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Physico-chemical Studies and Thermal Decomposition Kinetics of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Vanillin-2-Aminothiazole

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Manganese(II), cobalt(II), nikel(II), copper(II) and zinc(II) complexes of the Schiff base vanillin-2-aminothiazole have been synthesized. On the basis of spectral, magnetic and thermal data, octahedral structure was assigned to all complexes.

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 nonmechanistic integral equations.

Keywords: Transition metal complexes, Schiff bases, thermal decomposition, kinetics.

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 manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of the novel Schiff base vanillin-2-aminothiazole (Fig. 1). Non-iso-thermal 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 vanillin-2-aminothiazole from TG experiments. A comparison of the energy of activation, entropy and relative thermal stability of these complexes has also been made.

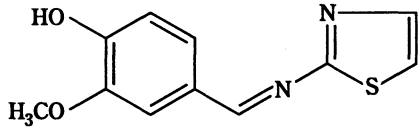

Fig. 1. Structure of vanillin-2-aminothiazole

EXPERIMENTAL

The ligand vanillin-2-aminothiazole (VAAT) was prepared by refluxing an ethanolic solution of vanillin (1.5 g, 0.01 mol.) and 2-aminothiazole (1 g, 0.01 mol) for 16 h on a water bath. The resulting solution was added to distilled water dropwise with constant stirring. Brownish yellow crystals separated were filtered, washed and dried over anhydrous $CaCl_2$. Melting point was found to be 98°C. The ligand was characterised on the basis of CHN analysis, UV, NMR and IR spectral data.

Preparation of Complexes: Metal complexes of vanillin-2-aminothiazole (LH) was prepared by adding a solution of metal salt (chloride or acetate) dropwise to a refluxing solution of ligand in ethanol until the metal to ligand ratio reached 1 : 2. Heating was continued for 2 h. The resulting solution was added in distilled water dropwise with constant stirring. The separated complexes were filtered, washed with 50% ethanol 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.

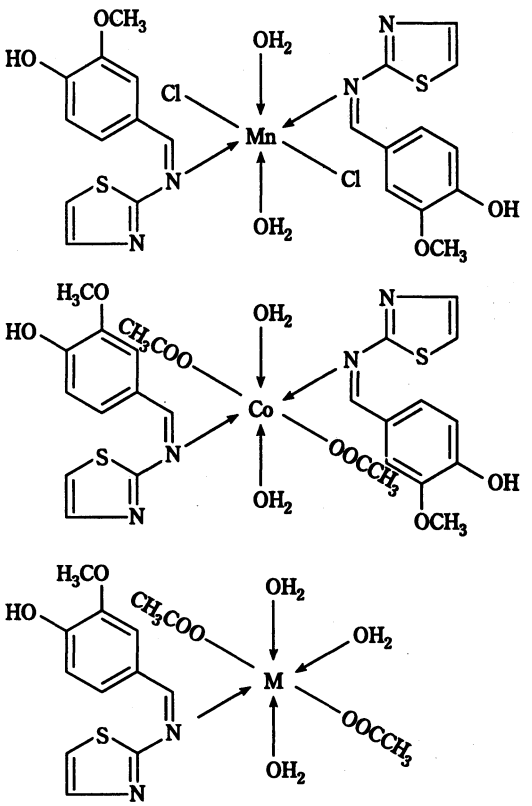

Fig. 2. M = Ni(II), Cu(II) or Zn(II)

Infrared spectra were recorded using a Shimadzu FTIR-8101 spectrophotometer. Thermal studies were carried out using a Perkin-Elmer 7 series thermal analysis system. A constant heating rate of 15°C min^{-1} and sample mass of *ca.* 5 mg were employed for the entire study. Computational work was done with a Horizon III minicomputer using the programming language FORTRAN.

The decomposition temperature ranges in TG for the metal chelates are presented in Tables 2 and 3. TG curve for Mn(II) complex of vanillin-2-aminothiazole shows a two stage decomposition pattern. The Co(II), Ni(II) and Cu(II) complexes exhibit a three-stage decomposition pattern in their TG graph, while the Zn(II) complex shows a four-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 Sestak 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.

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

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

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

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

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

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 solutions and is recommended by several authors[17, 18].

