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Mixed Ligand Complexes of Ni(II), Zn(II) & Cd(II) with 2,2'-Bipyridyl as a Primary Ligand & α -Amino Acids as Secondary Ligands

G. S. MALIK*, S. P. SINGH* & J. P. TANDON

Chemistry Department, University of Rajasthan, Jaipur 4

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Solution equilibria of the systems Ni(II), Zn(II) or Cd(II)-2,2'-bipyridyl(bipy)- α -amino acids [glycine (gly), α -alanine (ala) or norleucine (norleu)] have been studied. The pH-metric titration of the reaction mixture containing equimolar solutions of metal ion, bipy and one of the secondary ligands (gly, ala and norleu) have shown the formation of 1:1:1 mixed ligand complexes and their monohydroxo derivatives. The formation constants of the resulting complexes have been determined at $30 \pm 1^\circ$ ($\mu = 0.1$, KNO_3). The order of stability of complexes in terms of metal ions has been found to be: $\text{Ni(II)} < \text{Zn(II)} < \text{Cd(II)}$ and in terms of the secondary ligands: $\text{gly} > \text{ala} > \text{norleu}$.

THE ligand, 2,2'-bipyridyl (bipy) forms stable chelates particularly with all the transition metals^{1,2}. It is a good donor as well as a good acceptor³ and stabilizes both low and high valence states⁴. The 2,2'-bipyridyl complex of Fe(II) stimulates the respiration of rat brain cells⁵. Since glycine, α -alanine and norleucine are also of biological importance, it was therefore of interest to study the mixed ligand complexes of Ni(II), Zn(II) and Cd(II) with bipy as primary ligand and these amino acids as secondary ligands.

Stock solutions of the metal nitrates (AR, BDH) were prepared in doubly distilled water and standardized against a standard solution of disodium salt of EDTA using murexide [Ni(II)] and eriochrome black T [Zn(II) and Cd(II)] as indicators. 2,2'-Bipyridyl (BDH), glycine, α -alanine and norleucine solutions were prepared by direct weighing and standardized potentiometrically against a standard KOH solution.

Systronics pH-meter standardized against a 0.05M solution of potassium hydrogen phthalate (AR, BDH) was used for all the pH measurements and the titrations of the following solutions (total

vol. 50 ml) at $\mu = 0.1M$ (KNO_3) and temp. = $30 \pm 1^\circ$ were carried out.

(i) 10 ml (0.025M) ligand; (ii) 10 ml (0.025M) ligand + 10 ml (0.025M) metal nitrate [M(II)-ligand, 1:1] where M(II) = Ni(II) or Zn(II); and (iii) 10 ml (0.025M) each of primary and secondary ligands + 10 ml (0.025M) metal nitrate [M(II)-primary ligand-secondary ligand, 1:1:1].

In the case of systems involving Cd(II), the corresponding solutions were prepared using 10 ml (0.0125M) each of cadmium nitrate, 2,2'-bipyridyl and secondary ligand due to the low solubility of cadmium complexes.

The dissociation constant pK_1 of norleucine (9.60 ± 0.06) was determined by Chaberek and Martell's method⁶ and that of glycine (9.69), α -alanine (9.86) and 2,2'-bipyridyl (4.44) has been taken from the literature^{7,8}.

The pH titration curves of solutions containing equimolar quantities of nickel, zinc or cadmium nitrate and 2,2'-bipyridyl respectively exhibit a sharp inflection at $m = 1$ (where $m =$ moles of base added per mole of the metal ion) indicating the formation of 1:1 binary complex in the lower buffer region.

The pH titration curves of solutions containing nickel, zinc and cadmium nitrate in the presence of equimolar concentration of 2,2'-bipyridyl (HA^+) and one of the secondary ligands (HL) exhibit only one sharp inflection at $m = 1$, followed by buffer regions. In the initial stage, all these curves run slightly above the corresponding 1:1, M(II)-bipy titration curves and superimpose over these at $m \sim 1$. This may be due to the zwitterion formation tendency of the α -amino acids and it indicates that initially M(II)-bipy complex is formed in the above systems. The mixed ligand chelate formation occurs after $m = 1$ and this indicates that the chelation of the secondary ligand starts after the complete chelation of 2,2'-bipyridyl with the metal ion. It may be inferred from a comparison of the titration curves with the corresponding composite curves [which can be drawn by adding the horizontal distance of the secondary ligand curve to the horizontal distance of the M(II)-bipy curve at the same pH] that after $m = 1$ the formation of 1:1:1 mixed ligand chelate, MAL is the only possibility in the ternary systems studied. Further, poor inflection at $m = 2$ in the case of systems involving Ni(II) and no inflection at this stage in other systems probably indicate that the formation of 1:1:1 mixed ligand chelate and its conversion into hydroxo derivative overlap. It gets support by the analysis of the potentiometric data given below:

The equilibria involved in the mixed ligand chelate formation in the above systems may be expressed as: $\text{MA}^{2+} + \text{L}^- \rightleftharpoons \text{MAL}^+$... (1)

where M^{2+} stands for metal ion, A for bipy and L^- for the secondary ligand anion. The formation constant K_{MAL} of the 1:1:1 mixed ligand chelate may then be given by the relation (2)

$$K_{\text{MAL}} = \frac{[\text{MAL}^+]}{[\text{MA}^{2+}][\text{L}^-]} \quad \dots (2)$$

If T_{M} and T_{L} represent the total concentrations of all the metal and secondary ligand species res-

*Present address: Chemistry Department, J.V. College, Baraut.

pectively and T_{OH} is the concentration of the base added to the reaction mixture during the titration, that under the condition $T_M = T_A = T_L$.

$$K_{MAL} = \frac{T_M - X[L^-]}{X[L^-]^2} \quad \dots(3)$$

where $X = \frac{[H^+]}{k_1} + 1$ and

$$[L^-] = \frac{(2-m)T_M - [H^+] + [OH^+]}{[H^+]/k_1}$$

where k_1 is the dissociation constant of the secondary ligand.

