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Electrochemical Studies on Mixed Ligand Complexes of Cadmium Ion with Some Dicarboxylic Acids and Pyridoxine (Vitamin B_6)

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Ternary complexes of cadmium(II) with carboxylic acids (oxalic, malic, maleic, malonic and succinic acid) and pyridoxine have been studied at 30°C and at ionic strength 0.1 (KNO_3) and pH 8–9. Cadmium ion forms (0, 1), (0, 2), (0, 3) complexes. The reduction of the complexes in each case is reversible and diffusion-controlled. Cd(II) forms three mixed complexes, *viz.*, [Cd (carboxylate) (pyridoxynate)], [Cd (carboxylate) $(pyridoxynate)_2$] and [Cd $(carboxylate)_2$ (pyridoxynate)].

Key words: Electrochemical studies, mixed ligand complexes, cadmium(II), pyridoxine, dicarboxylic Acids.

INTRODUCTION

An increasing number of studies of mixed ligand complexes have appeared in the past by various techniques[1,2]. But polarographic studies have attracted little attention. The mixed-ligand complexes of cadmium with other ligands have been studied by many workers[3–5]. Simple complexes of Cd(II) with carboxylic acids and pyridoxine have been studied in our laboratory[6,7]. The mixed ligand complexes of cadmium with pyridoxine and amino acids have been studied recently[8].

However, polarographic studies on mixed complexes of Cd(II) with carboxylic acids (oxalic, malic, maleic, malonic and succinic acid) and pyridoxine have not been reported so far and hence have been considered for investigation.

EXPERIMENTAL

The chemicals used were of AnalaR grade. Pyridoxine and dicarboxylic acids were used as complexing agents. Potassium nitrate was used as supporting electrolyte to maintain the ionic strength constant. 0.004% solution of gelatin was added to suppress the maxima. pH of all the solutions was maintained at 8–9 with an Elico LI-120 digital pH meter.

Purified nitrogen gas was passed through the solution to remove oxygen. Polarograms of solutions were taken using a manual polarograph. Saturated calomel electrode was used as a reference electrode. The capillary had the following characteristies.

$m = 1.96$ mg s^{-1}, $t = 4.05$ s per drop and $h_{corr} = 40.0$ cm (at 303 ± 1 K in 0.1 M KNO_3 in open circuit) Temperature was maintained at 303 ± 1 K.

RESULTS AND DISCUSSION

The formation constants of simple systems were calculated with the help of Deford and Hume method[9] before the study of mixed systems. The values of formation constants of simple systems are presented in Table-6, which are in good agreement with values in the literature.[10, 11]

The mixed systems of Cd(II) with pyridoxine and dicarboxylic acids (oxalic, malic, maleic, malonic and succinic acid) were studied by keeping the concentration of weaker ligand (pyridoxine) constants at two different values while varying the concentration of dicarboxylic acids in each case. The free ligand concentration for each system has been calculated with the help of pH of the solution, pK values and amount of ligand. In each case a single well defined wave was obtained. The plots of Ede *vs.* log $i/(i_d - i)$ were linear with a slope of 30 ± 2 showing that the two-electron reduction is reversible. The direct proportionality of the diffusion current to the effective height of the mercury column indicated that the reduction is entirely diffusion-controlled.

The functions F_{00}, F_{10}, F_{20} and F_{30} were calculated by the method of Schaap and McMasters[12] and the functions A, B, C and D were calculated by Laden's graphical extrapolation method[13] and are presented in Tables 1–5.

TABLE-1 (A)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-SUCCINATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M)$ = 0.588 *vs.* SCE

$[X]\ 10^2$	$\Delta' E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{-1}$	$'F_{20} \times 10^{-2}$	$'F_{30} \times 10^{-3}$	F_{00} (cal)	$\Delta' F_{00}$ (%)
1.00	0.004	0.0092	1.39	3.90	8.60	2.50	1.39	0.00
1.25	0.005	0.0126	1.52	4.16	8.56	2.50	1.52	0.00
1.50	0.006	0.0179	1.65	4.46	8.60	2.51	1.65	0.00
1.75	0.007	0.0224	1.80	4.57	8.74	2.23	1.80	0.00
2.00	0.008	0.0261	1.96	4.81	8.80	2.25	1.96	0.00
2.25	0.009	0.0310	2.14	5.05	8.97	2.75	2.13	+0.46
2.50	0.010	0.0328	2.33	5.29	8.99	2.54	2.32	+0.49
2.75	0.011	0.0354	2.52	5.53	9.05	2.54	2.52	0.00
3.00	0.012	0.0369	2.73	5.71	9.10	2.50	2.73	0.00
3.25	0.013	0.0388	2.95	6.00	9.17	2.52	2.96	–0.03

