

Studies on Complex Formation by Di(2-pyridyl)amine & 2-Aminopyridine with Metal Ions in Aqueous Solution: Evaluation of Enthalpies & Entropies of Complex Formation with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) & Cd(II) & Ligand Field Stabilization Energies of the Metal Complexes

A. K. BASAK & D. BANERJEA*

Department of Chemistry, Calcutta University, Calcutta 700009

Received 20 August 1975; accepted 6 October 1975

The formation constants of the complexes formed by di(2-pyridyl)amine and 2-aminopyridine with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in aqueous solution have been evaluated *pH*-metrically at different temperatures in the range of 25-40°, following the method of Rossotti and Rossotti and from these data the corresponding values of enthalpies and entropies of complex formation have been evaluated, as well as the ligand field stabilization energies of the Co(II), Ni(II) and Cu(II) complexes following the method of George and McClure. The results have been compared with literature data on the complexes of 2,2'-dipyridyl. Di(2-pyridyl)amine has been found to form much more stable complexes than 2-aminopyridine and thus resembles 2,2'-dipyridyl. 2-Aminopyridine also forms complexes which are much more stable than those of pyridine. Ligand field stabilization energy values indicate that the bis-complex formed by Cu(II) with di(2-pyridyl)amine is of low tetragonality while the corresponding bis-complex of 2-aminopyridine has a high degree of tetragonal distortion.

FROM structural considerations the complexing ability of di(2-pyridyl)amine and a comparison of its behaviour in this regard with those of 2,2'-dipyridyl and 2-aminopyridine appeared worthy of investigation. The formation constants of the complexes formed by 2,2'-dipyridyl with Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ ions are reported in the literature¹. The results of studies on the complexes formed by these metal ions with di(2-pyridyl)amine and 2-aminopyridine are reported in this paper.

Materials and Methods

Di(2-pyridyl)amine, C₁₀H₉N₃ (Reilly Tar & Chemical Corp., USA) was purified before use by recrystallization from hot ethanol and its purity checked by its melting point (95°).

2-Aminopyridine, C₅H₆N₂, a pure product obtained from E. Merck was used. Its aqueous solution (~0.03M) was prepared and standardized by *pH*-metric titration with acid.

Stock solutions containing the metal ions were prepared by dissolving the corresponding nitrates (GR, E. Merck or AR, BDH) in doubly distilled water containing a small amount of reagent grade HNO₃ (freed from nitrous fumes by aeration after dilution with water as usual). The solutions were standardized by usual methods for the estimation of the metals. From a knowledge of the metal concentration the amount of the free acid in the solution was ascertained by eluting a known volume

of the solution through a strong cation exchanger (Dowex 50WX-8 in the H⁺ form) and titrating the HNO₃ in the effluent with standard alkali as usual.

All other chemicals used were of reagent quality; distilled water redistilled with a little KMnO₄ and KOH in an all-glass still was used in making all the solutions which were stored in Jena glass vessels.

A Philips *pH*-meter, PR 9405M, was used for *pH* measurements (accuracy better than ±0.01) using glass and calomel electrodes. The set was first calibrated before use with solutions of known [H⁺], so that from the measured *pH* values the corresponding [H⁺] could be ascertained accurately. Ionic strength of the experimental solution was maintained constant at 0.1M with requisite quantity of KNO₃ ([KNO₃] + [HNO₃] = 0.1 M).

Evaluation of equilibrium constant for the protonation of the ligands and the formation constants of the complexes—The equilibrium constants for the protonation of the ligands were evaluated graphically (cf. Figs. 1 and 2, for data at 25°) from measurements of *pH* values of solutions containing the ligand and HNO₃ in different proportions in the manner described earlier². The results indicate that both the ligands add only one proton with practically no tendency to add a second proton in weakly acidic solutions.

From the measured *pH* values of the solutions containing known concentrations of a metal ion, a ligand and HNO₃ the value of the formation function \bar{n} , i.e. the average number of moles of the ligand bound per mole of the metal ion, could

*Author to whom all correspondence to be made.

