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Study of Ternary Complexes of Bivalent Metal Ions with Dipyridyl and β-Diketones

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Abstract – Dipyridyl functions as a typical bidentate chelating agent through the N-atoms with the formation of a five-membered ring

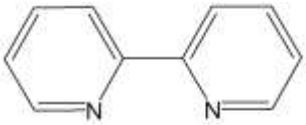

Figure 1

The metal ion chelates of dipyridyl are formed at low pH values and these remain stable at high pH also. So, dipyridyl has been used as a primary ligand in the formation of mixed ligand complexes. The lowering of the potentiometric curve for the mixed system in comparison to the curve for binary complex of the metal with the primary ligand indicates the formation of a mixed ligand complex.

The mixed ligand complexes of bivalent metal ions using dipyridyl as the primary ligand and β-diketones (p-Bromobenzoylacetone and p-Chlorobenzoylacetone) as the secondary ligands. The stability constants for these systems have been determined potentiometrically. The competition of these ligands in the inner sphere of the bivalent ions has been studied by calculating the reproportionation constants.

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INTRODUCTION

The presence of β-carbonyl group with proton on the carbon atom allows a Keto ⇌ Enol tautomerism. By the replacement of the proton by a metal ion β-ketoenolate complexes are obtained.

p-Bromobenzoylactone (p-BBA) and p-Chlorobenzoylacetone have been chosen to study the interaction with metal ions along with dipyridyl.

EXPERIMENTAL

A digital pH meter, model pH 5651 (EC, India) was used for pH measurements. The solutions of p-BBA and p-BCA were prepared in freshly distilled dioxane. Dipyridyl was (E Merck) was dissolved in doubly distilled water. The solutions of bivalent metal ions were prepared from reagent-grade bottles. Chemically pure sodium perchlorate was used to maintain the ionic strength of the medium Tetramethylammonium hydroxide (TMAH) in 75% (v/v) aqueous dioxane was used as titrant

pH TITRATION PROCEDURE

The following solutions were titrated potentiometrically against 0.04 M TMAH.

(i) 3.0 ml $HClO_4$ (0.02M) +1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 15 .0 ml dioxan +0.5 ml H_2O

(ii) 3.0 ml $HClO_4$ (0.02M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 0.5 ml dipyridyl (0.02 M) + 15.0 ml dioxan.

(iii) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 0.5 ml sec. ligand (0.02 M) +0.5 ml H_2O +14.5 ml dioxan.

(iv) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml dipyridyl (0.02 M) +0.5 ml metal ion (0.02 M) +15 ml dioxan.

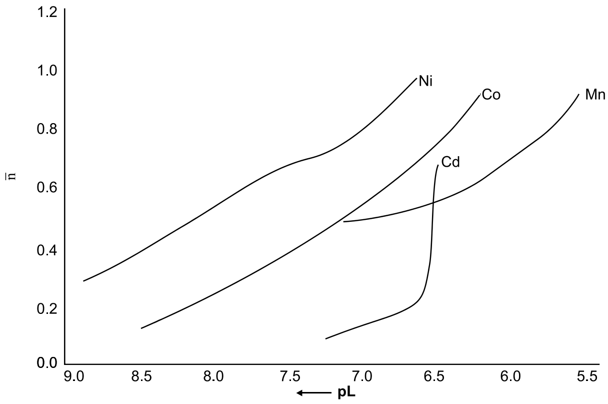


Fig. 1: Formation curves for mixed ligand complexes of bivalent metals with dipyridyl and p-bromobenzoyl acetone in 75% aqueoudioxanean at μ = 0.1 M $NaClO_4$ and T = 30°C.

