

Synthetic, spectral and thermal studies of cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes with amino acid schiff bases

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A few complexes of Co(II), Ni(II), Zn(II) and Cd(II) have been isolated by the metal ion template condensation of amino acids (L-phenylalanine, L-leucine, L-histidine or L-tryptophan) and aldehyde/ketone (salicylaldehyde, *o*-hydroxynaphthaldehyde, pyruvic acid, *o*-vanillin or isatin). The elemental analysis, conductivity and magnetic susceptibility measurements, IR, ¹H NMR and electronic spectral data indicate that the ligands function as dibasic terdentate with O, N, O donor set. The thermal degradation of Co(isa-L-phe)₂, Ni(OV-L-phe).3H₂O, Zn(OHN-L-phe).3H₂O, Zn(sal-L-leu).3H₂O, Zn(OV-L-his).3H₂O, Cd(OV-L-try).3H₂O and Cd(PyA-L-try).3H₂O is studied in air by differential thermal analysis and dynamic thermogravimetry technique from ambient temperature to 900°C.

Schiff bases are important class of ligands and have got wide applications in various fields^{1,2}. The literature survey revealed that the bivalent cobalt, nickel, zinc and cadmium complexes with imines derived from the above-mentioned amino acids and aldehyde/ketone have not been studied so far. Therefore, we thought it worthwhile to study the synthesis and characterization of some amino acid schiff base complexes of Co(II), Ni(II), Zn(II) and Cd(II) metal ions. The complexes have been subjected to thermal degradation using TG, DTG and DTA analysis. Various kinetic, thermodynamic parameters have been calculated using Broido³ and least squares⁴ methods, which give a better understanding of the various decomposition stages of metal derivatives.

Experimental

All the chemicals and solvents used were of AR grade. Amino acids were obtained from Loba-Chemie. Salicylaldehyde, *o*-hydroxynaphthaldehyde, *o*-vanillin, pyruvic acid and isatin were purchased from Sisco-Chem Industries. The metal acetates were obtained from Albright and

Wilson (MFG) Ltd., England and the metal contents were estimated using standard methods⁵.

Preparation of metal complexes

A general method involving the metal ion template reaction has been applied for the synthesis of metal derivatives with amino acid schiff bases derived by condensation of aldehyde/ketone [salicylaldehyde (sal), *o*-hydroxynaphthaldehyde (OHN), *o*-vanillin (OV), pyruvic acid (PyA) or isatin (isa)] with amino acids [L-phenylalanine (L-phe), L-leucine (L-leu), L-histidine (L-his) or L-tryptophan (L-try)].

The compound [Co(isa-L-phe)₂ (**1**)] (Table 1) was synthesized by refluxing first an aqueous solution of sodium salt of amino acid and an ethanolic solution of isatin in equimolar ratio for 30 min and then further refluxing it for half an hour after adding an aqueous ethanolic solution of metal acetates in 1:2 molar ratio. The compounds isolated were filtered, washed with water-ethanol mixture (1:1) and ether and the products were dried first on water-bath and then *in vacuo* over P₂O₅.

The compounds **2** to **7** (Table 1) were prepared by stirring aqueous solutions of sodium salts of amino acids with hot ethanolic solutions of aldehydes in 1:1 molar ratio and then aqueous ethanolic solutions of metal acetates were added in equimolar ratios with constant stirring for ~ 15 h. The products so formed were filtered, washed with aqueous ethanol and ether. The samples were dried first on a water-bath and then *in vacuo* over P₂O₅.

The metal complexes were solid and non-hygroscopic in nature with 80-90% yield. Their purity was checked by TLC. The R_f values of the complexes were found to be in the range 0.48-0.60 in benzene-acetic acid (15:1) mixture.

The thermal analyses of the metal derivatives were carried out in static air using a Stanton Redcroft Instrument (USIC, University of Roorkee). The specimen were heated at the rate of 10°/min in 0-900°C range. Al₂O₃ was used as standard. The IR spectra of the complexes were recorded on a Perkin-Elmer 842 spectrophotometer. The far-IR spectra were recorded using polythene sheets. The molar conductance values of dilute solutions (10⁻³ M) in DMF were measured on an Elico-conductivity bridge type CM82T. The dif-