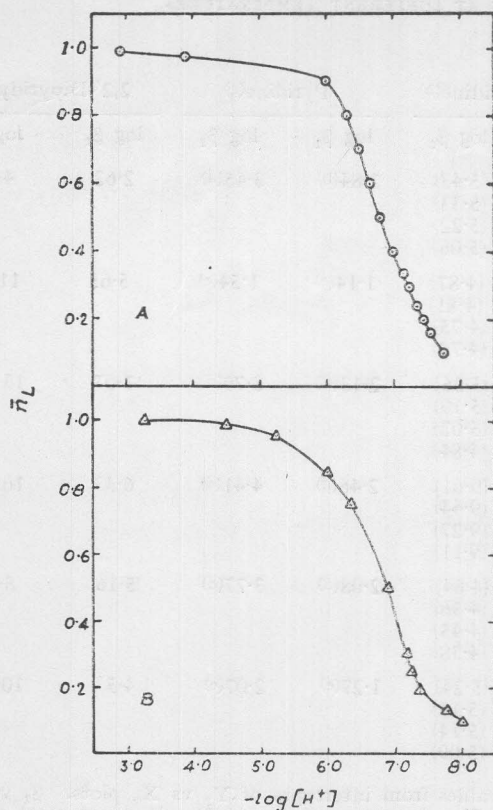


Fig. 1 — Protonation of the ligands (25°; μ , 0.1M) [(A) Di(2-pyridyl)amine, 0.005M and (B) 2-aminopyridine, 0.01M]

be evaluated². The formation curves for 25° are shown in Fig. 3 for the different metal complexes of both the ligands. From the \bar{n} values thus obtained for solutions having a particular concentration of metal ion and different concentrations of a ligand the values of the overall formation constants (β_1 and β_2) were evaluated graphically (cf. Figs. 4 and 5 for results at 25°) following the method of Rossotti and Rossotti³ as described earlier².

The nature of plots in Fig. 5 indicates that no detectable amount of the tris or higher complexes are formed under the experimental conditions.

Evaluation of thermodynamic parameters and ligand field parameters energies — From the values of the formation constants (β_1 and β_2) obtained at different temperatures the enthalpy (ΔH_x) and entropy (ΔS_x) of complex formation were evaluated graphically from the plot of $\log \beta_x$ ($x = 1, 2$) vs $1/T$ as usual. Using the ΔH_x values, the values of the ligand field stabilization energies, δH_1 and δH_2 , for the mono- and the bis-complexes respectively of the transition metal ions were evaluated following George and McClure⁴. The $\Delta H'_x$ ($x = 1, 2$) values which represent the enthalpy changes in the formation of the complexes in solution from the gaseous metal ion and the ligand in solution have been evaluated from Eq. (1)

$$\Delta H'_x = \Delta H_h + \Delta H_x \quad \dots(1)$$

where ΔH_h is the enthalpy of hydration of the gaseous metal ion.

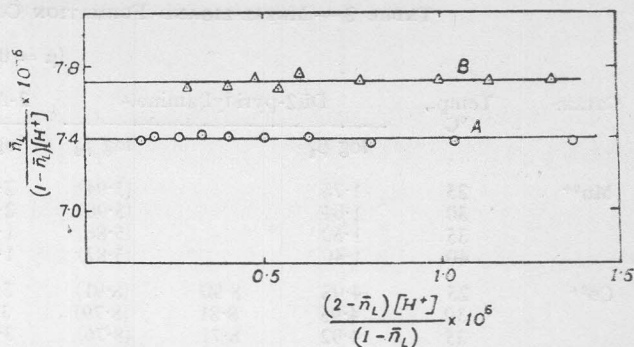


Fig. 2 — Graphical evaluation of protonation constant of ligand (25°; μ , 0.1M) [(A) Di(2-pyridyl)amine, 0.005 M and (B) 2-aminopyridine, 0.01M]

