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# Spectral Studies on Metal Complexes of a Newly Synthesized Azetidinone

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A dioxane solution of N-(4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-3′-carboxy-2′-hydroxybenzalideneimine, $LH_3$ (**I**) on reacting with chloroacetyl chloride, in the presence of triethylamine, undergoes cyclization to form N-(4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, $L'H_3$ (**II**). A methanolic solution of $L'H_3$ reacts with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Zr(IV), $MoO_2$(VI) and $UO_2$(VI) ions to form the complexes, $[M(L'H)\cdot MeOH]_2$ [where M = Mn(II), Co(II) or Ni(II)]; $[Cu(L'H)]_2$; [M(L'H)] [where M = Zn(II), Cd(II), $MoO_2$(VI) or $UO_2$(VI)]; $[Fe(L'H)Cl]_2$ and $[Zr(OH)_2(L'H)]_2$. The compounds have been characterized on the basis of elemental analyses, molar conductance, molecular weight, spectral (IR, UV-visible) studies and magnetic susceptibility measurements. $L'H_3$ behaves as a dibasic tridentate OON donor ligand in $[Cu(L'H)]_2$, while it acts as a dibasic tetradentate OONS donor ligand in rest of the compounds. The complexes, $[M(L'H)\cdot MeOH]_2$ [M = Mn(II), Co(II) or Ni(II)]; $[Cu(L'H)]_2$; $[Fe(L'H)Cl]_2$ and $[Zr(OH)_2(L'H)]_2$ are dimers, while others are monomers. The dimeric complex, $[Cu(L'H)]_2$ exhibits subnormal magnetic moment and is involved in antiferromagnetic exchange, while all other complexes are magnetically dilute. The octahedral structure for Mn(II), Co(II), Ni(II), Fe(III), $MoO_2$(VI) and $UO_2$(VI) complexes, square planar structure for Cu(II) complex, tetrahedral structure for Zn(II) and Cd(II) complexes and pentagonal bipyramidal structure for Zr(IV) complex have been suggested.

**Key Words: Azetidinones, Dimetallic coordination compounds.**

## INTRODUCTION

In recent years, there has been considerable research interest on the transition metal complexes derived from the sulphur donor ligands due to their carcinostatic, antibacterial and antifungal activities[1]. Sulphur donor ligands have been used as PVC stabilizers, agrochemicals and anti-fouling paints due to their low photo-toxicity and favourable environmental degradation[2]. A perusal of the literature reveals that

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very little work has been done on the coordination compounds of azetidinones[3]. In this paper, the syntheses and characterization of $L'H_3$ (**II**) and its Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Zr(IV), $MoO_2$(VI) and $UO_2$(VI) coordination compounds are reported.

## EXPERIMENTAL

Copper(II) acetate monohydrate, zinc(II) acetate dihydrate, nickel(II) acetate tetrahydrate, 1,4-dioxane [SD's]; cobalt(II) acetate monohydrate, cadmium(II) acetate dihydrate, dioxouranium(VI) acetate tetrahydrate, iron(III) chloride (anhydrous), hexadecaaquaoctahydroxotetrazirconium(IV) chloride [BDH] and manganese(II) acetate tetrahydrate [Sarabhai] were used for the syntheses. 3-Formyl salicylic acid, *bis*(acetylacetonato)dioxomolybdenum(VI), hexadecaaquaoctahydroxotetrazirconium(IV) acetate and 4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole were synthesized according to the published procedures[4,5].