A = 1.00 (cal) B = 30.40 C = 8.35×10^2 D = $(2.52 \pm .22) \times 10^3$

TABLE-1(B)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-SUCCINATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M) = 0.588$ *vs.* SCE

$[X]\ 10^2$	$\Delta' E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{-1}$	$'F_{20} \times 10^{-3}$	$'F_{30} \times 10^{-3}$	F_{00} (cal)	$\Delta' F_{00}$ (%)
1.00	0.005	0.0097	1.50	4.50	1.22	2.00	1.50	0.00
1.25	0.006	0.0191	1.65	4.82	1.23	2.40	1.66	+0.61
1.50	0.007	0.0272	1.82	5.13	1.23	2.00	1.82	0.00
1.75	0.008	0.0349	2.00	5.45	1.24	2.52	2.01	+0.50
2.00	0.009	0.0450	2.21	5.78	1.25	2.50	2.21	0.00
2.25	0.010	0.0510	2.42	6.10	1.25	2.22	2.43	+0.41
2.50	0.011	0.0589	2.66	6.43	1.26	2.40	2.66	0.00
2.75	0.012	0.0647	2.91	6.77	1.27	2.55	2.91	0.00
3.00	0.013	0.0700	3.18	7.12	1.28	2.67	3.18	0.00
3.25	0.014	0.0746	3.47	7.44	1.28	2.52	2.47	0.00

A = 1.05 (cal) B = 32.80 C = 1.20×10^3 D = $(2.52 \pm .52) \times 10^3$

TABLE-2(A)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALEATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M) = 0.588$ *vs.* SCE

$[X]\ 10^2$	$\Delta' E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{1}$	$'F_{20} \times 10^{2}$	$'F_{30} \times 10^{3}$	F_{00} (cal)	$\Delta' F_{00}$ (%)
1.00	0.005	0.0228	1.55	5.51	4.91	2.10	1.55	0.00
1.25	0.006	0.0322	1.71	5.64	4.96	2.08	1.71	0.00
1.50	0.007	0.0380	1.86	5.73	4.73*	2.00	1.87	–0.54
1.75	0.008	0.0435	2.04	5.94	5.07	2.12	2.03	+0.49
2.00	0.009	0.0450	2.20	6.05	5.15	2.25	2.21	–0.45
2.25	0.010	0.0457	2.39	6.18	5.16	2.04	2.39	0.00
2.50	0.011	0.0457	2.58	6.32	5.20	2.00	2.58	0.00
2.75	0.012	0.0480	2.78	6.47	5.27	2.07	2.78	0.00
3.00	0.012	0.0749	2.98	6.60	5.27	1.90	2.99	–0.34
3.25	0.012	0.1060	3.20	6.77	5.39	2.12	3.20	0.00

A = 1.00 (cal) B = 50.20 C = 4.70×10^2 D = $(2.10 \pm .03) \times 10^3$

TABLE-2(B)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALEATE SYSTEM

Pyridoxine = 2×10^{-3} M, $E_{1/2}(M)$ = 0.588 *vs.* SCE

$[X] 10^2$	$\Delta'E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{-1}$	$'F_{20} \times 10^{-2}$	$'F_{30} \times 10^{-3}$	F_{00} (cal)	$\Delta'F_{00}$ (%)
1.00	0.002	0.1483	1.64	5.91	6.82	2.10	1.64	0.00
1.25	0.003	0.1579	1.81	6.12	7.12	2.56	1.81	0.00
1.50	0.004	0.1658	1.99	6.31	7.20	2.66	2.00	–0.50
1.75	0.005	0.1664	2.19	6.49	7.20	2.28	2.18	+0.45
2.00	0.006	0.1770	2.38	6.67	7.20	2.10	2.39	–0.42
2.25	0.007	0.1804	2.59	6.89	7.28	2.57	2.59	0.00
2.50	0.008	0.1841	2.82	7.08	7.40	2.40	2.82	0.00
2.75	0.008	0.2180	3.05	7.27	7.42	2.22	3.05	0.00
3.00	0.009	0.2178	3.29	7.47	7.47	2.23	3.29	0.00
3.25	0.009	0.2496	3.54	7.66	7.48	2.09	3.54	0.00

