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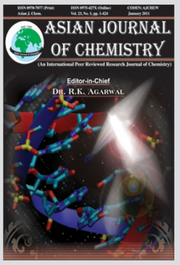

Ligational Behaviour of the Azetidinone Towards Some Di-, Tri-, Tetra- and Hexavalent Metal Ions

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A methanolic solution of salicylaldehyde reacts with *o*-hydroxyphenylurea in methanol to yield Schiff base (**1**) *via* nucleophilic addition reaction followed by the elimination of one water molecule. The cycloaddition reaction of **1** with chloroacetyl chloride in presence of Et_3N in dioxane affords the corresponding azetidin-2-one, LH_3 (**2**). The reaction of **2** with Cu(II), Zn(II), Cd(II), Mn(II), Co(II), Ni(II), Fe(III), MoO_2(VI), UO_2(VI) and $Zr(OH)_2$(IV) ions in methanol results in the formation of $[Cu(OAc)(LH_2)]$ (**3**), $[M(OAc)(LH_2)]$ (here M = Zn(II), Cd(II)) (**4**), $[M'(OAc)(LH_2)(MeOH)_2]$ (here M' = Mn(II), Co(II), Ni(II) (**5**), $[FeCl_2(LH_2)(MeOH)]$ (**6**), $[MoO_2(acac)(LH_2)(MeOH)]$ (**7**), $[UO_2(OAc)(LH_2)(MeOH)_2]$ (**8**) and $[Zr(OH)_2(OAc)(LH_2)]$ (**9**). The compounds have been characterized on the basis of elemental analyses, molecular weight, molar conductance, spectral (IR, UV-VIS, ESR) and magnetic susceptibility measurements. **2** acts as a monobasic tridentate ONO donor ligand in these monomeric complexes. A square-planar structure for **3**, a tetrahedral structure for **4** and an octahedral structure for **5**, **6** and **9** have been proposed. **7** and **8** afford an eight-coordinate structure.

Key Words: *o*-Hydroxyphenylurea, Schiff base, Azetidin-2-one, Cyclocondensation reaction.

INTRODUCTION

The 2-carbonyl derivatives of azetidine which contains a four membered heterocyclic ring with N as heteroatom, are known as 2-azetidinone or β-lactam. They are most widely used antibiotic, antimicrobial, anti-inflammatory, anticonvulsant and antitubercular substances[1]. They also function as enzyme inhibitors and are effective on central nervous system[2]. In view of the above importance of 2-azetidinone and in continuation of our earlier work on the metal complexes of 2-azetidinones[3] it was thought worthwhile to synthesize coordination compounds of **2** with Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, MoO_2^{2+}, UO_2^{2+} and $Zr(OH)_2^{2+}$ ions.

EXPERIMENTAL

Manganese(II) acetate tetrahydrate, salicylaldehyde (Sarabhai); cobalt(II) acetate tetrahydrate, cadmium(II) acetate dihydrate, dioxouranium(VI) acetate tetrahydrate, iron(III) chloride (anhydrous) (BDH); nickel(II) acetate tetrahydrate (Fluka); copper(II) acetate monohydrate (IDPL); zinc(II) acetate dihydrate (S.D.'s Fine Chemicals); urea (Nice) and *o*-aminophenol (CDH); methanol, triethylamine, chloroacetyl chloride and dioxane (Ranbaxy) were used as received for the syntheses. Hexadecaaquaoctahydroxotetrazirconium(IV)-acetate and *bis*(acetylacetonato)dioxomolybdenum(VI) were synthesized by following the published procedures[4].

Analyses and physical measurements: The metal contents of the respective coordination compounds were estimated by the methods reported earlier[3]. CHN analyses were carried out by Eager CHN analyzer model-300. The chlorine content was determined gravimetrically as silver chloride. The molecular weights of the coordination compounds were determined by the Rast method using diphenyl as the solvent[5]. The molar conductances were carried out in DMF with the help of a Toshniwal conductivity bridge (CL01-02A) and a dip type cell calibrated with KCl solutions. The IR spectra of **1-9** were recorded in KBr pellets (4000-400 cm^{-1}) on a Beckman-20 spectrophotometer. The reflectance spectra were recorded on a Beckmann DU spectrophotometer attached with a reflectance arrangement. ESR spectrum of the Cu^{2+} complex was recorded at LNT as polycrystalline solid on a Varian V 4502-12 X-band ESR spectrometer with 100 KHz modulation using DPPH as g-marker and monitoring the frequency with a frequency meter. The magnetic susceptibility measurements were carried out at room temperature, using $Hg[Co(NCS)_4]$ as the standard[6]. 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^{2+} and Co^{2+}, 60 × 10^{-6} cgs units for Cu^{2+} and zero for Mn^{2+} and Fe^{3+} ions.

