

Metal complexes of cobalt(II), nickel(II), copper(II) and zinc(II) with N-(2-hydroxy-1-naphthylidene)-L-amino acids

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Abstract. A new series of complexes of Co(II), Ni(II), Cu(II) and Zn(II) with imines derived from the condensation of 2-hydroxy-1-naphthaldehyde with L-amino acids (L-alanine and L-isoleucine) have been synthesized. The complexes are characterized by elemental analyses, ^1H NMR, IR, electronic spectra and conductivity and magnetic susceptibility measurements. Metal ions function as a trap for Schiff base intermediates. Spectroscopic studies reveal that the ligands are dibasic terdentate with the O, N, O donor set.

Keywords. Metal complexes; N-(2-hydroxy-1-naphthylidene)-L-amino acids; dibasic terdentate ligands.

1. Introduction

Schiff bases are an important class of ligands in coordination chemistry and have many applications in various fields (Jungreis and Thabet 1969; Gupta *et al* 1980; Bhattacharya 1982). As compared to metal complexes of Schiff bases derived from salicylaldehyde and amino acids (Burrows and Bailer 1966; Percy and Slenton 1976; Casella *et al* 1987; Shanthi *et al* 1987; Roy *et al* 1990; Akbarov and Shadmanov 1991), complexes of N-(2-hydroxy-1-naphthylidene)-amino acids have received very little attention. Only Cu(II) complexes with a few polyfunctional amino acids (MacDonald *et al* 1982) and some metal complexes with only one ligand i.e., N-naphthylidene-glycine (Thankarajan and Mohanan 1986) have been studied. In view of the above, it was thought of interest to synthesize and characterize Co(II), Ni(II), Cu(II) and Zn(II) complexes, isolated *in situ* by condensation of 2-hydroxy-1-naphthaldehyde and L-amino acids [where amino acids = L-alanine (L-Ala) and L-isoleucine (L-Ile)].

2. Experimental

All the chemicals and solvents were used of Analar grade. 2-Hydroxy-1-naphthaldehyde was obtained from Sisco-Chem industries and L-amino acids from Loba-Chemie. Metal acetates were purchased from Albright and Wilson (MGF) Ltd., England. Metal contents were estimated using standard methods (Vogel 1978).

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2.1 Preparation of metal complexes

A general method: Metal ion template condensation of 2-hydroxy-1-naphthaldehyde and L-amino acids was employed for the preparation and isolation of metal derivatives.

An aqueous solution of the sodium salt of amino acids was treated with hot ethanolic solution of 2-hydroxy-1-naphthaldehyde in 1:1 molar ratio. Aqueous ethanolic solution of metal acetates was added to hot ligand solution in 1:1, 1:2 and 1:excess molar ratios. The reactants were stirred for about 15 h. The products so formed were filtered, washed with aqueous alcohol and ether. The samples were dried first on a water-bath and then under vacuum over P_2O_5 , and the complexes obtained were solid and non-hygroscopic. Their purity was checked by TLC. The yield of the complexes varied from 80–90%. The analytical data (table 1) showed the following general formulae of the complexes:

- (1) (a) $Co(OHN-L-Ala)_2$; 1:1, 1:2 and 1:excess molar ratio;
(b) $Co(OHN-L-Ile).3H_2O$; 1:1, 1:2 and 1:excess molar ratio.
- (2) (a) $Ni(OHN-aa).3H_2O$; (aa = L-Ala, L-Ile; 1:1 and 1:2 molar ratio).
(b) $Ni(OHN-aa)_2$; (aa = L-Ala; 1:excess molar ratio).
- (3) (a) $Cu(OHN-aa).H_2O$; (aa = L-Ala, L-Ile; 1:1 molar ratio).
(b) $Cu(OHN-aa).H_2O$; (aa = L-Ala, L-Ile; 1:2 and 1:excess molar ratio).
- (4) (a) $Zn(OHN-aa).3H_2O$; (aa = L-Ala, L-Ile; 1:1 and 1:2 molar ratio).
(b) $Zn(OHN-aa)_2$; (aa = L-Ala, L-Ile; 1:excess molar ratio).

