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PHYSICOCHEMICAL STUDIES AND THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF CITRONELLAL ANTHRANILIC ACID

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Abstract

Cobalt(II), nickel(II), copper(II) and zinc(II) complexes of two new Schiff-bases, citronellal anthranilic acid and citronellal-5-bromoanthranilic acid have been synthesized. On the basis of spectral, magnetic and thermal data, octahedral structure was assigned to all complexes $[ML_2(H_2O)_2]$. Thermal decomposition of these complexes was studied by TG. Kinetic parameters, viz activation energy, E, pre-exponential factor, A, and order of reaction, n, were calculated from the TG curves using mechanistic and non-mechanistic integral equations.

Keywords: kinetics, Schiff-bases

Introduction

Transition metal complexes of Schiff-bases have important technical applications. Some workers [1–7] have studied thermal stabilities of metal chelates with azomethine ligands. In continuation of our work [8–11] on thermal decomposition kinetics of metal chelates, we report here the preparation, characterisation and thermoanalytical data of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of two novel Schiff-bases, citronellal anthranilic acid and citronellal-5-bromoanthranilic acid. Non-isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids [12–14]. This study therefore attempts to establish the mechanism of decomposition of some selected transition metal complexes of citronellal anthranilic acid and its 5-bromo derivative from TG experiments. A comparison of the energy of activation, entropy and relative thermal stability of these complexes has also been made.

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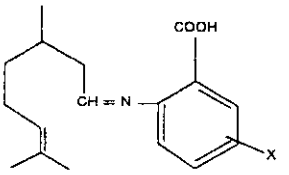

Fig. 1 (*X*=H or Br)

Experimental

Preparation of ligands

The ligand citronellal anthranilic acid was prepared as follows. Citronellal (1.8 ml, 0.01 mol) in ethanol was mixed with recrystallised anthranilic acid (1.37 g, 0.01 mol) and was kept overnight. The yellow crystalline precipitate obtained was filtered, recrystallised from ethanol and dried. Melting point was found to be 120°C.

Citronellal-5-bromoanthranilic acid was prepared from 5-bromoanthranilic acid following the same procedure adopted for parent ligand. Melting point was found to be 195°C. Both ligands were characterised on the basis of CHN analysis, mass and IR spectral data.

Preparation of complexes

Metal complexes of citronellal anthranilic acid (L'H) and citronellal-5-bromoanthranilic acid (L''H) were prepared by adding a solution of metal chlorides dropwise to a refluxing solution of ligand in methanol until the metal to ligand ratio reached 1:2. Sodium acetate (1 g) was added and heating was continued for 10 min. The separated complexes were filtered, washed with 50% methanol and dried over anhydrous $CaCl_2$. The purity of the samples was checked by elemental analysis for the metal and C, H, N analysis, spectral and thermal studies.

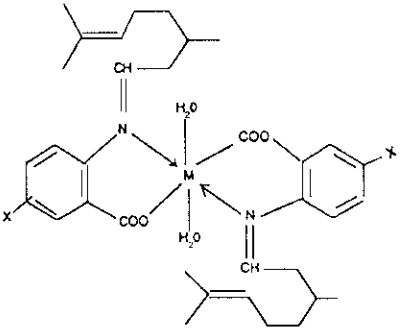

Fig. 2 *M*=Co(II), Ni(II), Cu(II) or Zn(II); (*X*=H or Br)

Instrumental

Infrared spectra were recorded using a Perkin-Elmer Model 283 infrared spectrophotometer. Thermal studies were carried out using a Perkin-Elmer 7 series thermal analysis system. A constant heating rate of 10°C min^{-1}, and sample mass of ~5 mg were employed for the entire study. Computational work was done with a Horizon III minicomputer using the programming language FORTRAN.