TABLE 1 — LIGAND PROTONATION CONSTANTS AT DIFFERENT TEMPERATURES

Ligand	$(\mu = 0.1M)$			
	log k_1^* at 25°	30°	35°	40°
Di(2-pyridyl)amine	6.87	6.79	6.76	6.73
2-Aminopyridine	6.89	6.66	6.48	6.28
Pyridine	5.33	—	—	—
2,2'-Dipyridyl	4.44	—	—	—

(ref. 1, Table No. 275)
(ref. 1.)

*Values better than ± 0.02 .

Results and Discussion

Values of the protonation constant, K_1 , of each ligand at four different temperatures are given in Table 1. The values of the formation constants at four different temperatures are given in Table 2.

It appears that although di(2-pyridyl)amine resembles 2-aminopyridine very closely in its basicity, it forms much more stable complexes than the latter and in this respects it resembles 2,2'-dipyridyl. This seems to suggest that in the formation of metal ion complexes of di(2-pyridyl)amine bonding from the nitrogen atoms of each of the two pyridine rings takes place as in the case of 2,2'-dipyridyl. Data in Table 2 further indicate that 2-aminopyridine forms more stable complexes than pyridine. The observed sequence of stabilities of both the mono- and the bis-complexes of di(2-pyridyl)amine and the mono-complexes of 2-aminopyridine with different metal ions of the first transition series studied is $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$, which is in agreement with the Irving-Williams natural order of stabilities⁵. Since the value of the formation constant depends on the ΔH and ΔS values (Table 3), the order of stabilities may show a deviation from the Irving-Williams sequence in some systems. Indeed for the bis-complexes of 2-aminopyridine the observed order of stabilities is $Cu^{2+} > Mn^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$ and the following order has been observed earlier² in the case of the

TABLE 2 — METAL-LIGAND FORMATION CONSTANTS AT DIFFERENT TEMPERATURES

($\mu = 0.1M$)

Cation	Temp., °C	Di(2-pyridyl)amine(a)		2-Aminopyridine(b)		Pyridine(c)		2,2'-Dipyridyl(c)	
		log β_1	log β_2	log β_1	log β_2	log β_1	log β_2	log β_1	log β_2
Mn ²⁺	25	1.78	(5.94)	2.19	(5.43)	1.84(b)	3.45(d)	2.62	4.62
	30	1.64	(5.90)	2.07	(5.33)				
	35	1.50	(5.86)	1.97	(5.22)				
	40	1.40	(5.82)	1.88	(5.06)				
Co ²⁺	25	4.98	8.90 (8.91)	3.06	(4.87)	1.14(e)	1.54(e)	5.65	11.25
	30	4.95	8.81 (8.79)	3.05	(4.81)				
	35	4.92	8.71 (8.76)	3.03	(4.75)				
	40	4.89	8.61 (8.63)	3.02	(4.70)				
Ni ²⁺	25	6.76	12.84 (13.05)	3.20	(5.36)	2.13(d)	3.79(d)	7.07	13.93
	30	6.70	12.72 (12.93)	3.17	(5.19)				
	35	6.64	12.62 (12.82)	3.14	(5.02)				
	40	6.60	12.52 (12.64)	3.11	(4.84)				
Cu ²⁺	25	7.60	14.40 (14.38)	5.43	(9.61)	2.46(d)	4.41(d)	6.33	16.28
	30	7.57	14.34 (14.30)	5.42	(9.44)				
	35	7.53	14.29 (14.27)	5.40	(9.27)				
	40	7.50	14.24 (14.20)	5.38	(9.11)				
Zn ²⁺	25	3.70	7.16 (7.27)	2.72	(4.64)	2.08(d)	3.77(d)	5.16	8.9
	30	3.62	7.07 (7.16)	2.69	(4.56)				
	35	3.56	6.98 (7.06)	2.66	(4.45)				
	40	3.49	6.90 (6.95)	2.63	(4.38)				
Cd ²⁺	25	2.89	(4.98)	2.54	(5.24)	1.27(e)	2.07(e)	4.5	10.0
	30	2.86	(4.86)	2.49	(5.19)				
	35	2.83	(4.74)	2.44	(5.14)				
	40	2.80	(4.64)	2.38	(5.09)				

