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Molar Conductometric and Stepwise Potentiometric Studies on Chromium(III)-, Manganese(II)-, Copper(II)-, and Silver(I)-2,2′-Dipyridyl-Salicylaldoxime-Benzamide Complexes

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Molar conductivity titrations and conductometric measurements as well as pH-metric studies were done on Cr(III), Mn(II), Cu(II), and Ag(I) with 2,2′-dipyridyl (Dipy), salicylaldoxime (SD) and benzamide (BAM) at 35° and 45°C. Conductivity and potentiometry studies indicated the formation of 1 : 1, 1 : 2 and 1 : 3 Cr(III)-, Mn(II) and Cu(II)- and 1 : 1 and 1 : 2 Ag(I)-Dipy or BAM, 1 : 1 and 1 : 2 Cr(III)-, Mn(II)-, Cu(II)- and Ag(I)-SD, 1 : 1 : 1 Cr(III)-, Mn(II)-, Cu(II)- and Ag(I)-Dipy-SD, Dipy-BAM and SD-BAM and 1 : 1 : 1 : 1 Cr(III)-, Mn(II)-, Cu(II)-, and Ag(I)-Dipy-SD-BAM complexes. Complexation takes place through two coordinate bonds between the metal ions and the two nitrogen atoms of Dipy, two covalent bonds between the metal ions and the phenolic OH and oximic OH groups of salicylaldoxime, and coordinate and covalent bonds between the metal ions and the benzoyl CO and amide NH groups of BAM. Proton-ligand and metal ligand(s) conditional stability constants at 35 and 45°C were estimated. Thermodynamic parameters (Δ°G, ΔH, ΔS) at 35 and 45°C of binary, ternary and quaternary complexes were evaluated.

INTRODUCTION

Conductometry and potentiometry are electroanalytical techniques for the determination of the stoichiometric composition of the formed complexes as well as the amount of substances in solution from the measurements of molar conductivity and electromotive force (pH) values, respectively. The literature survey reveals that extensive studies had been carried out on binary, ternary and quaternary systems involving transition metal ions.[1–5] Irving and Rossotti[6] studied the formation curves of proton-ligand and metal-ligand systems from pH titration curves in mixed ligand solutions.

The present investigation is conducted to throw further insights on applying conductometric titrations and conductometric measurements procedure for tracing complex formation, stoichiometric composition of complexes and introducing the method for microdetermination of metals under study, and potentiometric titrations as an analytical technique for evaluation of K_f, Δ°G, –ΔH and –ΔS of the formed complexes.

EXPERIMENTAL

All chemicals used were purchased from Aldrich, Sigma, BDH, E. Merck or Ridel de Haëm companies (A.R. 99.9%).

1×10^{-3} M solutions of Dipy, SD, and BAM were prepared[7] by dissolving the appropriate amounts of the reagents in bidistilled water while Dipy was dissolved in 50% ethanol (EtOH-H_2O mixture). 1×10^{-3} M Cr(III), Mn(II), Cu(II) or Ag(I) solutions were prepared by dissolving the appropriate amounts of $CrCl_3$, $MnCl_2 \cdot 4H_2O$, $CuCl_2$ or $AgNO_3$ in redistilled water. 1×10^{-2} M of a carbonate free NaOH solution was prepared by dissolving the appropriate amount of NaOH pellets in previously boiled bidistilled water and the resulting solution was standardised against standardised HCl. 1×10^{-2} M HNO_3 was prepared by appropriate dilution of the conc. A.R. acid using bidistilled water, and the resulting solution was standardised against standard Na_2CO_3 solution. 1×10^{-2} M $NaNO_3$ was prepared by dissolving the requisite amount of dried crystallised salt in bidistilled water.

The conductometric titrations were carried out by titrating a certain concentration (v_1) of the ligand or ligands mixture (25 mL of 1×10^{-4} M) with 0.25 mL of 1×10^{-3} M increments of the metal ion solution (v_2). The conductance values were measured at 35 and 45°C after each addition of metal ion and thoroughly stirring the reaction mixture for five minutes with a magnetic stirrer and the specific conductance, λ, was corrected due to dilution effect $\left[\frac{\lambda(v_1 + v_2)}{v_1}\right]$.

In conductometric measurements, two series of solutions were prepared. In the first series, the metal ion solution was kept constant at 5×10^{-5} M and the ligand (1×10^{-5}–1×10^{-4} M) or ligands mixture (biligand, 1×10^{-5}–1×10^{-4} M; triligand, 3×10^{-6}–25×10^{-6} M) was varied. In the second series, the ligand (ligands) concentration was kept constant at 1×10^{-4} M and the metal ion concentrations were varied [Cr(III), 1×10^{-10} g –2×10^{-6} g, Mn(II), 1×10^{-10} g– 25×10^{-7} g; Cu(II), 2×10^{-10} g–25×10^{-9} g and Ag(I), 2×10^{-10} g –2×10^{-9} g]. In the two series of solutions, the total volume of the reaction mixture was diluted to 25 mL in measuring flasks using bidistilled water. The mixtures were thermostated at 35 and 45°C for 2 h using Ultrathermostat, HAAKE, Model NB-22, then the specific conductance was measured using YSI Scientific Model 35 Conductometer.

