and 19220  $\text{cm}^{-1}$  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 octahedral symmetry<sup>[300]</sup>.

## ESR SPECTRAL STUDIES

The X-band ESR spectrum of **9** shows usual anisotropic pattern with two g values, which are characteristic of tetragonal type symmetry. Its spin Hamiltonian parameters are:  $A_{||} = 1.50 \times 10^{-2} \text{ cm}^{-1}$ ,  $A_{\perp} = 3.0 \times 10^{-3} \text{ cm}^{-1}$ ,  $g_{||} = 2.8$ ,  $g_{\perp} = 2.08$ ,  $\kappa = 0.49$ ,  $G = 3.50$ ,  $P_d = 1.54 \times 10^{-2} \text{ cm}^{-1}$ ,  $\kappa P_d = 7.55 \times 10^{-2} \text{ cm}^{-1}$ ,  $\alpha^2_{Cu} = 0.77$  and  $(\alpha')^2 = 0.33$ . The pattern  $g_{||} > g_{\perp} > 2$  is suggestive of  $d_{x^2-y^2}$  ground state. The value of  $g_{||}$  (2.28) indicates the covalent character in the metal-ligand bonding. The value of G (3.50) is indicative of strong field nature of the ligand in the complex. The values of  $\alpha^2_{Cu}$  (0.77) and  $(\alpha')^2$  (0.33) indicate the covalent nature of **9**. The positive value of  $\kappa$  (0.49) suggests that  $A_{||}$  should be greater than  $A_{\perp}$ . The  $P_d$  value ( $1.54 \times 10^{-2} \text{ cm}^{-1}$ ) is lower than free ion value ( $3.5 \times 10^{-2} \text{ cm}^{-1}$ ), which is suggestive of the presence of the covalent character between metal-ligand bonding. The absence of a band at ~1500 gauss due to  $\Delta M_s = 2$  transition in **9** rules out the presence of Cu—Cu interaction.

## MAGNETIC MEASUREMENTS

The room temperature magnetic moments of the compounds are presented in Table 2.2. The Cu(II) ion belongs to  $S = \frac{1}{2}$  system and since its spin-orbit coupling constant is negative, the magnetically dilute Cu(II) compounds, due to the presence of orbital contribution are expected to exhibit magnetic moments higher than the spin-only value (1.73 B.M.). The magnetic moment of **9** is 1.87 B.M. in the range expected for the monomeric Cu(II) compounds. The magnetic moment of **11** is 5.81 B.M., which lies in the normal range reported for the magnetically dilute octahedral compounds of Mn(II) ions<sup>[107]</sup>. The magnetic moment of **12** is 5.78 B.M. suggesting a high-spin octahedral environment around Fe(III) ion in the complex<sup>[317]</sup>. The coordination compounds of Cd(II) and MoO<sub>2</sub>(VI) ions are diamagnetic as expected.

## CONCLUSION

On the basis of analytical data, valence requirements and spectral studies, it is proposed that **8** behaves as a monobasic tridentate ONO donor ligand in these monomeric and non-electrolyte coordination compounds. The data suggest a square-planar structure for **9**, a tetrahedral structure for **10**, an octahedral structure for **11** and **12**. The compound, **13** is eight-coordinate.

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