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Kinetic, Spectroscopic and Polarographic Determination of Trivalent Ions in an Imine System

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Complexes of Al(III), Cr(III), Mn(III), Fe(III), Co(III) and Bi(III) with Schiff's base derived from the condensation of 2-oxo-1-benzopyran-3-carboxylic acid and *o*-aminothiophenol have been prepared. The kinetic parameters of decomposition have also been evaluated both by Freeman-Carroll and Sharp-Wentworth methods. D.C. electrical conductivity of the complexes has been studied. Differential pulse polarography has been chosen to follow the metal reduction process.

Key Words: Kinetics, Spectroscopy, Polarography, Trivalent ions, Imine.

INTRODUCTION

Coumarins are considered to be the building blocks for the synthesis of biologically active compounds which have been reported to act as nervous system depressants[1] and antibacterial agents[2]. Thus they occupy a central place in our armamentarium against various diseases afflicting mankind because of their diverse activities[3–5]. Besides the presence of potential coordination sites, they also possess interesting ligational properties which is in turn a deciding factor for many reactions to proceed. However, no work seems to have been reported on the trivalent metal complexes of Schiff's base derived from substituted coumarins and thiols. Therefore, it was thought of interest to prepare Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} and Bi^{3+} complexes of 2-oxo-1-benzopyran-3-carboxylic acid and *o*-aminothiophenol (H_2BCIT).

EXPERIMENTAL

Preparation of Schiff's Base

A DMF-ethanolic solution of coumarin-3-carboxylic acid and *o*-aminothiophenol in equimolar ratio (25 cm^3) was mixed with constant stirring. Refluxing was carried out for 4 h and then was cooled at room temperature. The formed crystals were collected and dried *in vacuo* (yield 60%).

Preparation of the Complexes

To the hot solution of the ligand H_2BCIT in DMF-ethanol (50 cm^3), a suspension of respective metal chloride/acetate in ethanol was added dropwise with stirring. The mixture was refluxed on a water bath for 4 h. The precipitated complexes were dried over fused calcium chloride (yield 65–70%).

RESULTS AND DISCUSSION

All the complexes (Table-1) are coloured solids, stable in air and insoluble in water and common solvents but soluble in DMF and DMSO. The satisfactory analytical data of these indicate 1 : 1 metal-ligand stoichiometry (Table-1). The conductivity data of the complexes in DMF at room temperature show that they are to some extent semi-conductors. The solids do not melt sharply but with decomposition.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compd. (Colour)	Metal % found (calcd.)	μ_{eff} (B.M.)	(σ) Elec. cond. (Ω^{-1} cm^{2} mol^{-2})	Decomp. temp. (°C)	Activation energy (kJ mol^{-1})	
					FC	SW
Cr—L (Rust)	18.18 (18.34)	4.89	4.4×10^{-9}	365	26.74	23.89
Mn—L (Brown)	19.23 (19.37)	4.81	6.3×10^{-8}	390	29.48	27.00
Fe—L (Black)	19.58 (19.64)	5.49	8.8×10^{-8}	410	34.10	33.99
Al—L (Grey)	9.44 (9.51)	Diamag.	9.1×10^{-8}	320	29.38	28.78
Co—L (Reddish brown)	20.62 (20.70)	Diamag.	10.4×10^{-8}	345	28.45	27.16
Bi—L (Dark brown)	72.72 (72.79)	Diamag.	11.6×10^{-8}	395	31.24	30.82

The infrared spectra of the ligand shows a broad band around 2900 cm^{-1} (intramolecular hydrogen bonded OH) which disappeared in the complexes as hydrogen is replaced by the metal[6]. The strong ligand band at 1620–1610 cm^{-1} (C═N) is lowered (20–30 cm^{-1}) in the spectra of the complexes, indicating coordination through azomethine nitrogen[7]. Bands at 1545 and 1265 cm^{-1} are due to the asym. and sym. COO stretching frequencies respectively. The disappearance of the band (2660 cm^{-1}) assigned to —SH indicates that the chelation has taken place through the sulphur of the thiol group[8]. The bands at 480 and 545 cm^{-1} may be assigned to ν(M—N) and ν(M—O) respectively. Appearance of new bands at 1570, 800 and 600 cm^{-1} in the complexes of Cr^{3+}, Fe^{3+} and Al^{3+} is attributed to the rocking and wagging modes of coordinated water.

The magnetic moments of the Cr^{3+}, Mn^{3+} and Fe^{3+} complexes show spin-only values. The spectra of the Cr^{3+}-complex exhibit three bands which can be assigned to transitions characteristic of an octahedral geometry[9]. The lowest energy spin-allowed transition (ν_1) is $^4A_{2g} \rightarrow {}^4T_{2g}(F)$. The other two bands at 25470 (ν_2) and 41055 cm^{-1} (ν_3) are assigned to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. The various ligand field parameters have also been evaluated. The value of first spin-allowed transition ν_1 at 19215 cm^{-1} is directly taken as 10 Dq. The value of Racah parameter (B), the nephelauxetic ratio (β) (B in complex/B in free ion) and CFSE calculated[10] are found to be 592 cm^{-1}, 0.643 and 229.57 kJ mol^{-1} respectively.