A = 1.05 (cal) B = 52.30 C = 6.80×10^2 D = $(2.10 \pm .04) \times 10^3$

TABLE-3(A)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALONATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M)$ = 0.588 *vs.* SCE

$[X] 10^2$	$\Delta'E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{1}$	$'F_{20} \times 10^{2}$	$'F_{30} \times 10^{3}$	F_{00} (cal)	$\Delta'F_{00}$ (%)
1.00	0.005	0.0062	1.56	5.60	5.80	–	1.57	–0.64
1.25	0.007	0.0062	1.73	5.82	6.37	2.99	1.73	0.00
1.50	0.008	0.0126	1.90	5.13	6.45	3.00	1.90	0.00
1.75	0.009	0.0183	2.08	6.16	6.53	3.00	2.08	0.00
2.00	0.010	0.0233	2.27	6.34	6.60	3.02	2.28	–0.44
2.25	0.011	0.0267	2.47	6.52	6.68	3.00	2.47	0.00
2.50	0.012	0.0281	2.68	6.71	6.75	3.01	2.68	0.00
2.75	0.013	0.0282	2.90	6.90	6.82	2.98	2.90	0.00
3.00	0.014	0.0291	3.13	7.09	6.90	2.99	3.13	0.00
3.25	0.015	0.0291	3.37	7.29	6.98	3.00	3.37	0.00

A = 1.00 (cal) B = 50.20 C = 6.0×10^2 D = $(3.00 \pm .02) \times 10^3$

TABLE-3(B)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALONATE SYSTEM

Pyridoxine = 2×10^{-3} M, $E_{1/2}(M)$ = 0.588 *vs.* SCE

[X] 10^2	$\Delta'E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{-1}$	$'F_{20} \times 10^{-2}$	$'F_{30} \times 10^{-3}$	F_{00} (cal)	$\Delta'F_{00}$ (%)
1.00	0.006	0.0126	1.72	6.21	9.60	3.00	1.72	0.00
1.25	0.008	0.0126	1.90	6.45	9.67	2.96	1.91	+0.56
1.50	0.009	0.0248	2.11	6.70	9.75	3.00	2.11	0.00
1.75	0.010	0.0328	2.32	6.97	9.83	2.02	2.32	0.00
2.00	0.011	0.0389	2.54	7.23	9.90	3.00	2.55	+0.39
2.25	0.013	0.0131	2.79	7.49	9.96	2.93	2.79	0.00
2.50	0.014	0.0171	3.04	7.76	10.04	2.96	3.04	0.00
2.75	0.015	0.0208	3.31	8.03	10.10	2.95	3.31	0.00
3.00	0.016	0.0228	3.59	8.31	10.20	3.00	3.59	0.00
3.25	0.017	0.0244	3.89	8.58	10.25	2.92	3.89	0.00

A = 1.10 (cal) B = 5.25×10^1 C = 9.30×10^2 D = $(3 \pm .08) \times 10^3$

TABLE-4(A)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M)$ = 0.588 *vs.* SCE

[X] 10^2	$\Delta'E_{1/2}$	log Im/Ic	F_{00}	$'F_{10} \times 10^{-1}$	$'F_{20} \times 10^{-2}$	$'F_{30} \times 10^{-3}$	F_{00} (cal)	$\Delta'F_{00}$ (%)
1.00	0.003	0.1697	1.86	8.65	6.95	2.52	1.86	0.00
1.25	0.004	0.1891	2.10	8.83	7.02	2.52	2.10	0.00
1.50	0.005	0.2047	2.35	9.00	7.03	2.00	2.35	0.00
1.75	0.006	0.2170	2.61	9.20	7.14	2.25	2.61	0.00
2.00	0.007	0.2265	2.88	9.40	7.16	2.30	2.88	0.00
2.25	0.008	0.2322	3.15	9.56	7.16	2.04	3.16	–0.32
2.50	0.009	0.2371	3.44	9.76	7.24	2.61	3.45	–0.29
2.75	0.010	0.2402	3.74	9.96	7.31	2.22	3.75	–0.26
3.00	0.011	0.2422	4.06	10.17	7.40	2.33	4.06	0.00
3.25	0.012	0.2422	4.38	10.37	7.44	2.52	4.38	0.00