In Potentiometric Studies [6] the proton-ligand and the metal-ligand(s) formation stability constants were computed by Bjerrum-Calvin pH titration as adopted by Irving-Rossotti using DR-LANGE Digital pH-Meter. Following sets of titrations were performed under nitrogen atmosphere against standard carbonate-free 0.01 M NaOH solution at fixed ionic strength (I = 0.01 M $NaNO_3$). ~~The solutions were~~ thermostated at 35 and 45°C and the total volume in each set was kept at 50 mL using bidistilled water: (i) 5 mL of 1×10^{-2} M HNO_3 + 1 mL of 1×10^{-2} M $NaNO_3$, (ii) mixture (i) + 5 mL of 1×10^{-3} M of ligand (Dipy, SD or BAM), (iii) mixture (i) +1 mL of 1×10^{-3} M of metal ion solution, (iv) mixture

(i) + 10 mL of 1×10^{-3} M of Dipy + SD, Dipy + BAM or SD + BAM, (v) mixture (iv) + 1 mL of 1×10^{-3} M of M^{n+}, (vi) mixture (i) + 15 mL of 1×10^{-3} M of Dipy + SD + BAM, (vii) mixture (vi) + 1 mL of 1×10^{-3} M of M^{n+}.

RESULTS AND DISCUSSION

Formation of binary, ternary and quaternary complexes is evidenced by the comparison of conductometric and potentiometric titration curves. Stoichiometric composition, protonation constants of the ligands (K), formation constants (K_f) of the complexes, free energy changes (Δ°G), enthaply (ΔH), and entropy (ΔS) values at 35 and 45°C are evaluated and collected in Tables 1–5. Ω^{-1}-V, pH-V, n^{-}A-pH and n^{-}-pL are calculated and represented graphically in Figures 1 and 2.

The results of the conductometric titrations and measurements (at constant metal ion or ligand concentration) reveal the formation of 1:1 and 1:2 Cr(III)-, Mn(II)-, Cu(II)- and Ag(I)-Dipy, SD and BAM complexes at 35 and 45°C, 2:1:1, 1:1:1 Cr(III)-, Mn(II)-, Cu(II)- and Ag(I)- Dipy-SD, Dipy-BAM and SD-BAM complexes at 35 and 45°C, 1:1:1:1 Cr(III)-, Mn(II)-, Cu(II)- and Ag(I)-Dipy-SD-BAM complexes at 35 and 45°C. The conductance values increase with the increase of ligand and/or metal ion concentration as a result of the increase of the diffusion coefficient of the diffusion particles. Increase of conductance may be ascribed to the liberation of chloride ions from $CrCl_3$, $MnCl_2$, $CuCl_2$ and nitrate ion from $AgNO_3$, and hydrogen ions from SD and BAM having faster movements and high mobility which are liable to increase the conductance power of the solution[8]. The formation of binary, ternary and quaternary complexes leads to increase in the conductance values. The conductometric measurement method was utilised as an analytical method for the microanalytical determination of Cr(III), Mn(II), Cu(II) and Ag(I) on using constant concentration of individuals or mixtures of ligands as microanalytical reagents and variable concentrations of metal ions. On using Dipy, $5–12.5 \times 10^{-7}$ g Cr(III), $5–12.5 \times 10^{-7}$ g Mn(II), $5–12.5 \times 10^{-10}$ g Cu(II), $7.5–12.5 \times 10^{10}$ g Ag(I) at 35°C, $7.5–12.5 \times 10^{-7}$ g Cr(III), $7.5–12.5 \times 10^{-7}$ g Mn(II), $10–25 \times 10^{10}$ g Cu(II), and $5–12.5 \times 10^{-10}$ g Ag(I) at 45°C were determined. Also, SD is made use of for the determination of $7.5–12.5 \times 10^{-7}$ g Cr(III) and Mn(II), $5–12.5 \times 10^{-10}$ g Cu(II) and $5–12.5 \times 10^{-10}$ g Ag(I) at 35°C, and $2.5–10 \times 10^{-10}$ g Cr(II), $5–12.5 \times 10^{-10}$ g Mn(II), $7.5–12.5 \times 10^{-10}$ g Cu(II) and $5–25 \times 10^{-10}$ g Ag(I) at 45°C. On introducing BAM as a microanalytical reagent, $5–12.5 \times 10^{-7}$ g Cr(III), $4.99–12.49 \times 10^{-7}$ g Mn(II), $5–25 \times 10^{10}$ g Cu(II) and $7.5–12.5 \times 10^{-10}$ g Ag(I) at 35°C. On using mixture of Dipy-SD, $5–25 \times 10^{-10}$ g Cr(III), $2.5–12.5 \times 10^{-10}$ g Mn(II), $7.5–12.5 \times 10^{-10}$ g Cu(II), and $5–12.5 \times 10^{-10}$ g Ag(I) at 35°C and $5–12.5 \times 10^{-10}$ g Cr(III), $1.25 \times 10^{-10}–2.5 \times 10^{-9}$ g Mn(II), $5–12.5 \times 10^{-10}$ g Cu(II) and $1–12.5 \times 10^{-10}$ g Ag(I) at 45°C. $7.5–12.5 \times 10^{-10}$ g Cr(III), $5–12.5 \times 10^{-10}$ g Mn(II) and Ag(I) and $2.5–12.5 \times 10^{-10}$ g Cu(II) and $7.5–12.5 \times 10^{10}$ g Cr(III), $0.1–1.25 \times 10^{-10}$ g Mn(II), $5–12.5 \times 10^{-10}$ g Cu(II) and Ag(I) can be estimated on using Dipy-BMA mixture at 35 and 45°C, respectively. On applying SD-BAM mixture as a microanalytical reagent, $7.5–12.5 \times 10^{-7}$ g Cr(III), $4.99–12.49 \times 10^{-7}$ g Mn(II), $5–25.5 \times 10^{-10}$ g Cu(II) and $2.5–11.25 \times 10^{-10}$ g Ag(I) at 45°C can be assayed.