**Analyses and physical measurements:** The estimation of metal, chlorine and the sulphur contents of the respective compounds were carried out by the standard methods as reported earlier[6]. The carbon, hydrogen and nitrogen contents were determined by the Eager analyzer model-300 CHN analyzer. The molar conductances of the coordination compounds were determined in DMSO with the help of a Toshniwal conductivity bridge (CL01-02A) and a dip type cell calibrated with KCl solutions. The molecular weights were determined by the Rast's method using diphenyl as the solvent[7]. Infrared spectra were recorded in KBr (4000-400 $cm^{-1}$) on a Nicolet 5DX FT-IR spectrophotometer. Reflectance spectra were recorded on the Shimadzu UV-visible spectrophotometer attached with a reflectance arrangement. The magnetic susceptibility measurements on the complexes were carried out at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. The magnetic susceptibilities were corrected using diamagnetic corrections of the ligand and metal atoms and for temperature independent paramagnetism (TIP) term[8].

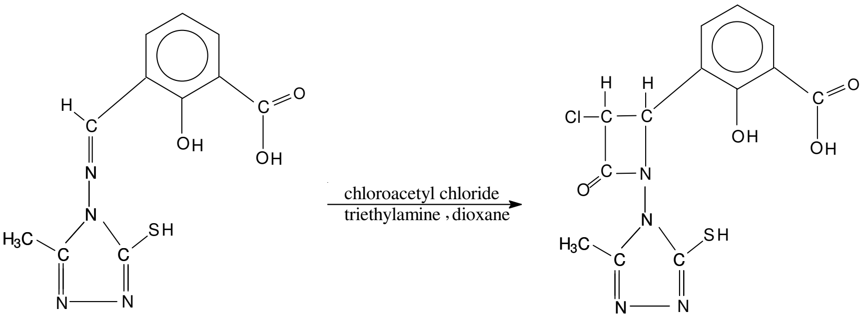
**Synthesis of Schiff base, $LH_3$ (I):** A MeOH solution of 4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole (1.30 g, 10 mmol in 30 mL) was added to a MeOH solution of 3-formylsalicylic acid (1.66 g, 10 mmol in 50 mL) and the mixture was then refluxed for 2 h. The yellow coloured precipitates formed were suction filtered, washed with MeOH and dried *in vacuo* at room temperature over silica gel for 24 h. Yield = 80 %, Anal: (**I**, $C_{11}H_{10}N_4O_3S$) [Found (%): C, 47.20; H, 3.70; N, 19.84; S, 11.28, Calcd. (%): C, 47.48; H, 3.60; N, 20.14; S, 11.51]; IR (KBr, $\nu_{max}$, $cm^{-1}$): 2530 (S–H), 1660 (C=O) carboxylic, 1625 (C=N) azomethine, 1510 (C–O) phenolic and 765 (C–S) thioalcoholic.

**Synthesis of N-(4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, $L'H_3$ (II):** Chloroacetyl chloride (2.26 g, 20 mmol) was added drop by drop during a period of 2 h to a dioxane solution of **I** (2.78 g, 10 mmol in 50 mL) in the presence of triethylamine (3.03 g, 30 mmol), while stirring constantly. 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 $CHCl_3$. The compound was dried as mentioned above. Yield = 50 %. Anal: (**II**, $C_{13}H_{11}N_4O_4SCl$) [Found (%): C, 43.87; H, 3.00; N, 15.62; S, 9.23; Cl, 10.18. Calcd. (%): C, 44.00; H, 3.10; N, 15.80; S, 9.03; Cl, 10.01]; IR (KBr, $\nu_{max}$, $cm^{-1}$): 2845 (O–H) intramolecular H-bonding, 2520 (S–H), 1735 (C=O) β-lactam, 1670 (C=O) carboxylic, 1515 (C–O) phenolic, 1407 (C–N) β-lactam, 775 (C-S) thioalcoholic and 750 (C–Cl) β-lactam.

**Syntheses of coordination compounds of L'H$_3$ (II):** A methanolic solution (30-50 mL) of the appropriate metal acetate/metal complex/iron(III) chloride (anhydrous) (10 mmol) was added to a MeOH solution (50 mL) of **II** (3.54 g, 10 mmol) and the mixture was then refluxed for 3-4 h. In case of the synthesis of respective iron(III) coordination compounds, the refluxion was carried out under anhydrous condition. The solid products formed were suction filtered, washed with methanol and were then dried as mentioned above. Yield = 48-67 %.