Table 1—Characterization data of the metal complexes

Sl. No.	Compounds	Colour & yield(%)	Found (Calcd.)%				Λ_M ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} (BM)
			M	C	H	N		
1.	[Co(isa-L-phe) ₂]	Dark brown	9.08	63.15	4.05	8.33	10.1	4.35
	Co(C ₁₁ H ₁₃ N ₂ O ₄) ₂	(80)	(9.14)	(63.26)	(4.03)	(8.68)		
2.	[Ni(OV-L-Phe).3H ₂ O]	Yellowish green	14.06	49.48	5.09	3.23	5.0	2.98
	Ni(C ₁₁ H ₁₃ NO ₄).3H ₂ O	(85)	(14.33)	(49.79)	(5.13)	(3.42)		
3.	[Zn(OHN-L-phe).3H ₂ O]	Yellow	15.03	54.87	4.53	3.01	5.2	Diamagnetic
	Zn(C ₁₁ H ₁₃ NO ₄).3H ₂ O	(90)	(14.98)	(54.99)	(4.81)	(3.20)		
4.	[Zn sal-L-leu).3H ₂ O]	Colourless	18.32	44.10	5.76	3.76	11.9	Diamagnetic
	Zn(C ₁₁ H ₁₃ NO ₄).3H ₂ O	(90)	(18.55)	(44.27)	(5.96)	(3.97)		
5.	[Zn(OV-L-his).3H ₂ O]	Yellow	15.80	41.12	4.43	10.62	8.1	Diamagnetic
	Zn(C ₁₄ H ₁₇ N ₃ O ₄).3H ₂ O	(85)	(16.09)	(41.34)	(4.68)	(10.34)		
6.	[Cd(OV-L-try).3H ₂ O]	Light yellow	22.25	45.17	4.09	5.50	5.0	Diamagnetic
	Cd(C ₁₀ H ₁₆ N ₂ O ₄).3H ₂ O	(90)	(22.37)	(45.38)	(4.38)	(5.57)		
7.	[Cd(PyA-L-try).3H ₂ O]	Colourless	25.35	38.10	4.12	6.18	6.6	Diamagnetic
	Cd(C ₁₄ H ₁₂ N ₂ O ₄).3H ₂ O	(80)	(25.64)	(38.32)	(4.11)	(6.39)		

fuse reflectance spectra were recorded on Cary 2390 spectrophotometer in the range 300-2,000 nm region at RSIC, IIT, Madras. The electronic spectra were also recorded on a U-2000 spectrophotometer. The magnetic susceptibilities of the complexes were determined at room temperature (25 ± 3°C) using a vibrating sample magnetometer model 155 at the USIC, University of Roorkee. The ¹H NMR spectra were recorded on a 90 MHz Perkin-Elmer R-32 spectrometer.

Results and discussion

The empirical composition of the complexes has been confirmed on the basis of analytical data (Table 1). The molar conductance values of 10⁻³ M solutions of the complexes (5-12 ohm⁻¹ cm² mol⁻¹) in DMF showed them to be non-electrolytic in nature. The compounds were found to be insoluble in most of the common organic solvents.

The infrared spectra of 1:1 complexes exhibited a broad band in the region ~3400-3200 cm⁻¹ due to $\nu(\text{OH})$ vibrations of coordinated water. A broad band centered ~3400 cm⁻¹ in 1:2 complexes indicates the coordination of phenolic OH group without loss of hydrogen. An intense band appearing at 1640-1620 cm⁻¹ for all the complexes is assigned to $\nu(\text{N}=\text{C})$ vibrations, indicative of imine structure. The $\Delta\nu(\text{COO}^-)$ is greater than 200 cm⁻¹ which [$\nu(\text{COO}^-)_{\text{asym}}$ at ~1600 cm⁻¹ and $\nu(\text{COO}^-)_{\text{sym}}$ at ~1400 cm⁻¹] indicates the unidenticity of the carboxylate group⁶. A band appearing in 1535-1520 cm⁻¹ region for all the complexes can be attributed to $\nu(\text{C}-\text{O})$ (phenol-

ic)-stretching⁷. The OH rocking and wagging bands appeared in the regions 800-750 cm⁻¹ and 720-700 cm⁻¹ respectively. Shukla *et al.*⁸ observed these bands in 900-650 cm⁻¹ region. The Far-IR spectra of the complexes showed bands in 520-480 cm⁻¹ and 440-400 cm⁻¹ regions which may be attributed to $\nu_{\text{M}-\text{N}}$ and $\nu_{\text{M}-\text{O}}$ vibrations^{9,10} respectively.

The UV spectra of all the metal derivatives showed absorption bands at ~260 nm and ~350 nm which may be assigned to $\pi-\pi^*$ transitions originating in the benzenoid and aldimine residue respectively. Similar bands were observed by Casella *et al.*¹¹ in zinc complexes derived from N-salicylidene- and N-pyridoxylideneamino acids.