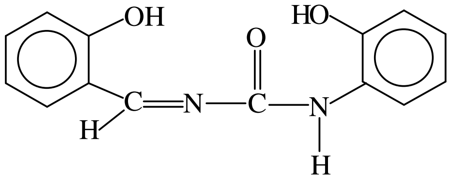
Synthesis of compound 1: An EtOH solution (50 mL) of *o*-hydroxyphenylurea (15.2 g, 0.1 mol) and salicylaldehyde (12.2 g, 0.1 mol) were refluxed on a water bath for 1 h. The excess of solvent was evaporated and the mixture was allowed to stand at room temperature. The brown compound separated out was suction filtered, washed with and recrystallized from EtOH. The compound was dried *in vacuo* at room temperature over silica gel. m.p. = 162 ºC, Yield = 70 %; Anal. [$C_{14}H_{12}N_2O_3$; found (calcd) % C = 65.58 (65.62); H = 4.75 (4.69); N = 10.88 (10.94); IR (KBr, ν_{max}, cm^{-1}): 1665 [(C=O)(carbonyl)], 1620 [(C=N)(azomethine)] and 1526 [(C-O)ϕ].

Synthesis of compound 2: To a dioxane solution (50 mL) of **1** (2.56 g, 10 mmol), chloroacetyl chloride (2.26 g, 20 mmol) was added dropwise, in presence of triethylamine (3.03 g, 30 mmol) during a period of 2 h with constant stirring. 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 and recrystallized from $CHCl_3$ and then dried as mentioned above. Yield = 30 %; Anal. [$C_{16}H_{13}N_2O_4Cl$; found (calcd) % C = 57.67 (57.74); H = 3.83 (3.91); N = 8.51 (8.42), Cl = 10.52 (10.68); IR (KBr, ν_{max}, cm^{-1}): 2765 [(O–H)(intramolecular H-bonding)], 1728 [(C=O)(β-lactam)], 1670 [(C=O)(amide)], 1510 [(C–O)ϕ], 1410 [(C–N)(β-lactam)] and 780 [(C–Cl)(β-lactam)].

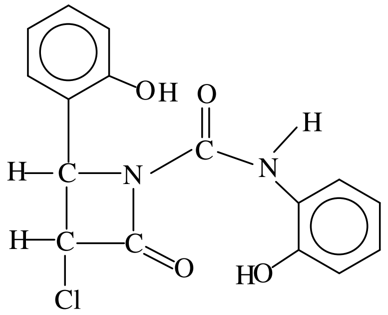
General procedure for the syntheses of compounds 3-9: A MeOH solution (30-50 mL) of appropriate metal acetate/chloride/complex (10 mmol) was added to a MeOH solution (50 mL) of 2 (3.32 g, 10 mmol) and the mixture was than refluxed for *ca.* 4 h on a water bath. The solid product obtained was suction filtered, washed with MeOH and dried as mentioned above (Yield = 50-60 %).

RESULTS AND DISCUSSION

The Schiff base, sal-*o*-hydroxyphenylurea (**1**), in dioxane in the presence of Et_3N undergoes cyclocondensation reaction with chloroacetyl chloride and forms **2**. The reaction of latter with appropriate metal ions in 1:1 molar ratio produces [$Cu(OAc)(LH_2)$] (**3**), [$M(OAc)(LH_2)$] (here M = Zn^{2+}, Cd^{2+}) (**4**), [$M'(OAc)(LH_2)(MeOH)_2$] (here M' = Mn^{2+}, Co^{2+}, Ni^{2+}) (**5**), [$FeCl_2(LH_2)(MeOH)$] (**6**), [$MoO_2(acac)(LH_2)(MeOH)$] (**7**), [$UO_2(OAc)(LH_2)(MeOH)_2$] (**8**) and [$Zr(OH)_2(OAc)(LH_2)$] (**9**). The coordination compounds are insoluble in common solvents such as H_2O, MeOH, EtOH but are soluble in DMF and DMSO. The molar conductance data of these monomeric complexes are indicative of their non-electrolytic nature in DMF. The analytical data of compound **2** and its coordination compounds are presented in Table-1.