## RESULTS AND DISCUSSION

N-(4-Amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, L'H$_3$ (**II**) was synthesized by the reaction of chloroacetyl chloride with N-(4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-3′-carboxy-2′-hydroxybenzalideneimine, LH$_3$ (**I**) in the presence of triethylamine in dioxane (**Scheme-I**). The reaction of L'H$_3$ with appropriate metal salt/metal complex in 1:1 molar ratio in MeOH produces the coordination compounds, $[Cu(L'H)]_2$, $[M(L'H)]$ [where M = Zn(II), Cd(II), $MoO_2$(VI) or $UO_2$(VI)], $[M(L'H)\cdot MeOH]_2$ [where M = Mn(II), Co(II) or Ni(II)], $[Fe(L'H)Cl]_2$ and $[Zr(OH)_2(L'H)]_2$. The formation of coordination compounds of L'H$_3$ takes place according to the **Scheme-II**.



LH$_3$ (**I**) L'H$_3$ (**II**)

**Scheme-I:** Preparative scheme of L'H$_3$ (**II**)

$$2L'H_3 + 2M(CH_3COO)_2\cdot xH_2O \xrightarrow[\text{Reflux}]{\text{MeOH}} [M(L'H)\cdot MeOH]_2 + 4CH_3COOH + 2xH_2O$$

[M = Mn(II), Co(II) or Ni(II)]

$$2L'H_3 + 2Cu(CH_3COO)_2\cdot H_2O \xrightarrow[\text{Reflux}]{\text{MeOH}} [Cu(L'H)]_2 + 4CH_3COOH + 2H_2O$$

$$L'H_3 + M(CH_3COO)_2\cdot yH_2O \xrightarrow[\text{Reflux}]{\text{MeOH}} [M(L'H)] + 2CH_3COOH + yH_2O$$

$$[M = Zn(II), Cd(II) \text{ or } UO_2(VI)]$$

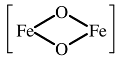
$$2L'H_3 + 2FeCl_3 \xrightarrow[\text{Reflux}]{\text{MeOH}} [Fe(L'H)Cl]_2 + 4HCl$$

$$4L'H_3 + [Zr_4(OH)_8(H_2O)_{16}](CH_3COO)_8 \xrightarrow[\text{Reflux}]{\text{MeOH}} 2[Zr(OH)_2(L'H)]_2 + 8CH_3COOH + 16H_2O$$

$$L'H_3 + [MoO_2(acac)_2] \xrightarrow[\text{Reflux}]{\text{MeOH}} [MoO_2(L'H)] + 2acacH$$

**Scheme-II:** Preparative scheme of coordination compounds of $L'H_3$ (**II**)

The coordination compounds are insoluble in $H_2O$, MeOH, EtOH, partially soluble in $CHCl_3$, $Me_2CO$, $C_6H_6$ and completely soluble in DMSO and DMF. They are non-electrolytes in DMF ($\Lambda_M$ = 2.5-9.7 mho cm$^2$ mol$^{-1}$).

