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Thermal Spectral and Magnetic Studies of Citral-anthranilic Acid and Citral-5-bromo-anthranilic Acid Complexes of Co(II), Ni(II) and Cu(II)

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Citral-anthranilic acid and citral-5-bromo-anthranilic acid a novel Schiff base, form 1 : 1 complexes with Co(II), Ni(II) and Cu(II) acetates. All the complexes are found to be non-electrolytes in methanol and octahedral structures are assigned to them. IR studies reveal that the complexes are formed by the replacement of hydrogen atom of COOH group by the metal with the azomethine nitrogen co-ordinating to the metal. The thermal decomposition of $[ML'(OAc)(H_2O)_3]$, and $[ML''(OAc)(H_2O)_3]$, where M = Co, Ni, Cu, was studied by TG technique. The mechanism of the decomposition has been established from TG data. The kinetic parameters E, activation energy preexpoential factor (A) and entropy of activation (ΔS) were calculated from TG curves using mechanistic and non- mechanistic equations. On the basis of our findings the relative thermal stabilities of the chelates have been evaluated.

INTRODUCTION

Schiff bases constitute an important class of nitrogen donor ligands and occupy a prominent position among the recent achievements in the field of coordination chemistry. The synthesis and properties of Schiff bases are widely reviewed.[1, 2] Schiff bases contain the azomethine group and the bonding ability of ligands depends on the nature of atoms which act as co-ordination sites, their electronegativity and steric factors. Wendtlandt *et al.*[3] and Scency *et al.*[4] studied the thermal properties of metal chelates with different types of complexing ligands. A few workers[5] have done such studies on the thermal decomposition and kinetics of metal chelates with azomethine ligands. In the work we report here the preparation, characterisation and thermo-analytical data of these transition metal complexes of citral-anthranilic acid (CAA) and citral-5 bromo-anthranilic acid (CBrAA).

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EXPERIMENTAL

All the chemicals used were of AnalaR grade. The solvents used were purified by distillation. Magnetic moments were calculated using the Gouy balance. Molar conductivity was determined by using Elico conductivity bridge. IR and UV studies were conducted in Shimadzu spectrophotometer. Thermogravimetric analysis was conducted on a Shimadzu thermal analysis system.

All the transition metal complexes were prepared by reported methods[5]. The analytical data of the complexes are presented in Table 1.

TABLE-1
MICRO-ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF TRANSITION METAL COMPLEXES OF CAA (L_1) AND CBrAA (L_2)

Complex (colour)	%Analysis, found (calcd.)				μ_{eff} (B.M)	Conductance ohm^{-1} cm^2 mole^{-1}
	M	C	H	N		
$[CoL_1(OAc)(H_2O)_3]$ (Pink)	13.54 (13.01)	49.57 (49.05)	6.01 (5.98)	3.24 (3.06)	5.6	4.23
$[NiL_1(OAc)(H_2O)_3]$ (Light Green)	13.47 (13.18)	49.57 (49.08)	5.96 (5.67)	3.21 (3.12)	4.6	5.61
$[CuL_1(OAc)(H_2O)_3]$ (Green)	14.42 (14.18)	49.03 (48.87)	5.90 (5.87)	3.17 (3.05)	1.9	7.51
$[CoL_2(OAc)(H_2O)_3]$ (Light violet)	11.44 (11.12)	41.90 (41.32)	5.05 (4.67)	2.71 (2.53)	5.7	3.40
$[NiL_2(OAc)(H_2O)_3]$ (Light)	11.04 (11.02)	41.90 (41.28)	5.05 (4.64)	2.72 (2.37)	2.9	7.64
$[CuL_2(OAc)(H_2O)_3]$ (Green)	12.23 (12.01)	41.58 (41.07)	5.00 (4.87)	2.69 (2.42)	2.0	6.50

RESULTS AND DISCUSSION

Spectra of complexes of both the ligands are similar and bands were assigned by comparison to their parent compounds. Strong bands appearing in the region 2950–2900 cm^{-1} and 2900–2800 cm^{-1} can be attributed to asymmetric and symmetric stretching vibrations due to methyl and methylene groups present in the citral part. These bands are retained in the metal chelates also. In the metal chelates of Co(II), Ni(II) and Cu(II) bands appearing in the region 3400–3100 cm^{-1} are assigned to coordinated water. The bands appearing in the spectra of complexes at *ca.*1585 cm^{-1} may be due to ν(C=N). The asymmetric stretching vibration of carboxyl group is seen in 1625–1610 cm^{-1} region, while symmetric stretching frequency of carboxyl group is present at 1419 cm^{-1}. The $\Delta\nu$ in the range 180–170 cm^{-1} between these two vibrations is indicative of the monodentate nature of carboxylate group. Bands or shoulders due to skeletal vibrations of aromatic nucleus can be identified in the region 1600–1450 cm^{-1}. The conclusive evidence of bonding of the ligand to the central metal ion is provided by the