(**1**)



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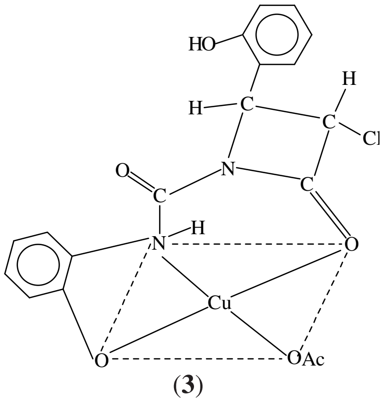


(**3**)

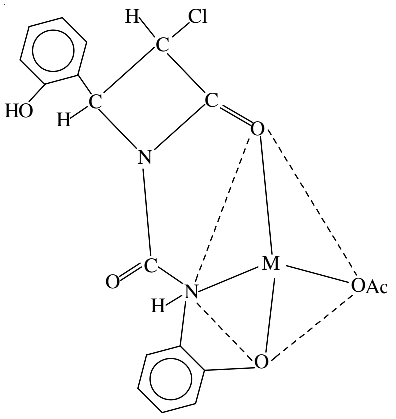
TABLE-1
ANALYTICAL, MOLAR CONDUCTANCE AND MOLECULAR WEIGHT OF COMPOUNDS

Compd.	Stoichiometry	Λ_M (mho cm^2 mol^{-1})	Found (calcd.) (%)					
			m.w.	M	C	H	N	Cl
1	$C_{14}H_{12}N_2O_3$	–	256.0[a] (256.0)	–	65.58 (65.62)	4.75 (4.69)	10.88 (10.94)	–
2	$C_{16}H_{13}N_2O_4Cl$	–	332.5[a] (332.5)	–	57.44 (57.74)	3.82 (3.91)	8.45 (8.42)	10.43 (10.68)
3	$CuC_{18}H_{15}N_2O_6Cl$	8.3	423.4 (454.0)	13.78 (13.99)	47.45 (47.58)	3.12 (3.30)	6.25 (6.17)	7.95 (7.82)
4 (M = Zn)	$ZnC_{18}H_{15}N_2O_6Cl$	3.8	436.7 (455.9)	14.28 (14.34)	47.21 (47.38)	3.34 (3.29)	6.08 (6.14)	7.63 (7.79)
4 (M = Cd)	$CdC_{18}H_{15}N_2O_6Cl$	6.3	513.8 (502.9)	22.58 (22.35)	42.72 (42.95)	2.92 (2.98)	5.63 (5.57)	7.17 (7.06)
5 (M' = Mn)	$MnC_{20}H_{23}N_2O_8Cl$	5.3	530.2 (509.4)	10.61 (10.78)	47.25 (47.11)	4.62 (4.52)	5.67 (5.50)	6.84 (6.97)
5 (M' = Co)	$CoC_{20}H_{23}N_2O_8Cl$	2.6	542.7 (513.4)	11.33 (11.47)	46.88 (46.75)	4.56 (4.48)	5.32 (5.45)	6.73 (6.91)
5 (M' = Ni)	$NiC_{20}H_{23}N_2O_8Cl$	6.3	537.4 (513.2)	11.27 (11.44)	46.57 (46.76)	4.54 (4.48)	5.49 (5.46)	7.08 (6.92)
6	$FeC_{17}H_{16}N_2O_5Cl_3$	7.2	478.6 (490.5)	11.36 (11.42)	40.78 (41.59)	3.19 (3.26)	5.58 (5.71)	21.93 (21.71)
7	$MoC_{22}H_{23}N_2O_9Cl$	8.3	561.2 (590.5)	16.35 (16.26)	44.52 (44.71)	3.81 (3.90)	4.62 (4.74)	6.14 (6.01)
8	$UC_{20}H_{23}N_2O_{10}Cl$	4.3	698.9 (724.5)	32.62 (32.85)	33.28 (33.13)	3.28 (3.17)	3.75 (3.86)	4.73 (4.90)
9	$ZrC_{18}H_{17}N_2O_8Cl$	6.1	546.3 (515.7)	17.57 (17.68)	41.65 (41.88)	3.37 (3.30)	5.57 (5.43)	6.72 (6.88)