A = 1.00 (cal) B = 7.95×10^1 C = 6.7×10^2 D = $(2.52 \pm .5) \times 10^3$

TABLE-4(B)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-MALATE SYSTEM

Pyridoxine = 2×10^{-3} M, $E_{1/2}(M) = 0.588$ *vs.* SCE

$[X]\ 10^2$	$\Delta'E_{1/2}$	log Im/Ic	F_{00} $\times 10^{-1}$	$'F_{10}$ $\times 10^{-1}$	$'F_{20}$ $\times 10^{-2}$	$'F_{30}$ $\times 10^{-3}$	F_{00} (cal) $\times 10^{-1}$	$\Delta'F_{00}$ (%)
1.00	0.002	0.2301	1.98	9.35	12.50	2.52	1.96	+1.01
1.25	0.003	0.2585	2.26	9.68	12.64	2.64	2.22	+1.76
1.50	0.004	0.2649	2.57	10.13	13.53	2.35	2.50	+2.70
1.75	0.005	0.2793	2.79	9.92	10.44	2.00	2.79	0.00
2.00	0.006	0.2903	3.09	10.20	10.50	2.52	3.09	0.00
2.25	0.007	0.2986	3.40	10.49	10.62	2.75	3.40	0.00
2.50	0.008	0.3067	3.74	10.76	10.64	2.52	3.74	0.00
2.75	0.009	0.3123	4.09	11.05	10.73	2.65	4.09	0.00
3.00	0.010	0.3157	4.45	11.33	10.77	2.57	4.44	+0.22
3.25	0.011	0.3180	4.83	11.63	10.86	2.65	4.83	0.00

A = 1.05 (cal) B = 8.0×10^1 C = 1×10^3 D = $(2.52 \pm 0.3) \times 10^3$

TABLE-5(A)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-OXALATE SYSTEM

Pyridoxine = 2×10^{-4} M, $E_{1/2}(M) = 0.588$ *vs.* SCE

$[X]\ 10^2$	$\Delta'E_{1/2}$	log Im/Ic	F_{00} $\times 10^{-1}$	$'F_{10}$ $\times 10^{-2}$	$'F_{20}$ $\times 10^{-4}$	$'F_{30}$ $\times 10^{-5}$	F_{00} (cal) $\times 10^{-1}$	$\Delta'F_{00}$ (%)
1.00	0.004	0.0192	1.42	12.63	5.63	7.30	1.42	0.00
1.25	0.005	0.1215	1.94	14.26	5.81	7.28	1.94	0.00
1.50	0.006	0.2069	2.55	15.95	5.95	7.00	2.55	0.00
1.75	0.007	1.2803	3.26	17.73	6.13	7.03	3.26	0.00
2.00	0.008	1.3445	4.08	19.62	6.31	7.05	4.08	0.00
2.25	0.009	1.3995	5.00	21.52	6.45	6.89	5.01	–0.20
2.50	0.010	1.4498	6.06	23.63	6.65	7.00	6.06	0.00
2.75	0.011	1.4605	7.24	25.76	6.82	6.98	7.24	0.00
3.00	0.012	1.5332	8.56	28.01	7.00	7.00	8.56	0.00
3.25	0.013	1.5680	10.01	30.32	7.18	7.02	10.01	0.00

A = 1.57 (cal) B = 7.0×10^2 C = 4.9×10^4 D = $(7 \pm .30) \times 10^5$

TABLE-5(B)
DATA AND RESULTS OF CADMIUM-PYRIDOXYNATE-OXALATE SYSTEM

Pyridoxine = 2×10^{-3} M, $E_{1/2}(M) = 0.588$ *vs.* SCE

$[X]\ 10^2$	$\Delta'E_{1/2}$	log Im/Ic	$F_{00} \times 10^{-1}$	$'F_{10} \times 10^{-2}$	$'F_{20} \times 10^{-4}$	$'F_{30} \times 10^{-5}$	F_{00} (cal) $\times 10^{-1}$	$\Delta'F_{00}$ (%)
1.00	0.010	2.289	3.87	3.87	–	–	3.88	–0.25
1.25	0.011	2.363	4.96	4.96	4.39	7.20	4.95	+0.20
1.50	0.012	2.385	6.09	6.09	4.40	6.67	6.09	0.00
1.75	0.013	2.429	7.27	7.27	4.42	6.86	7.27	0.00
2.00	0.014	2.464	8.51	8.52	4.45	7.50	8.52	–0.11
2.25	0.015	2.494	9.83	9.83	4.46	7.02	9.82	+0.10
2.50	0.016	2.517	11.19	11.19	4.48	7.20	11.18	+0.09
2.75	0.017	2.535	12.62	12.62	4.49	6.91	12.61	+0.07
3.00	0.018	2.550	14.10	14.10	4.50	6.67	14.10	0.00
3.25	0.019	2.562	15.10	15.63	14.52	6.77	15.63	+0.06