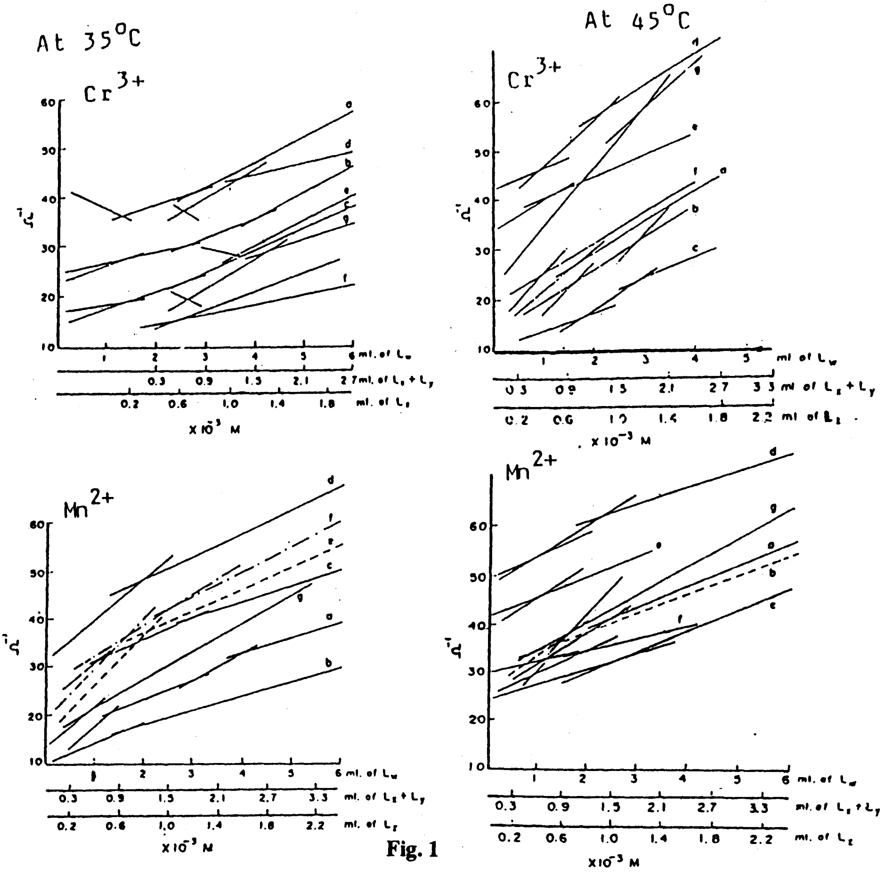

At 35°C
At 45°C
Cr3+
Mn2+
λ⁻¹
10
20
30
40
50
60
1 2 3 4 5 6 ml. of Lw
0.3 0.9 1.5 2.1 2.7 3.3 ml. of Lz + Ly
0.2 0.6 1.0 1.4 1.8 2.2 ml. of Lz
x10⁻³ M
a
b
c
d
e
f
g

Fig. 1

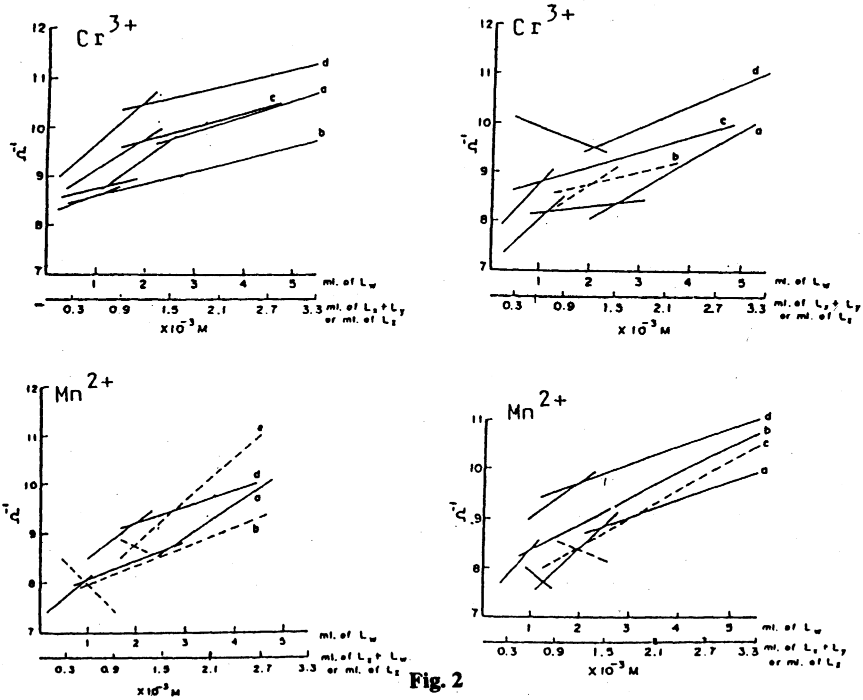

Cr3+
Mn2+
λ⁻¹
7
8
9
10
11
12
1 2 3 4 5 ml. of Lw
0.3 0.9 1.5 2.1 2.7 3.3 ml. of Lz + Ly or ml. of Lz
x10⁻³ M
a
b
c
d

Fig. 2

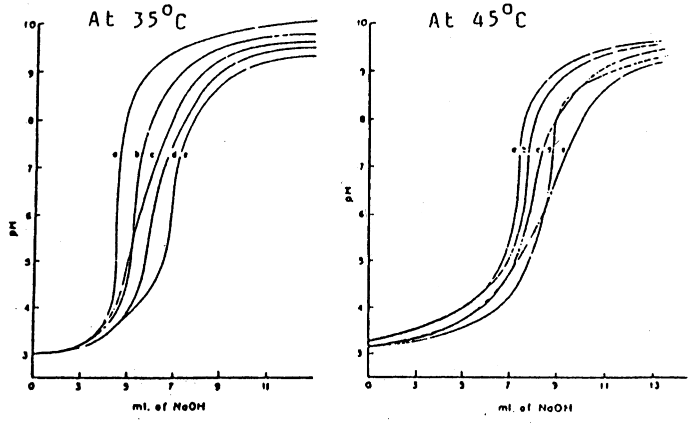


Fig. 3a. Formation curres of (a) $HNO_3 + NaNO_3$; (b) a + Dipy; (c) b + SD; (d) b + BAM; (e) C + BAM