(a) This work: β_1 values from intercepts of Y_1 vs X_1 plot and β_2 values from intercepts of Y_2 vs X_2 plots. β_2 values given within parentheses were obtained from the slopes of the Y_1 vs X_1 plots (see ref. 2 and 3). In those cases where for practical reasons n values much higher than 1 could not be reached within the permissible range of pH even with excess of the ligand, the β_2 values obtained from the slopes of the Y_1 vs X_1 plots are only available. Accuracy of log β_x values is better than ± 0.02 . (b) At 25°; cf. ref. 1, Table 275. (c) At 25°; cf. ref. 1. (d) At $\mu = 1.0M$. (e) At $\mu = 0.5M$.

TABLE 3 — VALUES OF ENTHALPY (ΔH , kcal mole⁻¹) AND ENTROPY (ΔS , e.u) CHANGES AND LIGAND FIELD STABILIZATION ENERGIES (δH , kcal mole⁻¹)(a)

Thermo-dynamic parameters	H ⁺	Mn ²⁺	Co ²⁺	Ni ³⁺	Cu ³⁺	Zn ²⁺	Cd ²⁺
DI-(2PYRIDYL)AMINE							
$\Delta H_h^{(b)}$	—	-654	-697	-716	-716.9	-701.1	—
ΔH_1	-2.8	-10.9	-2.7	-4.4	-2.5	-5.6	-2.1
$\Delta H_1'$	—	-664.9	-699.7	-720.4	-719.4	-706.7	—
ΔS_1	+22.1	-28.3	+13.9	+16.3	+26.6	-1.8	+6.2
δH_1	—	0	18.1	30.5	21.1	0	0
ΔH_2	—	-3.3	-8.5	-9.0	-4.8	-7.3	-10.0
$\Delta H_2'$	—	-657.3	-705.5	-725	-721.7	-708.4	—
ΔS_2	—	+16.2	+12.4	+28.9	+50.1	+8.4	-10.7
δH_2	—	0	27.7	37.0	23.4	0	0
2-AMINOPYRIDINE							
ΔH_1	-17.3	-9.1	-1.2	-2.3	-1.5	-2.6	-4.6
$\Delta H_1'$	—	-663.1	-698.2	-718.3	-718.4	-703.7	—
ΔS_1	-26.4	-20.4	+10.0	+7.0	+19.9	+3.8	-3.7
δH_1	—	0	19.2	31.0	22.9	0	0
ΔH_2	—	-10.7	-4.9	-14.8	-14.3	-7.7	-4.2
$\Delta H_2'$	—	-664.7	-701.9	-730.8	-731.2	-708.8	—
ΔH_2	—	-10.9	+6.0	-25.0	-3.8	-4.5	+10.0
δH_2	—	0	20.7	40.4	31.7	0	0

(a) ΔH_x and ΔS_x values reported here account for log β_x (and log K_1) values at the different temperatures (25-40°) to within ± 0.02 of the experimental values.

(b) The values of the enthalpy of hydration (ΔH_h) of the metal ions which were used in calculating the δH_x ($x = 1, 2$) values were obtained from ref. 4.

