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Role of π -interaction in Ternary Complexes of Zinc(II) or Cadmium(II) + 2,2'-Bipyridyl + Amino Acids

J. D. JOSHI

Department of Chemistry, South Gujarat University,
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MIXED ligand complexes MAL, where M = Ni²⁺, Cu²⁺; A = 2,2'-bipyridyl or 1,10-phenanthroline; and L = amino acids, have been studied earlier¹. In the present investigation an attempt has been made to determine the stability constants of the title systems using modified form of Irving-Rossotti titration technique. The [M(2,2'-bipy)]²⁺, 1:1 complex formed before pH ~ 4 and stable up to pH ~ 8 where the secondary ligand gets coordinated. Formation of 1:1 complexes of both [Ni(2,2'-bipy)]²⁺ and [Zn(2,2'-bipy)]²⁺ at low pH and their stability at high pH has been shown earlier^{2,4}.

Experimental

All the reagents used were of A.R. quality. Metal perchlorates were used in the present study to avoid the complexing tendency of the anion.

The experimental set-up and calculations described by Bhattacharya *et al.*⁵ were employed. The ionic strength was maintained at 0.2 M in each case. Systronics 355 digital pH meter was employed for pH measurements. Potentiometric titrations were carried out at 30° using 0.2M NaOH.

The interpretation of the potentiometric curves was similar to that reported¹. From the titration data \bar{n}_H , \bar{n} and P_Z were calculated as described earlier⁵. Precise values of K_{MAL}^{MA} were determined by the method of averages⁶ and the values are presented in the Table 1.

Results and Discussion

The order of the formation constants of the mixed ligand chelates is the same as that for the binary complexes. It is observed that the values of K_{MAL}^{MA} are nearly equal to K_{ML}^M . This can be explained in terms of secondary ligands basicities. The order of mixed ligand formation constant is, glycine \approx α -alanine \approx leucine; valine \approx serine \approx threonine \approx methionine.

The higher values of mixed ligand formation constants can be explained by the special behaviour of 2,2'-bipyridyl. The 2,2'-bipyridyl molecule is bound to the metal ion by σ -bonding. Besides that there is also π -bonding formation by the back donation of electrons from M \rightarrow L. The d π -p π interaction has been observed by earlier workers⁷. The positive charge on the metal ion in [M(2,2'-bipy)]²⁺ and [M(aq)]²⁺ complexes is same, because the d π -p π interaction does not allow the concentration of electrons on the metal ion to increase significantly. Therefore, the electronegativity of the metal ion in [M(2,2'-bipy)]²⁺ remains same as in [M(aq)]²⁺. So, the tendency of the secondary ligand L to combine with [M(2,2'-bipy)]²⁺ and [M(aq)]²⁺ is comparable. Therefore, K_{MAL}^{MA} values are nearly equal to K_{ML}^M . Thus, π -interaction is playing an important role for the lowering of Δ values in all the cases.

TABLE 1—MIXED LIGAND FORMATION CONSTANTS OF SOME HETEROCHELATES OF Zn²⁺ AND Cd²⁺ AT 30°
Ionic strength, 0.2M

Ligand (L)	$\log K_{Zn.L}^{Zn*}$	$\log K_{Zn.bipy.L}^{Zn.bipy*}$ (1:1:1)	$\log K_{Cd.L}^{Cd*}$	$\log K_{Cd.bipy.L}^{Cd.bipy*}$ (1:1:1)
Glycine	5.22	4.81 \pm 0.06	4.24	4.20 \pm 0.04
α -Alanine	5.17	4.54 \pm 0.04	4.27	4.05 \pm 0.02
Leucine	4.74	4.48 \pm 0.05	3.92	3.93 \pm 0.04
Valine	4.74	4.69 \pm 0.06	3.91	3.81 \pm 0.04
Serine	5.06	4.79 \pm 0.03	3.95	3.76 \pm 0.05
Threonine	5.16	4.89 \pm 0.06	4.02	3.86 \pm 0.02
Methionine	4.69	4.59 \pm 0.04	4.30	3.89 \pm 0.03

* M. V. Chidambaram, Ph.D. Thesis, M. S. University, Baroda, 1971; J. D. Joshi, Ph.D. Thesis, M. S. University, Baroda, 1974.