The Mn^{3+} complexes show an intense charge transfer band around 23000 cm^{-1} and a broad band at 18180 cm^{-1}. Usually the spin-free Mn^{3+} complexes[11] with octahedral geometry give one charge transfer band around 25000 and a spin-allowed *d-d* transition band $^5E_{2g} \rightarrow {}^5T_{2g}$ around 20000 cm^{-1}. In the present case, the band around 18180 cm^{-1} is assignable to the *d-d* transition. This broad band occurring at lower frequency with increased intensity indicates the lowering of symmetry from the octahedral configuration to square-pyramidal structure which seems to be the most probable one. The magnetic moment value (4.81 B.M.) of the complex is very close to the value expected for a high-spin complex with unpaired electrons. Electronic spectra of the Fe^{3+} complexes show bands at 14867–18833, 22691–24315 and 31876–32300 cm^{-1}. The first two bands may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions respectively, for an octahedral stereochemistry[12]. The third band may be due to ligand-metal charge transfer. The effective magnetic moment value (5.49 B.M.) for the complex is in the range expected for a spin free octahedral system. The Al^{3+}, Co^{3+} and Bi^{3+} complexes are found to be diamagnetic and the diffuse reflectance spectra did not show any band in the visible region.

The thermal studies indicate that the complexes decompose in two steps after dehydration. The loss of coordinated water molecules takes place at around 140°C for Cr^{3+}, Fe^{3+} and Mn^{3+} and around 160° for the remaining complexes. The first step of decomposition is fast as compared to the second step. This may be due to the fact that the non-coordinated part of the ligand decomposes first, while the actually coordinated part decomposes later and finally forms metallic oxide[13]. No attempt was made to characterize the products formed at the end of each step. To obtain the relative thermal stabilities of the various complexes the methods described by Sharp-Wentworth and Freeman-Carroll[15] were adopted and the values which are comparable are summarized in Table-1. The complexes were found to be thermally more stable than the ligand itself and decompose in the range 310–440°C. From the decomposition temperature (Table-I), the relative thermal stabilities of the complexes were found to be: Fe > Bi > Mn > Cr > Co > Al.

The d.c. electrical conductivityies of the complexes were studied over a wide range of temperature. The conductivity (σ) varies exponentially with the absolute temperature according to the relationship $\sigma = \sigma_0 \exp -E_a/KT$, where σ_0 is a constant, E_a is activation energy and K is Boltzmann constant. Over a wide range of temperature (60–220°C), linear dependence of $\log \sigma = f(10^3/T)$ was observed, which confirms the semiconductor behaviour of the complexes.[16] The low value of conductivity may be attributed to low molecular weight due to which the extent of conjugation becomes low or of undesirable morphology due to pressing of the samples into hard brittle pellet form.

The differential pulse polarographic behaviour of 1×10^{-5} M solutions of the compound in aqueous 0.01 M NH_4Cl, NH_3 and gelatin was determined and it was observed that d.c. polarographic limiting current increases linearly with the square-root of the mercury height, demonstrating that the reduction is diffusion controlled (Table-2).

TABLE-2
VARIATION OF MERCURY PRESSURE ON THE LIMITING CURRENT

Supporting electrolyte = NH_3/NH_4Cl/Gelatin; pH = 8.6; Cr(III) = 1×10^{-5} M

S. No.	Height of Hg-Column (h) (cm)	Current (i_0) (μA)	i_0/h	$i_0/\sqrt{h}$
1.	35	3.4	0.097	0.574
2.	40	3.6	0.090	0.569
3.	45	3.7	0.082	0.551
4.	50	3.9	0.078	0.551
5.	55	4.1	0.074	0.552
6.	60	4.3	0.071	0.555
7.	65	4.6	0.070	0.570

The complexation reaction has been investigated by measuring both potential and current evolution of the differential pulse polarographic peak of 1×10^{-5} M Cr^{3+} solution by increasing the concentrations of the ligand from 1×10^{-5} to 10.0×10^{-4} M (Table-3). In order to investigate the complex formation and calculate the stability constants, the reduction potential is plotted against the logarithm of the ligand concentration. This gives rise to a smooth curve. By applying the method of Deford and Hume[17] modified by Health and Hefter[18], the following function is used for calculations:

$$f_n[x] = \frac{f_{(n-1)}[x] - \beta_{n-1}}{[x]}$$

where [x] is ligand concentration. By plotting $f_n[x]$ function against the ligand concentrations, the stability constants can be determined from the intercepts. The functions are derived until a straight line parallel to x-axis is obtained, thereby concluding 1 : 1 metal to ligand stoichiometry.

TABLE-3
VARIATION OF THE PEAK POTENTIAL (E_p) AND THE PEAK CURRENT (I_p) AS A FUNCTION OF LIGAND CONCENTRATION [X] IN THE PRESENCE OF 1×10^{-5} M OF METAL(III) IONS

Compound	[x] (10^{-4} M)	$-E_p$ (v)	$-I_p$ (μA)	I_p/C
Cr(III)	2.0	1.43	2.21	1.105
	4.0	1.43	5.5	1.375
	5.0	1.43	6.2	1.240
	6.0	1.43	8.0	1.333
	7.0	1.45	9.3	1.328
	8.0	1.45	10.4	1.300
	10.0	1.45	13.1	1.310

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