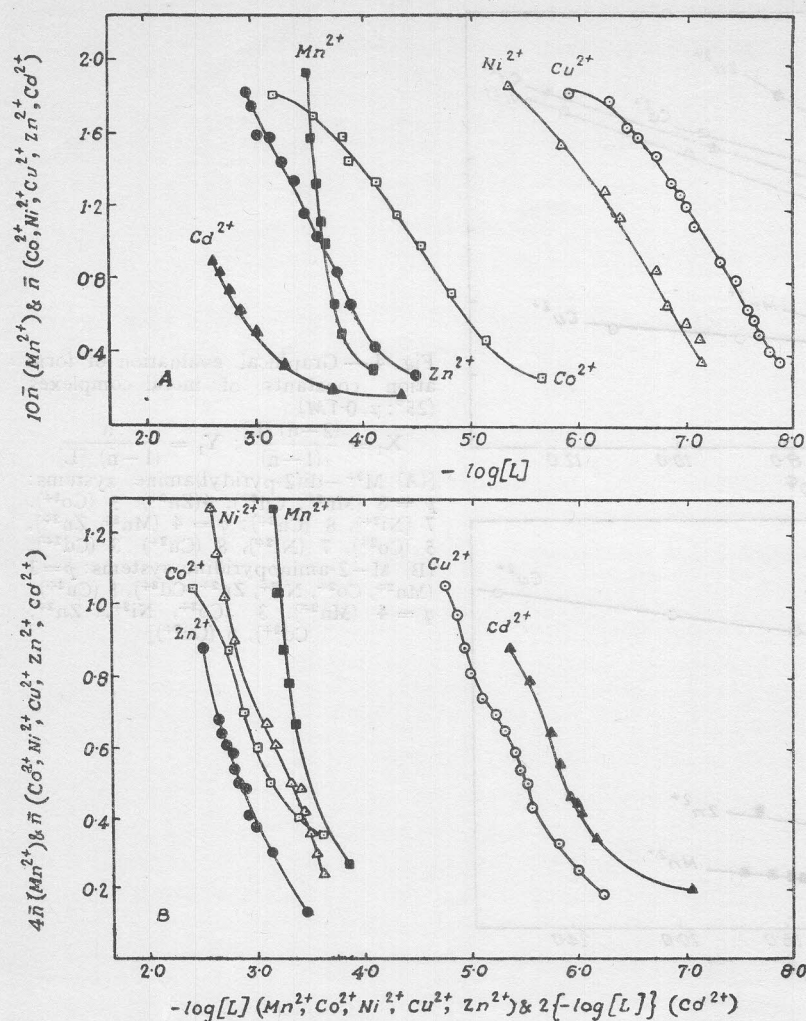


Fig. 3 — Complex formation curves (25°; μ , 0.1M) [(A) M^{2+} — di(2-pyridyl)amine systems: ligand, 0.005M; M^{2+} , 0.001M in all the cases except Mn^{2+} , 0.00085M and (B) M^{2+} — 2-aminopyridine systems: ligand, 0.01M; M^{2+} , 0.001M in all the cases except Mn^{2+} , 0.00085M]

monocomplexes of these metal ions with hydrazine: $Cu^{2+} > Mn^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$.

From the $\Delta H'_x$ values (Table 3) it is seen that for a particular series of complexes of the different transition metal ions the sequence of $\Delta H'_x$ is $Mn^{2+} < Co^{2+} < Ni^{2+} \sim Cu^{2+} < Zn^{2+}$ which is in keeping with the expected trend. It is also seen from the data in Table 3 that of the mono- and the bis-complexes of di(2-pyridyl)amine and of 2-aminopyridine, Ni^{2+} complexes have the highest δH_x values (Table 3), with the values for the Co^{2+} and Cu^{2+} complexes being much less; the order being $Ni^{2+} \gg Cu^{2+} > Co^{2+}$ for the mono-complexes of both the ligands and $Ni^{2+} \gg Co^{2+} > Cu^{2+}$ for the bis-complexes of di(2-pyridyl)amine, while for the bis-complexes of 2-aminopyridine the observed sequence is $Ni^{2+} \gg Cu^{2+} \gg Co^{2+}$.