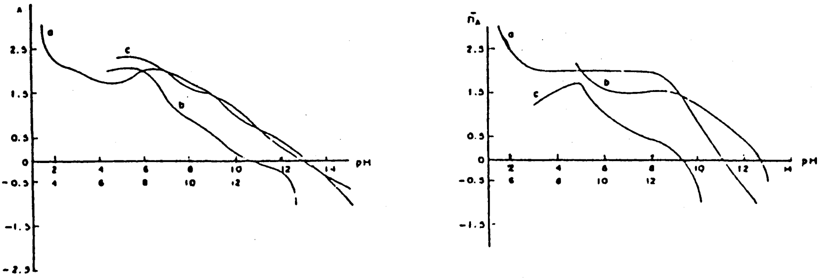


Fig. 3b. $N\bar{A}$-pH relation (a) $HNO_3 + NaNO_3$ + Dipy + SD + BAM; (b) $HNO_3 + NaNO_3$ + Dipy + SD; (c) $HNO_3 + NaNO_3$ + Dipy + BAM

On using mixed Dipy-SD-BAM ligands, $5–10 \times 10^{-10}$ g Cr(III), Mn(II), and Ag, 2.5×10^{-10} g Cu(II), and $12.5–25 \times 10^{-10}$ g Cr(III), $2.5–10 \times 10^{-10}$ g Mn(II), Cu(II) and $5–10 \times 10^{-10}$ g Ag(I) at 35 and 45°C, respectively, can also be estimated.

Proton-Ligand Stability Constants:

In the absence of metal ions, the ligands offered two well-separated buffer regions, pH (3.9–9.5) and pH (4.0–9.0), pH (3.5–8.75), and pH (3.0–8.5) and pH (3.5–8.5) obviously due to successive protonation of the two nitrogen atoms of the dipyridyl, deprotonation of the phenolic OH and the oximic OH groups of salicylaldoxime and protonation of the benzoyl CO and deprotonation of the amide NH groups of benzamide at 45°C, respectively, accordingly,

$$\text{(a)}\quad \underset{(L)}{C_6H_4NNC_6H_4} \overset{K_{CN}}{\rightleftharpoons} \overset{H}{C_6H_4NHNC_6H_4} \overset{K_{CNH}}{\rightleftharpoons} \underset{(LH_2)^{+2}}{C_6H_4NHNHC_6N_4} \quad (1)$$

(b) $$\underset{(LH_2)}{HO{\cdot}C_6H_4{\cdot}CH{\cdot}NOH} \underset{H}{\overset{K^{H}_{OH}}{\rightleftharpoons}} O^{-}{\cdot}C_6H_4{\cdot}CH{\cdot}NOH + H^{-}$$

$$\underset{(LH^{-})}{O{\cdot}C_6H_4{\cdot}CH{\cdot}NOH} \overset{K^{H}_{NOH}}{\rightleftharpoons} O^{-}{\cdot}C_6H_4{\cdot}CH{\cdot}NO^{-} + H^{+} \qquad (2)$$

(c) $$\underset{(LH^{-})}{OC{\cdot}C_6H_4{\cdot}NH_2} \overset{K^{H}_{CO}}{\rightleftharpoons} \underset{(LH_2)}{HOC{\cdot}C_6H_4{\cdot}NH_2} \overset{K^{H}_{NH_2}}{\rightleftharpoons} \underset{(L^{-})}{OC{\cdot}C_6H_4{\cdot}NH^{-} + 2H^{+}} \qquad (3)$$

This is evident that Dipy is titrated as nonprotic acid, SD as biprotic and BAM as monoprotic acid under the same experimental conditions in the entire pH range (3.0–10.0). The proton-ligand stability constants (Table 1) of Dipy, SD, BAM, Dipy-SD, Dipy-BAB, SD-BAM and Dipy-SD-BAM at 35 and 45°C are obtained from the formation curves [(representative Figures 1–2). n_A vs. pH at $n_A = 0.5$, 1.5 and 2.5 (half integral method)] and by pointwise calculations applying the following equations:

$$pk_1 = pH + \log (2 - n_A)/(1 - n_A) \qquad (4)$$

where pH is in the range $1 < n_A > 2$;

$$pk_2 = pH + \log n_A/(1 - n_A) \qquad (5)$$

where pH is in the range $n_A < 1$;

$$pk_3 = pH \log (3 - n_A)/(2 - n_A) \qquad (6)$$

where pH is in the range $2 < n_A > 3$;

The $\bar{n}_A$ at different pH values can be determined applying the following equation:

$$\bar{n}_A = \frac{y - (v_2 - v_1)(N^\circ + E^\circ)}{(v_0 + v_1)TCL^\circ} \qquad (7)$$

where

y = total number of dissociable protons (dissociable hydrogen atoms) attached to the ligand (or ligands).

N° = normality of NaOH solution or the initial concentration.

E° = normality of the acid (HNO_3)

v_1 = volume of alkali of normality N required for the acid at definite pH,

v_2 = volume of alkali of normality N required for the ligand (or ligands) at a given pHs

v_0 = initial volume of the solution (25 mL).

TCL° = total ligand (or ligands) concentration.

