

LETTERS TO THE EDITOR

FORMATION AND REPROPORTIONATION CONSTANTS OF BINARY AND TERNARY COMPLEXES

STUDY of solution equilibria of mixed ligand complexes is of great importance, as this leads to the finding of the definite thermodynamic conditions for the compatibility of different ligands in the coordination sphere of the metal ion. In the present communication, we are reporting the values of reproportionation constant and the change in bond energies during the complexation of dipyrldyl (dipy) phenanthroline (Phen) and thiotropolone (T.T.) with Ni^{2+} , Co^{2+} and Mn^{2+} .

Solutions of thiotropolone (T.T.)^{1,2}, 2-2 dipyrldyl and O-phenanthroline were prepared in dioxan. The solutions of bivalent metal ions (Analar B.D.H.) were prepared in double distilled water and were standardised by usual methods. Sodium perchlorate was used to keep ionic strength constant ($\mu = 0.1 \text{ M}$). The following solutions (total vol. 20.0 ml) were titrated potentiometrically in 50% (v/v) dioxan medium, against 0.05 M tetramethylammonium hydroxide solution, using a Beckman pH meter (SS-2 model, in conjugation with a glass and calomel electrode assembly) at $30 \pm 1^\circ \text{C}$.

a. (i) HClO_4 ($3.0 \times 10^{-3} \text{ M}$); (ii) HClO_4 ($3.0 \times 10^{-3} \text{ M}$) + T.T. ($2.5 \times 10^{-3} \text{ M}$); (iii) HClO_4 ($3.0 \times 10^{-3} \text{ M}$) + T.T. ($2.5 \times 10^{-3} \text{ M}$) + metal ion ($5.0 \times 10^{-3} \text{ M}$).

b. (i) HClO_4 ($3.0 \times 10^{-3} \text{ M}$); (ii) HClO_4 ($3.0 \times 10^{-3} \text{ M}$) + T.T. ($5.0 \times 10^{-4} \text{ M}$); (iii) HClO_4 ($3.0 \times 10^{-3} \text{ M}$) + dipy or phen ($5.0 \times 10^{-4} \text{ M}$) + metal ion ($5.0 \times 10^{-4} \text{ M}$); (iv) HClO_4 ($3.0 \times 10^{-3} \text{ M}$) + dipy or phen ($5.0 \times 10^{-4} \text{ M}$) + T.T. ($5.0 \times 10^{-4} \text{ M}$) + metal ion ($5.0 \times 10^{-4} \text{ M}$).

Using Irving and Rossotti³ method, the value of \bar{n} and pL of the different binary and ternary complexes have been calculated from titration sets (a) and (b) respectively. The corresponding values of stability constants, $\beta_{0,1}$ and $\beta_{0,2}$ for different binary complexes and $\beta_{1,1}$ for ternary complexes were obtained using weighted least squares method of Sullivan *et al.*,⁴ with the help of IBM 360 computer. The S_{min} values (χ^2) have also been calculated⁵.

Reproportionation Constant⁶. The formation constant of the mixed ligand complex is directly proportional to the geometrical mean of the formation constants of the parent complexes, and the proportionality

factor is termed as Reproportionation constant (K_d) i.e.,

$$\beta_{j,i} = K_d \cdot \beta_{m,o}^{j/m} \cdot \beta_{o,m}^{i/m} \quad (i + j = m)$$

When the ligands L and A are not compatible the mixed ligand complex formed is less stable than the parent complexes and the value of reproportionation constant is smaller than unity, whereas in compatibility of the ligands, it is greater than one. The results of present investigations are given in Tables I and II.

TABLE I

Stepwise stability constants of various T.T. complexes at $30 \pm 1^\circ \text{C}$

Metal ion	$\log k_1$	$\log k_2$	$\log \beta_{0,2}$
H ⁺	7.20
Ni ²⁺	6.75	5.81	12.56
Co ²⁺	6.20	5.70	11.90
Mn ²⁺	5.80	4.85	10.65

$\log k_1$ and $\log k_2$ values for Cd^{2+} could not be calculated as the binary complexes of T.T. are insoluble in 50% dioxan.

