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Synthesis and Characterization of Mn(II), Fe(III), Co(II) and Ni(II) Complexes of Anthracene Carboxaldehyde Semicarbazone

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Complexes of Mn(II), Fe(III), Co(II) and Ni(II) with Schiff base formed by condensation of semicarbazide hydrochloride and anthracene carboxaldehyde have been synthesized and their physico-chemical properties have been investigated by elemental analysis, magnetic measurements, molar conductance, electronic spectroscopy, Infra-red spectroscopy and thermal studies. The ligand was found to be bidentate chelating agent for the metal ions. Thermal decomposition data of Co(II), Ni(II) and Mn(II) have been analysed 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

$$[CoL_2(H_2O)_2] \approx [NiL_2(H_2O)] > [MnL_2(H_2O)_2]$$

INTRODUCTION

Many metal complexes of semicarbazone have been known for their pharmacological properties including activity against tuberculosis[1], bacterial[2] and viral functions[3]. In continuation of our work[4–7] on thermal decomposition kinetics of metal chelates, we report here the preparation, characterization and thermo analytical data of Mn(II), Fe(III), Co(II) and Ni(II) complexes of the novel schiff base, anthracene carboxaldehyde semicarbazone.

EXPERIMENTAL

Synthesis of the ligand: Anthracene carboxaldehyde (2 g) dissolved in ethanol was added to an aqueous solution of semicarbazide hydrochloride (1 g) and sodium acetate (100 mg). The reaction mixture was stirred and refluxed for about 4 h. The yellow crystals separated were washed with water, dried and recrystallized from alcohol and characterized on the basis of analytical and spectral data.

General method for preparing the complexes: An aqueous solution of the metallic salt, semicarbazide hydrochloride and sodium acetate was refluxed with hot ethanolic solution of anthracene carboxaldehyde in 1 : 2 molar ratio for about 3 h. The mixture was cooled and ammonium hydroxide was added till ammoniacal and refluxed again for 2 h and cooled. The precipitate was filtered, washed with water and alcohol and dried in vacuum over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The physical appearance and analytical data of the various complexes are summarised in Table-1. The complexes are found to be bright coloured and hence give a broad absorption in the visible region. The molar conductance of the complexes in nitrobenzene is in the range 0.3–1.3 ohm^{-1} mol^{-1} cm^2. The very low values indicate that complexes are non-electrolytes in nitrobenzene and are neutral in nature.

TABLE-1
ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS

	Complex	Colour	Found (Calcd.) % metal	μ_{eff} B.M.	Molar conductance cm^{-1} cm^2 mol^{-1}
1.	$[MnL_2(H_2O)_2]$	Brownish yellow	8.93 (9.21)	6.30	0.7
2.	$[FeL_2Cl_2]_2$	Brown	8.50 (8.90)	4.50	0.9
3.	$[CoL_2(H_2O)_2]$	Greenish yellow	9.50 (10.20)	4.76	0.6
4.	$[NiL_2(H_2O)_2]$	Yellow	9.48 (10.15)	2.84	0.3

The observed magnetic moment of Fe(III) complex is 4.5 B.M. The low value of magnetic moment indicates a possible contribution from intramolecular antiferromagnetic exchange process and a dimeric structure has been suggested for the complex.

The observed value of 6.3 B.M. in the case of Mn(II) complex suggests an octahedral geometry. Co(II) complex possesses a magnetic moment value of 4.76 B.M. The observed magnetic moment for the spin free octahedral $Co^{2+}(^4T_{1g})$ have excess of spin only value and it may be due to the orbital contribution of both the ground state $(^5T_{2g}{}^2E_g)$ and the first excited state $(^4T_{2g}{}^3E_g)$. Nickel(II) complex possesses a magnetic moment of 2.84 B.M. which is very close to the spin only value of 2.83 B.M. indicating the presence of 2 unpaired electrons with the electronic configuration $^6T_{2g}{}^2E_g$ $(^3A_2)$. An octahedral geometry can be assigned to the Ni(II) complex.