For perfectly octahedral weak field complexes of Ni(II), Co(II) and Cu(II) it is known that the ligand field stabilization energy values are 12, 8 and 6Dq respectively. However, due to Jahn-Teller distortion the complexes of Cu(II) are always tetragonal which further stabilizes this d^9 system. In most cases because of this additional stabilization due to Jahn-Teller effect the overall stabili-

zation energies of complexes of Cu(II) are higher than those of the corresponding complexes of Co(II). However, in the case of Cu(II) complexes of low tetragonality, ligand field stabilization energy of the copper(II) complex may be nearly the same as or even lower than that of the corresponding cobalt(II) complex. According to Jorgensen⁶ the relatively low value of $\bar{\nu}_{Cu}/\bar{\nu}_{Ni} = 1.2$, where $\bar{\nu}_{Cu}$ and $\bar{\nu}_{Ni}$ are the wavenumbers of the principal ligand field bands of the tris-dipyridyl complexes of Cu(II) and Ni(II) respectively, is indicative of low tetragonality of $Cu(dipy)_3^{2+}$ and in agreement with this the order of δH_3 for the tris-dipyridyl complexes is $Ni^{2+} \gg Cu^{2+} \sim Co^{2+}$, with the value for the Cu(II) complex being only 1 kcal mole⁻¹ higher than that of the Co(II) complex⁴. Hence, the sequence which has been observed now for the bis-complexes of di(2-pyridyl)amine indicates low tetragonality of the bis-complex of Cu(II) with di(2-pyridyl)amine. However, for the bis-complexes of 2-aminopyridine the observed sequence, particularly the much higher δH_2 value of the Cu(II) complex compared to that of the Co(II) complex, indicates a tetragonal distortion of high degree in this Cu(II) complex.

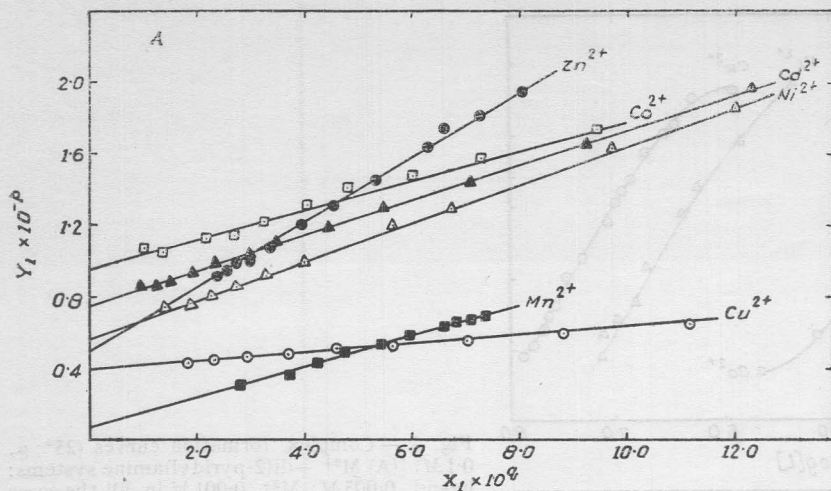


Fig. 4—Graphical evaluation of formation constants of metal complexes (25°; μ, 0.1M)

$$X_1 = \frac{(2-\bar{n}) [L]}{(1-\bar{n})}; Y_1 = \frac{\bar{n}}{(1-\bar{n}) [L]}$$

[(A) M²⁺-di(2-pyridyl)amine systems: p = 3 (Mn²⁺, Cd²⁺), 4 (Zn²⁺), 5 (Co²⁺), 7 (Ni²⁺), 8 (Cu²⁺); q = 4 (Mn²⁺, Zn²⁺), 5 (Co²⁺), 7 (Ni²⁺), 8 (Cu²⁺), 3 (Cd²⁺). (B) M-2-aminopyridine systems: p = 3 (Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺), 5 (Cu²⁺); q = 4 (Mn²⁺), 3 (Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺), 6 (Cu²⁺)]