**Infrared spectral studies:** The infrared spectra of $LH_3$ (**I**), $L'H_3$ (**II**) and the coordination compounds of **II** were recorded in KBr and the prominent peaks (in cm$^{-1}$) are shown in Table-2. $LH_3$ exhibits the $\nu$(C=N) (azomethine) stretch at 1625 cm$^{-1}$. This band disappears in $L'H_3$ and a new band due to $\nu$(C–N) ($\beta$-lactam) stretch[9] appears at 1407 cm$^{-1}$ indicating the conversion of **I** into **II**. The formation of **II** is further supported by the appearance of a new band due to $\nu$(C–Cl) ($\beta$-lactam) stretch[10] at 750 cm$^{-1}$. The $\nu$(C–N) ($\beta$-lactam) stretch[9] of **II** shifts from 1407 cm$^{-1}$ to lower energy by 15-35 cm$^{-1}$ in the complexes indicating the involvement of the N atom of $\beta$-lactam moiety towards coordination. $L'H_3$ exhibits a strong band at 2845 cm$^{-1}$ due to the intramolecular H-bonded -OH group of phenolic and/or carboxylic acid moieties[11]. This band disappears in the complexes indicating the breakdown of H-bonding and subsequent deprotonation of the OH group followed by the involvement of phenolic and carboxylic O atoms towards coordination. The presence of a broad band at *ca.* 3410 cm$^{-1}$ and the decrease of $\nu$(C–O) (alcoholic) stretch of MeOH from 1034 cm$^{-1}$ to lower energy by 39-54 cm$^{-1}$ in $[M(L'H)\cdot MeOH]_2$ [M = Mn(II), Co(II) or Ni(II)] indicate the involvement of the O atom of MeOH towards coordination[12]. A medium intense band at 2520 cm$^{-1}$ in **II** is assigned to the $\nu$(S–H) stretch[11]. This band remains at the same energy in $[Cu(L'H)]_2$ indicating the non-involvement of the S atom towards coordination in this coordination compound. The $\nu$(C–S) (thioalcoholic) stretch[11] of **II** occurs at 775 cm$^{-1}$. This band remains at the same energy in $[Cu(L'H)]_2$ indicating the non-involvement of the S atom towards coordination. However, this band undergoes a negative shift by 20-55 cm$^{-1}$ in rest of the coordination compounds indicating the involvement of the S atom towards coordination[11]. The $\nu$(C=O) ($\beta$-lactam) stretch[13] of **II** occurring at 1735 cm$^{-1}$ remains unchanged in the coordination compounds suggesting the non-involvement of the O atom of $\beta$-lactam moiety towards coordination. The $\nu$(C=O) (carboxylic) stretch[14] of **II** occurring at 1670 cm$^{-1}$ disappears in the coordination compounds and two new bands at 1598-1570 $cm^{-1}$ and 1395-1360 $cm^{-1}$ assignable to $\nu_{as}$(COO) and $\nu_s$(COO) stretches, respectively appear in the coordination compounds. The energy separation ($\Delta\nu$) between these bands is 203-225 $cm^{-1}$. The magnitude of the above energy separation is > 144 $cm^{-1}$ which indicates the monodentate behaviour of carboxy group in the present case, since in the event of bidentate coordination the energy separation[15] is < 200 $cm^{-1}$. The $\nu$(C–O) (phenolic) stretch[12] of **II** occurring at 1515 $cm^{-1}$ shifts to higher energy by ≤ 10 $cm^{-1}$ in [M(L'H)] [M = Zn(II), Cd(II), $MoO_2$(VI) or $UO_2$(VI)] and by 25-35 $cm^{-1}$ in rest of the coordination compounds supporting the involvement of phenolic O atom towards coordination. The magnitude of the above shift of the $\nu$(C-O) (phenolic) stretch indicates the monomeric structure for [M(L'H)] [M = Zn(II), Cd(II), $MoO_2$(VI) or $UO_2$(VI)] and the dimeric structure for the rest of the coordination compounds as in the event of a dimeric structure, the $\nu$(C–O) (phenolic) stretch shifts to higher energy[16] by >10 $cm^{-1}$. The $\nu$(C–Cl) ($\beta$-lactam) stretch[10] of **II** occurring at 750 $cm^{-1}$ remains unchanged in the coordination compounds indicating the non-involvement of the Cl atom of $\beta$-lactam moiety towards coordination. The presence of a new band at 835 $cm^{-1}$ in $[Fe(L'H)Cl]_2$ due to $\nu_{as}$(Fe–O–Fe) stretch suggests the presence of an oxo bridged  structure[17]. The molecular weight data also suggests the dimeric nature of the present iron(III) coordination compound. The absence of a band in 955-835 $cm^{-1}$ region is due to the $\nu$(Zr=O) stretch in the present Zr(IV) compound suggests its formulation as $[Zr(OH)_2(L'H)]_2$ and not as $[ZrO(H_2O)(L'H)]_2$. The presence of a broad band at 3445 $cm^{-1}$ due to $\nu$(OH) stretch and the appearance of a new medium intense band at 1135 $cm^{-1}$ due to the $\delta$(Zr–OH) bending mode[14] also support the proposed structure of the present Zr(IV) compound. $[MoO_2(L'H)]$ exhibits the $\nu_s$(O=Mo=O) and $\nu_{as}$(O=Mo=O) stretches at 935 and 905 $cm^{-1}$, respectively[14]. These bands occur in the usual ranges: $\nu_{sy}$(O=Mo=O) stretch, 892-964 $cm^{-1}$ and $\nu_{asy}$(O=Mo=O) stretch, 842-928 $cm^{-1}$, reported for the majority of $MoO_2$(VI) complexes[14]. The presence of two bands due to the $\nu$(O=Mo=O) stretch is indicative of a *cis*-$MoO_2$ configuration as the complex with *trans*-$MoO_2$ structure shows only $\nu_{as}$(O=Mo=O) stretch since the $\nu_s$(O=Mo=O) stretch is IR inactive[18]. The *cis*-$MoO_2$ structure forces the tetradentate ligand to coordinate in a non-planar fashion (**VIII**)[19]. The absence of a band at *ca.* 775 $cm^{-1}$ in the $MoO_2$(VI) complex indicates the absence of an oligomeric chain with Mo···Mo···Mo··· interaction[19]. $[UO_2(L'H)]$ exhibits the $\nu_{as}$(O=U=O) stretch at 900 $cm^{-1}$ and this band occurs in the usual range (950-870 $cm^{-1}$) observed for the majority of *trans*-$UO_2$(VI) compounds[14]. The new non-ligand bands in the present coordination compounds in the low frequency region are assigned to the $\nu$(M-O) (580-550 $cm^{-1}$) and the $\nu$(M–N) (455-430 $cm^{-1}$) and these bands are in the expected order of increasing energy: $\nu$(M–N) < $\nu$(M–O)[20]. On the basis of analytical data (Table-1), valence requirements and the infrared spectral studies, it is proposed that **II** behaves as a dibasic tridentate OON donor ligand in $[Cu(L'H)]_2$ and as a dibasic tetradentate OONS donor ligand in the rest of the coordination compounds.

