

## Conductometric Study of Complexation of Some Transition Metal Cations with 1,10-Phenanthroline, 2,2'-Bipyridine and 8-Hydroxyquinoline in Acetonitrile Solution

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Complexation of  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Cd^{2+}$  with 1,10-phenanthroline, 2,2'-bipyridine and 8-hydroxyquinoline in acetonitrile has been studied conductometrically at 25°C. The stoichiometry and stability constants of the resulting complexes were evaluated from non-linear least-square fitting of the conductometric data to appropriate equations. The stabilities of the resulting complexes vary in the order of phen > bipy > oxine.

### INTRODUCTION

1,10-Phenanthroline and 2,2'-bipyridine are the parents of a very important class of chelating agents<sup>1, 2</sup>. The reagents of this class form stable chelates with transition metal ions<sup>3, 4</sup>. In these chelates, bipyridine and phenanthroline behave as a bidentate uncharged ligand to form  $ML_3^{n+}$  and  $ML_2^{n+}$ -type chelates with a metal ion ( $M^{n+}$ ) of coordination numbers 6 and 4 respectively; the chelating properties of 1,10-phenanthroline have been utilized in a variety of analytical reagents and probes as well as herbicides<sup>5</sup>. In recent years several natural products incorporating 1,10-phenanthroline have been isolated, several of which show incorporating anticancer properties<sup>6</sup>. 8-Hydroxyquinoline forms chelates with a variety of metal ions so that oxine has been accepted as one of the commonest organic reagents for metal analysis<sup>4</sup>.

Since transition metals occupy an important position in matter and life, their coordination chemistry has received considerable attention. Extensive work has been done on complexation of transition metal cations with different ligands in aqueous solutions<sup>4</sup>. Since in the complexation process, the ligand must compete with solvent molecules for the cations, variation of the solvent is expected to change the apparent binding properties of the ligand. Thus, an interesting possibility for understanding the nature of the interactions between cations and conventional ligands in solution is the use of nonaqueous solvents of lower solvating abilities and dielectric constants than water.

In this work, the complexation reactions between  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$  and  $Cu^{2+}$  ions with 8-hydroxyquinoline, 2,2'-bipyridine and 1,10-phenanthroline have been studied conductometrically in acetonitrile solution. Formation constants of the resulting complexes have been compared with those reported in

aqueous solution and the effect of the structure of ligands on the stability of the resulting complexes has been discussed.

## EXPERIMENTAL

Reagent grade cobalt nitrate, nickel nitrate, copper nitrate, zinc nitrate, manganese nitrate (all from Merck), 1,10-phenanthroline (phen, Fluka), 2,2-bipyridine (Bipy, Merck) and 8-hydroxyquinoline (Oxine, Merck) were of the highest purity available and used without any further purification except for vacuum drying over  $P_2O_5$  for several days.

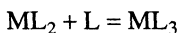
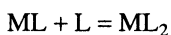
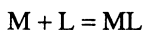
HPLC grade acetonitrile (Fluka) was used as received. The conductivity of the solvent was less than  $1 \times 10^{-7} \text{ cm}^{-1}$ . The conductance measurements were carried out with a 712 metrohm conductometer. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.800 was used. In all measurements the cell was thermostated at  $25 \pm 0.1^\circ\text{C}$ .

The experimental procedure used to obtain the formation constants of the complexes of transition metal cations was as follows. A solution of each cation ( $2 \times 10^{-4} \text{ mol dm}^{-3}$ ) in acetonitrile solution was placed in the titration cell, thermostated at  $25^\circ\text{C}$ , and its conductance was measured. A known amount of the ligand solution prepared in the same solvent was then added in the stepwise manner using a calibrated microsyringe. The conductance of the solution was measured after each addition. Addition of the ligand solution was continued until the desired ligand to metal ion mole ratio was achieved.