Electronic spectrum of the ligand are characterized by two bands lying at 37600 and 24000 cm^{-1} which can be assigned to $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ respectively. These transitions are observed with high intensity.

The electronic spectrum of Fe(III) complexes shows an intense band at 23148 cm^{-1} which is due to charge transfer transition. A weak shoulder is located at 30303 cm^{-1}. These bands have been observed by Martin and White. Since the ground state for Fe(III) high spin complexes is $^6A_1$, all transitions are expected to be weak and frequently obscured by charge transfer bands.

The electronic spectrum of Co(III) complex is characterized by 2 bands at

95900 cm^{-1} and 22723 cm^{-1} due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. The expected octahedral transitions of cobalt are:

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$; $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.

The middle band is due to a transition of two electrons, which is forbidden and gives a weak band. And again $^4A_{2g}(F)$ and $^4T_{1g}(P)$ are very close in octahedral transition. Due to these factors detection of the middle band is very difficult. Ni(II) complexes also exhibit two d–d transitions in the regions at *ca.* 14725 and 20733 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition respectively.

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 ANTHRACENE CARBOXALDEHYDE SEMICARBAZONE AND ITS METAL CHELATES

Complex	ν(C=N)	ν(C=O)	ν(M—N)	ν(M—O)
Ligand	1610	–	–	–
Mn(II) complex	1575	1034	524	418
Fe(III) complex	1570	1034	524	419
Co(II) complex	1575	1082	525	416
Ni(II) complex	1579	1082	525	410

The ligand exhibits bands of high intensity at about 3480, 3300, 3210 and 3120 cm^{-1}. The group —NH—$CONH_2$ accounts for these bands. These may be assigned to the asymmetric ν(NH) of terminal —NH_2 group and the symmetric ν(NH) of the NH_2 and two NH group[8]. It has been suggested that the vibrations of the terminal —NH_2 group are responsible for the two bands at higher frequency region, as they are all present in the spectra of complexes at about the same frequencies or a slight shift to the higher frequency region. Therefore in these semicarbazones the secondary —NH group would be responsible for the lower frequency bands between 3210 and 3150 cm^{-1}. In the metal complexes, the intensity of these bands is considerably lowered. Moreover, the number of bands in this region decreases, and they become broad. These observations are attributed to the fact that the hydrazine nitrogen atom of —N—NH—CO— participates in coordination.

The bands at 1624 cm^{-1} may be assigned to ν(C=O) group. This band is not observed in the spectrum of the chelates and a new band appears around 1034 cm^{-1}. This may be due to enolization and subsequent coordination of this carbonyl group in this complex.[9]

A strong band in the spectrum of the ligand at 1610–1580 cm^{-1} may be assigned to azomethine stretching modes[10]. In the metal complexes, this band is shifted to lower frequency region indicating the participation of the azomethine nitrogen atom in coordination. However, there is likely to be overlap with aromatic ring absorptions in the region. The bands between 1075–950 cm^{-1} may be assigned to ν(N—N). The bands of medium intensity between 1210–1150 cm^{-1} may be due to the deformation and rocking modes of NH_2.

The combination bands due to ν(C—N) and π(C—H) appear at approximately 880–830 cm^{-1} in the spectrum of the chelates. A broad feature at approximately 3500 cm^{-1} in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecule. In addition, a strong band at approximately 950–870 cm^{-1} suggests that the water molecules are coordinated[11]. The medium intensity bands at 525–500 and 430–400 cm^{-1} may be assigned to ν(M—N) and ν(M—O) respectively[12].

Based on the above observation, it has been inferred that the ligand behaves as a univalent bidentate coordinating through the azemethine nitrogen and enolic oxygen atoms.