The $\bar{n}_A$ values are plotted against pH and the values of proton-ligand stability constants (pK) can be determined by interpolation at $\bar{n}_A = 0.5$, and 2.5.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS AT 35° AND 45°C

Ligand	35°C		
	pK_1	pK_2	pK_3
Dipy	4.4, (4.4), (4.35)*	—	—
SD	1.6, (1.6), (1.37)*	9.5, (9.45), (9.18)*	12.6, (12.6), (12.11)*
BAM	13.2, (13.2), (13.14)*	—	—
Dipy-SD	8.7, (8.7)	11.50, (11.45)	—
Dipy-BAM	8.8, (8.8)	11.40, (11.45)	—
SD-BAM	9.2, (9.2)	12.40, (12.30)	—
Dipy-SD-BAM	1.7, (1.7)	8.90, (08.85)	11.70, (11.75)
Ligand	**45°C**		
	pK_1	pK_2	pK_3
Dipy	4.4, (4.4)	—	—
SD	1.5, (1.5)	9.3, (9.25)	12.0, (11.95)
BAM	13.0 (13.0)	—	—
Dipy-SD	9.2, (9.2)	11.80, (11.75)	—
Dipy-BAM	9.4, (9.4)	11.90, (11.85)	—
SD-BAM	9.4, (9.4)	12.60, (12.50)	—
Dipy-SD-BAM	1.9, (1.9)	9.20, (09.30)*	11.80, (11.85)

— values evaluated by the half integral method
( ) values evaluated by the pointwise calculation
( )* reported evaluated values (II)

The pH regions 3.5–9.5, 3.5–9.0 and 3.5–8.5 corresponding to the protonation of Dipy, deprotonation of SD and protonation and deprotonation of BAM are not lowered in the presence of M^{n+} [M = Cr(III), Mn(II), Cu(II), Ag(I)] ions (representative fig. 3). This indicates the absence of any metal-ligand complex formation in this pH range. The pH regions corresponding to metal-ligand-equilibria are observed around pH (3.5–9.0) with Cr(III), pH (3.5–8.5) with Mn(II), pH (3.5–9.0) with Cu(II) and pH (4.0–8.5) with Ag(I) at 35 and 45°C where free Dipy exists exclusively in the L form, SD in the LH^- and L^{2-}, and BAM exists in the L^- form. Formation of binary, ternary and quaternary complexes equilibria in solution expected to exist:

$$M^{(n+)} + \text{Dipy} \longrightarrow M^{n+} \cdot \text{Dipy}$$

$$M^{(n+)} + H_2SD \longrightarrow M^{(n-1)+} \cdot HSD$$

$$M^{(n+)} + HBAM \longrightarrow M^{(n-1)+} \cdot BAM$$

$$M^{(n+)} + \text{Dipy} + H_2SD \longrightarrow M^{(n-1)+} \cdot \text{Dipy} \cdot HSD$$

$$M^{(n+)} + 2\text{Dipy} + 2H_2SD \longrightarrow M^{(n-2)+} \cdot 2\text{Dipy} \cdot 2HSD$$

$$M^{(n+)} + \text{Dipy} + \text{HBAM} \longrightarrow M^{(n-1)+} \cdot \text{Dipy} \cdot \text{BAM}$$
$$M^{(n+)} + 2\text{Dipy} + 2\text{HBAM} \longrightarrow M^{(n-2)+} \cdot 2\text{Dipy} + 2\text{BAM}$$
$$M^{(n+)} + H_2SD + \text{HBAM} \longrightarrow M^{(n-2)+} \cdot \text{HSD} \cdot \text{BAM}$$
$$M^{(n+)} + \text{Dipy} + H_2SD + \text{HBAM} \longrightarrow M^{(n-2)+} \cdot \text{Dipy} \cdot \text{HSD} \cdot \text{BAM}$$

The average number of ligand (or ligands) molecules attached per mole of metal ion, $\bar{n}$, and the free ligand exponent, pL, can be evaluated by the following equations:

$$\bar{n} = \frac{(v_3 - v_2)[(N^\circ + E^\circ) + TCL^\circ(y - \bar{n}_A)]}{(V_0 + v_2).\bar{n}_A \quad TCM^\circ} \tag{8}$$

$$pL = \log\left[\sum_{n=0}^{n=j} \frac{\beta_n^H[H]^{+n}}{TCL^\circ - n \cdot TCM^\circ} \times \frac{(v_0 + v_3)}{v_0}\right] \tag{9}$$

or

$$pL = \log \frac{(1 + [H^+]/K_1 + [H^+]^2/K_1 \cdot K_2)}{(T_l^\circ - n \cdot TCM^\circ)} \times \frac{(v_0 + v_3)}{v_0}$$

where

TCM° = total concentration of the metal ions

V_3 = volume of alkali required to reach the acid + ligand + metal titration curve.

On plotting the $\bar{n}$ values against the pL values and interpolation at $\bar{n} = 0.5$, 1.5 and 2.5 values, the stepwise stability constants of the chelates (1 : 1, 1 : 2, 1 : 3) can be evaluated, respectively.

The stability constant values are also calculated by half integral method ($\bar{n}$ vs. pL) and confirmed by the pointwise calculations applying the equations:

$$\log n^{-}/(1 - \bar{n}) = \log K^{\text{metal}}_{\text{metal complex}} - pL \tag{10}$$

where values of $\bar{n}$ are selected between 0.2 and 0.8 (at $\bar{n} = 0.5$) for $pK_{1:1}$

$$\log (2 - n^{-})/(1 - n^{-}) = \log K^{\text{metal complex}}_{\text{metal complex}} - pL \tag{11}$$

where values of n^{-} are selected between 1.2 and 1.8 (at $n^{-} = 1.5$) for $pK_{1:2}$.

$$\log (3 - \bar{n})/(1 - \bar{n}) = \log K^{\text{metalcomplex}}_{\text{metalcomplex}} - pL \tag{12}$$

where values of $\bar{n}$ are selected between 2 and 3 (at $\bar{n} = 2.5$) for $pK_{1:3}$.