Data processing

The decomposition temperature ranges in TG and DTG for the metal chelates are presented in Tables 3 and 4. TG curves for Co(II) complexes of two ligands show single stage decomposition pattern, while Ni(II) and Zn(II) complexes of two ligands show double stage decomposition pattern. Cu(II) complex of citronellal anthranilic acid shows three-stage decomposition pattern while that of citronellal-5-bromoanthranilic acid shows two stage decomposition pattern. Mechanistic and non-mechanistic methods were used to determine kinetic data from TG curves.

Thermal decomposition kinetics

Kinetic parameters, viz activation energy E, pre-exponential factor A, and order parameter n, for the thermal decomposition of the complexes were determined from the TG data. Fractional decomposition, α, for respective temperatures was calculated from TG curves.

Determination of the mechanism of reaction from non-isothermal methods has been discussed by Šesták and Berggren and Satava [15, 16]. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation.

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha) \tag{1}$$

where A is the pre-exponential factor, t is the time and $f(\alpha)$ depends on the mechanism of the process.

For a linear heating rate, Φ, $dT/dt = \Phi$ and substitution into Eq. (1) gives

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\Phi}\exp(-E/RT)dT \tag{2}$$

Integration of the left hand side of Eq. (2) gives

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^{T} \frac{A}{\Phi} \exp(-E/RT)dT \tag{3}$$

where $g(\alpha)$ is the integrated form of $f(\alpha)$. A series of $f(\alpha)$ forms are proposed, and the mechanism is obtained from the one that gives the best representation of the experimental data. Nine probable reaction mechanisms are given by Satava [16]. To determine kinetic parameters from the mechanistic equations, the right-hand side of Eq. (3), the temperature integral which is an incomplete gamma function, was used in the form given by Coats and Redfern, which produces one of the best solution and is recommended by several authors [17, 18].

The general form of the equation used is

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\Phi E}\right] - \frac{E}{RT} \tag{4}$$

Along with the mechanistic equations, three non-mechanistic methods suggested by Coats and Redfern [19], Horowitz and Metzger [20] and MacCallum and Tanner were also used for comparison [21]. The reaction order can easily be estimated by comparing the values using n=0.33, 0.5, 0.66 and 1 in equations

$$\ln[1-(1-\alpha)^{1-n}/(1-n)T^2] \; vs. \; 1/T \quad \text{for} \quad n \neq 1 \tag{5}$$

$$\log[-\log(1-\alpha)]/T^2 \; vs. \; 1/T \quad \text{for} \quad n=1 \tag{6}$$

Coats-Redfern equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)/T^2}\right] = \ln\left[\frac{AR}{\Phi E}\left(\frac{1-2RT}{E}\right)\right] - \frac{E}{RT} \tag{7}$$

Horowitz-Metzger equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \ln\frac{ARTs^2}{\Phi E} - \frac{E}{RTs} + \frac{E\theta}{RTs^2} \tag{8}$$

where $\theta = T - Ts$.

MacCallum-Tanner

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \log\frac{AE}{R} - 0.483E^{0.435} - \left[\frac{0.449+0.217E}{T}\right]10^3 \tag{9}$$

From the slope and intercept, E, A, and ΔS were calculated.

Table 1 Analytical data and characteristics of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal anthranilic acid (L'H)

Complex	Colour	*M*	C	H	N	μ_{eff}	Conductance $ohm^{-1}\ cm^2\ mol^{-1}$
		%					
$[CoL'_2(H_2O)_2]$	greyish brown	8.96 (9.22)	64.23 (63.82)	7.52 (7.57)	4.64 (4.38)	5.0	2.3
$[NiL'_2(H_2O)_2]$	greenish brown	9.29 (9.19)	65.34 (63.84)	8.12 (7.57)	4.26 (4.38)	2.8	7.6
$[CuL'_2(H_2O)_2]$	greenish brown	9.37 (9.87)	62.84 (63.36)	7.63 (7.51)	4.82 (4.35)	19	4.2
$[ZnL'_2(H_2O)_2]$	light yellow	10.59 (10.12)	62.76 (63.18)	7.34 (7.49)	3.98 (4.34)	*D*	2.9