The complex Co(isa-L-phe)₂ showed two absorption bands at 9,600 and 15,200 cm⁻¹ assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) which indicates octahedral geometry for the complex¹². The chelate Ni(OV-L-phe).3H₂O exhibited three spin-allowed absorption bands at 8,615, 18,900 and 25,695 cm⁻¹ which may be attributed to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions respectively, indicative of octahedral environment around Ni(II). The effective magnetic moment values (Table 2) for both the complexes were found to be well within the expected range 4.3-5.2 B.M. and 2.8-3.5 B.M. (ref. 13).

The zinc(II) and cadmium(II) complexes are diamagnetic as expected for d^{10} configuration.

Table 2—Kinetic and thermodynamic parameters for the decomposition stages of metal derivatives

Compound	E_a (kJ mol ⁻¹)	z (s ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J/K)	ΔG^* (kJ mol ⁻¹)	T_m (K)
[Co(isa-L-phe) ₂]	35.67	28.03	31.55	-229.72	145.26	495
[Ni(OV-L-phe).3H ₂ O]	46.81	6.42 × 10 ²	42.69	-203.69	143.52	495
[Zn(OHN-L-phe).3H ₂ O]	61.11	6.01 × 10 ³	56.99	-184.58	148.36	495
[Zn(sal-L-leu).3H ₂ O]	29.68	3.54	25.81	-246.43	140.40	465
[Zn(OV-L-his).3H ₂ O]	25.77	0.0246	21.90	-287.75	155.70	465
[Cd(OV-L-try).3H ₂ O]	57.28	2.67 × 10 ²	53.25	-210.84	155.51	485
[Cd(PyA-L-try).3H ₂ O]	39.06	36.40	35.02	-227.39	145.30	485

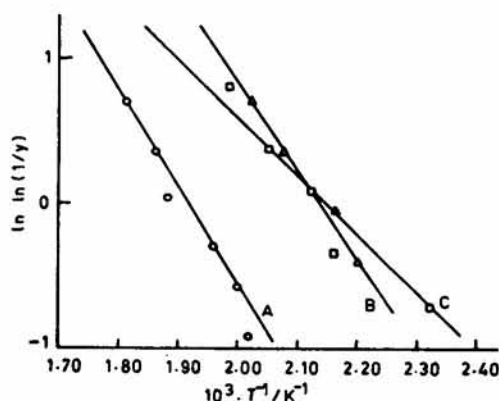


Fig. 1—Plots of $\ln [\ln(1/y)]$ vs. $10^3 \cdot T^{-1}/K^{-1}$ using Broido equation for decomposition stage of thermal degradation of (A) Zn(OHN-L-phe).3H₂O, (B) Ni(OV-L-phe).3H₂O and (C) Co(isa-L-phe)₂

The ¹H NMR spectra for only Zn(OHN-L-phe).3H₂O [A], Zn(sal-L-leu).3H₂O [B], Zn(OV-L-his).3H₂O [C] and Cd(OV-L-try).3H₂O [D] complexes have been recorded because of their solubility in DMSO-*d*₆/TFA, while the spectra of other complexes could not be recorded due to their insolubility.

The azomethine protons of A, B, C and D at δ 8.29, 8.28, 8.62 and 8.00 clearly showed the presence of imine structure. The integration of a multiplet between δ 6.46 and 7.70 accounted for the aromatic protons in these complexes. The different aliphatic protons present in the complexes are shown between δ 0.90 and 5.28.

The thermal behaviour of the complexes are almost identical, hence only that of Ni(OV-L-phe).3H₂O complex is being given. The DTG curve indicated the decomposition in three steps, 30–55°C, 105–130°C and 135–235°C. The loss of first water molecule occurred at 51°C with a mass loss of about 4.09% (theoretical-4.39%). The second and third water molecules were lost at 125°C [mass loss 12.96% (theoretical-13.18%)]. The organic moiety starts decomposing after 135°C. The

formation of nickel oxide and carbon dioxide was indicated at 220°C with loss in mass of 70.71% (theoretical-71.03%). Nickel oxide was found to be the end-product at 280°C and above.

The various kinetic parameters activation energy (E_a) and frequency factor (z) for the decomposition stages of metal derivatives were determined from the TG curves using Broido's and least squares methods (Fig. 1; Table 2). The thermodynamic parameters, enthalpy (ΔH^*), entropy (ΔS^*) and free energy of activation (ΔG^*) were calculated using standard equations and the values are given in Table 2. The data clearly indicates that the basic steps are similar in the thermal degradation of these complexes.

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