

SPECTRAL STUDIES M^{2+} COMPLEXES WITH SALICYLALDEHYDE (NH)- PHENYL THIOSEMICARBAZONE

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INTRODUCTION

All the complexes of ligand Salicylaldehyde (NH)- phenyl thiosemicarbazone with metal (II) ions (Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) are anhydrous as also supported from their analytical and spectral studies. All these complexes are stable upto $180^{\circ}C$. The complexes are generally soluble in water and ethanol, sparingly soluble in DMSO and DMF and insoluble in benzene, ether and acetone. All these complexes with Cr^{2+} , Mn^{2+} and Fe^{2+} were found non-electrolytic in nature. The molar conductance of these complexes have been recorded in nitrobenzene in digital systonic conductivity meter-304 and given in following table.

| Complexes | Colour | M.Pt. ($^{\circ}C$) | Soluble | μ_{eff} | Conductance (Ω -1cm ² mol ⁻¹) |
|---------------------------------------|--------------|--------------------------|-------------------------|-------------|---|
| [CrL(H ₂ O) ₂] | Deep red | 192 | In benzene and ether | 3.48 | 4.02 |
| [MnL(H ₂ O) ₂] | Light yellow | 210 | In benzene and ether | 3.60 | 4.50 |
| [FeL(H ₂ O) ₂] | Red | 225 | In benzene and ether | 1.61 | 3.91 |
| [Co(L)] | Orange | 240 | In benzene and ether | 1.71 | 3.17 |
| [Ni(L)] | Green | 220 | In benzene and ether | Diamagnetic | 3.43 |
| [Cu(L)] | Light Green | 215 | In benzene and ether | 1.72 | 4.23 |
| [Zn(L)] | Colourless | 230 | In benzene and ether | Diamagnetic | 3.68 |

EXPLANATION :

The IR spectral data and assignment of bands of transition metal (II) complexes are given in following table.

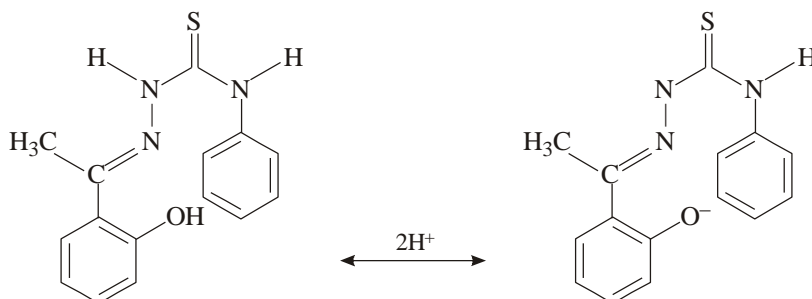
| Compound | $\nu_{(C=N)}$ | $\nu_{(OH)}$ phenolic | $\nu_{(CS)}$ | $\nu_{(NH)}$ | $\nu_{(MO)}$ | $\nu_{(MN)}$ | $\nu_{(H_2O)}$ | $\nu_{(Cl)}$ |
|---------------------------------------|---------------|--------------------------|--------------|--------------|--------------|--------------|----------------|--------------|
| AMPD | 1610 | 3590 | 1110 | 3300 | --- | --- | --- | |
| [CrL(H ₂ O) ₂] | 1595 | --- | 1090 | 3250 | 450 | 600 | 885 | 705 |
| [MnL(H ₂ O) ₂] | 1580 | --- | 1060 | 3240 | 435 | 580 | 880 | 710 |
| [FeL(H ₂ O) ₂] | 1550 | --- | 1080 | 3265 | 430 | 595 | 875 | 708 |
| [Co(L) ₂] | 1565 | --- | 1070 | 3245 | 455 | 590 | 882 | 700 |
| [Ni(L) ₂] | 1555 | --- | 1075 | 3260 | 465 | 570 | 890 | 705 |
| [Cu(L) ₂] | 1570 | --- | 1040 | 3250 | 475 | 585 | 880 | 700 |
| [Zn(L) ₂] | 1575 | --- | 1065 | 3265 | 460 | 575 | 860 | 710 |

The ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone has many donor sites such as phenolic hydroxyl group, -NH group, C=N group, thiocarbonylamide group and carbonyl lactone group. However, the infrared frequencies in the ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone associated with the phenolic hydroxyl group and C=N group have been influenced on complex formation with Metal (II) ions.