The general form of the equation used is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\phi E} \frac{E}{RT} \tag{4}$$

Along with the mechanistic equations, one non-mechanistic method suggested by Coats and Redfern[19] was also used for comparison. The reaction order can easily be estimated by comparing the values using n = 0.33, 0.50, 0.66 and 1.00 in the equations:

$$\ln \frac{1-(1-2)^{1-n}}{(1-n)T^2} \quad vs. \quad \frac{1}{T} \quad \text{for } n \neq 1 \tag{5}$$

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

Coats-Redfern equation

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

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

RESULTS AND DISCUSSION

The structures (Fig. 2) of the five complexes were found to be $[Mn(LH)_2CL_2(H_2O)_2]$, $[Co(LH)_2(OAc)_2(H_2O)_2]$, $[NiLH(OAc)_2(H_2O)_3]$, $[CuLH(OAc)_2(H_2O)_3]$ and $[ZnLH(OAc)(H_2O)_3]$.

Analytical, molar conductance and magnetic data are presented in Table-1. The complexes exhibit molar conductance in the range 1.25–8.63 ohm^{-1} mol^{-1} cm^2 in ethanol. The magnetic and electronic spectral data are also consistent with an octahedral structure in all complexes.

TABLE 1
ANALYTICAL DATA AND CHARACTERISTICS OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF VANILLIN-2-AMINOTHIAZOLE (LH)

Complex (colour)	% Analysis, found (calcd.)						μ_{eff}	Λ_m (ohm^{-1} cm^2 mol^{-1})
	M	C	H	N	S	Cl		
$[Mn(LH)_2Cl_2(H_2O)_2]$ (brown)	8.24 (8.72)	41.15 (41.92)	3.07 (3.81)	8.12 (8.89)	10.84 (10.16)	10.88 (11.26)	5.91	2.38
$[Co(LH)_2(OAc)_2(H_2O)_2]$ (Brownish yellow)	8.42 (8.66)	45.11 (45.82)	3.97 (4.40)	8.77 (8.22)	9.52 (9.40)	—	5.24	1.92
$[Ni(LH)(OAc)_2(H_2O)_3]$ (Greenish yellow)	12.54 (12.63)	38.46 (38.73)	5.01 (4.73)	6.33 (6.02)	6.57 (6.89)	—	2.43	8.63
$[Cu(LH)(OAc)_2(H_2O)_3]$ (Coffee brown)	13.31 (13.52)	37.84 (38.34)	4.84 (4.68)	5.66 (5.96)	6.21 (6.82)	—	2.08	1.25
$[Zn(LH)(OAc)_2(H_2O)_3]$ (Lemon yellow)	13.36 (13.87)	38.54 (38.19)	4.21 (4.67)	5.81 (5.94)	5.99 (6.79)	—	Diamag	1.87

The electronic spectrum of the ligand showed two characteristic bands at 32258 cm^{-1} and 27027cm^{-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 octahedral environment of the ligands around the central Mn(II) ion is confirmed by the appearance of a broad band[20] at 24875 cm^{-1}. The $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions expected for Co(II) complex with octahedral geometry was very clear in the spectrum at 10530–9500 cm^{-1} and 22000–20000 cm^{-1} respectively. The bands at 10755 cm^{-1} in Ni(II) complexes

are assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition and another at 23600 cm^{-1} to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition of octahedral geometry. The distorted octahedral geometry for Cu(II) complex is indicated by the band[21] at 16123 cm^{-1}. In the case of Zn(II) complex no absorption band other than ligand absorption is seen.

The IR spectrum of the ligand shows a band at 1620 cm^{-1}, which may be attributed to ν(C=N) of Schiff base[22]. This band shifts to lower frequencies at about 1570 cm^{-1} in the complexes indicating a reduction of electron density in the azomethine linkage as the nitrogen coordinates to the metal ion[23].

In all the complexes, the presence of coordinated water is confirmed by the observation of a broad band at 3300–3100 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 600–500 cm^{-1} and 500–400 cm^{-1} regions, respectively, in the metal complexes[24]. The IR data suggest that the ligand behaves as a monodentate chelating agent coordinating through azomethine nitrogen. Its probable structure is shown in Fig. 2.

The decomposition temperature ranges for the metal chelates are given in Table-2.