The stability constants of the mixed ligand complexes can be calculated making use of $\bar{n}$ vs. pL relations [eqs. (8), (9) and (10)]. The data obtained are recorded in Tables 1–5. With increasing temperature, the dissociation constants of the ligands and the formation constants of the metal complexes at constant ionic strength show an increasing trend (Tables 1–5). The thermodynamic parameters $\Delta^\circ G$, ΔH and ΔS (Tables 2–5) are calculated making use of the following equations:

$$\Delta^\circ G = -RT \ln K \tag{13}$$

$$\Delta H = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_2}{K_1} \tag{14}$$

$$\Delta S = R \ln K + \frac{\Delta H}{T}$$

where

$\Delta^\circ G$ = free energy changes,

ΔH = enthalpy changes (heat content),
ΔS = entropy changes,
R = gas constant,
T = absolute temperature
K = dissociation constant.

TABLE-2
STEPWISE FORMATION CONSTANT, FREE ENERGY CHANGE, ENTHALPY AND ENTROPY VALUES (in kcal/mol) AT 35° AND 45°C of M^{n+} -DIPY COMPLEXES

Ratio	T, °C	log k	$\Delta^{\circ}G$	$-\Delta H$	$-\Delta S$
			Cr(III)-Dipy		
1:1	35	4.60, (4 .70)	6.53, (6.67)	9.02, (4.96)	21.22, (26.61)
	45	4.80, (4.81)	7.01, (7.05)	9.02, (4.96)	22.12, (27.11)
1:2	35	10.60, (10.05)	15.05, (15.05)	9.02, (10.38)	48.05, (49.55)
	45	10.08, (10.98)	15.77, (16.08)	9.02, (10.38)	49.77 (60.95)
1:3	35	14.00, (14.00)	19.88, (19.88)	9.02, (9.02)	63.51, (63.51)
	45	14.20, (14.20)	20.73, (20.73)	9.02, (9.02)	65.43, (65.43)
			Mn(II)-Dipy		
1:1	35	4.20, (4.21), (4.6)*	5.96, (5.95)	18.04, (21.65)	19.4, (41.01)
	45	4.6, (4.69)	6.72, (6.87)	18.04, (21.65)	21.25, (43.25)
1:2	35	7.80, (7.97), (7.84)*	11.08, (11.31)	18.04, (19.40)	35.98, (56.11)
	45	8.20, (8.40)	11.97, (12.30)	18.04, (19.40)	37.83, (58.09)
1:3	35	11.60, (11.60), (11.47)*	16.47, (16.47)	18.04, (18.04)	53.49, (53.49)
	45	11.20, (11.20)	16.35, (16.35)	18.04, (18.04)	51.64, (51.64)
			Cu(II)-Dipy		
1:1	35	8.2, (8.2) (8.0)*	11.64, (11.64)	27.07, (27.07)	37.85, (37.86)
	45	8.80, (8.81)	8.47, (8.47)	27.07 (27.07)	40.62, (70.10)
1:2	35	13.60, (13.60), (13.60)*	19.31, (19.31)	9.02, (6.77)	62.02, (06.77)
	45	13.80, (13.75)	20.15, (20.14)	9.02, (6.77)	63.54 (63.54)
1:3	35	17.2, (17.2), (17.08)*	24.42, (24.42)	18.04, (18.04)	79.28 (79.28)
	45	17.6, (17.6)	25.70, (25.70)	18.04 (18.04)	81.12 (81.12)
			Ag(I)-Dipy		
1:1	35	3.6, (3.6), (3.65)*	5.11, (5.11)	9.02 (10.83)	16.61, (27.41)
	45	3.8, (3.84)	5.55, (5.62)	9.02, (10.83)	17.53, (28.52)
1:2	35	7.4, (7.4), (7.15)*	10.51, (10.51)	9.02, (9.02)	34.11, (34.11)
	45	7.6, (7.6)	11.10 (11.10)	9.02 (9.02)	35.03, (35.30)
1:3	35	—	—	—	—
	45	—	—	—	—

TABLE-3
FORMATION STABILITY CONSTANT, FREE ENERGY CHANGE, ENTHALPY AND ENTROPY VALUES (in kcal/mol) AT 35° AND 45°C OF aM^{n+}-SD COMPLEXES

Ratio	T, °C	log k	Δ°G	−ΔH	−ΔS
			Cr(III)-SD		
1:1	35	4.6, (4.6)	6.53, (6.53)	9.02, (9.45)	21.22, (21.19)
	45	4.8, (4.6)	6.82, (6.75)	9.02, (9.45)	22.12, (21.24)
1:2	35	9.3, (8.3)	11.78, (11.78)	13.53, (13.53)	38.27, (38.27)
	45	8.6, (8.6)	12.21, (12.21)	13.53, (13.53)	39.65, (39.65)
			Mn(II)-SD		
1:1	35	3.2, (3.4)	4.54, (4.82)	18.04, (9.02)	14.80, (14.68)
	45	3.6, (3.6)	5.11, (5.11)	18.04 (9.02)	16.64, (16.64)
1:2	35	8.5, (8.5)	11.06, (12.06)	22.56, (9.02)	39.22, (35.6)
	45	9.0, (9.0)	22.56, (12.77)	22.56, (9.02)	41.53, (41.53)
			Cu(II)-SD		
1:1	35	5.2, (5.20)	7.38, (7.38)	27.07, (24.81)	24.04, (48.76)
	45	5.8, (5.75)	8.24, (8.42)	27.07, (24.81)	26.89, (51.29)
1:2	35	8.0(8.0), (18.13)*	11.35, (11.35)	54.13, (54.13)	36.87, (36.87)
	45	9.2 (9.2)	13.06, (13.06)	54.13, (54.13)	42.54, (42.54)
			Ag(I)-SD		
1:1	35	4.6 (4.74)	6.72, (6.72)	18.04, (13.53)	21.25, (25.37)
	45	5.0, (5.04)	7.10 (7.38)	18.04, (13.53)	23.10, (23.10)
1:2	35	10.5, (10.5)	14.90, (14.90)	13.53, (13.53)	48.41 (35.74)
	45	10.8, (10.8)	15.54, (15.54)	13.53, (13.53)	49.70, (49.70)

