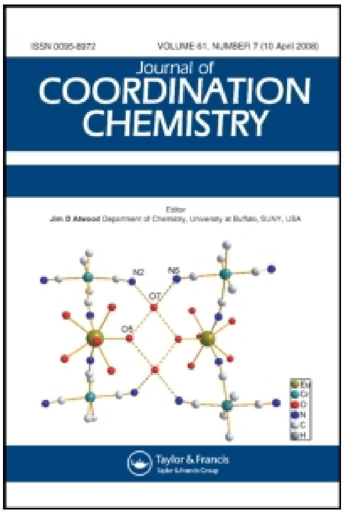

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Badar Taqui Khan[a]; R. Madhusudhan Raju[a]; S. M. Zakeeruddin[a]
[a] Department of Chemistry, Osmania University, Hyderabad, India

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BINARY AND TERNARY METAL COMPLEXES OF URIDINE AND THERMODYNAMIC QUANTITIES ASSOCIATED WITH THE INTERACTION OF URIDINE WITH BIVALENT METAL IONS IN SOLUTION

BADAR TAQUI KHAN†, R. MADHUSUDHAN RAJU and
S.M. ZAKEERUDDIN
Department of Chemistry, Osmania University, Hyderabad 500 007, India.

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Formation of binary and ternary complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II), Ca(II), metal ions with uridine as a primary ligand and 2,2′-bipyridyl, 1,10-phenanthroline and 5-sulphosalicylic acid as secondary ligands was studied by a potentiometric technique at 15°, 25°, 35° and 45°C and 0.10 M (KNO_3) ionic strength. The ternary complex formation was found to take place in a stepwise manner. The stability constants of these binary and ternary systems were calculated and the Δ log K values obtained were found to be negative. The lower stability of 1:2 complexes of uridine and those of the ternary systems compared to the corresponding binary systems is in accord with statistical considerations. Thermodynamic parameters are reported for all the systems studied.

Key words: Uridine, stability constants, divalent metals, *N*-heterocycles, complexes

INTRODUCTION

Ternary complexes of nucleosides and nucleotides have attracted the attention of many investigators.[1–7] This is because of the fact that metal ions participate in many biological processes such as replication, transcription and translation.[8–12] In recent years, considerable research has been carried out on model mixed-ligand complexes in an effort to understand the nature of metal ion complexation in biochemical systems. The uridine complexes of 3d metal ions and Ru(III) have been investigated in the solid state.[13,14]

As very little work has been carried out on binary and ternary complexes of uridine in aqueous media, it seemed worthwhile to study the formation of binary uridine metal complexes and the effect of secondary ligands on the stabilities of these complexes. In the present work we have investigated the interaction of Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II) and Ca(II) with uridine and the effect of secondary ligands such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (*o*-phen), 5-sulphosalicylic acid (SSA).

EXPERIMENTAL

The experimental method consisted of the potentiometric titration of each ligand with standard sodium hydroxide solution in the absence and presence of the metal ions being investigated. The ionic strength of the solution was maintained constant

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†Author for correspondence.

during the course of titration at 0.10 M (KNO_3) and relatively low concentrations of ligand and metal ion were used. Presaturated nitrogen was passed through the solution throughout each titration and the temperature was maintained constant ± 0.1°C. A Digisun model D1-707 pH meter, with a Toshniwal combination glass electrode was used to determine hydrogen ion concentration. The electrode system was calibrated by direct titration with acetic acid and the observed pH was compared with the actual hydrogen ion concentration as calculated from the data tabulated by Harned and Owen.[15] The pH regions below 3.5 and above 10.5 were calibrated by measurements in HCl and NaOH solutions respectively.

Reagents

Chromatographically pure uridine was obtained from the Sigma Chemical Company, USA; 2,2′-bipyridyl, 1,10-phenanthroline and 5-sulfosalicylic acid were obtained from E. Merck, Dermstedt. The metal salt solutions were standardised by titration with the disodium salt of EDTA as described by Schwarzenbach.[16] Carbonate-free sodium hydroxide was prepared by the method of Schwarzenbach and Biedermann[17] and was standardized by titration with pure potassium acid phthalate. Fresh solid ligand was weighed out for each titration to ensure against loss by hydrolysis or photochemical decomposition.