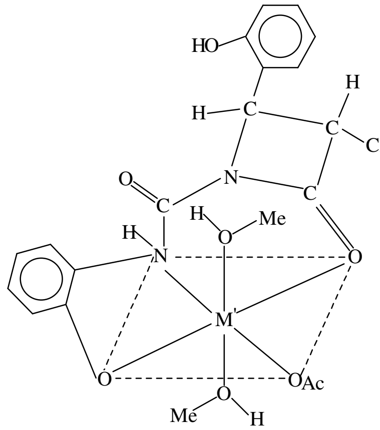
[a] Mass spectral data

TABLE-2
IR, REFLECTANCE SPECTRAL DATA (cm^{-1}) AND MAGNETIC MOMENTS OF THE COORDINATION COMPOUNDS

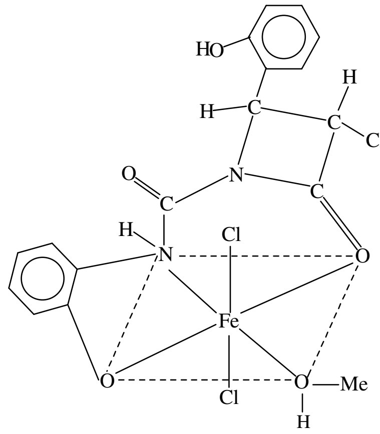
Compound	ν(C=O) (β-lactam)	ν(C–O) (ϕ)	ν_{as}(OAc)	ν_{s}(OAc)	ν(C–O) (MeOH)	ν_{max}	Magnetic moment (BM)
2	1728	1510	–	–	–	–	–
3	1713	1512	1586	1375	–	17450	1.87
4 (M = Zn)	1708	1516	1580	1370	–	–	Diamagnetic
4 (M = Cd)	1716	1517	1595	1372	–	–	Diamagnetic
5 (M' = Mn)	1698	1514	1592	1380	992	16236, 23400, 25570	5.81
5 (M' = Co)	1710	1514	1610	1395	982	8600, 16300, 19220	4.64
5 (M' = Ni)	1706	1516	1597	1382	990	9200, 16920, 25220	3.34
6	1714	1512	–	–	994	12450, 15000, 19220	5.78
7	1700	1516	–	–	974	–	Diamagnetic
8	1704	1513	1602	1390	978	–	Diamagnetic
9	1708	1515	1600	1388	–	–	Diamagnetic



(**4**; M = Zn^{2+}, Cd^{2+})



(**5**; M' = Mn^{2+}, Co^{2+}, Ni^{2+})



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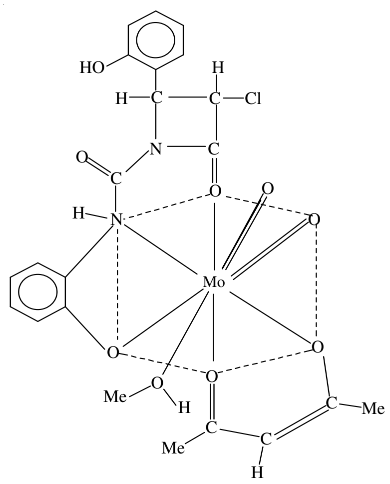

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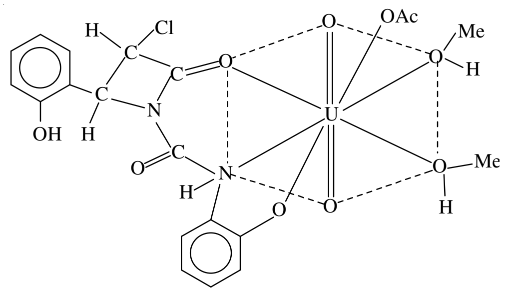

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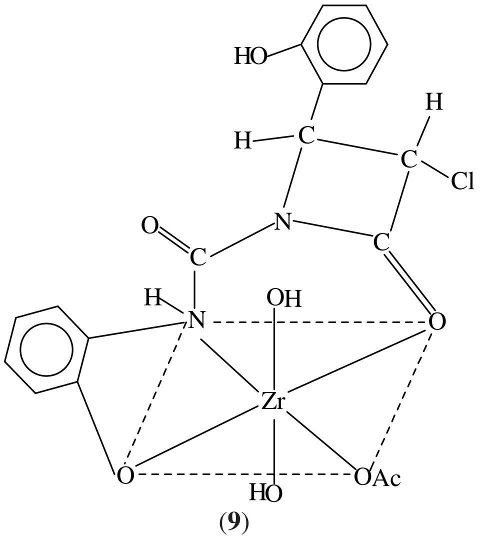