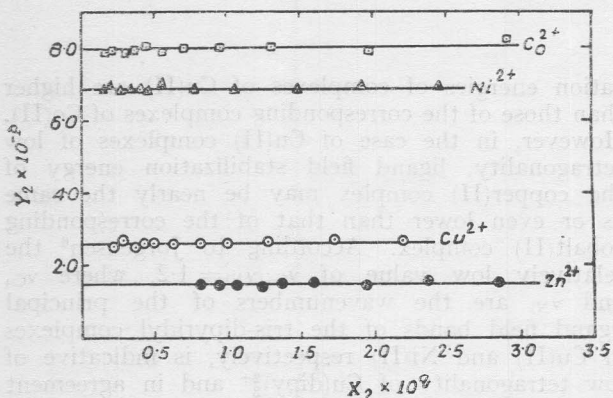
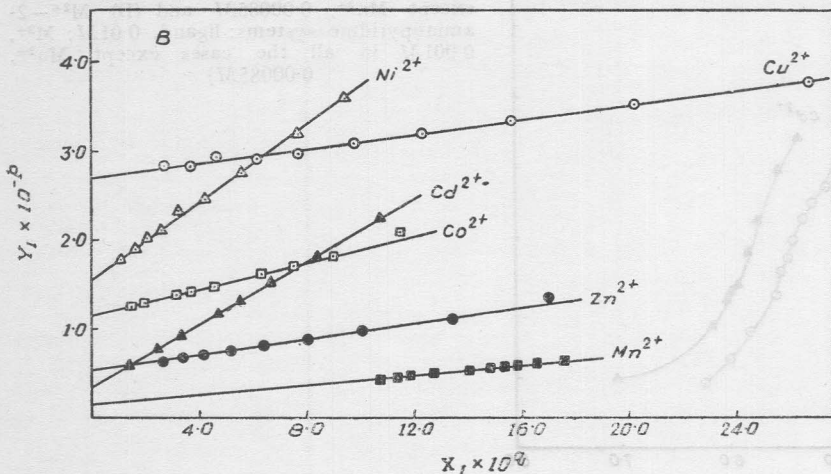


Fig. 5—Graphical evaluation of β₂ values of the metal complexes of di(2-pyridyl)amine (25°; μ, 0.1M) [M²⁺ and ligand concentrations as in Fig. 4

$$X_2 = \frac{(3-\bar{n}) [L]}{(2-\bar{n})}; Y_2 = \frac{\bar{n} - (1-\bar{n})\beta_1 [L]}{(2-\bar{n}) [L]^2}; p = 4 (Cd^{2+}), 7 (Zn^{2+}), 8 (Co^{2+}), 12 (Ni^{2+}), 14 (Cu^{2+}); q = 2 (Cd^{2+}), 3 (Co^{2+}, Zn^{2+}), 5 (Ni^{2+}), 6 (Cu^{2+})]$$

Acknowledgement

This investigation has been carried out with financial assistance from the CSIR, New Delh. The award of a research fellowship to one of us (A.K.B.) by the said council is thankfully acknowledged.

References

- SILLEN, L. G., *Stability constants of metal-ion complexes* (The Chemical Society, London), spl. publication No. 17, 1964 and No. 25, 1971, Table No. 783.
- BANERJEA, D. & SINGH, I. P., *Z. anorg. allgem. Chem.*, **349** (1967), 213.
- ROSSOTTI, F. J. C. & ROSSOTTI, H. S., *Acta. chem. Scand.*, **9** (1955), 1166.
- GEORGE, P. & MCCLURE, D. S., *Progress in inorganic chemistry* Vol. 1, edited by F. A. Cotton (Interscience, New York), 1959, 428.
- IRVING, H. & WILLIAMS, R. J. P., *Nature, Lond.*, **162** (1948), 746.
- JORGENSEN, C. K., *Absorption spectra and chemical bonding in complexes* (Pergamon Press, Oxford), 1962, 124.