

Synthesis, Thermal and Spectral Studies of Mn(II), Co(II), Cu(II) and Zn(II) Complexes of Cinnamaldehydeanthranilic Acid

B. SLEEMA and GEETHA PARAMESWARAN*

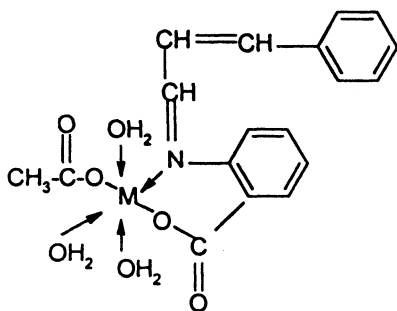
Department of Chemistry, University of Calicut, Calicut-673 635, India

Complexes of Mn(II), Co(II), Cu(II) and Zn(II) with Schiff base formed by condensation of cinnamaldehyde and anthranilic acid have been synthesized and their physicochemical properties have been investigated by elemental analysis, magnetic measurement, molar conductance, electronic spectroscopy, infrared spectroscopy and thermal studies. The ligand was found to be bidentate chelating agent for the metal ions. Thermal decomposition data of the complexes have been analyzed to obtain the activation energy, entropy of activation and frequency factor based on Coats-Redfern equation. The relative thermal stability of the chelates can be given as $[\text{MnLOAc}(\text{H}_2\text{O})_3] \approx [\text{ZnLOAc}(\text{H}_2\text{O})] < [\text{CoLOAc}(\text{H}_2\text{O})_3] < [\text{CuLOAc}(\text{H}_2\text{O})]$

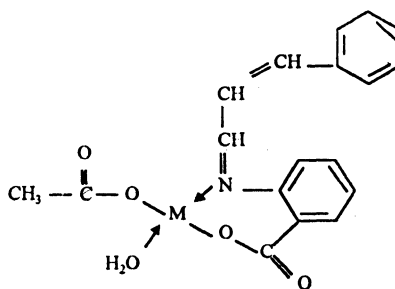
Key Words: Synthesis, Thermal, Spectral, Mn(II), Co(II), Cu(II), Zn(II), Complexes, Cinnamaldehydeanthranilic acid.

INTRODUCTION

Many metal complexes of anthranilic acid have been known for their analytical properties including estimation¹ and quantitative separation². In continuation of our work³⁻⁶ on thermal decomposition kinetics of metal chelates we report here the preparation, characterization and thermoanalytical data of Mn(II), Co(II), Cu(II) and Zn(II) complexes of the novel Schiff base, cinnamaldehydeanthranilic acid.



M = Mn or Co



M = Cu or Zn

EXPERIMENTAL

Synthesis of the ligand: Cinnamaldehyde (3 mL) dissolved in ethanol was added to an ethanolic solution of anthranilic acid (2.8 g). The reaction mixture was stirred well for a few minutes. The yellow crystals separated were washed with alcohol, dried and recrystallized from alcohol and characterized on the basis of analytical and spectral data.

General method for preparing the complexes: Complexes were prepared by refluxing an aqueous or alcoholic solution of metallic salts with an alcoholic solution of the ligand in 1 : 2 molar ratio for about 1 h. The resulting solution was cooled and filtered. The product formed was washed with alcohol and dried in vacuum over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The physical appearance and analytical data of the various complexes are summarized in Table-1. Elemental analysis shows that Mn(II), Co(II), Cu(II) and Zn(II) form 1 : 1 complexes with the ligand. All these complexes are found to be insoluble in all common available solvents.

TABLE-1
ANALYTICAL DATA AND MAGNETIC MOMENTS

Complex	Colour	Elemental Analysis (%), Found (Calcd.)				μ_{eff} (B.M.)
		M	C	H	N	
[MnLOAc(H ₂ O) ₃]	Yellow	13.3 (13.1)	51.42 (51.68)	5.06 (5.02)	3.62 (3.35)	5.98
[CoLOAc(H ₂ O) ₃]	Purple	14.7 (14.0)	51.21 (51.19)	4.97 (4.98)	3.36 (3.32)	4.80
[CuLOAc(H ₂ O)]	Blue	16.9 (16.2)	55.37 (55.31)	4.33 (4.35)	3.61 (3.58)	1.80
[ZnLOAc(H ₂ O)]	Colourless	17.2 (16.7)	55.27 (55.05)	4.39 (4.33)	3.61 (3.57)	Diamag.