2.2 Physical measurements

Infrared spectra of the complexes were recorded on a Perkin–Elmer 842 spectrophotometer in the region $4,000\text{--}350\text{ cm}^{-1}$. Far-IR spectra were recorded using polythene sheets. The conductivity of dilute solutions ($1 \times 10^{-3}\text{ M}$) in DMF was measured on an Elico-conductivity bridge type CM 82T. Diffuse reflectance spectra were recorded on a Cary 2390 in the $300\text{--}2,000\text{ nm}$ region at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. The UV and visible spectra were also recorded on a U-2000 spectrophotometer. $^1\text{H NMR}$ spectra were taken using TMS as the internal standard on a 90 MHz Perkin–Elmer R-32 spectrometer.

3. Results and discussion

The analytical results and magnetic moment data are tabulated in table 1. The structure given in figure 1 is based on IR, $^1\text{H NMR}$ and electronic spectra, and conductivity and magnetic measurements.

The molar conductance values ($5\text{--}30\text{ ohm}^{-1}\text{ cm}^{-2}\text{ mol}^{-1}$) of 10^{-3} M solutions of metal derivatives in DMF showed that the complexes are nonelectrolytic in nature.

3.1 Infrared spectra

The broad band in the region $\sim 3400\text{--}3200\text{ cm}^{-1}$ in the infrared spectra of 1:1 complexes may be assigned to the $\nu(\text{OH})$ vibration of coordinated water. A strong band at $1640\text{--}1620\text{ cm}^{-1}$ in the IR spectra of all complexes may be evidently due to

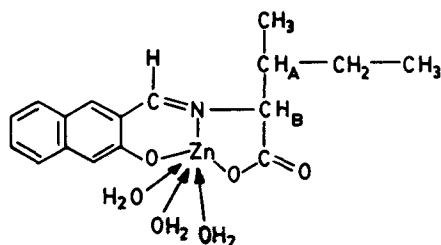


Figure 1. Structure of the zinc-isoleucine complex.

Table 1. Analytical and magnetic moment data of metal complexes.

Compound	Colour	Analysis - Found (Calcd.) %				μ_{eff} (BM)
		M	C	H	N	
Co(OHN-L-Ala) ₂	Dark green	10.64	61.41	4.20	5.13	5.01
Co(C ₂₈ H ₂₄ N ₂ O ₆)		(10.85)	(61.88)	(4.42)	(5.16)	
Co(OHN-L-Ile).3H ₂ O	Light brown	14.53	51.30	4.14	3.32	4.85
Co(C ₁₇ H ₁₇ NO ₃).3H ₂ O		(14.88)	(51.52)	(4.29)	(3.53)	
Ni(OHN-L-Ala).3H ₂ O	Green	16.28	47.31	3.00	3.72	2.99
Ni(C ₁₄ H ₁₁ NO ₃).3H ₂ O		(16.59)	(47.49)	(3.10)	(3.95)	
Ni(OHN-L-Ala) ₂	Green	10.61	62.74	4.33	5.01	3.13
Ni(C ₂₈ H ₂₄ N ₂ O ₆)		(10.82)	(61.91)	(4.42)	(5.16)	
Ni(OHN-L-Ile).3H ₂ O	Yellowish green	14.51	51.30	4.15	3.38	3.45
Ni(C ₁₇ H ₁₇ NO ₃).3H ₂ O		(14.80)	(51.55)	(4.30)	(3.54)	
Cu(OHN-L-Ala).H ₂ O	Dark green	19.43	51.90	3.20	4.27	1.78
Cu(C ₁₄ H ₁₁ NO ₃).H ₂ O		(19.69)	(52.08)	(3.41)	(4.34)	
Cu(OHN-L-Ala) ₂	Green	11.49	61.17	4.13	4.98	2.10
Cu(C ₂₈ H ₂₄ N ₂ O ₆)		(11.60)	(61.37)	(4.38)	(5.11)	
Cu(OHN-L-Ile).H ₂ O	Dark green	17.22	55.64	4.40	3.78	1.88
Cu(C ₁₇ H ₁₇ NO ₃).H ₂ O		(17.43)	(55.96)	(4.66)	(3.84)	
Cu(OHN-L-Ile) ₂	Dark green	9.87	64.50	5.51	4.34	1.90
Cu(C ₃₄ H ₃₆ N ₂ O ₆)		(10.06)	(64.60)	(5.70)	(4.43)	
Zn(OHN-L-Ala).3H ₂ O	Light yellow	17.95	46.66	3.00	3.71	Diamagnetic
Zn(C ₁₄ H ₁₁ NO ₃).3H ₂ O		(18.13)	(46.61)	(3.05)	(3.88)	
Zn(OHN-L-Ala) ₂	Light yellow	11.68	61.20	4.19	5.03	Diamagnetic
Zn(C ₂₈ H ₂₄ N ₂ O ₆)		(11.88)	(61.16)	(4.37)	(5.10)	
Zn(OHN-L-Ile).3H ₂ O	Colourless	16.03	50.31	4.03	3.22	Diamagnetic
Zn(C ₁₇ H ₁₇ NO ₃).3H ₂ O		(16.24)	(50.69)	(4.22)	(3.47)	
Zn(OHN-L-Ile) ₂	Light yellow	10.10	64.14	4.91	4.29	Diamagnetic
Zn(C ₃₄ H ₃₆ N ₂ O ₆)		(10.32)	(64.42)	(5.05)	(4.42)	