Calculated values are given in parenthesis, *D*-diamagnetic, *M*-Metal

Table 2 Analytical data and characteristics of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal-5-bromoanthranilic acid (L"H)

Complex	Colour	*M*	C	H	N	Br	μ_{eff}	Conductance $ohm^{-1}\ cm^2\ mol^{-1}$
		%						
$[CoL''_2(H_2O)_2]$	brown	7.42 (7.39)	50.68 (51.17)	5.84 (5.82)	3.72 (3.51)	21.42 (20.07)	4.6	5.6
$[NiL''_2(H_2O)_2]$	light yellow	7.80 (7.37)	52.14 (51.19)	5.85 (5.82)	3.26 (3.51)	22.34 (20.07)	2.9	4.8
$[CuL''_2(H_2O)_2]$	greenish brown	7.43 (7.92)	48.63 (50.88)	5.74 (5.78)	3.23 (3.49)	20.14 (19.95)	2.0	7.3
$[ZnL''_2(H_2O)_2]$	light yellow	7.56 (8.13)	48.63 (50.76)	5.86 (5.77)	3.54 (3.48)	20.56 (19.95)	*D*	8.4

Calculated values are given in parenthesis, *D*-diamagnetic, *M*-Metal

Results and discussion

The structure of the eight complexes was found to be $[ML_2(H_2O)_2]$. Analytical, molar conductance and magnetic data are presented in Tables 1 and 2. The complexes exhibit molar conductance in the range 1–10 ohm^{-1} mol^{-1} cm^2 in nitrobenzene. The magnetic and electronic spectral data are also consistent with an octahedral structure in all complexes.

The electronic spectra of the ligands showed two characteristic bands near 37 736 cm^{-1} and 27 400 cm^{-1}. The shift of these bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligands to metal ions.

The $4_{T1g}(F) \rightarrow 4_{T2g}(F)$ and $4_{T1g}(F) \rightarrow 4_{T1g}(P)$ transitions expected for Co(II) complexes with octahedral geometry was clear in the spectra at 9 500–10 530 cm^{-1} and 20 000–22 000 cm^{-1}, respectively. The band at 10 000 cm^{-1} in Ni(II) complexes are assignable to $3_{A2g}(F) \rightarrow 3_{T1g}(F)$ transition and other at 23 000 cm^{-1} to $3_{A2g}(F) \rightarrow 3_{T1g}(P)$ transition of octahedral geometry. The distorted octahedral geometry for Cu(II) complexes is indicated by the band at 15 300 cm^{-1} [22]. In the case of other complexes no absorption bands other than ligand absorption is seen.

The IR spectrum of the ligand shows a band of medium intensity at about 1500 cm^{-1}, which may be attributed to ν C=N of Schiff-base [23]. This band shifts to lower frequencies at 1470 cm^{-1} in the complexes indicating a reduction of electron density in the azomethine linkage as the nitrogen coordinates to the metal ion [24].

In all the complexes, the presence of coordinated water is confirmed by the observation of a broad band at 33 00 cm^{-1}. However, conclusive evidence regarding the bonding of nitrogen and oxygen was provided by the occurrence of M–N and M–O in the 500–600 cm^{-1} and 400–500 cm^{-1} regions, respectively, in the metal complexes [25]. The IR data suggest that the ligand behaves as a bidentate chelating agent coordinating through enolic oxygen and azomethine nitrogen. Its probable structure is shown in Fig. 2.

The decomposition temperature ranges for the metal chelates are given in Tables 3 and 4. Data from independent pyrolytic experiments are also included in these Tables. The values of E, A, ΔS and r from non-mechanistic equations (Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner) and the comparable values obtained from nine mechanistic equations are given in Tables 5 and 6.