The acid dissociation of neutral uridine is related to the usual equilibrium dissociation

$$HL \rightleftharpoons L + H^+$$

by the equation

$$K_a = [H^+]\,(aT_L + [H^+] - [OH^-])/\{T_L - (aT_L + [H^+] - [OH^-])\} \qquad (1)$$

where a = mole of base added per mole of ligand and T_L = total ligand concentration. The equilibrium involved in the formation of 1:1 metal uridine complex may be represented by

$$M + L \overset{K}{\rightleftharpoons} ML$$

$$K^{M}_{ML} = \{T_M - [M]\}/[M][L] \qquad (2)$$

where

$$[L] = \{(1 - m)\,T_m - [H^+] + [OH^-]\}\,K_a/[H^+],$$

$$[M] = [L]\,([H^+]/K_a + 1), \text{ and}$$

T_M = total metal ion concentration.

The equations involved in the formation of 1:2-metal-uridine complexes may be represented by the following equations.

$$M + L \rightleftharpoons ML$$

$$ML + L \rightleftharpoons ML_2$$

$$K^{ML}_{ML_2} = [ML_2]/[ML][L] \qquad (3)$$

where

$$[L] = \{(2 - m)\, T_m - [H^+] + [OH^-]\}\, Ka/[H^+],$$

$$[M] = [L]\, ([H^+]/K_a + 1)/(2 + K_1[L],)$$

$$[ML_2] = T_m - [M]\, (1 + K_1\, [L]), \text{ and}$$

$$[ML] = K_1[M][L].$$

K_1 is the stability constant of 1:1 normal complex.

For the formation of the ternary complexes of metal ions in presence of uridine and 2,2′-bipyridyl or 1,10-phenanthroline the following equilibria may be considered by the equations given.

$$M + A \overset{K}{\rightleftharpoons} MA$$

$$MA + L \rightleftharpoons MAL$$

$$K^{MA}_{MAL} = [MAL]/[MA][L] \qquad (4)$$

where A = bipy or o-phen, MA = 1:1 metal-bipy or 1:1 metal-*o*-phen normal complex, and L = neutral ligand uridine.

Here complex formation is considered to take place in a stepwise manner. The calculation of the stability constant K^{MA}_{MAL} is similar to that of a 1:1 metal-uridine complex.

The stability constants for the ternary metal-SSA-uridine were calculated by the help of the following equations

$$MHA + L \overset{K}{\rightleftharpoons} MHAL$$

$$K^{MHA}_{MHAL} = [MHAL]/[MHA][L] \qquad (5)$$

where MHA = monoprotonated 1:1 metal-SSA complex, L = neutral uridine, and MHAL = monoprotonated ternary complex. The values of ΔH°_f, ΔG°_f, ΔS°_f were calculated by using the usual relationships as described in an earlier paper.[18] All calculations were carried out using a Casio FX-702P personal computer with appropriate programmes.

RESULTS

The potentiometric titration curve of uridine is shown in Fig. 1(a). Acid dissociation constants calculated at 15°, 25°, 35° and 45° C by using equation (*1*) are presented in Table 1. Titraton curves of uridine in the presence of Cu(II) and Mg(II) at a 1:1 ratio at 35°C are given in Fig. 1(b) and 1(d). Similar titration curves were obtained for Ni(II), Co(II), Zn(II), Mn(II) and Ca(II) with uridine. The titration curves at other temperatures are similar to those obtained at 35°C. It was assumed that normal 1:1 complexes of uridine are formed between a = 0 to 1 with the abovementioned metal ions. The stability constants were calculated in this region by using equation (*2*) and the resulting values are presented in Table I. The corresponding thermodynamic parameters are given in Table II. The titration curve for Mg(II)-uridine at a 1:2 ratio of metal ion to ligand is shown in Figure 1(c). Similar titration curves were obtained for

TABLE I

Stability constants[+] of 1:1 metal-uridine and 1:2 metal-uridine complexes and Δ log K values for these systems; $\mu = 0.10$ M (KNO_3).