TABLE II

Formation and reproportionation constants of mixed ligand complexes with S_{min} values at $30 \pm 1^\circ \text{C}$

L	M ²⁺	$\log \beta_{1,1}$	S_{min}	K_d
Bipyridyl	Ni ²⁺	6.73	2.1	0.52
	Co ²⁺	6.16	0.10	0.52
	Mn ²⁺	5.70	1.79	0.61
	Cd ²⁺	5.85	7.00	..
Phenanthroline	Ni ²⁺	6.72	0.79	0.45
	Co ²⁺	5.92	0.39	0.45
	Mn ²⁺	5.29	0.25	0.56
	Cd ²⁺	5.79	1.5	..

TABLE III

Change in bond strengths of various mixed complexes (cal/mole) at $30 \pm 1^\circ \text{C}$

L	M ²⁺	M-L (parent)	M-L (mixed)	Change in bond strength	M-T.T. (parent)	M-T.T. (mixed)	Change in bond strength
Bipyridyl	Ni ²⁺	4580	2342	-2238	4337	2308	-2029
	Co ²⁺	3876	2010	-1866	4129	2245	-1884
	Mn ²⁺	2798	1403	-1395	3678	2535	-1143
Phenanthroline	Ni ²⁺	6078	2960	-3118	4337	1682	-2655
	Co ²⁺	4800	2580	-2220	4129	1510	-2619
	Mn ²⁺	2832	1295	-1537	3678	2297	-1381

Bond Strengths⁶: The strengths of the individual M-A and M-L bonds in the complex MA₂L₂ have been calculated from the formation constants of the mixed complexes and the parent MA₂ and ML₂ complexes using the following relations:

$$F_L' = \frac{RT}{4} \ln \beta_{1,1} \frac{\beta_{1,0}}{\beta_{0,1}} ; F_A' = \frac{RT}{4} \ln \beta_{1,1} \frac{\beta_{0,1}}{\beta_{j,0}}$$

while the bond strengths of the parent complexes MA₂ (F_A) and ML₂ (F_L) were calculated from their formation constants using equations:

$$F_L = \frac{RT}{2} \ln \beta_{m,0} ; F_A = \frac{RT}{2} \ln \beta_{0,m}$$

The values, thus obtained, are recorded in Table III.

In the present investigations, it is found that the value of reproportionation constant for mixed complexes is less than one and the bond strengths of all the metal to ligand bonds decrease, showing that the ligands are incompatible and the mixed complex is less stable than either of the parent complexes.

In the case of Ni²⁺, the formation constants of the mixed complexes are not significantly lowered, as observed in other cases. This may be attributed to the fact that Ni-N bonds of Ni-Dipy complexes have some amount of M → L *dπ-pπ* interaction along with the L → M bond⁷.

The mixed complexes of phenanthroline show similar trends as dipyrldyl complexes. But because of its greater size, their formation constants are slightly lower than the formation constants of dipyrldyl complexes.

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Department of Chemistry, University of Delhi,
Delhi 110 007, India,
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JAWAHAR LAL SHARMA,
J. N. SRIVASTAVA,
B. S. GARG,
R. P. SINGH.

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CIS-HYDROXYLATION OF OLEFINIC COMPOUNDS WITH SILVER SUCCINATE AND IODINE

SILVER salts of carboxylic acids and iodine have been employed for the preparation of *vic*-glycols from olefinic compounds. Prevost¹ showed that the complex formed from silver benzoate (2 moles) and iodine (1 mole), reacted with an olefin to give the corresponding *vic*-glycol dibenzoate. This reaction has been made use of by Witcoff and Miller² and Raman³ for the preparation of *vic*-dihydroxy acids from typical monoethenoid acids, the products being the corresponding *threo*-dihydroxy compounds when dry benzene is used as the medium for the reaction.

It has now been found that the use of silver succinate and iodine in molecular proportions in dry benzene medium is a very efficient method of preparing *vic*-dihydroxy acids from olefinic acids. Oxidation of octadec-9-enoic acid and of docos-13-enoic acid thus has given 9, 10-dihydroxy stearic