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Research Article

## Synthesis and Spectral Characterization of Mn(II), Zn(II) and Cd(II) Complexes with Thiosemicarbazone as Primary Ligand and 2,2'-Bipyridyl as Secondary Ligand

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### ABSTRACT

*Complexes of Mn(II), Zn(II) and Cd(II) with 2,5-Dihydroxy butyrophenone thiosemicarbazone(L<sub>1</sub>)/2,5-Dihydroxy benzophenone thiosemicarbazone(L<sub>1</sub>') as primary ligands and 2,2'-bipyridyl(L<sub>2</sub>) as secondary ligand have been isolated and characterized by elemental analysis, molar conductance, magnetic measurements, electronic spectra, IR spectra and thermogravimetric analysis. Conductivity data of the complexes in DMSO suggested their non-electrolytic nature. The molecular weight of the complexes determined by the Rast Camphor method corresponds with the weight of the formula, indicating their monomer nature. TG analysis confirms the presence of one coordinated water molecule in all the complexes. On the basis of above observations the complexes are proposed to be octahedral in nature.*

**Keywords:** 2,5-Dihydroxy butyrophenone thiosemicarbazone(L<sub>1</sub>) / 2,5-Dihydroxy benzophenone thiosemicarbazone(L<sub>1</sub>') and 2,2'-bipyridyl(L<sub>2</sub>), Mn(II), Zn(II) and Cd(II) complexes.

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### INTRODUCTION

Interest in thiosemicarbazone chemistry has flourished for many years, largely as a result of its wide range of uses, for example, as antibacterial, antifungal, chemotherapeutic, and bioanalytical agents. One particular area of thiosemicarbazone chemistry that has been increasing in importance recently involves biologically active metal complexes of thiosemicarbazone-based chelating (NNS) agents. As the coordination of the metal ions to thiosemicarbazones improves their efficacy and improve their bioactivity<sup>1-4</sup>. Co-ordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound and the type of ligand. These metal complexes have found extensive applications in various fields of human interest<sup>5</sup>. Keeping the above facts in mind, in the present paper, synthesis and spectral studies of Mn(II), Zn(II) and Cd(II) mixed ligand complexes with L<sub>1</sub>/L<sub>1</sub>' as primary ligand and L<sub>2</sub> as secondary ligand have been reported.

## MATERIALS AND METHODS

All the reagents used were of Analytical grade. The ligands as well as metal complexes were analyzed by standard methods<sup>6</sup>. The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr pellets. Conductivity measurements were made on Systronic conductometer using DMF Magnetic susceptibility were measured by Guoy method using Hg [Co (CNS)<sub>4</sub>] as a calibrant. The analytical data, color, conductivity measurements and magnetic moments have been recorded in **Table-1**.

**Table-1: Analytical Data of Mn(II), Zn(II) and Cd(II) Mixed Ligand Complexes**

S. No.	Complex	% chemical analysis: Found (Calculated)					$\Omega$ M in DMSO (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	M. P.(°C) Colour	$\mu_{\text{eff}}$ (B. M.)	Mol. Wt. Found (Calcd)
		C	H	N	S	Metal				
1	[Mn(C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	52.42 (52.50)	4.70 (4.79)	14.50 (14.58)	6.58 (6.66)	11.40 (11.44)	19.70	175 Orange	5.92	468.0 (479.94)
2	[Mn(C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	55.95 (56.03)	4.00 (4.08)	13.52 (13.62)	6.25 (6.22)	10.60 (10.68)	20.80	236 Orange	5.94	500.6 (513.94)
3.	[Zn(C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	51.31 (51.40)	4.60 (4.69)	14.20 (14.27)	6.44 (6.52)	13.21 (13.30)	13.60	172 Light yellow	Diamagnetic	480.0 (490.2)
4	[Zn(C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	54.85 (54.94)	3.85 (4.00)	13.26 (13.35)	6.00 (6.10)	12.35 (12.43)	17.50	170 Light yellow	Diamagnetic	512.0 (524.2)
5	[Cd(C <sub>11</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	46.78 (46.89)	4.18 (4.27)	12.90 (13.02)	5.88 (5.95)	20.80 (20.91)	13.20	235 Light yellow	Diamagnetic	524.6 (537.4)
6	[Cd(C <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N <sub>3</sub> S)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )H <sub>2</sub> O]	50.30 (50.40)	3.58 (3.94)	12.15 (12.25)	5.52 (5.60)	19.60 (19.67)	14.20	245 White	Diamagnetic	562.0 (571.4)