The thermal decomposition studies of Mn(II), Fe(III), Co(II) and Ni(II) chelates have been carried out. The T.G. traces exhibit a three stage decomposition pattern. The first step corresponds to the loss of water molecules, which occurs in the temperature range 150–250°C in these complexes. The mass loss of the second step corresponds to the loss of one ligand part and third step also denotes the loss of the second ligand. The final products of decomposition are identified an oxides. The decomposition was found to be very rapid for the second step in the case of Co(II) and Ni(II) complexes. As a result, the second decomposition step in the TG traces was steep and so mathematical analysis of this part was not carried out owing to much difficulty. The first step in these traces was subjected to kinetic study. These observed mass loss agrees fairly well with the value calculated from pyrolytic experiments.

The percentage mass loss as shown by the TG cruves is 49% for stage I and 38.5% for stage II in the case of $[MnL_2(H_2O)_2]$, 48% and 39% for stage I and stage II in the case of $[CoL_2(H_2O)_2]$ and 60 and 31% for stage I and stage II in the case of $[NiL_2(H_2O)_2]$ respectively. The calculated percentage mass losses are as shown in Table-3.

TABLE-3

Complex	Stage	Mass loss % (Calcd)
$[MnL_2(H_2O)_2]$	I	48.5%
	II	39%
$[CoL_2(H_2O)_2]$	I	48%
	II	38.8%
$[NiL_2(H_2O)_2]$	I	59.9%
	II	30.7%

The kinetic parameters obtained from the application of the Coats Redfern Equation[13].

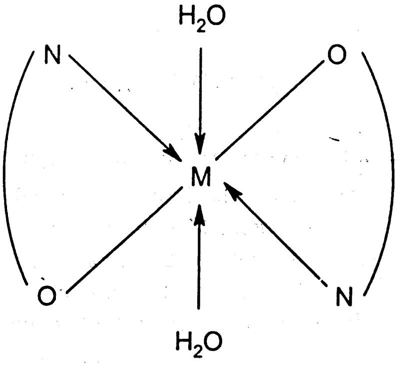
$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\ln\left[\frac{AR}{\phi E^*}\left(1-\frac{2RT}{E^*}\right)\right]-\frac{E^*}{RT}$$

are given in Table-4.

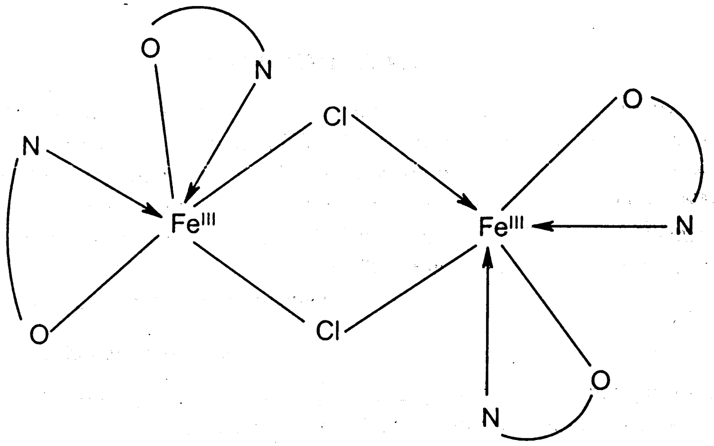
TABLE-4
KINETIC DATA

Chelate	Stage	E (kcal mol^{-1})	A (s^{-1})	ΔS (cal K^{-1} mol^{-1})
$[MnL_2(H_2O)_2]$	I	20.4	2.8×10^4	–39.4
	II	4.5	7.9	–56.1
$[CoL_2(H_2O)_2]$	I	13.9	1.6×10^3	–58.8
	II	rapid		
$[NiL_2(H_2O)_2]$	I	29.0	6.9×10^5	–33.2
	II	rapid		

All these studies suggest octahedral structures for Fe(III), Co(II), Ni(II) and Mn(II) complexes. Based on the available data, a chlorine bridged dimeric structure has been tentatively suggested for Fe(III) complex.



where M = Mn(II) Co(II) and Ni(II).



On the basis of the experimental findings, the relative thermal stability of the chelates can be given as

$$[CoL_2(H_2O)_2 \approx [NiL_2(H_2O)_2] > [MnL_2(H_2O)_2]$$

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