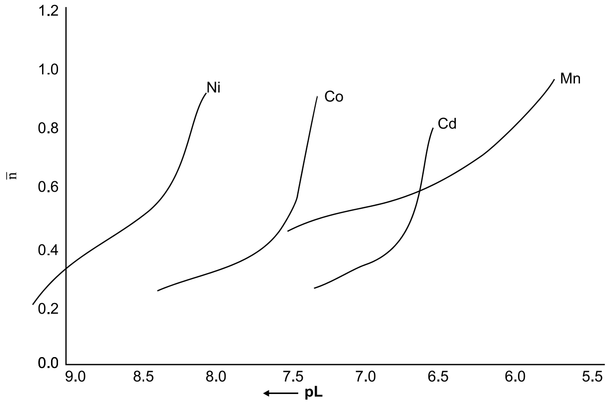


Fig. 2: Formation Curves for mixed ligand complexes of bivalent metals with dipyridyl and p-chlorobenzoyl acetone in 75% aqueous dioxane at μ = 0.1 M $NaClO_4$ and T = 30°C.

(v) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml dipyridyl (0.02 M) + 0.5 ml metal ion (0.02 M) + 0.5 ml sec ligand (0.02 M) + 14.5 ml dioxan.

RESULTS AND DISCUSSION

The values of stability constants and reproportionation constants are given in table 1. The $\bar{n}$ values obtained lie below 1.0 in all the cases. Hence only 1:1:1 mixed ligand complex is formed in each system.

The complex formation between metal ions and dipyridyl was found to take place at low pH whereas with secondary ligands it takes place at a high pH range. The titration curves for the solutions (iv) and (v) overlap in the lower pH range, indicating that secondary ligands do not combine with metal ions in this pH range and only complexation with dipyridyl takes place. At high pH values, the titration curve of solution (v) diverges from the solutions (iii) and (iv) shows the coordination of the secondary ligands with $[M\text{-dipy}]^{2+}$. The reaction may be represented as

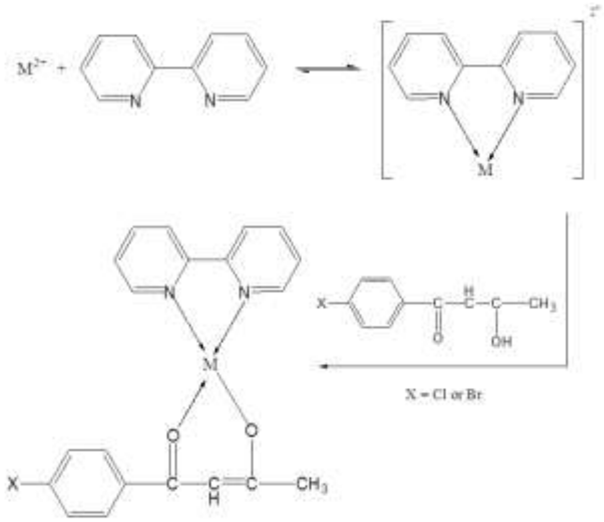
$$M^{2} + \text{dipy} \rightleftharpoons [M\,(\text{dipy})]^{2+}$$

$$[M\,(\text{dipy})]^{2+} + [L]^{-} \rightleftharpoons [M\,(\text{dipy})\,(L)]^{+}$$

$K_{M.dipy.L}$ can be written as

$$\beta_{1,1} = \frac{[M(\text{dipy})(L)]^{+}}{[M(\text{dipy})]^{2+}[L]^{-}}$$

The reactions can be written as

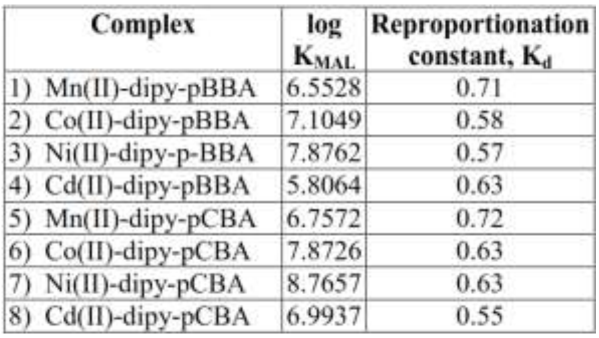


The values of stability constants of the mixed ligand complexes have been calculated and are given in Table 3.