**Synthesis of ligands:** 2, 5-Dihydroxy butyrophenone / benzophenone was prepared by the literature method<sup>7-8</sup>. Their thiosemicarbazone were obtained by refluxing their ethanolic solution with thiosemicarbazide in conc. HCl for about 2-3 hours on water bath. On cooling, light yellow compound separated out. It was filtered, washed with ethanol and dry ether and dried well under anhydrous conditions. Yield ~ 62%

**Synthesis of Complexes:** An ethanolic solution of ligand L<sub>1</sub> / L<sub>1</sub> as primary ligand and L<sub>2</sub> as secondary ligand was added slowly, into hot equimolar ethanolic solution of metal chloride, with stirring to get a clear solution. The resulting solution was refluxed for 4-5 hours on water bath. The solid coloured product separated on cooling. The precipitated complex was filtered, washed with ethanol and then dried in vacuum. Yield ~ 60%

## RESULTS AND DISCUSSION

All the metal complexes are colored and solid. They are insoluble in acetone, ethanol, benzene and chloroform but soluble in DMF and DMSO. The complexes are fairly stable at room temperature, non-hygroscopic and could be stored for a long period without decomposition. Elemental analysis reported in Table-1 suggested 1:1:1 (M:L:L') (where M = metal ion, L = 2,5-Dihydroxy butyrophenone thiosemicarbazone / 2,5-Dihydroxy benzophenone thiosemicarbazone ligand and L' = 2,2'-bipyridyl) stoichiometry for the isolated complexes. The analytical data, colour, molecular weight, conductivity, magnetic measurements and magnetic moment value have been recorded in **Table-1** and main IR band frequencies have been recorded in **Table-2**.

**Table 2: Main IR Bands ( $\text{cm}^{-1}$ ) observed in the Spectra of Mn (II), Zn (II) and Cd (II) Mixed Ligand complexes**

S. No.	Complexes	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}-\text{N}=\text{C})$	$\nu$ (C-S)	$\nu$ (N-N)	$\nu(\text{M}-\text{N})$ Bipy	$\nu$ (M-N)	$\nu$ (M-O)	$\nu$ (M-S)
1	$[\text{Mn}(\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1620	1565	645	1055	265	470	500	295
2	$[\text{Mn}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1635	1575	640	1050	265	470	515	310
3	$[\text{Zn}(\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1640	1575	640	1060	265	470	515	300
4	$[\text{Zn}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1640	1565	635	1055	265	465	500	280
5	$[\text{Cd}(\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1630	1570	635	1060	265	470	510	290
6	$[\text{Cd}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_3\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{O}]$	1635	1565	640	1055	270	465	515	300

**Magnetic Measurements:** Mn (II) complexes under study show magnetic moment values 5.92 and 5.94 B.M respectively and lie in the range of 5.70-6.00 B.M. indicating octahedral nature<sup>9</sup>. The magnetic moment values of the Zn (II) and Cd (II) complexes are in the range of 0.18 to 0.26 B.M. which shows their diamagnetic nature<sup>10</sup>.

**Electronic spectra:** The electronic spectra of Mn(II) complexes in DMF shows bands in the range 18300-18550, 22500-23000, 24600-25500, 28500-29300 and 34200-35400  $\text{cm}^{-1}$  which may be assigned to  ${}^6\text{A}_{1g}(\text{G}) \rightarrow {}^4\text{T}_{1g}(\text{G})$ ;  ${}^6\text{A}_{1g}(\text{G}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ ;  ${}^6\text{A}_{1g}(\text{G}) \rightarrow {}^4\text{E}_g(\text{G})$ ,  ${}^4\text{A}_{1g}(\text{G})$ ;  ${}^6\text{A}_{1g}(\text{G}) \rightarrow {}^4\text{T}_{2g}(\text{D})$  and  ${}^6\text{A}_{1g}(\text{G}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ , transitions, respectively. These transitions are indicative of octahedral geometry<sup>11</sup>. The calculated values of ligand field parameters viz. 10 Dq, B,  $\text{F}_2$  and  $\text{F}_4$  are also in accordance with the octahedral stereochemistry of the Mn(II) complexes. The value of  $\beta$  is less than unity indicating the considerable amount of covalency in the bond formed between the metal atom and the donor atom of the ligand. Zn(II) and Cd(II) complexes are found to be diamagnetic as expected for  $\text{d}^{10}$  system because d-d transitions are not possible hence electronic spectra did not give any fruitful information.