$\nu(\text{N}=\text{CH})$ vibration, which indicates the presence of an imine structure. A band appearing at $\sim 1600 \text{ cm}^{-1}$ may be assigned to $\nu(\text{COO}^-)_{\text{asym}}$ vibrations, while $\nu(\text{COO}^-)_{\text{sym}}$ vibrations appearing at $\sim 1400 \text{ cm}^{-1}$. $\Delta\nu(\text{COO}^-) \sim 200 \text{ cm}^{-1}$ indicates the unidenticity of the carboxylate group (Nakamoto 1978). All complexes showed an absorption band in the region $1535\text{--}1520 \text{ cm}^{-1}$ which can be attributed to $\nu(\text{C}-\text{O})$

(phenolic) vibration (Gruber *et al* 1968). The two weaker bands appearing in the regions 800–750 and 720–700 cm^{-1} may be due to rocking and wagging vibrations respectively for lattice water in the complexes. These two bands were observed by Fuzita *et al* (1956) and Shukla *et al* (1983) in the region 900–650 cm^{-1} . In 1:2 complexes, a broad band centred around 3400 cm^{-1} indicates the coordination of phenolic OH group without loss of hydrogen. Far-IR spectra of the compounds showed bands in 520–480 and 440–400 cm^{-1} regions which can be attributed to $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ stretchings (Singh and Singh 1982; Saha and Bhattacharya 1982), respectively.

3.2 Electronic spectra and magnetic properties

The UV spectra of all the metal complexes possess a high energy absorption band with maxima at ~ 260 nm which can be assigned to benzenoid $\pi - \pi^*$ transition. At low energies, metal complexes exhibit an absorption band at ~ 350 nm indicative of $\pi \rightarrow \pi^*$ transitions mainly originating in the aldimine residues. Similar bands were observed in zinc complexes derived from N-salicylidene- and N-pyridoxilideneamino acids (Casella and Gullotti 1981).

Cobalt(II) forms a number of complexes as shown in table 1. In these complexes, absorption bands appear in the regions 8,000–10,000 and 18,000–20,000 cm^{-1} for ν_1 and ν_3 transitions, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$, which indicate octahedral geometries for the complexes (Lever 1968). The electronic spectrum of $\text{Co}(\text{OHN-L-Ala})_3\text{H}_2\text{O}$ showed two bands at 7,360 (ν_1) and 19,600 cm^{-1} (ν_3) suggesting octahedral geometry. ν_2 transition is not observed in these cases. The effective magnetic moment values (table 1) were found to be well within the range (4.30–5.20 BM) as expected for octahedral cobalt(II) complexes (Lewis and Wilkins 1967).

Nickel(II) complexes generally exhibit three absorption bands in the regions 7,000–13,000, 13,000–19,000 and 20,000–27,000 cm^{-1} for ν_1 , ν_2 and ν_3 transitions [${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$], respectively. The electronic spectrum of $\text{Ni}(\text{OHN-L-Ala})_3\text{H}_2\text{O}$ showed three spin-allowed bands at 7,250 (ν_1), 13,570 (ν_2) and 22,800 cm^{-1} (ν_3) indicating octahedral geometry. The magnetic moment values (table 1) for Ni(II) complexes are within normal range (2.8–3.5 BM) (Lewis and Wilkins 1967).