A = 1.57 (cal) B = 7.0×10 C = 4.9×10 D = $(7.00 \pm .30) \times 10$

TABLE-6
FORMATION CONSTANTS FOR SIMPLE COMPLEXES

Systemes	$\log \beta_{01}$	$\log \beta_{02}$	$\log \beta_{03}$
Pyridoxine	1.38	2.33	–
Succinate	1.48	2.90	3.40
Maleate	1.70	2.65	3.38
Malonate	1.70	2.75	3.22
Malate	1.90	2.80	3.40
Oxalate	2.45	3.84	3.89

The stability constants β_{11} and β_{12} were evaluated from two values of B; two values of C gave two values of β_{21} which are in good agreement with each other. $\log \beta_{30}$ will agree with the mean values of D. The results are presented in Table-7.

TABLE-7
VALUES OF STABILITY CONSTANTS OF MIXED-LIGAND COMPLEXES OF Cd(II) WITH CARBOXYLIC ACIDS AND PYRIDOXINE

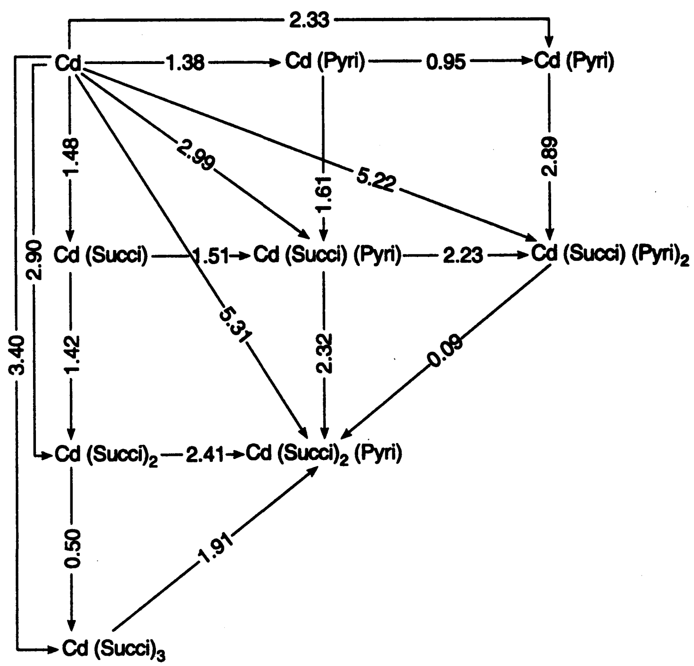
Systems	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$
Cd-Pyri-Succi	2.99	5.22	5.31
Cd-Pyri-Malea	2.99	4.92	5.06
Cd-Pyri-Malo	2.99	5.14	5.27
Cd-Pyri-Mala	2.67	5.22	5.28
Cd-Pyri-Oxa	3.68	5.90	6.36

The experimental values of D should also coincide with β_{30} at the final concentration of dicarboxylate.