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Stabilisation of Molybdenyl Cation(V) in Diverse Anionic Environment by 2(2'-Pyridyl)benzimidazole

H. K. SAHA, (Miss) ANIMA SAHA and S. S. MANDAL

Department of Pure Chemistry, University College of Science, Calcutta-700 009

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WE have reported in details¹⁻² the chemistry of MoO^{5+} in the environment of some diverse anions. The present communication deals with the isolation and study of some oxomolybdenum(V)chloro complexes with 2(2'-pyridyl)benzimidazole (Pybmz) in spin-free state.

Experimental

The ligand was prepared following the standard procedure³ and the other reagents used were of A.R. grade. Molybdenum and chloride were estimated gravimetrically as molybdenum trioxide and silver chloride. Nitrogen was estimated by Dumas' method. The oxidation state of the metal was determined by ceric sulphate method.

2(2'-Pyridyl) benzimidazoliniumoxopentachloromolybdate(V), $\text{PybmzH}_2 [\text{MoOCl}_5]$:

Molybdenum trioxide (~1 g) was dissolved in HCl (10 ml, 12 M) with stirring followed by addition of hydriodic acid (1 ml). The solution was boiled to drive off the liberated iodine. The concentrated small mass was taken up with minimum quantity of conc. HCl when a bright green solution was obtained. To this solution containing MoOCl_5^{2-} , was added with stirring a solution of 0.8 g ligand in minimum quantity of HCl when a greenish yellow precipitate was obtained. The precipitate was filtered and dried *in vacuo* over solid KOH to yield the product (1.9 g).

Oxotrichloro [2 (2'-pyridyl)benzimidazole]molybdenum(V), $[\text{MoOCl}_4 \cdot \text{Pybmz}]$, (pink): A sample of the parent salt, $\text{PybmzH}_2 [\text{MoOCl}_5]$ (~1 g) was refluxed with dehydrated ethanol (15 ml) for 0.5 h. The pink coloured crystalline solid so formed was filtered and dried in vacuum desiccator to yield the product (0.75 g).

Oxotrichloro [2 (2'-pyridyl)benzimidazole]molybdenum(V), $[\text{MoOCl}_4 \cdot (\text{Pybmz})]$, (orange): The orange coloured crystalline compound was obtained by refluxing 1g of the original salt (1g) with acetonitrile (15 ml) for 2 h. The solid mass was filtered, washed with acetonitrile and dried *in vacuo* to yield the product (0.73 g).

Alternatively, the orange compound was also prepared by refluxing the parent salt with acetylacetone for 2.5 h. Analytical data of the complexes are given in Table 1.

Results and Discussion

The extensive hydrolysis and ionisation of oxopentahalomolybdate(V) ion was confirmed by conductance measurement of the salt in aqueous medium. The non-electrolytic nature of $[\text{MoOCl}_5 \cdot \text{Pybmz}]$ compound was established by conductance measurement in acetonitrile. The conductance values in $10^{-3}M$ solution of the pink and the orange forms are 11.73 and 11.28, $11.68 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively which are much less than those for binary electrolytes⁴.

The μ_{eff} values of the complexes, $\text{PybmzH}_2 [\text{MoOCl}_5]$, $[\text{MoOCl}_4 \cdot \text{Pybmz}]$ (pink) and $[\text{MoOCl}_4 \cdot \text{Pybmz}]$ (orange, two product) are 1.51, 1.62, 1.53

TABLE 1—ANALYTICAL, OXIDATION STATE, MAGNETIC AND CONDUCTANCE DATA FOR OXOMOLYBDENUM(V) COMPLEXES

Compound	Colour	Analysis % : Found/(Calcd.)			Oxidation state	μ_{eff} B.M.	Molar conductance Ω^{-1}
		Mo	Cl	N			
$\text{PybmzH}_2 [\text{MoOCl}_5]$	Greenish yellow	20.32 (19.72)	35.69 (36.48)	9.43 (8.68)	5.07	1.513	—
$[\text{MoOCl}_4 \cdot \text{Pybmz}]$	Pink	23.82 (23.23)	25.72 (25.78)	10.56 (10.16)	4.89	1.62	11.73
$[\text{MoOCl}_4 \cdot \text{Pybmz}]$	Orange	23.74 (23.23)	25.87 (25.78)	10.76 (10.16)	4.88	1.53	11.28
$[\text{MoOCl}_4 \cdot \text{Pybmz}]$ (from acetylacetone)	Orange	23.73 (23.23)	25.80 (25.78)	9.91 (10.16)	4.91	1.46	11.68