The observed magnetic moment of Mn(II) complex is 5.98 BM. This value is nearer to the spin only value of 5.92 BM which points out the presence of 5 unpaired electrons. The corresponding electronic configuration will be d^5 , ${}^3T_{2g}$, 2E_g which does not show any orbital contribution to the magnetic moment and therefore an OH symmetry can be assigned to Mn(II) complex. Co(II) complex possesses a magnetic moment value 4.78 BM. It is reported that octahedral, high spin symmetry can be assigned to Co(II) complex, if the measured μ_{eff} values are in the range of 4.3–5.2 BM.

Magnetic moment of 1.86 BM observed for Cu(II) complex indicate the presence of one unpaired electron. The corresponding electronic configuration will be (d^9) ; $T_{2g}{}^6E_g{}^3$ and one can expect a square planar geometry. The Zn(II) complex is diamagnetic as expected for d^{10} configuration.

Electronic spectrum of the ligand is characterized by three bands lying in the region $31000\text{--}27000\text{ cm}^{-1}$, $38000\text{--}30300\text{ cm}^{-1}$, which can be assigned to $n \rightarrow \pi$, $\pi \rightarrow \pi$ and $n \rightarrow \sigma$, transitions respectively. These transitions are observed with high intensity.

During complex formation a red shift is detected for the bands which indicate the involvement of Schiff base in coordination. In addition to this, spectra of complexes are characterized by a strong band of maximum absorption at a region of $34000\text{--}26000\text{ cm}^{-1}$ which can be assigned to the charge transfer transition from ligand to metal.

The electronic spectrum of the Mn(II) complex contained a band at 24800 cm^{-1} which support the presence of Mn(II) in an octahedral environment⁸. The electronic spectrum of Co(II) is characterized by two bands at 10604 cm^{-1} and 21000 cm^{-1} due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ respectively. The expected octahedral transitions of cobalt are ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The middle band is due to a transition of 2 electrons which is forbidden and gives a weak band. And again ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$ are very close in octahedral. Due to these factors, detection of the middle band is very difficult.

Cu(II) complex shows only one band at 15873 cm^{-1} . This frequency may be due to the transition of $E \rightarrow T_2$ which is suggestive of its square planarity⁹. Zn(II) complex exhibits strong charge transfer bands at 19000 cm^{-1} .

The significant IR spectral bands of the ligand and the complexes along with their probable assignments are given in Table-2.

TABLE-2
SELECTED INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF
CINNAMALDEHYDE ANTHRANILIC ACID AND ITS METAL CHELATES

Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Ligand	1616	1707	—	—
[MnLOAc(H ₂ O) ₃]	1590	1614	510	400
[CoLOAc(H ₂ O) ₃]	1592	1614	510	419
[CuLOAc(H ₂ O)]	1595	1604	480	430
[ZnLOAc(H ₂ O)]	1593	1605	510	400

Infrared spectra of cinnamaldehydeanthranilic acid shows a strong band at 1707 cm^{-1} due to $\nu(\text{C}=\text{O})$; another band at 1616 cm^{-1} due to $\nu(\text{C}=\text{N})$. As compared to the spectra of the ligands, those of the metal chelates show considerable differences, particularly in the 1700–1570 cm^{-1} .

The sharp band at 1616 cm^{-1} in the ligand due to $\nu(\text{C}=\text{N})$ of Schiff base residue shifts to lower frequencies at *ca.* 1590 cm^{-1} in the complexes showing the coordination of N atom of the azomethine linkage to the metal atom^{10, 11}.

The band at 1707 cm^{-1} may be due to the carbonyl stretching frequency of the carboxyl group. A shift of this band to lower frequencies (1604 cm^{-1}) indicates chelation of the ligand to the metal atom through carbonyl oxygen.