The activation energies obtained in the present complexes are comparable to those of the coordination compounds of 3d transition metals having similar structure. In all the complexes H_2O molecules are lost around 130–150°C. According to Nikolaev *et al.* [26] water eliminated at this temperature can be considered as coordinated water. Initial decomposition temperature and inflection temperature have been used to determine the thermal stability of metal chelates.

Table 3 Thermal decomposition data of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal anthranilic acid (L'H)

Complex	Stage	$T_{range\ in\ TG}$	$T_{peak\ in\ TG}$	$T_{peak\ in\ DTG}$	Loss of mass %			Probable assignment
			°C		from TG	calc.	from pyrolysis	
$[CoL'_2(H_2O)_2]$	I	100–460	375	377.5	87.5	87.46	87.75	loss of $2H_2O$+2L'
$[NiL'_2(H_2O)_2]$	I	220–465	455	457.5	70	29.84	–	loss of $2H_2O$+L'+citronellal
	II	465–520	470	470	18	58.48	–	loss of anthranilic acid
					88	88.32	87.24	
$[CuL'_2(H_2O)_2]$	I	60–160	180	180	8.5	5.59	–	loss of $2H_2O$
	II	160–280	250	255	63.5	63.86	–	loss of L'+citronellal
	III	280–560	535	530	15.5	18.29	–	loss of anthranilic acid
					87.5	87.74	86.95	
$[ZnL'_2(H_2O)_2]$	I	180–380	355	357.5	72.5	69.12	–	loss of $2H_2O$+L'+citronellal
	II	390–520	485	482.5	15.5	18.3	–	loss of anthranilic acid
					88	87.42	85.05	

Table 4 Thermal decomposition data of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal-5-bromoanthranilic acid (L'H)

Complex	Stage	$T_{range\ in\ TG}$	$T_{peak\ in\ TG}$	$T_{peak\ in\ DTG}$	Loss of mass %			Probable assignment
			°C		from TG	calc.	from pyrolysis	
$[CoL'_2(H_2O)_2]$	I	220–670	440	445	89.5	89.91	87.75	loss of $2H_2O$+2L'
$[NiL'_2(H_2O)_2]$	I	120–300	255	255	50	48.54	–	loss of $2H_2O$+L'
	II	310–610	535	540	40.50	42.06	–	loss of L'
					90.50	90.60	89.51	
$[CuL'_2(H_2O)_2]$	I	160–280	275	272.5	51	48.28	–	loss of $2H_2O$+L'
	II	290–520	345	345	39	41.78	–	loss of L'
					90	90.06	87.94	
$[ZnL'_2(H_2O)_2]$	I	120–420	325	322.5	50	48.13	–	loss of $2H_2O$+L'
	II	430–680	565	565	40.50	42.72	–	loss of L'
					90.50	90.85	91.78	

Table 5 Kinetic parameters for the decomposition of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal anthranilic acid (L'H) from TG using non-mechanistic equations

Complex	*Parameter	Coats-Redfern	Horowitz-Metzger	MacCallum-Tanner	Mechanistic equation followed		Order of reaction n
$[CoL'_2(H_2O)_2]$	E	17.56	42.59	21.25	19.03	Eq.(8)	
	A	$2.6027 \cdot 10^{-2}$	8.60176	$2.2638 \cdot 10^{2}$	$2.0463 \cdot 10^{-2}$	phase boundary reaction	2/3
	ΔS	−282.83	−234.44	−207.14	−284.84	cylindrical symmetry	
	r	0.9514	0.9726	0.9590	0.9399		
$[NiL'_2(H_2O)_2]$ I Stage	E	8.90	21.93	10.79	8.90	Eq.(5)	
	A	$5.47 \cdot 10^{-4}$	$3.040 \cdot 10^{-4}$	$4.76 \cdot 10^{-4}$	$5.47 \cdot 10^{-4}$	Mampel equation	1
	ΔS	−316.09	−301.77	−331.21	−316.04		
	r	0.9428	0.9974	0.9634	0.9428		
$[CuL'_2(H_2O)_2]$ II Stage	E	72.41	79.21	73.16	72.41	Eq.(5)	
	A	$6.8579 \cdot 10^{-4}$	$4.49437 \cdot 10^{5}$	$5.1654 \cdot 10^{7}$	$6.8579 \cdot 10^{-4}$	Mampel equation	1
	ΔS	−157.71	−142.04	−102.40	−157.71		
	r	0.9539	0.9518	0.9634	0.9539		