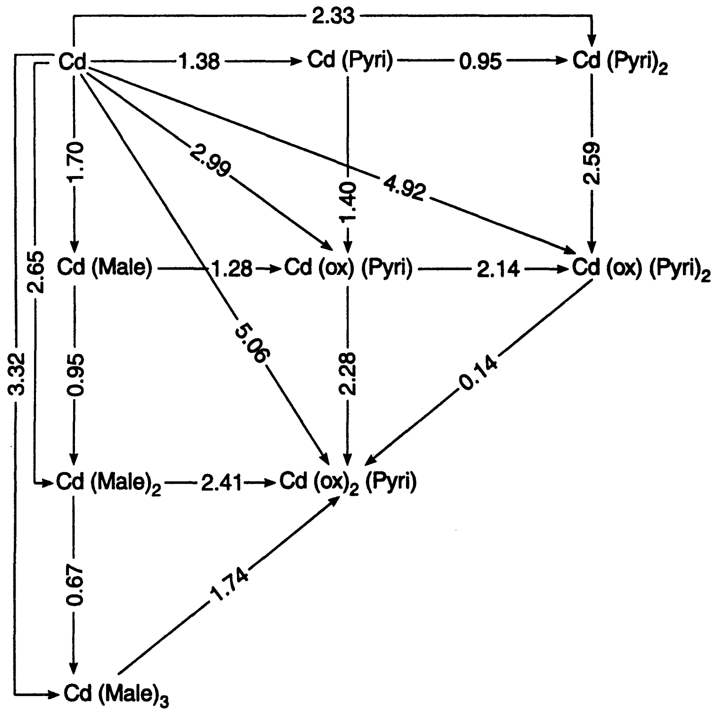
All the pyridoxynate ions have been replaced and only Cd (carboxylate)$_3$ complexes exist in solution. This indeed is found to be so (log $\beta_{30} = 11.79$).

The results are summarised in the form of **Schemes 1–5** where the numerical values indicate the log of equilibrium constants.

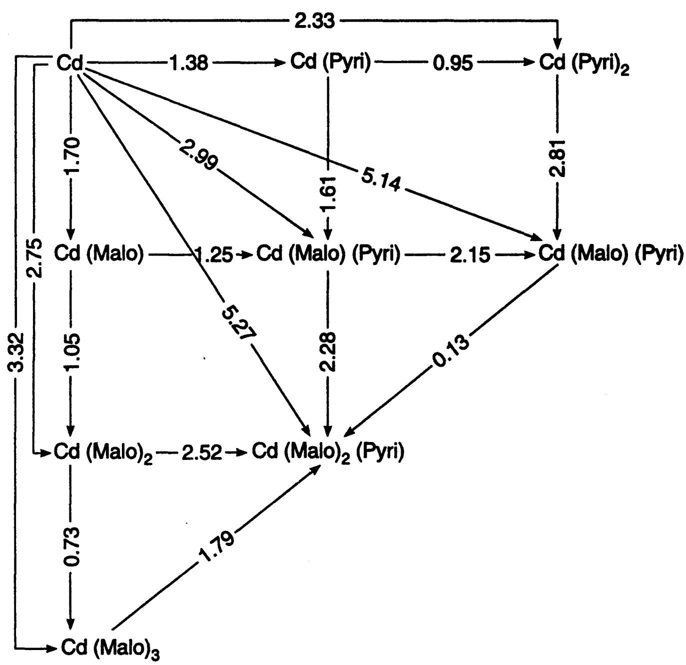
The mixed ligand complex formation may also be explained by considering **Schemes 1 to 5**. The tendency to add x (x = oxalic, malic, maleic, malonic and succinic acid) can be compared. The logarithm of stability constants of the above complexation are (0.95, 6.36), (0.95, 5.28), (0.95, 5.06), (0.95, 5.27), (0.95, 5.31) for Cd-pyridoxynate-oxalate, Cd-pyridoxynate-malate, Cd-pyridoxynate-maleate, Cd-pyridoxynate-malonate, Cd-pyridoxynate-succinate systems respectively and shows that the mixed ligand complexation is fovoured. Log values of stability constants for the addition of carboxylic acids to [Cd(Pyridoxynate)$_2$], [Cd(pyridoxynate)(dicarboxylate) and [Cd(di-carboxylate)$_2$ (3.57, 2.68, 1.05), (2.89, 2.61, 0.6), (2.59, 2.28, 0.67), (2.81, 2.28, 0.73) and (2.89, 2.32, 0.50) for (Cd-pyridoxynate-oxalate), (Cd-pyridoxynate-malate), (Cd-pyridoxynate-maletate), (Cd-pyridoxynate-malonate) and (Cd-pyridoxinate-succinate) systems respectively.