TABLE-2

SELECTED IR FREQUENCIES (cm^{-1}) OF METAL COMPLEXES OF CAA AND CBrAA

Substance	ν(OH) of H_2O	ν_{asy} ($CH_3 + CH_2$)	ν_{sym} ($CH_3 + CH_2$)	ν(C=N)	ν_{sym} $\mathrm{C}{<}^{\mathrm{O}^-}_{\mathrm{O}}$	ν_{asym} $\mathrm{C}{<}^{\mathrm{O}^-}_{\mathrm{O}}$	In-plane deformation	Out-of-plane deformation	ν(M—N)	ν(M—O)
[$CoL_1(OAc)(H_2O)_3$]	3120 b 3300 b	2900 s	2830 m	1580 s	1625 s	1458 s	872 m	756 s	519 w	424 m
[$NiL_1(OAc)(H_2O)_3$]	3306 b 3231 b	2974 s	2930 w	1580 s	1616 s	1458 s	872 m	754 m	519 w	424 s
[$CuL_1(OAc)(H_2O)_3$]	3120 b 3280 b	2920 s	2850 w	1585 s	1606 s	1458 s	862 m	775 s	584 w	420 s
[$CoL_2(OAc)(H_2O)_3$]	3310 b 3135 b	2970 s	2920 m	1585 s	1608 s	1419 s	883 s	727 s	517 m	421 m
[$NiL_2(OAc)(H_2O)_3$]	3308 b 3123 b	2950 s	2924 m	1587 s	1608 s	1419 s	883 m	727 s	517 m	426 m
[$CoL_2(OAc)(H_2O)_3$]	3400 b 3250 b	2950 s	2928 m	1598 s	1650 s	1477 s	883 m	729 m	617 m 517 m	453 m

appearance of bands at 500 cm^{-1} and 410 cm^{-1} which can be assigned to $\nu(M—N)$ and $\mu(M—O)$ respectively (Table-2).

The electronic spectral data were found to be confirmative to the conclusions arrived at from magnetic susceptibility measurements.

The electronic spectra of Co(II) complexes are characterised by bands at 27470–15,500 cm^{-1} and 11140 cm^{-1} corresponding to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. Octahedral Ni(II) complexes will usually have these absorption bands in the regions 13000–8000 cm^{-1}, 19000–15000 cm^{-1} and 29000–25000 cm^{-1}. The absorption bands correspond to the excitations $^3A_{2g} \rightarrow {}^3T_{2g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. In the present case Ni(II) complex showed well resolved bands at 10350, 18500 and 27777 cm^{-1}. Hence Ni(II) complexes assume an octahedral geometry.

TABLE-3
THERMAL DECOMPOSITION DATA OF Co(II), Ni(II) AND Cu(II) COMPLEXES

Complex	Temp. ranges in TG °C	Peak temp. (°C)	Loss of mass%			Probable assignment
			TG	Calcd	Pyrolysis	
$[CoL_1(OAc)(H_2O)_3]$	180–380	336.9	77.2	81.5	80.1	Loss of $3H_2O$ + acetate + L_1
$[NiL_1(OAc)(H_2O)_3]$	180–380	362.9	81.0	83.0	82.4	Loss of $3H_2O$ + acetate + L_1
$[CuL_1(OAc)(H_2O)_3]$	230–400	269	78.0	82.1	81.2	Loss of $3H_2O$ + acetate + L_1
	Stage					
$[CoL_2(OAc)(H_2O)_3]$	I. 120–370	356	37.7	37.0	—	Loss of $3H_2O$,
	II. 370–520	415	39.9	47.6	—	1 Br + 1 acetate
			77.6	84.6	83.5	Loss of CAA part
$[NiL_2(OAc)(H_2O)_3]$	I. 120–390	382	42.0	37.0		Loss of $3H_2O$ +,
	II. 390–520	440	39.0	48.6		1Br + 1 acetate
			81.0	85.66	84.0	
$[CuL_2(OAc)(H_2O)_3]$	I. 120–220	220	26.0	25.5		Br + $3H_2O$
	II. 220–600	452	56.3	59.4		Loss of acetate +
			82.3	84.8	84.0	CAA

Cu(II) ion being tetragonal, its octahedral components show excitations from $^2B_{1g}$ and $^2B_{1g}{}^2E_g$ terms. These transitions occur in the energy region 20000–1000 cm^{-1}. In the present investigation absorption band at 16129–2000 cm^{-1} indicates that Cu(II) is in octahedral environment.