## RESULTS AND DISCUSSION

The molar conductance of the cation solutions in acetonitrile was monitored as a function of ligand to metal ion mole ratio at  $25^\circ\text{C}$  and the corresponding plots are shown in Figures 1–3. It is evident that, in general, the conductance-mole ratio plots can be approximately divided into three groups: (1) Plots with a slight slope and without any indication of an abrupt change in slope at any given mole ratio (*e.g.* cases 2, 3 and 6 in Fig. 1). (2) Plots with a pronounced change in curvature at the mole ratios of either 1 : 1 or 1 : 3 (metal to ligand) which beyond mole ratio of 1 : 3 conductance remains more or less constant (*e.g.* cases 2, 3 and 5 in Figs. 2 and 3). (3) Plots with a gradual change in conductivity which do not tend to level off, even at high mole ratios (*e.g.* cases Mn and Cu in Fig. 2). Qualitatively these mole ratio behaviours indicate: (1) Formation of weak complexes (weak complexes of oxine with metal ions compared to bipy and phen has been reported previously<sup>7</sup>). (2) Stepwise formation of quite stable complexes with the stoichiometries of 1 : 1, 1 : 2 and 1 : 3 metal to ligand. (3) Formation of relatively stable complexes of the same stoichiometries 1 : 1, 1 : 2 and 1 : 3 metal to ligand.

The stepwise binding of metal ions with the ligands can be expressed by the following equilibrium.



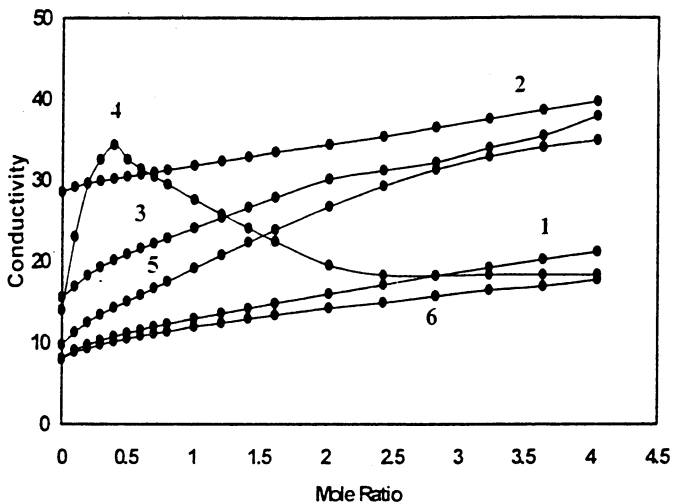


Fig. 1. Conductivity mole-ratio plots for complexation of oxine and different transition metal cations in acetonitrile solution, 1, Mn; 2, Ni; 3, Co; 4, Cu; 5, Zn; 6, Cd

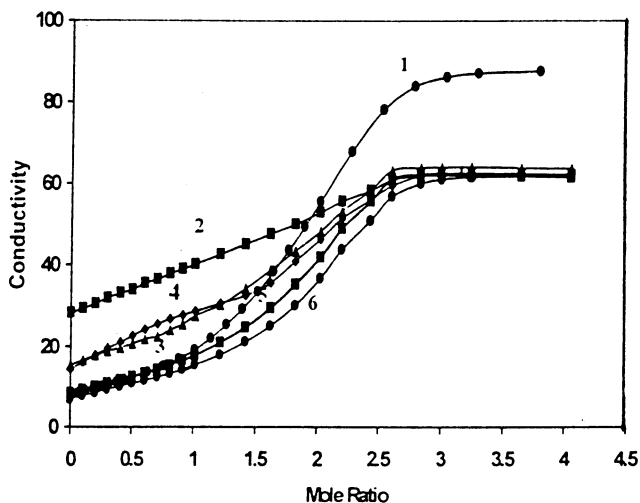


Fig. 2. Conductivity mole-ratio plots for complexation of phenanthroline and different transition metal cations in acetonitrile solution, 1, Mn; 2, Ni; 3, Co; 4, Cu; 5, Zn; 6, Cd

The corresponding equilibrium constants  $K_1$ ,  $K_2$  and  $K_3$  are given by

$$K_1 = \frac{[ML]}{[M][L]}$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$

where  $[M]$ ,  $[ML]$ ,  $[ML_2]$ ,  $[ML_3]$  and  $[L]$  represent the equilibrium molar