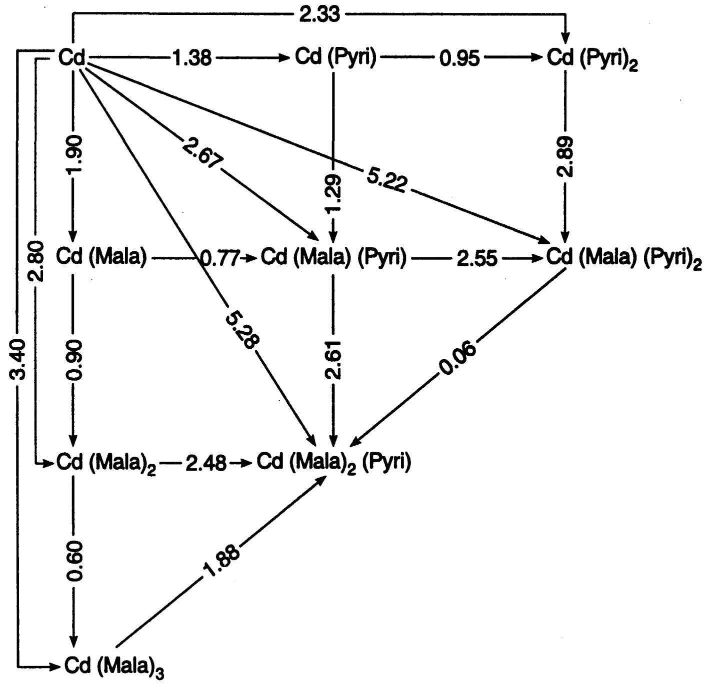
Scheme-1. Cadmium-Pyridoxynate-Succinate System



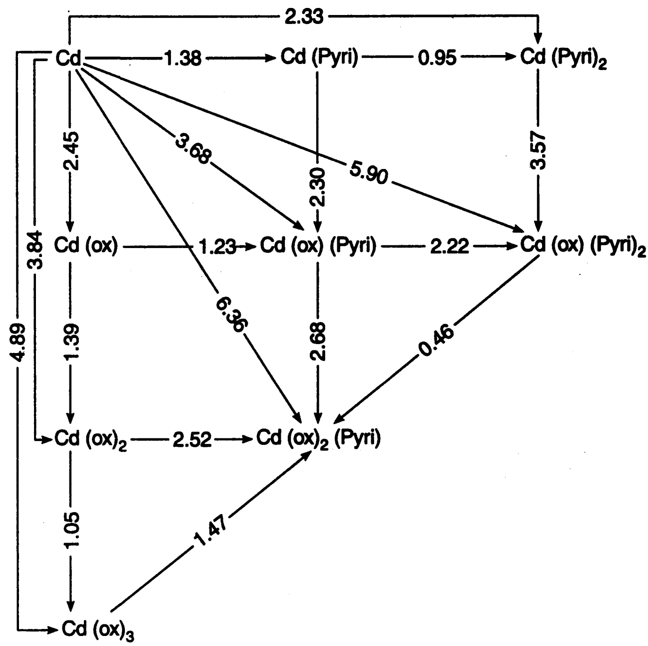
Scheme-2. Cadmium-Pyridoxynate-Maleate System



Scheme-3. Cadmium-Pyridoxynate-Malonate System



Scheme-4. Cadmium-Pyridoxynate-Malate System



Scheme-5. Cadmium-Pyridoxynate-Oxalate System

This shows that the addition of dicarboxylic acid is preferred to a weaker ligand (pyridoxine). The tendency to add dicarboxylic acids to Cd(pyridoxynate) and Cd(di-carboxylate) can also be compared. The log K values are (2.30, 1.39), (1.29, 0.9), (1.40, 0.95), (1.61, 1.05), (1.61, 1.42) for all the systems and shows that formation of mixed complexes is favoured by an amount corresponding to that predicted by the statistical factor.

The values of β_{21} are much higher than β_{30}; so [Cd(dicarboxylate) (pyridoxynate)] is more stable than $Cd(ox)_3$ and this is because of the very close values of the stability constants of both the ligands (stronger and weaker).

The tendency of formation of simple and mixed complexes can be easily expressed by calculating the disproportion constant K^D for the equilibria:

$$2Cd(xy) \Leftrightarrow Cd(x)_2 + Cd(y)$$

The value of log K^D is –0.6 statistically but the observed values are found to be –1.19, –0.21, –1.00, –0.9 and –0.75 for the Cd(pyridoxinate) (oxalate), Cd(pyridoxynate)(malate), Cd(pyridoxynate)(maleate), Cd(pyridoxynate)(malonate), Cd(pyridoxynate)(succinate) respectively. Nagative values of log K^D for each equilibriium account for the stability of the mixed ligand complexes.

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