**IR Spectra:** The IR spectra of free ligands and their complexes are carefully analyzed to get information of active coordination sites of ligands with the metal ions. The N-N stretching band at 1040-1030  $\text{cm}^{-1}$  in the spectra of thiosemicarbazones shows a positive shift of 20-25  $\text{cm}^{-1}$  in the spectra of the complexes, indicating the bonding of metal ion with azomethine N of the ligand<sup>12</sup>. The IR spectra of thiosemicarbazone ligands show  $\nu(\text{CH}=\text{N})$  around 1660-1640  $\text{cm}^{-1}$ . The lowering in this frequency region observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination. A band observed at 3210  $\text{cm}^{-1}$  assigned to  $\nu\text{NH}_2$  in the thiosemicarbazones, which remain unchanged, indicating the non-participation of the  $-\text{NH}_2$  group in complexation<sup>13</sup>. The spectra of the mixed ligand complexes shows change in frequency of (N-C-N), (C=S) and (NH-C=S). The disappearance of  $(-\text{NH}-\text{C}=\text{S})$  absorption frequency with the formation of new band for azine ( $\text{C}=\text{N}-\text{N}=\text{C}$ ) at 1565-1575  $\text{cm}^{-1}$  suggests coordination of the metal ion through the azine nitrogen and thiol sulphur of the enolic form of thiosemicarbazones<sup>14</sup>. The schiff base has undergone thio-keto  $\leftrightarrow$  thio-enol tautomerism in the alkaline medium and following coordination to the metal ion by deprotonation of C-SH group is indicated by the absence of bands in the region 2750-2500  $\text{cm}^{-1}$ . The IR spectra of thiosemicarbazone ligands show  $\nu(\text{NH}) \sim 3210 \text{ cm}^{-1}$  and  $\nu(\text{C}=\text{S}) \sim 930 \text{ cm}^{-1}$ . These bands disappear in the spectra of their complexes. The appearance of new band at 640  $\text{cm}^{-1}$  in the IR spectra of all the complexes is assigned to  $\nu(\text{C}-\text{S})$ .

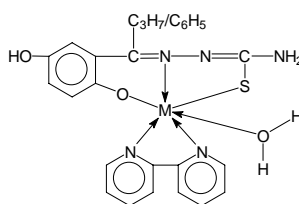
A broad frequency band, due to phenolic  $\text{-OH}$  at  $3490\text{ cm}^{-1}$  in the spectra of thiosemicarbazone ligands is observed almost at the same position in the spectra of all the complexes, indicating that only a single  $\text{-OH}$  group (deprotonated) takes part in the reaction with metal ions. The  $\nu(\text{C-O})$  phenolic stretch shifts to higher energy by  $10\text{ cm}^{-1}$  in all the complexes indicating coordination of phenolic  $\text{-O}$  with metal ion<sup>15</sup>. The coordination of 2, 2'-bipyridyl is indicated by the positive shift of  $(\text{C}=\text{C})$ ,  $(\text{C}=\text{N})$  ring stretching frequencies and the presence of their deformation modes at  $1170$  and  $1980\text{ cm}^{-1}$ . The position of the bands found in the spectrum of 2,2'-bipyridyl has been completely changed in the spectra of the complexes where it is used as co-ligand and new bands appeared at  $\sim 1590$  and  $1560\text{ cm}^{-1}$  confirming the coordination nature of bipyridyl ligand<sup>16</sup>. The  $400\text{ cm}^{-1}$  band of bipyridyl ( $\text{C-C}$  out of plane bending) shifts to higher frequency and splits into two components in the complexes, again confirms the coordination of bipyridyl through nitrogen. An additional band at  $\sim 270\text{ cm}^{-1}$  in the spectra of all the complexes also confirms the coordination of bipyridyl - nitrogen with the metal ion.

The IR-spectra of all the complexes exhibit bands in region  $3400\text{-}3360\text{ cm}^{-1}$  and  $850\text{-}920\text{ cm}^{-1}$  assignable to coordinated water molecule<sup>17</sup>. Some new non-ligand bands appeared in the far IR region around  $515\text{-}295\text{ cm}^{-1}$  have been noticed in the spectra of metal complexes, are assigned to  $\nu(\text{M-N})$ ,  $\nu(\text{M-O})$  and  $\nu(\text{M-S})$ , respectively. The above discussions indicate that both the thiosemicarbazone ligands act as tridentate while 2,2'-bipyridyl acts as bidentate in all the complexes.

**Thermogravimetric analysis:** The existences of coordinated water molecule suggested from IR spectra are confirmed by TG studies. All the complexes show a weight loss in the temperature range  $170\text{-}250^\circ\text{C}$  corresponds to the removal of one molecule of water and supports further the presence of one coordinated water molecule.

## CONCLUSION

On the basis of elemental analysis, magnetic moment value, conductivity measurements, electronic spectra, IR spectra and thermogravimetric analysis, octahedral geometry has been proposed to all the complexes as shown in Figure: 1



**Figure: 1.**

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