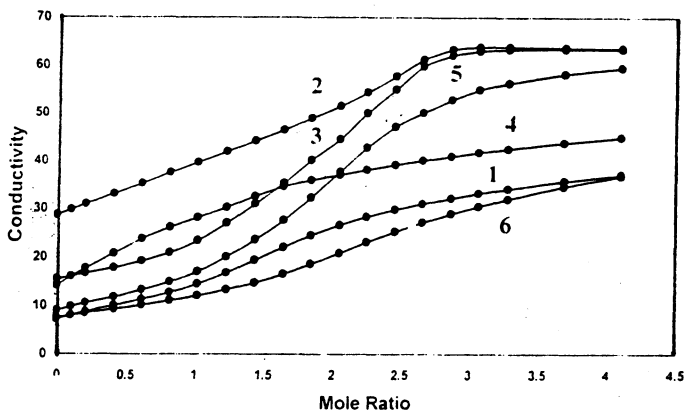


Fig. 3. Conductivity mole-ratio plots for bipyridine and different transition metal cations in acetonitrile solution, 1, Mn; 2, Ni; 3, Co; 4, Cu; 5, Zn; 6, Cd

concentrations of metal ion, 1 : 1, 1 : 2, 1 : 3 complexes and free ligand. The observed molar conductance can be expressed by the following equation.

$$\Lambda_{\text{obs}} C_M = \Lambda_M [M] + \Lambda_{ML} [ML] + \Lambda_{ML_2} [ML_2] + \Lambda_{ML_3} [ML_3]$$

for the evaluation of the formation constants from conductivity *vs.* mole ratio data (20–23 data points), a nonlinear least squares curve fitting program, KINFIT, was used<sup>8</sup>. The program is based on the iterative adjustment of the calculated values of the conductance to the observed values by using either the Wintworth matrix technique<sup>9</sup> or the Powell procedure<sup>10</sup>. Adjustable parameters are the stepwise formation constants of all complexes present and the corresponding molar conductance of the complexes.

The mass balance equations used in computer program KINFIT for evaluation of conductance data are:

$$C_M = [M] + [ML] + [ML_2] + [ML_3]$$

$$C_L = [L] + [ML] + 2[ML_2] + 3[ML_3]$$

Solutions of mass-balance equations in terms of the free ligand concentration [L] give:

$$k_1 k_2 k_3 [L]^4 + (3k_1 k_2 k_3 C_M + k_1 k_2 - C_L k_1 k_2 k_3) [L]^3 + (2C_M k_1 k_2 + k_1 - k_2 C_L) [L]^2 + (k_1 C_M - k_1 C_L + 1) [L] - C_L = 0$$

The free ligand concentrations were calculated by means of a Newton-Raphson procedure. Once the value of [L] had been obtained, the concentrations of all other species involved were calculated by using the estimated values of the stability constants at the current iteration step of the program. Refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the conductance for all experimental points is minimized. The output of the program KINFIT comprises refined parameters, the

sum-of-squares and the standard deviation of the data. All the calculated formation constants are summarized in Table-1.

As seen in all cases, cations form 1 : 1, 1 : 2 and 1 : 3 complexes with phen, bipy and oxine. Since all three molecules act as bidentate ligands in the process of complexation with different metal ions in different solvents<sup>4, 11-12</sup>, it is not surprising to witness the stepwise formation of 1 : 1, 1 : 2 and 1 : 3 (metal to ligand) complexes in acetonitrile solution.

A sample computer fit of the mole ratio data is shown in Fig. 4. Our assumption of presence of stepwise complex formation with stoichiometrics of 1 : 1, 1 : 2 and 1 : 3 seems reasonable in the light of the fair agreement between the observed and calculated molar conductances. It should be noticed that, in the procedure used for calculating stability constants, corrections for viscosity changes were neglected since the concentration of ligands was kept below  $7 \times 10^{-4}$  during these experiments.

It is interesting to note that in the case of all cations used the overall stability of the resulting complexes ( $\log \beta_3$ ) varies in the order phen > bipy > oxine. As expected, both the nature of donating atoms and the rigidity of the ligand structure could be responsible for determining the stability of the resulting complexes. Compared to bipy, phen has a distinct property; the rigid structure imposed by the central benzene ring of this molecule means that the two nitrogen atoms are always held in juxtaposition, whereas in bipy free rotation of the two pyridine rings about the linking band allows the two donating nitrogens to be separated. This entropic advantage for phen results in the formation of more stable complexes with metals ions<sup>14</sup>. On the other hand, although the two donor atoms of oxine (*i.e.*, the pyridine nitrogen and the —OH group) have structurally fixed positions, suitable for simultaneous binding with metal ions, bipy usually forms more stable complexes than this ligand with metal ions. It seems reasonable to assume that the pyridine nitrogens act as more effective donating groups than hydroxyl oxygens for metal ions in the solvent used. This is possibly due to the specific hydrogen bonding of hydroxy group with solvent molecules, which reduces its donating ability towards complexation. It should be noted that although oxine usually complexes the metal ions as its anion in water and protic solvents, in the aprotic solvent like acetonitrile its dissociation to protons and the corresponding conjugated base could be reasonably assumed negligible.