(**9**)

The IR spectra of compounds **1-9** were recorded in KBr and the prominent peaks are presented in Table-2. The Schiff base (**1**) exhibits the ν(C=O)(carbonyl), ν(C=N)(azomethine) and ν(C–O)ϕ stretches at 1665, 1620 and 1526 cm^{-1}, respectively. The ν(C=N)(azomethine) stretch of **1** disappears in **2** and a new band due to the ν(C–N)(β-lactam) stretch appears at 1410 cm^{-1} supporting the formation of corresponding 2-azetidinone[7]. The formation of **2** is further supported by the appearance of a new band at 1728 cm^{-1} and other at 780 cm^{-1} due to the ν(C=O)(β-lactam) and the ν(C–Cl)(β-lactam) stretches, respectively[8]. The ν(C–O)ϕ stretch of **2** occurring at 1510 cm^{-1} shifts to higher energy by ≤ 10 cm^{-1} in **3-9** indicating the involvement of phenolic O atom towards coordination. The magnitude of above shift of the ν(C–O)ϕ stretch indicates the monomeric nature of present coordination compounds. The molecular weight data also suggest their monomeric nature. Compound **2** occurs in keto form as evident by the presence of a band at 1670 cm^{-1} due to the ν(C=O)(amide) stretch[9]. The persistence of this band at the same energy in **2** as well as in **3-9** indicates the non-involvement of ketonic O (amide) towards coordination. The ν(C=O)(β-lactam) stretch of **2** occurring at 1728 cm^{-1} shifts to lower energy by 12-30 cm^{-1} indicating the involvement of O atom of β-lactam moiety towards coordination[10]. The Cl atom of the β-lactam ring does not participate in coordination as evident by the presence of the ν(C--Cl)(β-lactam) stretch at the same energy in **2** and **3-9**. The presence of a broad band between 3440-3360 cm^{-1} due to the ν(O-H)(MeOH) stretch and the decrease of the ν(C–O)(MeOH) stretch from 1034 cm^{-1} to lower energy by 40-60 cm^{-1} in **5-8** indicates the presence of coordinated MeOH molecule(s)[11]. The ν_{as}(OAc) and ν_s(OAc) stretches of free acetate ions occur at 1560 and 1416 cm^{-1} respectively[11]. These bands occur between 1610-1580 and 1395-1370 cm^{-1} respectively in **3-9**. The magnitude of energy separation (Δν = 211-223) between ν_{as}(OAc) and ν_s(OAc) is >144 cm^{-1} indicates the monodentate nature of acetato group in **3-9** except **6** and **7**. The occurrence of two bands, one at 940 cm^{-1} and other at 880 cm^{-1} in **7**, due to the ν_s(O=Mo=O) and ν_{as}(O=Mo=O) stretches, respectively, indicates the presence of a *cis*-MoO_2 configuration in it[12]. Acetylacetone is coordinated here as a monobasic bidentate OO donor ligand as evident by the presence of a band at 1695 cm^{-1} due to the ν(C=O) stretch[13]. Compound **8** exhibits the ν_{as}(O=U=O) stretch at 884 cm^{-1}, which lies in the usual range (950-870 cm^{-1}) observed for the majority of *trans*-UO_2(VI) compounds[14]. The presence of a band at 3420 cm^{-1} due to the ν(OH) stretch and appearance of a new medium intense band at 1136 cm^{-1} due to the δ(Zr–OH) bending mode support the proposed structure of the **9**[15]. The new non-ligand bands in the present coordination compounds in the low frequency region are assigned as ν(M–O)(575-550 cm^{-1}) and ν(M–N)(465-430 cm^{-1}) and these bands are in the expected order of increasing energy: ν(M–N) < ν(M–O)[16].