The infrared spectra of complexes of ligand salicylaldehyde (NH)-phenyl thiosemicarbazone with Metal (II) ions and the ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone were recorded in the range of 400 – 4000 cm⁻¹. The highest frequency of the bands of the ligand at ~1610 cm⁻¹ can be assigned to the ν_{CN} vibration. This band is shifted to lower frequency 1595 – 1550 cm⁻¹ on complexation indicating the involvement of -C=N group in complex formation. The absence of a band at 3590 cm⁻¹ characteristics of phenolic hydroxyl group in all complexes, suggest that the hydroxyl group participate in coordination with metal ions. The band at 110 cm⁻¹ shifted to lower frequency 1090 – 1040 cm⁻¹ in complexes, indicating the involvement of thiocarbonyl group in complexation. The band at 3300 cm⁻¹ shifted to lower frequency in complexes in the range of 3265 – 3240 cm⁻¹. It may be due to the participation of the -NH group in complexation. The occurrence of band at 600 – 570 cm⁻¹ (M-N) and 450 – 430 cm⁻¹ (M-O) prove the bonding of nitrogen and oxygen to the metal ions. The spectra of the complexes exhibited a broad band about 3600 -3400 cm⁻¹ which may be due to water molecules. The presence of a band at about 890 – 860 cm⁻¹ indicates the coordinated water molecules in the complexes.

Thus on account of infrared spectral properties it can be said that ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone acts as quadridentate ligand.

The singlet peak at $\delta = 9$ ppm of phenolic hydroxyl hydrogen of the lactone ring is disappeared in all complexes of M^{2+} ions with ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone. It may be due to the deprotonation of the hydroxyl group before the complexation as :



The spectral data for the solution of transition metal (M^{2+}) ion complexes with ligand Salicylaldehyde (NH)-phenyl thiosemicarbazone investigated in acetonitrile are presented in the following table.

CONCLUSION :

TABLE : Electronic spectral data of Salicylaldehyde (NH)-phenyl thiosemicarbazone with M^{2+} ions in cm^{-1} .

| M^{2+} complexes | Spectral bands (in cm^{-1}) | Transitions |
|--------------------------------------|--|---|
| $[\text{CrL}(\text{H}_2\text{O})_2]$ | 14, 450 | ${}^5\text{E}_g \rightarrow 5\text{T}_{2g}$ |
| $[\text{MnL}(\text{H}_2\text{O})_2]$ | 16500, 22300, 24800, 24850, 25200, 27800, 29500, and 32000 | ${}^6\text{E}_{1g} \rightarrow {}^4\text{T}_{1g}, {}^4\text{T}_{2g}$ (G) ${}^4\text{E}_g, {}^4\text{A}_{1g}$ and ${}^4\text{T}_{2g}$ (D) |
| $[\text{FeL}(\text{H}_2\text{O})_2]$ | 10,250 | ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ |
| $[\text{Co}(\text{L})_2]$ | 7850, 19,00 and 21,400 | ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}, {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g}$ |
| $[\text{Ni}(\text{L})_2]$ | 8,400, 14,200 and 25,000 | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}, {}^3\text{T}_{1g}$ (F) and ${}^3\text{T}_{1g}$ (P) |
| $[\text{Cu}(\text{L})_2]$ | 12,210 | ${}^2\text{E}_{2g} \rightarrow {}^2\text{T}_{2g}$ |

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