**Reflectance spectral studies:** The complexes being insoluble or sparingly soluble in common non-coordinating organic solvents, the solution electronic spectra could not be recorded and hence, the reflectance spectra were recorded (Table-2). The six-coordinate high-spin Mn(II) ion belongs to $3d^5$ system. The high spin state Russell-Saunders term is $^6S$ which changes its notation to $^6A_{1g}$ in an octahedral environment. The complex, $[Mn(L'H){\cdot}MeOH]_2$ exhibits three bands at 17980, 23100 and 25370 cm$^{-1}$ due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions, respectively in an octahedral environment[21]. The presence of three bands at 9050, 14900 and 19000 cm$^{-1}$ due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ($\nu_1$), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ($\nu_2$) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ ($\nu_3$) transitions, respectively in $[Co(L'H){\cdot}MeOH]_2$ suggests an octahedral arrangement of $L'H_3$ around Co(II) ions[21]. The $\nu_3/\nu_1$ value in the present Co(II) compound is 2.10 and it lies in the usual range (2.00-2.80), reported for the majority of octahedral Co(II) complexes[21]. The electronic spectral parameters for $[Co(L'H){\cdot}MeOH]_2$ were calculated using the standard methods[21-23] and the values are as follows: Dq = 1017 cm$^{-1}$, B' = 738 cm$^{-1}$, $\beta$ = B'/B = 0.76, $\beta^0$ = 24 % and CFSE = -99.78 kJ mol$^{-1}$. The reduction of Racah parameter from the free ion value of 971 to 738 cm$^{-1}$ and the $\beta^0$ value of 24 % indicate the covalent nature of the compound and the strong field nature of the tetradentate ligand **II**[8]. The complex, $[Ni(L'H){\cdot}MeOH]_2$ exhibits three bands at 9100, 15600 and 25280 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[21]. The $\nu_2/\nu_1$ value in the present Ni(II) compound is 1.71 and it lies in the usual range (1.60-1.82), reported for the majority of octahedral Ni(II) complexes[21,22]. The electronic spectral parameters calculated[21-23] for $[Ni(L'H){\cdot}MeOH]_2$ are as follows: Dq = 910 cm$^{-1}$, B' = 858 cm$^{-1}$, $\beta$ = B'/B = 0·83, $\beta^0$ = 17 % and CFSE = -130.46 kJ mol$^{-1}$. The reduction of the Racah parameter from the free ion value (1030 cm$^{-1}$) to 858 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 tetradentate ligand **II**[8]. For a given ligand and given stereochemistry, the covalent character of the corresponding Co(II) and Ni(II) coordination compounds is comparable since Co(II) and Ni(II) occupy the adjacent positions in the nephelauxetic metal ion series [*i.e.* Co(II)~Ni(II)][8]. In the present Co(II) and Ni(II) coordination compounds, the $\beta^0$ values are quite comparable: $[Co(L'H){\cdot}MeOH]_2$: 24 %; $[Ni(L'H){\cdot}MeOH]_2$: 17 %. For a given ligand and given stereochemistry, the spectrochemical series of metal ions on the basis of increasing 10Dq values is[8]: Ni(II) < Co(II). In present case, the calculated 10Dq values indicate that the 10Dq values are in the expected order[8]: Ni(II) < Co(II). The greater negative CFSE value (-130.46 kJ mol$^{-1}$) for $[Ni(L'H){\cdot}MeOH]_2$ in comparison to that of $[Co(L'H){\cdot}MeOH]_2$ (CFSE = - 97.20 kJ mol$^{-1}$) is as expected[23]. The presence of an asymmetric broad band at 17210 cm$^{-1}$ due to the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and $^2E_g$ transitions in $[Cu(L'H)]_2$ suggests a square planar arrangement of $L'H_3$ around Cu(II) ion[24]. The absence of a band in the range 8000-10000 cm$^{-1}$ precludes the presence of a tetrahedral structure[25]. The complex, $[Fe(L'H)Cl]_2$ exhibits three bands at 17830, 21740 and 26350 cm$^{-1}$ due to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and $^6A_{1g} \rightarrow {}^4A_{1g}$ (G) transitions, respectively in an octahedral environment[26].