Reproportionation constants

The correlation between the stability constants of the parent complexes and the mixed ligand complex formed with the same ligands is given as

Table 3: Stability constants and reproportionation constant (K_d) values of mixed ligand complexes of p-chloro-benzoyl acetone (p-CBA) and p-bromobenzoyl acetone (p-BBA) at μ = 0.1 M $NaC1O_4$ and T = 30°C



Complex	log K_{MAL}	Reproportionation constant, K_d
1) Mn(II)-dipy-pBBA	6.5528	0.71
2) Co(II)-dipy-pBBA	7.1049	0.58
3) Ni(II)-dipy-p-BBA	7.8762	0.57
4) Cd(II)-dipy-pBBA	5.8064	0.63
5) Mn(II)-dipy-pCBA	6.7572	0.72
6) Co(II)-dipy-pCBA	7.8726	0.63
7) Ni(II)-dipy-pCBA	8.7657	0.63
8) Cd(II)-dipy-pCBA	6.9937	0.55

Table 4: Stability constants of Binary Complexes of p-CBA, p-BBA and dipyridyl at $\mu = 0.1$ M NaC10$_4$ and T = 30°C

Ligand	Mn(II)		Co(II)		Ni(II)		Cd(II)	
	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$
p-chlorobenzoylacetone	6.89	10.80	6.98	13.41	8.13	14.52	5.63	19.76
p-bromobenzoylacetone	6.73	10.48	6.93	13.13	7.97	14.40	5.92	10.56
dipyridyl*	4.16	8.10	6.06	11.42	6.80	13.26	4.50	8.00

* Values reported in the literature

Table 5: Change in bond energies of M-A and M-L bonds during mixed ligand complex formation of bivalent metal ions at $\mu = 0.1$ M NaClO$_4$ and Temp. = 30°C

Secondary ligand	Metal ion	M-dipy bonds			M-L bonds		
		F'_A (parent) Cal mole^{-1}	F_A (mixed) Cal mole^{-1}	$F_A - F'_A$ (change in bond energy) Cal mole^{-1}	F'_L (parent) Cal mole^{-1}	F_L (mixed) Cal mole^{-1}	$F_L - F'_L$ (Change in bond energy) Cal mole^{-1}
p-chlorobenzoyl acetone	Co(II)	3944	2400	-1544	4632	3036	-1596
	Mn(II)	2798	1391	-1407	3730	3276	-454
	Cd(II)	2763	2024	-739	6825	2804	-4021
	Ni(II)	4580	2566	-2014	5015	3485	-1530
p-bromobenzoyl acetone	Co(II)	3944	2152	-1792	4535	2753	-1782
	Mn(II)	2798	1375	-1423	3620	3151	-469
	Cd(II)	2763	1513	-1250	3647	2494	-1153
	Ni(II)	4580	2314	-2266	4974	3122	-1852

$$\beta_{j,i} = K_d \cdot \beta_{m,o}^{1/m} \cdot \beta_{0,m}^{j/m}$$

(i + j = m)

The value of K_d = Reproportionation constant. The value of K_d gives an idea about the compatibility of the two ligands in the coordination sphere of the metal ion. If the $K_d > 1$ then the ligands are compatible and the mixed ligand complex formed should be more stable than the parent complexes. In the present case, K_d values are less than one (Table 3) so the mixed ligand complex formed is less stable than the parent complexes. Hence dipyridyl and β-diketones (p-BBA and p-CBA) are non-compatible ligands.

Change in Bond Energies

The strength of the individual M–A and M–L bonds in the complex MA_jL_i have been calculated from the stability constants of the mixed complex (MA_jL_i) and parent complexes (MA_m and ML_m) by using the following relations –

$$F_A = \frac{RT}{4j} \ln \beta_{j,i} \frac{\beta_{j,0}}{\beta_{0,i}}$$

$$F_L = \frac{RT}{4i} \ln \beta_{j,i} \frac{\beta_{0,i}}{\beta_{j,0}}$$

The strengths of the metal-ligand bonds in the parent complexes MA_m and ML_m have been calculated from their stability constants by using the following relations:

$$F'_A = \frac{RT}{2m} \ln \beta_{m,0}$$

$$F'_L = \frac{RT}{2m} \ln \beta_{0,m}$$

The results obtained are given in table 5. From the values of bond energies calculated it is found that the mixed ligand complexes have weaker bonds as compared to the parent complexes hence their stabilities will also be lower.

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