Table 5 Continued

Complex	*Parameter	Coats-Redfern	Horowitz-Metzger	MacCallum-Tanner	Mechanistic equation followed		Order of reaction n
$[ZnL'_2(H_2O)_2]$	E	31.37	56.24	35.03	32.76	Eq.(8)	
I Stage	A	$6.1572 \cdot 10^{-1}$	$1.4973 \cdot 10^{2}$	$2.9441 \cdot 10^{3}$	$4.5122 \cdot 10^{-1}$	phase boundary reaction	2/3
	ΔS	−245.62	−210.34	−185.47	−258.76	cylindrical symmetry	
	r	0.9826	0.9878	0.9863	0.9813		
II Stage	E	26.25	43.81	30.03	26.25	Eq.(5)	
	A	$3.2798 \cdot 10^{-1}$	8.9475	$6.7896 \cdot 10^{2}$	$3.2798 \cdot 10^{-1}$	Mampel equation	1
	ΔS	−262.92	−235.33	−228.65	−262.92		
	r	0.9474	0.9304	0.9252	0.9474		

*E in kJ mol^{-1}; A in s^{-1}; ΔS in J K^{-1} mol^{-1}

Table 6 Kinetic parameters for the decomposition of Co(II), Ni(II), Cu(II) and Zn(II) complexes of citronellal-5-bromoanthranilic acid (L''H) from TG using non-mechanistic equations

Complex	*Parameter	Coats-Redfern	Horowitz-Metzger	MacCallum-Tanner	Mechanistic equation followed		Order of reaction n
$[CoL''_2((H_2O)_2]$	E	9.28	16.38	14.14	11.21	Eq.(8)	
	A	$1.7804 \cdot 10^{-3}$	5.1762	$5.1845 \cdot 10^{1}$	$1.6208 \cdot 10^{3}$	phase boundary reaction	2/3
	ΔS	−306.56	−220.75	−246.37	−307.31	cylindrical symmetry	
	r	0.9752	0.9862	0.9862	0.9708		
$[NiL''_2((H_2O)_2]$	E	35.07	44.35	35.41	35.07	Eq.(5)	
	A	3.4429	$3.2646 \cdot 10^{1}$	$2.8154 \cdot 10^{1}$	3.4429	Mampel equation	1
	ΔS	−240.32	−221.55	−184.34	−240.32		
	r	0.9702	0.9730	0.9809	0.9702		
II Stage	E	18.86	41.23	22.30	18.86	Eq.(5)	
	A	$3.9298 \cdot 10^{-2}$	2.4647	1.0731^{2}	$3.9298 \cdot 10^{-2}$	Mampel equation	1
	ΔS	−281.32	−246.79	−215.29	−281.32		
	r	0.8860	0.9252	0.8962	0.8860		