TABLE-4
CONDITIONAL STABILITY CONSTANT, FREE ENERGY CHANGE, ENTHAPLY AND ENTROPY VALUES (in Kcal/mol) AT 35° AND 45°C OF M^{n+}-BAM COMPLEXES

Ratio	T, °C	log K	Δ°G	−ΔH	−ΔS
			Cr(III)-BAM		
1:1	35	6.80, (6.41)	9.65, (9.09)	18.04, (36.09)	31.38, (23.6)
	45	7.20, (7.21)	10.22, (10.22)	18.04, (36.09)	33.22, (25.91)
1:2	35	10.50, (10.76)	14.90, (15.25)	4.51, (2.26)	48.38, (80.91)
	45	10.60, (10.80)	15.05, (15.82)	4.51, (2.26)	48.48, (80.49)
1:3	35	12.8, (12.8)	18.16, (18.16)	18.04, (18.04)	59.02, (59.02)
	45	13.2, (13.2)	18.74, (18.74)	18.04, (18.04)	60.86 (60.86)

		Mn(II)-BAM			
1:1	35	2.20, (2.21)	3.12, (2.12)	18.04, (9.02)	10.19, (10.2)
	45	2.60, (2.41)	3.69, (3.53)	18.04, (9.02)	12.03 (11.13)
1:2	35	6.3, (6.4)	8.94, (9.08)	13.53, (9.02)	29.06 (38.5)
	45	6.6, (6.6)	9.37, (9.37)	13.53, (9.02)	30.44 (39.42)
1:3	35	10.4, (10.4)	14.75, (14.75)	9.02, (9.02)	38.86, (38.86)
	45	10.2, (10.2)	14.48, (14.48)	9.02, (9.02)	47.01, (47.01)
		Cu(II)-BAM			
1:1	35	6.8, (6.94)	9.65, (9.84)	27.07, (29.77)	31.41, (31.74)
	45	7.4, (7.6)	10.51, (11.13)	27.07, (29.77)	34.17, (34.78)
1:2	35	9.3, (9.3)	13.19, (13.19)	13.53, (13.53)	42.88, (42.88)
	45	9.6, (9.6)	13.63, (13.63)	13.53, (13.53)	44.26, (4.26)
		Ag(I)-BAM			
1:1	35	3.2, (3.14)	4.54, (4.45)	27.07, (27.07)	14.83, (15.655)
	45	3.8, (3.94)	5.40, (5.77)	27.07, (27.07)	17.59, (18.24)
1:2	35	8.6, (8.6)	12.20, (12.20)	36.09, (36.09)	39.73, (39.73)
	45	9.4, (9.4)	13.53, (13.53)	36.09, (36.09)	43.41, (43.41)

TABLE-5
FORMATION STABILITY CONSTANT, FREE ENERGY CHANGE, ENTHALPY AND ENTROPY CHANGES (in kcal/mol) AT 35° AND 45°C OF MIXED LIGAND COMPLEXES

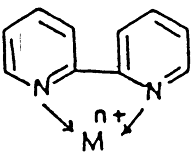
Ratio	T, °C	log K	$\Delta°G$	$-\Delta H$	$-\Delta S$
		Cr(III)-Dipy-SD			
1:1:1	35	14.2, (14.2)	20.14, (20.14)	18.04, (18.04)	83.34, (83.45)
	45	14.6, (14.6)	21.38, (21.38)	18.04, (18.04)	85.29, (85.29)
		Cr(III)-Dipy-BAM			
1:1:1	35	13.8, (13.8)	19.58, (19.58)	09.02, (09.02)	72.58, (72.58)
	45	14.0, (14.0)	20.51, (20.51)	09.02, (09.02)	73.50, (73.50)
		Cr(III)-SD-BAM			
1:1:1	35	10.8, (10.8)	15.30, (16.40)	18.04, (18.04)	67.79, (67.79)
	45	11.2, (11.2)	16.40, (16.40)	18.04, (18.04)	69.63, (69.63)
		Cr(III)-Dipy-SD-BAM			
1:1:1:1	35	14.8, (14.8)	21.02, (21.02)	18.04, (18.04)	68.23, (68.23)
	45	15.2, (15.2)	22.19, (22.19)	18.04, (18.04)	70.04, (70.04)
		Mn(II)-Dipy-SD			
1:1:1	35	11.7, (11.7)	16.60, (16.60)	04.15, (04.51)	58.40, (58.40)
	45	11.8, (11.8)	17.28, (17.28)	04.51, (04.51)	58.86, (58.86)