The appearance of an asymmetric band at 17450 cm^{-1} in the reflectance spectrum of **3** due to the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions is consistent with the Cu^{2+} ion in square-planar environment[17]. Compound **5** (M' = Mn^{2+}) exhibits three bands at 16236, 23400 and 25570 cm^{-1} due to the $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ (ν_1), $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ (ν_2) and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$($\nu_3$) transitions, respectively in an octahedral symmetry[18]. The corresponding Co^{2+} complex shows three bands at 8600, 16300 and 19220 cm^{-1}, due to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2), $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively in an octahedral symmetry[18]. The ν_3:ν_1 value (2.3) lies in the usual range (2.0-2.8) for the majority of the octahedral Co^{2+} complexes. The spectral data are: Dq = 972.24 cm^{-1}, B = 782.82, β = 0.81 and % covalance = 19.0. The reduction of Racah parameter from the free ion value of 971 to 782.82 cm^{-1} and the % covalance value indicate the covalent nature of the compound and strong field nature of the ligand[19]. Compound **5** (M' = Ni^{2+}) shows three bands at 9200, 16920 and 25220 cm^{-1}, due to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_3) transitions, respectively in an octahedral symmetry[19]. The ν_2:ν_1 value is 1.8, which lies in the usual range (1.6-1.82) for octahedral Ni^{2+} complexes. The spectral parameters are: Dq = 920 cm^{-1}, B = 840.08, β = 0.81 and % covalace = 19.0. The reduction of Racah parameter from the free ion value of 1030 to 840.08 cm^{-1} and the % covalancy value indicate the covalent nature of the compound and strong field nature of the ligand[19]. Our calculated 10Dq values indicate that the 10Dq values are in the expected order: $Ni^{2+} < Co^{2+}$. Compound **6** exhibits three bands; at 12450, 15000 and 19220 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[18].

The X-band ESR spectrum of **3** shows usual anisotropic pattern with two g values, which are characteristic of tetragonal type symmetry. The spin Hamiltonian parameters of the complex are: $A_{ll} = 1.50 \times 10^{-2}$ cm^{-1}, $A_{\perp} = 3.0 \times 10^{-3}$ cm^{-1}, g_{ll} = 2.8, $g_{\perp}$ = 2.08, κ = 0.49, G = 3.50, $P_d = 1.54 \times 10^{-2}$ cm^{-1}, $\kappa P_d = 7.55 \times 10^{-2}$ cm^{-1}, α^2_{Cu} = 0.77 and $(\alpha')^2$ = 0.33. The pattern $g_{11} > g_{\perp} > 2$ is suggestive of $d_{x^2-y^2}$ ground state. The value of g_{11} (2.28) indicates 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 α^2_{Cu} (0.77) and $(\alpha')^2$ (0.33) indicate the covalent nature of **3**. The positive value of κ (0.49) suggests that All should be. greater than $A_{\perp}$ and this trend in A_{ll} and $A_{\perp}$ values has also been observed by us. The P_d value (1.54×10^{-2} cm^{-1}) in the present complex is lower than free ion value (3.5×10^{-2} cm^{-1}), which is suggestive of presence of covalent character between metal-ligand bonding. The absence of a band at *ca.* 1500 gauss due to ΔMs = 2 transition in [Cu(OAc)(LH_2)] rules out the presence of Cu-Cu interaction.

The room temperature magnetic moments of the compounds are presented in Table-2. The Cu^{2+} ion belongs to S = ½ system and since its spin orbit coupling constant is negative, the magnetically dilute Cu^{2+} complexes, due to presence of orbital contribution are expected to exhibit magnetic moments higher than the spin-only value (1.73 BM). The magnetic moment of **3** is 1.87 BM in the range expected for the monomeric Cu^{2+} complexes. The magnetic moment of **5** (M' = Mn^{2+}) is 5.81 BM, which lies in the normal range reported for the magnetically dilute octahedral compounds of Mn^{2+} ions[20]. The magnetic moment of **5** (M' = Co^{2+}) is 4.64 BM, which lies in the usual range reported for octahedral Co^{2+} complexes. Compound **5** (where M' = Ni^{2+}) exhibits the magnetic moment 3.34 BM which is indicative of the presence of Ni^{2+} ion in octahedral geometry[20]. The magnetic moment of **6** is 5.78 BM suggesting a high-spin octahedral environment around Fe^{3+} ion in the complex[20]. The coordination compounds of Zn^{2+}, Cd^{2+}, MoO_2^{4+}, UO_2^{6+} and $Zr(OH)_2^{2+}$ ions are diamagnetic as expected.

Thus, on the basis of analytical data, valence requirements and spectral studies, it is proposed that **2** behaves as a monobasic tridentate ONO donor ligand in these monomeic and non-electrolyte coordination compounds. The data suggest a square-planar structure for **3**, a tetrahedral structure for **4**, an octahedral structure for **5**, **6** and **9**. The compounds, **7** and **8** are eight-coordinate.

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