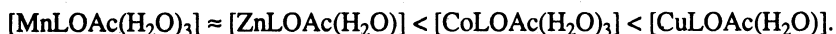
Since there are two carboxylate groups (benzoate and acetate) in the complexes, its effect on the frequencies is not easily predictable. In all the complexes, the symmetric and asymmetric stretching vibrations of the carboxylate groups occur at 1600–1590 and 1445–1440 cm^{-1} showing a $\Delta\nu$ of < 160–145 cm^{-1} . Monodentate carboxylate group has a difference of 160–150 cm^{-1} , but a bidentate carboxylate has a much closer difference (< 120 cm^{-1})¹²⁻¹³. Monodentate carboxylate groups are, therefore, indicated in the above chelates.

The broad band ranging from 3400–3000 cm^{-1} in the infrared spectra of the metal complexes is attributed to coordinated water¹⁴. The medium intensity bands at 510–480 and 430–400 cm^{-1} may be assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively¹⁵.

Based on the above observation, it has been inferred that the ligand behaves as a univalent bidentate coordinating through the azomethine nitrogen and carboxylate anion.

The thermal decomposition studies of Mn(II), Co(II), Cu(II) and Zn(II) chelates have been carried out. These complexes do not show any detectable change upto 100°C when heated. This shows there is no water of hydration. At a range of 110–180°C, a loss of mass is noted in all the four complexes. This is due to coordinated water molecules in these complexes.

The initial decomposition temperature is frequently used to define the relative thermal stability of metal complexes. On the basis of experimental findings in the present course of studies the relative thermal stabilities of the chelates under examination can be given as



TG curves of Mn(II) and Co(II) chelates show very sharp single stage process. This peculiar behaviour may be due to the rapid decomposition of the complex. The decomposition of $[\text{CuLOAc}(\text{H}_2\text{O})]$ takes place in two steps. The first decomposition step in the TG curve is steep and hence the first step was not studied further. It was found to be impractical to subject the very steep TG curve to a mathematical analysis. The second step forms the main decomposition step and hence this was subjected to kinetic study.

Decomposition of $[\text{ZnL}(\text{OAc})(\text{H}_2\text{O})]$ is also a two step process. The first step corresponds to the loss of one water molecule and cinnamaldehyde part whereas the second step denotes the loss of anthranilic acid and acetate.

The final products of decomposition of all these complexes are identified as oxides. The observed mass loss of these complexes agrees well with the value calculated properly from experiment. The percentage mass losses shown by the TG curves and those obtained by theoretical method are shown in Table-3 along with the temperature ranges and peak temperature.

The kinetic parameters obtained from the application of the Coats-Redfern equation¹⁶ are given in Table-4.

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^2} \right] = \ln \left[\frac{AR}{\phi E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{RT}$$

TABLE-3
THERMAL DECOMPOSITION DATA

Complex	Temp. range in TG (°C)	Peak temp. in TG (°C)	Loss of mass	
			From TG	Theoretical
1. $[\text{MnLOAc}(\text{H}_2\text{O})_2]$	120–340	330	81	81.76
2. $[\text{CoLOAc}(\text{H}_2\text{O})_3]$	150–300	345	81	80.97
3. $[\text{CuLOAc}(\text{H}_2\text{O})]$				
Stage I	180–290	270	69	68.70
Stage II	290–410	350	11	11.01
4. $[\text{ZnLOAc}(\text{H}_2\text{O})]$				
Stage I	120–370	350	34	34.15
Stage II	370–430	420	45	45.39

TABLE-4
KINETIC DATA

Complex	Stage	E	A	ΔS
1. [MnLOAc(H ₂ O) ₃]	I	Rapid	—	—
2. [CoLOAc(H ₂ O) ₃]	I	Rapid	—	—
3. [CuLOAc(H ₂ O)]	I	Rapid	—	—
	II	119.72	6.4×10^7	-101.5
4. [ZnLOAc(H ₂ O)]	I	136.80	2.4×10^9	-70.7
	II	212.80	1.2×10^{14}	0.0176

All these studies suggest octahedral structures for Mn(II) and Co(II) complexes, a square-planar structure for Cu(II) complex and tetrahedral structure for Zn(II) complex.

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