Table 6 Continued

Complex	*Parameter	Coats-Redfern	Horowitz-Metzger	MacCallum-Tanner	Mechanistic equation followed		Order of reaction n
$[CuL''_2(H_2O)_2]$ I Stage	E	26.12	43.76	28.01	27.04	Eq.(8)	
	A	$2.9045 \cdot 10^{-1}$	$2.5760 \cdot 10^{1}$	$1.0970 \cdot 10^{3}$	$1.9341 \cdot 10^{-1}$	phase boundary reaction	2/3
	ΔS	−261.24	−223.82	−192.49	−264.8	cylindrical symmetry	
	r	0.8854	0.9454	0.9222	0.8837		
II Stage	E	20.00	29.4	22.09	20.00	Eq.(5)	
	A	$1.1444 \cdot 10^{-1}$	1.0184	$2.288 \cdot 10^{2}$	$1.1444 \cdot 10^{-1}$	Mampel equation	1
	ΔS	−270.14	−251.87	−206.68	−270.04		
	r	0.9042	0.9472	0.9568	0.9042		
$[ZnL''_2(H_2O)_2]$ I Stage	E	21.00	35.41	21.46	21.00	Eq.(5)	
	A	$4.9424 \cdot 10^{-1}$	1.3664	$6.9381 \cdot 10^{1}$	$4.9424 \cdot 10^{-2}$	Mampel equation	
	ΔS	−276.74	−249.16	−216.26	−276.74		1
	r	0.9852	0.9870	0.9938	0.9852		
II Stage	E	27.97	31.58	20.33	27.97	Eq.(9)	
	A	$1.0986 \cdot 10^{-1}$	$1.44398 \cdot 10^{-1}$	$6.767 \cdot 10^{1}$	$3.6613 \cdot 10^{-2}$	phase boundary reaction	2/3
	ΔS	−272.92	−270.65	−219.28	−282.07	spherical symmetry	
	r	0.9569	0.9860	0.9836	0.9570		

*E in kJ mol^{-1}; A in s^{-1}; ΔS in J K^{-1} mol^{-1}

On the basis of our findings the relative thermal stabilities of the metal chelates can be given as,

$$[CuL_2^{'}(H_2O)_2]<[ZnL_2^{'}(H_2O)_2]<[CoL_2^{'}(H_2O)_2]<[NiL_2^{'}(H_2O)_2]$$

$$[NiL_2^{''}(H_2O)_2]<[CuL_2^{''}(H_2O)_2]<[ZnL_2^{''}(H_2O)_2]<[CoL_2^{''}(H_2O)_2]$$

Decomposition kinetics

The values of kinetic parameters obtained from nine mechanistic equations show that more than one equation gives good linear curves with high values of correlation coefficients, so it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function $f(\alpha)$, which gives kinetic parameters in agreement with those obtained by the numerical method.

In the present study it is observed that the values of E, A and ΔS for the single stage decomposition of $[CoL_2^{'}(H_2O)_2]$ and $[CoL_2^{''}(H_2O)_2]$ obtained from Coats-Redfern with n=2/3 are in good agreement with the corresponding values obtained for R2 mechanism based on phase boundary reaction, cylindrical symmetry.

For the first stage decomposition of $[NiL_2^{'}(H_2O)_2]$ and second stage decomposition of $[CuL_2^{'}(H_2O)_2]$ and $[ZnL_2^{'}(H_2O)_2]$ the values of kinetic parameters obtained for Coats-Redfern equation with n=1 are in good agreement with those values obtained for F_1 mechanism based on random nucleation (Mampel equation). First stage decomposition of $[ZnL_2^{'}(H_2O)_2]$ follows R_2 mechanism based on phase boundary reaction, cylindrical symmetry.

First and second stage decomposition of $[NiL_2^{''}(H_2O)_2]$, second stage decomposition of $[CuL_2^{''}(H_2O)_2]$, and first stage decomposition of $[ZnL_2^{''}(H_2O)_2]$ follow F_1 mechanism based on random nucleation (Mampel equation). First stage decomposition of $[CuL_2^{''}(H_2O)_2]$ follows R_2 mechanism based on phase boundary reaction, cylindrical symmetry and the second stage decomposition of $[ZnL_2^{''}(H_2O)_2]$ follows R_3 mechanism based on phase boundary reaction spherical symmetry.

All these mechanisms are proposed since the values of E, A and ΔS computed from the mechanistic equation agree well with those from the non-mechanistic equation (Coats-Redfern) having maximum correlation coefficient. These values of E, A and ΔS obtained for these complexes are comparable. The negative values for entropy of activation indicates that the activated complexes have a more ordered structure than the reactants and the reactions are slower than normal.

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