TABLE 2
THERMAL DECOMPOSITION DATA OF Mn(II), Co(II), AND Ni(II) COMPLEXES OF VANILLIN-2-AMINOTHIAZOLE (LH)

Complex	Stage	T_{range} in TG (°C)	T_{peak} in TG (°C)	Loss of mass (%)			Probable assignments
				from TG	theore-tical	from pyrolysis	
$[Mn(LH)_2Cl_2(H_2O)_2]$	I	70–260	160	22.00	21.28	—	Loss of $2H_2O$ + aminothiazole part
	II	270–520	430	68.00	66.72	—	Loss of 2(vanillin part) + L + 2 chlorine atoms
				90.00	88.00	89.20	
$[Co(LH)_2(OAc)_2(H_2O)_2]$	I	110–300	190	20.00	19.68	—	Loss of $2H_2O$ + aminothiazole part of 1st ligand
	II	310–450	330	30.00	34.36	—	Loss of vanillin part of 1st ligand + aminothiazole part of 2nd ligand
	III	450–520	480	40.00	34.25	—	Loss of vanillin part of 2nd ligand + 2 acetate
				90.00	88.29	88.90	
$[Ni(LH)(OAc)_2(H_2O)_3]$	I	100–300	230	13.00	11.62	—	Loss of $3H_2O$
	II	300–450	410	20.00	21.08	—	Loss of aminothiazole part
	III	450–550	490	51.00	51.21	—	Loss of vanillin part + 2 acetate
				84.00	83.91	84.02	

Data from independent pyrolytic experiments are also included in the Table-2. The values of E, A, Δs and γ from non-mechanistic equation (Coats-Redfern) and the comparable values obtained from nine mechanistic equations are given in Tables 3 and 4.

TABLE 3
THERMAL DECOMPOSITION DATA OF Cu(II) AND Zn(II) COMPLEXES OF VANILLIN-2-AMINOTHIAZOLE (LH)

Complex	Stage	T_{range} in TG (°C)	T_{peak} in TG (°C)	Loss of mass (%)			Probable assignments
				from TG	theoretical	from pyrolysis	
$[Cu(LH)(OAc)_2(H_2O)_2]$	I	80–150	150	3.50	3.80	—	Loss of 1 H_2O
	II	160–530	530	36.50	36.60	—	Loss of $2H_2O$ + vanillin part
	III	530–620	600	45.00	42.60	—	Loss of aminothiazole part + 2 acetate
				85.00	83.00	84.02	
$[Zn(LH)(OAc)_2(H_2O)_3]$	I	150–240	170	20.50	20.20	—	Loss of $2H_2O$ + 1 acetate
	II	250–320	270	16.00	16.30	—	Loss of $1H_2O$ + 1 acetate
	III	340–420	360	21.40	20.80	—	Loss of 2-aminothiazole part
	IV	440–500	450	26.00	25.40	—	Loss of vanillin part
				83.90	82.70	83.50	

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 100–200°C. According to Nikolaev *et al.*[25] 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.

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

$$[Mn(LH)_2Cl_2(H_2O)_2] < [Cu(LH)(OAc)_2(H_2O)_2] < [Ni(LH)(OAc)_2(H_2O)_3]$$
$$< [Co(LH)_2(OAc)_2(H_2O)_2] < [Zn(LH)(OAc)_2(H_2O)_3]$$

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 methods.

TABLE 4
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Mn(II) AND Co(II) COMPLEXES OF VANILLIN-2-AMINOTHIAZOLE (LH) FROM TG USING COATS-REDFERN EQUATION AND ACCEPTED MECHANISTIC EQUATION

Complex	*Parameter	From Coats-Redfern equation	From mechanistic equation	Reaction mechanism	Order of reaction
$[Mn(LH)_2Cl_2(H_2O)_2]$	E	23.5345	23.5345	Equation (5)	
I stage	A	2.0030×10^{-1}	2.0030×10^{-1}	F_1 mechanism	
	ΔS	–452.5891	–452.5891	Random nucleation	1
	γ	0.9206	0.9235	Mampel equation	
II stage	E	20.9271	20.9262	Equation (8)	
	A	2.9860×10^{-2}	2.4600×10^{-2}	R_2 mechanism	
	ΔS	–473.4249	–474.4827	Phase boundary reaction	1/2
	γ	0.9794	0.9794	Cylindrical symmetry	
$[Co(LH)_2(OAc)_2(H_2O)_2]$	E	28.1437	29.1383	Equation (6)	
	A	3.1860×10^{-1}	1.8320×10^{-1}	A_2 mechanism	
I stage	ΔS	–449.3847	–453.9880	Random nucleation	2/3
	γ	0.9396	0.9417	Avrami equation I	
	E	5.7859	5.7716	Equation (8)	
II stage	A	2.5092×10^{-4}	2.5582×10^{-4}	A_3 mechanism	
	ΔS	–511.0520	–510.9640	Random nucleation	2/3
	γ	0.9658	0.9657	Avrami equation II	
III stage	So rapid that could not be studied				

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

In the present study it is observed that R_2 mechanism based on phase boundary reaction, cylindrical symmetry gives the maximum correlation for the first stage of Ni(II), second stage of Mn(II) and third stage of Zn(II) complexes. The order of decomposition of all the above stages were found to be 1/2.