Mn(II)-Dipy-BAM					
1:1:1	35	10.9, (10.9)	15.46, (15.46)	22.56, (22.56)	72.76, (72.76)
	45	11.4, (11.4)	16.70, (16.70)	22.56, (22.56)	75.07, (75.07)
Mn(II)-SD-BAM					
1:1:1	35	9.20, (09.2)	13.02, (13.02)	36.59, (36.59)	78.46, (78.46)
	45	10.0, (10.0)	14.65, (14.65)	36.09, (36.09)	86.15, (86.15)
Mn(II)-Dipy-SD-BAM					
1:1:1:1	35	13.7, (13.7)	19.45, (19.45)	76.69, (76.69)	62.85, (62.85)
	45	12.0, (12.0)	17.52, (17.52)	76.69, (76.69)	55.51, (55.51)
Cu(II)-Dipy-SD					
1:1:1	35	17.0, (17.0)	24.12, (24.12)	18.04, (18.04)	96.35, (96.35)
	45	17.4, (17.4)	25.49, (25.49)	18.04, (18.04)	98.18, (98.18)
Cu(II)-Dipy-BAM					
1:1:1	35	16.9, (16.9)	23.98, (23.98)	13.53, (13.53)	91.37, (91.37)
	45	17.2, (17.2)	25.19, (25.19)	13.53, (13.53)	92.75, (92.75)
Cu(II)-SD-BAM					
1:1:1	35	12.0, (12.0)	17.02, (17.02)	72.18, (72.18)	127.45, (127.45)
	45	13.6, (13.6)	19.92, (19.92)	72.18, (72.18)	134.82, (134.82)
Cu(II)-Dipy-SD-BAM					
1:1:1:1	35	16.9, (16.9)	23.98, (23.98)	13.53, (13.53)	91.37, (91.37)
	45	18.6, (18.6)	27.16, (27.16)	18.04, (18.04)	85.73, (85.73)
AG(I)-Dipy-SD					
1:1:1	35	08.0, (08.0)	11.35, (11.35)	09.02, (09.02)	45.87, (45.87)
	45	08.2, (08.2)	12.00, (12.01)	09.02, (09.02)	46.79, (46.79)
Ag(I)-Dipy-BAM					
1:1:1	35	07.6, (07.6)	10.78, (10.78)	09.02, (09.02)	44.03, (44.03)
	45	07.8, (07.8)	11.42, (11.42)	09.02, (09.02)	44.95, (44.95)
Ag(I)-SD-BAM					
1:1:1	35	09.8, (09.8)	13.90, (13.90)	09.02, (09.02)	54.16, (54.16)
	45	10.0, (10.0)	14.65, (14.65)	09.02, (09.02)	55.08, (55.08)
Ag(I)-Dipy-SD-BAM					
1:1:1:1	35	09.3, (09.3)	13.21, (13.12)	04.51, (04.51)	42.85, (42.85)
	45	09.8, (09.8)	14.31, (14.31)	04.51, (04.51)	45.15, (45.15)

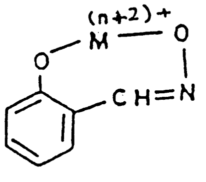
Values evaluated by the half integral method
( ) values evaluated by the pointwise calculation
( )* reported evaluated values (II)

Release of one proton per metal in the case of 1:1 metal:ligand (H_2SD or HBAM) could be explained on the basis of metal-promoted deprotonation of one phenolic OH group moiety, while a release of two protons per metal ion in the case of H_2SD could be explained on the basis of metal-promoted deprotonation of one oximic N—OH and one phenolic OH group moieties of the ligand L^{2-} ion. Therefore, the metal ions are coordinated by two deprotonated oximic and phenolic oxygen atoms of the ligand. Formation of mixed ligand complexes (1 : 1 : 1 and 1 : 1 : 1 : 1) may thus be interpreted as involving the displacement of some of the oximic NOH and phenolic OH groups. The order of stabilities of the various metal complex species formed is Cu(II) > Cr(III) > Mn(II) > Ag(I) with respect to $\log k_1$, $\log k_2$, $\log k_3$ values. The small differences between $\log k_1$, $\log k_2$, $\log k_3$, $\log k^{\text{metal-ligand}}_{\text{metal-biligand}}$ and $\log k^{\text{metal-ligand}}_{\text{metal-ligand}}$ complexes suggest the simultaneous formation of the 1 : 1, 1 : 2, 1 : 3, 1 : 1 : 1 and 1 : 1 : 1 : 1 complexes. The increase in stability from Ag(I) to Cr(III) may be related to solvation effect and with the increase of charge density except in the case of Cu(II) complexes. This may be due to expansion of the coordination sphere of Cu(II). However, the formation constant values of mixed ligand complexes are high and favour the view of expansion of the coordination number.

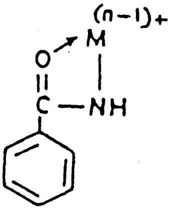
The positive $\Delta°G$ values indicate that all complexes are unspontaneously formed in solution. Furthermore, the negative values of enthalpy change (ΔH) indicate exothermic nature of chelation and their magnitudes suggest strong metal-ligand bond formation. The negative values of the entropy changes (ΔS) indicate that reactions suffer from a loss of some internal degrees of freedom



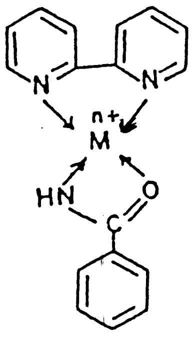
M^{n+}-Dipy



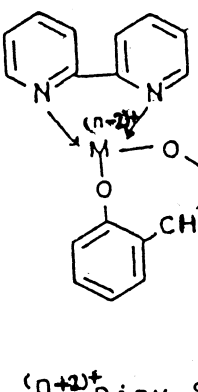
$M^{(n+2)+}$-SD



$M^{(n-1)+}$-BAM



$M^{(n-1)+}$-Dipy-BAM



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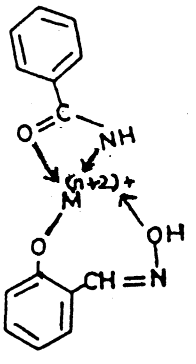
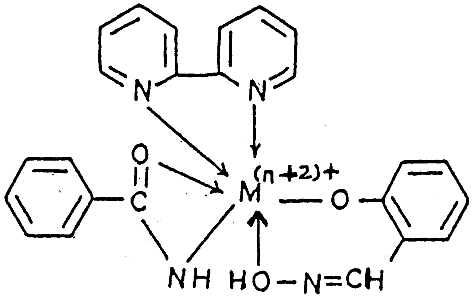


$M^{(n+2)+}$-SD-BAM



$M^{(n+2)+}$—Dipy-SD-BAM

during the complexation processes and can be attributed to the extensive solvation of metal chelates in aquo-organic media. Such modes of coordination also possibly bring the Dipy, SD and BAM moieties of the ligands at positions suitable for chelation. as suggested:

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