Comparison of the stability constants of the complexes obtained in this study with the stability constants of these complexes in water<sup>22-24</sup> shows that the solvent properties have an important influence on the stability of the resulting complexes. In fact, there is an inverse relationship between the overall stabilities of the complexes formed and the solvating ability of the solvents, as expressed by the Gutmann donor number, DN<sup>16</sup>. Since the complexation reaction takes place by replacement of the inner solvation shell of the cation by the ligand donating sites, competition exists between the ligand and solvent molecules for the cation in solution. Acetonitrile is the solvent with a lower donicity (DN = 14) than water (DN = 18) and therefore shows less competition with the ligands for metal ions which in turn results in the more stable complexes. The same type of solvent effects have already been reported for different complexes in various

solvents<sup>17-20</sup>. As can be seen from Table-1, the overall stability of the resulting complexes ( $\log \beta_3$ ) varies in the order  $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ . This order is in accordance with Irving-Williams series<sup>21</sup> which for some ligands and also for  $k_1$ ,  $k_2$  and  $k_3$  is followed.

TABLE-1  
STABILITY CONSTANTS  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  COMPLEXES WITH PHEN. OX-  
INE AND BIPY IN ACETONITRILE

Ligand	Cation	$\log K_1$	$\log K_2$	$\log K_3$
Phen	$Mn^{2+}$	$6.80 \pm 0.18$	$5.95 \pm 0.06$	$4.92 \pm 0.02$
	$Co^{2+}$	$7.87 \pm 0.01$	$7.46 \pm 0.06$	$6.23 \pm 0.01$
	$Ni^{2+}$	$7.98 \pm 0.02$	$7.68 \pm 0.01$	$6.54 \pm 0.03$
	$Cu^{2+}$	>7	$7.75 \pm 0.20$	$6.93 \pm 0.05$
	$Zn^{2+}$	$7.01 \pm 0.03$	$6.12 \pm 0.01$	$5.43 \pm 0.01$
	$Cd^{2+}$	$6.95 \pm 0.05$	$6.35 \pm 0.11$	$5.22 \pm 0.15$
Bipy	$Mn^{2+}$	$5.43 \pm 0.05$	$4.26 \pm 0.15$	$3.64 \pm 0.25$
	$Co^{2+}$	$7.03 \pm 0.11$	$6.40 \pm 0.02$	$5.81 \pm 0.02$
	$Ni^{2+}$	$7.12 \pm 0.01$	$6.42 \pm 0.03$	$5.92 \pm 0.05$
	$Cu^{2+}$	$7.23 \pm 0.02$	$6.85 \pm 0.05$	$6.08 \pm 0.11$
	$Zn^{2+}$	$5.73 \pm 0.12$	$5.53 \pm 0.05$	$4.62 \pm 0.11$
	$Cd^{2+}$	$5.83 \pm 0.01$	$4.68 \pm 0.01$	$4.11 \pm 0.05$
Oxine	$Mn^{2+}$	$4.70 \pm 0.01$	$3.86 \pm 0.02$	$3.54 \pm 0.05$
	$Co^{2+}$	$5.07 \pm 0.05$	$3.87 \pm 0.01$	$3.49 \pm 0.11$
	$Ni^{2+}$	$4.95 \pm 0.21$	$3.65 \pm 0.01$	$3.46 \pm 0.04$
	$Cu^{2+}$	$5.01 \pm 0.05$	$3.82 \pm 0.11$	$3.54 \pm 0.01$
	$Zn^{2+}$	$4.23 \pm 0.05$	$3.68 \pm 0.01$	$3.12 \pm 0.02$
	$Cd^{2+}$	$4.48 \pm 0.23$	$3.91 \pm 0.01$	$3.72 \pm 0.03$

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