Order of the reaction is found to be 2/3 for 1st and 2nd stage of $[Co(LH)_2(OAc)_2(H_2O)_2]$ and for the fourth stage of $[ZnLH(OAc)_2(H_2O)_3]$. First

stage of Co(II) complex followed A_2 mechanism while the second stage A_3 mechanism. Both the mechanisms are based on Random nucleation. The fourth stage decomposition of Zn(II) complex shows good agreement with the D_1 mechanism based on one-dimensional diffusion.

Kinetic parameters computed for F_1 mechanism based on random nucleation (Mampel equation) gives the maximum correlation with the corresponding values obtained for Coats-Redfern equation with n = 1, for the first stage decomposition of $[Mn(LH)_2Cl_2(H_2O)_2]$, second stage decomposition of $[Ni(LH)(OAc)_2(H_2O)_3]$, $[Cu(LH)(OAc)_2(H_2O)_3]$ and for the first and second stage decomposition of $[Zn(LH)(OAc)_2(H_2O)_3]$.

TABLE 5
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Ni(II) AND Cu(II) COMPLEXES OF VANILLIN-2-AMINOTHIAZOLE (LH) FROM TG USING COATS-REDFERN EQUATION AND ACCEPTED MECHANISTIC EQUATIONS

Complex	*Parameter	From Coats-Redfern equation	From mechanistic equation	Reaction mechanism	Order of reaction
$Ni(LH)(OAc)_2(H_2O)_3]$					
I stage	E	24.9163	24.9004	Equation (8)	
	A	1.7353×10^{-1}	-8.6325×10^{-2}	R_2 mechanism	1/2
	ΔS	–454.7013	–460.5090	Phase boundary reaction	
	γ	0.9946	0.9947	Cylindrical symmetry	
II stage	E	8.9622	8.9622	Equation (5)	
	A	1.5066×10^{-3}	1.5066×10^{-3}	F_1 mechanism	1
	ΔS	–497.4768	–497.4768	Random nucleation	
	γ	0.9280	0.9280	Mampel equation	
III stage	So rapid that could not be studied				
$[Cu(LH)(OAc)_2(H_2O)_3]$	Weight loss is to small to carryout the kinetic study				
I stage					
II stage	E	9.4105	9.4105	Equation (5)	
	A	2.2474×10^{-3}	2.2474×10^{-3}	F_1 mechanism	1
	ΔS	–493.9020	–493.9020	Random nucleation	
	γ	0.9615	0.9615	Mampel equation	
III stage	So rapid that could not be studied				

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

TABLE 6
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Zn(II) COMPLEX OF VANILLIN-2-AMINOTHIAZOLE (LH) FROM TG USING COATS-REDFERN EQUATION AND ACCEPTED MECHANISTIC EQUATIONS

Complex	*Parameter	From Coats-Redfern equation	From mechanistic equation	Reaction mechanism	Order of reaction
$[Zn(LH)(OAc)_2(H_2O)_3]$					
I stage	E	14.3019	14.3019	Equation (5)	
	A	1.1501×10^{-2}	1.1501×10^{-2}	F_1 mechanism	1
	ΔS	–476.6175	–476.6175	Random nucleation	
	γ	0.9460	0.9460	Mampel equation	
II stage	E	24.6015	24.6015	Equation (5)	
	A	2.0551×10^{-1}	2.0551×10^{-1}	F_1 mechanism	1
	ΔS	–454.6829	–454.6829	Random nucleation	
	γ	0.9771	0.9771	Mampel equation	
III stage	E	11.3700	11.3700	Equation (8)	
	A	4.6905×10^{-3}	2.3451×10^{-3}	R_2 mechanism	
	ΔS	–487.3982	–493.1640	Phase boundary reaction	1/2
	γ	0.9864	0.9864	Cylindrical symmetry	
IV stage	E	33.7534	37.0331	Equation (1)	
	A	6.3235×10^{-1}	6.0849×10^{-1}	D_1 mechanism	
	ΔS	–443.7352	–448.0351	One dimensional diffusion	2/3
	γ	0.9783	0.9686		

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

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