TABLE-I

ANALYTICAL DATA OF N- (4-AMINO-5-METHYL-3-THIOHYDROXY-1,2,4-TRIAZOLE)-4- (3'-CARBOXY-2'-HYDROXYPHENYL)AZETIDIN-2-ONE AND ITS METAL COORDINATION COMPOUNDS

| Compound | m.f. | m.w. Found (calcd.) | Elemental analysis (%): Found (calcd.) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | M | C | H | N | S | Cl |
| $L'H_3$ (**II**) | $C_{13}H_{11}N_4O_4SCl$ | 354.5 (354.5)[a] | – | 43.87 (44.00) | 3.00 (3.10) | 15.62 (15.80) | 9.23 (9.03) | 10.18 (10.01) |
| $[Mn (L'H)\cdot MeOH]_2$ | $Mn_2C_{28}H_{26}N_8O_{10}S_2Cl_2$ | 878.8 (872.8)[b] | 12.05 (12.49) | 38.00 (38.23) | 2.58 (2.96) | 12.40 (12.74) | 7.12 (7.28) | 7.80 (8.08) |
| $[Co (L'H)\cdot MeOH]_2$ | $Co_2C_{28}H_{26}N_8O_{10}S_2Cl_2$ | 886.8 (881.8)[b] | 12.92 (13.28) | 37.55 (37.89) | 2.62 (2.93) | 12.24 (12.63) | 7.10 (7.22) | 7.98 (8.01) |
| $[Ni (L'H)\cdot MeOH]_2$ | $Ni_2C_{28}H_{26}N_8O_{10}S_2Cl_2$ | 886.4 (882.4)[b] | 13.12 (13.24) | 37.72 (37.91) | 2.56 (2.93) | 12.22 (12.64) | 7.10 (7.22) | 7.53 (8.01) |
| $[Cu (L'H)]_2$ | $Cu_2C_{26}H_{18}N_8O_8S_2Cl_2$ | 832.0 (826.0[b] | 15.20 (15.26) | 37.40 (37.50) | 2.08 (2.16) | 13.13 (13.46) | 7.45 (7.69) | 8.24 (8.53) |
| $[Zn (L'H)]$ | $ZnC_{13}H_9N_4O_4SCl$ | 417.9 (414.8)[b] | 15.20 (15.65) | 37.38 (37.33) | 2.10 (2.15) | 13.28 (13.40) | 7.50 (7.66) | 8.22 (8.50) |
| $[Cd (L'H)]$ | $CdC_{13}H_9N_4O_4SCl$ | 464.9 (461.8)[b] | 23.88 (24.18) | 33.16 (33.56) | 1.56 (1.95) | 12.00 (12.05) | 6.28 (6.88) | 7.24 (7.64) |
| $[Fe (L?H)Cl]_2$ | $Fe_2C_{26}H_{18}N_8O_8S_2Cl_4$ | 863.6 (888)[b] | 12.48 (12.61) | 35.33 (35.14) | 2.17 (2.03) | 12.78 (12.61) | 7.34 (7.20) | 15.86 (15.99) |
| $[Zr (OH)_2 (L'H)]_2$ | $Zr_2C_{26}H_{22}N_8O_{12}S_2Cl_2$ | 955.4 (953.4)[b] | 18.90 (19.09) | 32.23 (32.66) | 2.10 (2.30) | 11.21 (11.72) | 6.31 (6.70) | 7.28 (7.43) |
| $[MoO_2 (L'H)]$ | $MoC_{13}H_9N_4O_6SCl$ | 480.4 (477.4)[b] | 19.36 (19.96) | 31.88 (32.47) | 1.66 (1.87) | 11.10 (11.66) | 6.22 (6.66) | 7.10 (7.39) |
| $[UO_2 (L'H)]$ | $UC_{13}H_9N_4O_6SCl$ | 622.5 (620.5)[b] | 38.00 (38.23) | 24.86 (25.06) | 1.25 (1.45) | 8.38 (9.00) | 4.84 (5.14) | 5.10 (5.70) |

[a]Mass spectral data, [b]Rast camphor method data.