Formation constants of the hydroxo derivative of 1:1:1 mixed ligand chelates — A gradual increase in the values of $\log K_{MAL}$ at $m > 1.8$; 1.5, 1.32, 1.36; 1.56, 1.40 and 1.64 in the case of Ni(II)-bipy-gly, ala or norleu; Zn(II)-bipy-gly, ala or norleu; Cd(II)-bipy-gly, ala or norleu probably indicates that the addition of the hydroxyl groups starts before the complete formation of 1:1:1 mixed ligand chelate resulting in the formation of a hydroxo derivative. The equilibria involved in the formation of monohydroxo derivative of 1:1:1 mixed ligand chelate may be represented by



and the overall formation constant $K_{MAL(OH)}$ of the monohydroxo derivative in these systems may be defined as:

$$K_{MAL(OH)} = \frac{[MAL(OH)]}{[MA^{2+}][L^-][OH^-]} \quad \dots(5)$$

Other pertinent equations are:

$$T_M = [MA^{2+}] + [MAL^+] + [MAL(OH)] \quad \dots(6)$$

$$T_{OH} + [H^+] - T_A - [OH^-] = [MAL^+] + 2[MAL(OH)] + [L^-] \quad \dots(7)$$

$$T_L = [MAL^+] + [MAL(OH)] + [HL] + [L^-] \quad \dots(8)$$

Eliminating $[MAL(OH)]$ from Eqs. (6)-(8) and rearranging the terms, we obtain

$$a[MA^{2+}]^2 + b[MA^{2+}] - c = 0 \quad \dots(9)$$

where $a = K_{MAL}$, $b = \frac{2[H^+]}{k_1} + 1$ and $c = \{(3-m)T_M - [H^+] + [OH^-]\}X$.

The equilibrium concentration of MA^{2+} present in the reaction mixture may be obtained by solving Eq. (9) and the concentrations of other species involved in the equilibrium relations can then be calculated from the above equations and also the value of formation constant, $K_{MAL(OH)}$.

The values of the formation constants of the mixed ligand chelate K_{MAL} and its monohydroxo derivative $K_{MAL(OH)}$ are presented in Table 1. The formation constants of monohydroxo derivative of Ni(II)-bipy-gly, Ni(II)-bipy-ala, Ni(II)-bipy-norleu, Zn(II)-bipy-ala and Zn(II)-bipy-norleu could not be calculated, as the precipitation occurs at an early stage after the addition of hydroxyl group starts.

The order of stability of mixed complexes in terms of metal ions is: Ni(II) > Zn(II) > Cd(II) as expected from Mellor and Maley order. Further, the order of stability in terms of secondary ligands has been found to be: gly > ala > norleu and this can be ex-

TABLE 1 — FORMATION CONSTANTS OF MIXED LIGAND CHELATE AND MONOHYDROXO DERIVATIVE

System	$\log K_{MAL}$	$\log K_{MAL(OH)}$
Ni(II)-bipy-gly	5.50 ± 0.03	—
Ni(II)-bipy-ala	5.15 ± 0.07	—
Ni(II)-bipy-norleu	4.90 ± 0.09	—
Zn(II)-bipy-gly	4.67 ± 0.04	9.90 ± 0.04
Zn(II)-bipy-ala	4.32 ± 0.13	—
Zn(II)-bipy-norleu	4.11 ± 0.12	—
Cd(II)-bipy-gly	3.97 ± 0.12	8.06 ± 0.07
Cd(II)-bipy-ala	3.72 ± 0.11	8.04 ± 0.07
Cd(II)-bipy-norleu	3.64 ± 0.08	7.92 ± 0.12

plained on the basis of the enlargement of the chain in α -alanine and norleucine systems.

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Mixed Ligand Complexes of Lanthanides with Diacetylmonoxime as a Primary Ligand & N-Substituted Anthranilic Acids as Secondary Ligands

V. D. DESHPANDE & S. S. DARA

Department of Chemistry
Visvesvaraya Regional College of Engineering, Nagpur 440011

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Mixed complexes of lanthanide ions Y^{3+} , La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} with diacetylmonoxime as primary ligand and N-phenylanthranilic acid and N-methylanthranilic acid as secondary ligands have been synthesized and characterized on the basis of analytical, spectral and thermal data.

SEVERAL simple lanthanide complexes with various oximes have been reported and characterized¹⁻⁵. Mixed ligand complexes of lanthanides have also received much interest in recent years⁶⁻⁹. Mixed complexes of lanthanides using oximes as primary ligands and 1,10-phenanthroline, oxine and pyridine-2-aldoxime as the secondary ligands have also been reported¹⁰. Preparation and characterization of several mixed complexes of lanthanides using DAMO as the primary ligand and NPAA and NMAA¹¹ as the secondary ligands are reported in this note.