The electronic absorption spectra of Cu(II) complexes showed a band in the visible region around 16,000 cm^{-1} . In the case of $\text{Cu}(\text{OHN-L-Ile})_2\text{H}_2\text{O}$, a band appearing at 15,675 cm^{-1} is attributed to the transition ${}^2E_g \rightarrow {}^2T_g$ and is characteristic of square-planar geometry (Lever 1968; Weeks and Fackler 1968). The band often exhibits a broad tail into the near-infrared region (in case of $\text{Cu}(\text{OHN-L-Ile})_2\text{H}_2\text{O}$ at 5,850 cm^{-1}). The magnetic moment values are within the required range (1.70–2.20 BM) for d^9 systems (Lewis and Wilkins 1967).

Zinc(II) complexes are diamagnetic as expected for the d^{10} configuration.

3.3 ${}^1\text{H}$ NMR spectra

${}^1\text{H}$ NMR spectra of zinc(II) complexes were studied and the δ values are given in table 2. Other metal complexes were insoluble in most of the organic solvents, but were soluble in DMSO, DMF and acetic acid. ${}^1\text{H}$ NMR spectra were studied for only Zn(II) complexes because their TFA solutions were clear, while for other metal complexes they were viscous.

Table 2. ¹H NMR spectra of zinc(II) complexes.

Compound	Solvent	δ(ppm)
Zn(OHN-L-Ala).3H ₂ O	TFA	1.55(d, 3 H, CH ₃), 4.65(q, 1 H, α-CH), 6.90–7.80(m, 6 H, aromatic protons), 8.95(s, 1 H, azomethine proton)
Zn(OHN-L-Ile).3H ₂ O (figure 1)	TFA	1.35(m, 6 H, 2xCH ₃), 1.80(m, 2 H, CH ₂), 2.60(m, 1 H, H _A), 5.05(d, 1 H, H _B), 7.50–8.60(m, 6 H, aromatic protons), 9.55(s, 1 H, azomethine proton).

The azomethine proton of Zn(OHN-L-Ala).3H₂O and Zn(OHN-L-Ile).3H₂O at δ 8.95 and 9.55 clearly showed the presence of the imine structure. Integration of the multiplet between δ 6.90 and 8.60 accounted for six aromatic protons in these complexes. The aliphatic protons present in the complexes are shown in table 2.

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References

- Akbarov A B and Shadmanov K K 1991 *Zh. Neorg. Khim.* **36** 2090
 Bhattacharya P J 1982 *J. Indian Chem. Soc.* **59** 505
 Burrows R C and Bailer J C 1966 *J. Am. Chem. Soc.* **88** 4150
 Casella L and Gullotti M 1981 *J. Am. Chem. Soc.* **103** 6338
 Casella L, Gullotti M, Pintar A, Messori L, Rockenbauer A and Gyor M 1987 *Inorg. Chem.* **26** 1031
 Fuzita I, Nakamoto K and Kobayashi M 1956 *J. Am. Chem. Soc.* **78** 3963
 Gupta V K, Jain N C and Sharma O K 1980 *Curr. Sci.* **49** 459
 Gruber S J, Harris C M and Sinn E 1968 *J. Inorg. Nucl. Chem.* **30** 1805
 Jungreis E and Thabet S 1969 *Chelates Anal. Chem.* **2** 149
 Lever A B P 1968 *Inorganic electronic spectroscopy* (Amsterdam: Elsevier) pp. 275–361
 Lewis J and Wilkins R G 1967 *Modern coordination chemistry* (New York: Interscience)
 MacDonald L G, Brown D H, Morris J D and Smith W E 1982 *Inorg. Chim. Acta* **67** 7
 Nakamoto K 1978 *Infrared and Raman spectra of coordination compounds* (New York: John Wiley) pp. 143–253
 Percy G C and Slenton H S 1976 *J. Inorg. Nucl. Chem.* **38** 1255
 Roy R, Saha M C and Roy P S 1990 *Transition Met. Chem.* **15** 51
 Saha N and Bhattacharya D 1982 *Indian J. Chem.* **A21** 574
 Shanthi R, Nagaraja K S and Udupa M R 1987 *Inorg. Chim. Acta* **133** 211
 Shukla P R, Singh V K, Jaiswal A M and Narain J 1983 *J. Indian Chem. Soc.* **60** 321
 Singh B and Singh R D 1982 *Indian J. Chem.* **A21** 648
 Thankarajan N and Mohanan K 1986 *J. Indian Chem. Soc.* **63** 861
 Vogel A I 1978 *A textbook of quantitative inorganic analysis* 4th edn (London: Longmans Green)
 Weeks J and Fackler J P 1968 *Inorg. Chem.* **7** 2548