TABLE-2

IR, REFLECTANCE SPECTRAL DATA (cm$^{-1}$) AND MAGNETIC MOMENTS OF METAL COORDINATION COMPOUNDS OF **II**

| Compound | $\nu_{as}$(COO) | $\nu_s$(COO) | $\nu$(C–O) ($\phi$) | $\nu$(C–N) ($\beta$-lactam) | $\nu$(C–S) (thioalcoholic) | $\nu_{max}$ | $\mu_{eff}$ (BM) |
|---|---|---|---|---|---|---|---|
| $L'H_3$ (**II**) | - | - | 1515 | 1407 | 775 | – | Diamagnetic |
| $[Mn(L'H)\cdot MeOH]_2$ | 1585 | 1360 | 1545 | 1387 | 735 | 17980, 23100, 25370 | 5.86 |
| $[Co(L'H)\cdot MeOH]_2$ | 1595 | 1385 | 1540 | 1377 | 725 | 9050, 14900, 19000 | 4.80 |
| $[Ni(L'H)\cdot MeOH]_2$ | 1578 | 1395 | 1550 | 1392 | 755 | 9100, 15600, 25280 | 3.10 |
| $[Cu(L'H)]_2$ | 1570 | 1362 | 1540 | 1380 | 775 | 17210 | 1.52 |
| $[Zn(L'H)]$ | 1580 | 1402 | 1525 | 1385 | 735 | – | Diamagnetic |
| $[Cd(L'H)]$ | 1575 | 1390 | 1525 | 1380 | 740 | – | Diamagnetic |
| $[Fe(L'H)Cl]_2$ | 1580 | 1395 | 1540 | 1375 | 735 | 17830, 21740, 26350 | 5.87 |
| $[Zr(OH)_2(L'H)]_2$ | 1572 | 1375 | 1545 | 1372 | 720 | – | Diamagnetic |
| $[MoO_2(L'H)]$ | 1590 | 1400 | 1523 | 1382 | 750 | – | Diamagnetic |
| $[UO_2(L'H)]$ | 1585 | 1385 | 1525 | 1378 | 730 | – | Diamagnetic |

**Magnetic measurements:** The room temperature magnetic moments of the compounds are presented in Table-2. The magnetic moments of $[Mn(L'H)\cdot MeOH]_2$, $[Co(L'H)\cdot MeOH]_2$, $[Ni(L'H)\cdot MeOH]_2$ and $[Fe(L'H)Cl]_2$ are 5.86, 4.80, 3.10 and 5.87 BM, respectively. These values lie in the usual ranges, reported for the majority of octahedral Mn(II), Co(II), Ni(II) and Fe(III) complexes, respectively[27]. The Cu(II) ion belongs to the S = ½ system and since its spin-orbit coupling constant is negative[8], the magnetically dilute Cu(II) complexes are expected to exhibit magnetic moments higher than the spin-only value of 1.73 BM due to the presence of orbital contribution[28]. The magnetic moment (1.52 BM) of the present Cu(II) complex is substantially less than the above range of magnetic moment and this indicates the presence of anti-ferromagnetic type of magnetic exchange interaction[8]. The coordination compounds of Zn(II), Cd(II), Zr(IV), $MoO_2$(VI) and $UO_2$(VI) are diamagnetic as expected. Thus, on the basis of analytical, molecular weight, spectral and magnetic studies, we suggest octahedral structure, **III** for Mn(II), Co(II), Ni(II) complexes, **VI** for Fe(III) complex, **VIII** for $MoO_2$(VI) complex, **IX** for $UO_2$(VI) complex; square planar structure, **IV** for Cu(II) complex; tetrahedral structure, **V** for Zn(II) and Cd(II) complexes and pentagonal bipyramidal structure, **VII** for Zr(IV) complex[11].

## Conclusion

The newly synthesized N-(4-amino-5-methyl-3-thiohydroxy-1,2,4-triazole)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, $L'H_3$ (**II**) behaves as a dibasic tridentate OON donor ligand in $[Cu(L'H)]_2$, while it acts as a dibasic tetradentate OONS donor ligand in rest of the compounds. $[M(L'H)\cdot MeOH]_2$ [M = Mn(II), Co(II) or Ni(II)], $[Cu(L'H)]_2$, $[Fe(L'H)Cl]_2$ and $[Zr(OH)_2(L'H)]_2$ are dimers, while [M(L'H)] [M = Zn(II), Cd(II), $MoO_2$(VI) or $UO_2$(VI)] is monomer. The complexes are magnetically dilute, except $[Cu(L'H)]_2$ which exhibits subnormal magnetic moment and is involved in antiferromagnetic exchange. A square planar structure for Cu(II) complex; a tetrahedral structure for Zn(II) and Cd(II) complexes; an octahedral structure for Mn(II), Co(II), Ni(II), Fe(III), $MoO_2$(VI) and $UO_2$(VI) complexes and a pentagonal bipyramidal structure for Zr(IV) complex have been suggested.

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