The TG curve for $[ML'(OAc)(H_2O)_3]$ exhibits a single stage decomposition pattern. Mass loss considerations from TG traces and direct pyrolytic data confirm the products to be the corresponding oxides (Table-3). The kinetic parameters were calculated from TG data by using the non-mechanistic and mechanistic equations. Details are given in Table-4 and 5.

A single stage decomposition pattern was observed for Co(II), Ni(II) and Cu(II) complexes of CAA. Stage I stands for the removal of one coordinated water molecule and one acetate part and Stage II for loss of citral anthranilic acid part. Since water is eliminated above 150°C it can be considered as co-ordination water.^{6} Details are given in Table-3.

TABLE-4

KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF CITRAL ANTHRANILIC ACID FROM TG USING CR EQUATION

Complex	Parameters from CR		From mechanistic equation		Order of reaction
$[CoL_1(OAc)(H_2O)_3]$	E kJ/mol	61.02	58.69	Phase boundary	1/3
	A sec^{-1}	2.5×103	2.5×103	reaction R_2	
	ΔS J/K mol^{-1}			cylindrical symmetry	
	r	–146.9	–146.9		
		0.9723	0.9723		
$[NiL_1(OAc)(H_2O)_3]$	E kJ/mol	44.67	44.67	Random nucleation	0
	A sec^{-1}	4.4×102	4.4×102	A_2	
	ΔS J/K mol^{-1}				
	r	–161.9	–161.9		
		0.9506	0.9506	Avrami equation I	
$[CuL_1(OAc)(H_2O)_3]$	E KJ/mol	119.1	119.1	Random nucleation F_1	1
	A sec^{-1}	5.4×109	5.4×109	One nucleus at each	
	ΔS J/K mol^{-1}			particle	
	r	–26.21	–26.21		
		0.9456	0.9456		

CR: Coats-Redfern

Initial decomposition temperature and inflection temperature have been used to determine the stability of metal chelates. In the present course of studies based on observations made by earlier workers the relative stabilities of metal chelates are

$$[CuL'(OAc)(H_2O)_3] < [CoL'(OAc)(H_2O)_3] < [NiL'(OAc)(H_2O)_3]$$

In the present case it is observed that the kinetic parameters calculated for F_1 mechanism based on random nucleation with one nucleus at each particle (Mampel equation) give good agreement with those obtained for Coats-Redfern (CR) equation with $n = 1$ for $[CuL'(H_2O)_3(OAc)_3]$ and $[CuL'(H_2O)_3(OAc)]$. $[NiL'(H_2O)_3(OAc)]$ was found to agree with A_2 mechanism based on random nucleation with $n = 0$ (Table-4).

From decomposition kinetics it has been observed that greater the thermal stability of the complex larger the activation energy for decomposition. The kinetic parameters obtained from Coats-Redfern and mechanistic equation for $[CuL''(OAc)(H_2O)_3]$, $[CoL''(OAc)(H_2O)_3]$ and $[NiL''(OAc)(HO)_3]$ follow F_1 mechanism with $n = 1$ (Table-5).

TABLE-5
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co(II), Ni(II) and Cu(II) COMPLEXES OF CITRAL-5-BROMO-ANTHRANILIC ACID FROM TG USING CR EQUATION

Complex	Parameters from CR		From mechanistic equation		Order of reaction
$[CoL_2(OAc)(H_2O)_3]$	E kJ/mol	319.8	324.9	Random nucleation F_1 are nucleus at each particle Mampel equation	1
	A sec^{-1}	2.7 × 1021	5.6 × 1022		
	ΔS* J/K mol^{-1}	162.1	222		
	r	0.9916	0.9921		
$[NiL_2(OAc)(H_2O)_3]$	E kJ/mol	108.6	113	Random nucleation at each particle Mampel equation	1
	A sec^{-1}	4.4 × 104	3.1 × 106		
	ΔS* J/K mol^{-1}	-159.5	-90.2		
	r	0.9772	0.9817		
$[CuL_2(OAc)(H_2O)_3]$	E kJ/mol	50.74	50.03	Phase boundary R_3 spherical symmetry	1
	A sec^{-1}	1.511	3.2 × 101		
	ΔS* J/K mol^{-1}	-214.8	-185.3		
	r	0.9876	0.9906		

CR: Coats-Redfern

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