	Log K^{M}_{ML}				log $K^{ML}_{ML_2}$				Δ log K			
T(°C)	45°	35°	25°	15°	45°	35°	25°	15°	45°	35°	25°	15°
pKa	8.91	9.07	9.21	9.33								
Cu(II)	4.24	4.16	4.03	3.93	3.43	3.34	3.20	3.10	−0.81	−0.82	−0.88	−0.83
Ni(II)	4.08	4.00	3.90	3.79	3.97	3.89	3.75	3.65	−0.11	−0.11	−0.15	−0.14
Co(II)	3.91	3.85	3.79	3.70	3.83	3.75	3.64	3.55	−0.08	−0.10	−0.15	−0.15
Zn(II)	3.80	3.72	3.67	3.58	3.40	3.30	3.19	3.08	−0.40	−0.42	−0.48	−0.50
Mn(II)	3.59	3.52	3.44	3.37	3.66	3.55	3.44	3.31	−0.07	+0.03	0.00	−0.06
Mg(II)	3.36	3.25	3.14	3.02	3.21	3.10	2.98	2.87	−0.15	−0.15	−0.16	−0.15
Ca(II)	3.25	3.15	3.05	2.95								

[+] The constants are accurate to ± 0.03 log K units. Δ log K = (log $K^{ML}_{ML_2}$ − log K^{M}_{ML}).

TABLE II

Thermodynamic parameters[+] associated with the interaction of metal ions with uridine at a 1:1 and 1:2 ratio of metal ion to ligand, and $\Delta\Delta H^\circ_f$, $\Delta\Delta S^\circ_f$ values for these systems.

	log K^{M}_{ML}			log $K^{ML}_{ML_2}$				
	ΔH°_f (kJ mol^{-1})	ΔG°_f(25°) (kJ mol^{-1})	ΔS°_f(25°) (J mol^{-1} K^{-1})	ΔH°_f (kJ mol^{-1})	ΔG°_f(25°) (kJ mol^{-1})	ΔS°_f(25°) (J mol^{-1} K^{-1})	$\Delta\Delta H^\circ_f$ (kJ mol^{-1})	$\Delta\Delta S^\circ_f$ (J mol^{-1} K^{-1})
Cu(II)	+18.5	−23.0	139	+19.8	−18.3	128	+1.3	−11
Ni(II)	+17.0	−22.2	131	+19.2	−21.4	136	+2.2	+5
Co(II)	+12.1	−21.7	113	+16.6	−20.8	125	+4.5	+12
Zn(II)	+12.5	−20.9	112	+18.8	−18.2	124	+6.3	+12
Mn(II)	+13.0	−19.6	109	+20.4	−19.6	134	+7.4	+15
Mg(II)	+19.8	−17.9	126	+20.0	−17.0	124	+0.2	−2
Ca(II)	+17.7	−17.4	118					

[+] The ΔH°_f values are accurate to ± 0.5 kJ mol^{-1} and the ΔS°_f values to ± 2 J mol^{-1} K^{-1}.

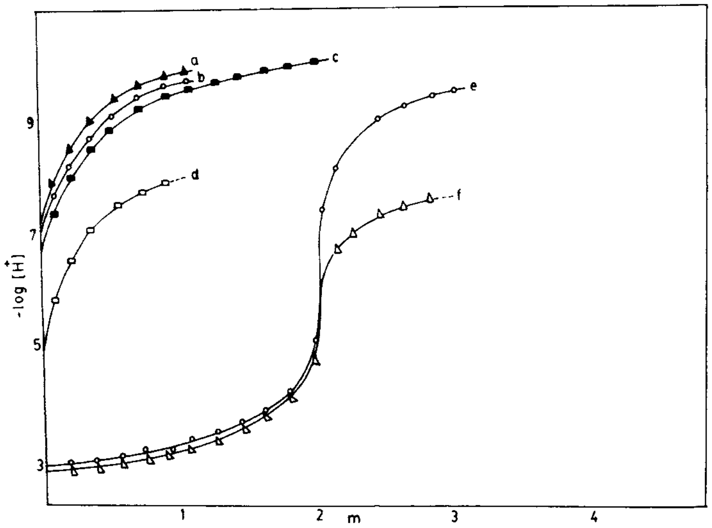


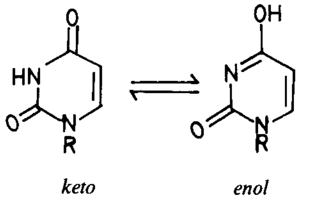
FIGURE 1 Petentiometric titration curves for uridine with Mg(II) and Cu(II) at 35°C, $\mu = 0.10$ M (KNO_3). a: free ligand; b: 1:1 Mg(II)-uridine; c: 1:2 Mg(II)-uridine; d: 1:1 Cu(II):uridine; e: (1:1:1)Mn(II)-2,2'-bipyridyl-uridine; f: (1:1:1) Cu(II)-2,2'-bipyridyl-uridine; m: mol of base added per mol of metal ion.

Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) ions. The stability constants $K^{ML}_{ML_2}$ were calculated by using equation (3). The stability constants at 15°, 25°, 35° and 45° C and the corresponding thermodynamic constants are given in Tables I and II respectively.

Potentiometric titration curves for M-A-L (M = metal ion; A = 2,2′-bipyridyl, 1,10-phenanthroline or 5-sulfosalicylic acid and L = uridine) show an inflection at m = 2 indicating stepwise complex formation. The titration curves for Mn(II)-bipy-uridine and Cu(II)-bipy-uridine at 35°C are given in Figs. 1(e) and 1(f), respectively. Similar curves were obtained at other temperatures and for the other systems. The stability constants of these ternary complexes were calculated as outlined in the earlier section are given in Table III and the corresponding thermodynamic parameters are listed in Table IV.

DISCUSSION

Uridine is a weak base, as compared to uracil. The dissociation constant of cationic uridine could not be calculated potentiometrically, because of the highly acidic nature of the associated proton ($pKa < 0.5$). IR data show that uridine predominantly exists in the diketo form[19].



R = Ribose

Schurukow *et al.*[20], have reported that the site of proton dissociation in uracil and thymine is the N_1H or N_3H group, whereas Taqui Khan *et al.*[21], have reported proton

TABLE III

Stability constants† for ternary metal complexes of uridine with 2,2-bipyridyl 1,10-phenanthroline or 5-sulfosalicyclic acid; $\mu = 0.10$ M (KNO_3).

	Metal-2,2-bipyridyl-uridine				Metal-1,10-phenathroline-uridine				Metal-SSA-uridine			
	log K^{MA}_{MAL}				log K^{MA}_{MAL}				log K^{MHA}_{MHAL}			
T(°C)	45°	35°	25°	15°	45°	35°	25°	15°	45°	35°	25°	15°
Cu(II)	3.82	3.90	4.01	4.08	3.74	3.81	3.91	3.98	3.75	3.66	3.55	3.43
Ni(II)	3.97	4.04	4.15	4.27	3.83	3.89	3.98	4.04	3.61	3.53	3.42	3.35
Co(II)	3.82	3.91	4.01	4.08	3.70	3.79	3.89	4.00	3.49	3.40	3.31	3.20
Zn(II)	3.51	3.56	3.60	3.64								
Mn(II)	3.39	3.43	3.49	3.54	3.59	3.62	3.67	3.70	3.61	3.66	3.75	3.85
Mg(II)	3.22	3.12	3.00	2.87	3.02	2.84	2.70	2.51				
Ca(II)	3.01	2.94	2.85	2.78								

†The values are accurate to ± 0.07 log K units.

TABLE IV

Thermodynamic parameters[†] associated with the interaction of metal ions with uridine and 2,2′bipyridyl, 1,10-phenanthroline or 5-sulfosalicylic acid; $\mu = 0.10$ M (KNO_3).

	Metal:bipy:uridine (1:1:1)			Metal:phen:uridine (1:1:1)			Metal:SSA:uridine (1:1:1)		
(kJ mol^{-1})	ΔH_f° (kJ mol^{-1})	ΔG_f° (25°) (kJ mol^{-1})	ΔS_f° (25°) (J mol^{-1} K^{-1})	ΔH_f° (kJ mol^{-1})	ΔG_f° (25°) (kJ mol^{-1})	ΔS_f° (25°) (J mol^{-1} K^{-1})	Δ H_f° (25°) (kJ mol^{-1})	Δ G_f° (25°) (kJ mol^{-1})	ΔS_f° (25°) (J mol^{-1} K^{-1})
Cu(II)	−15.4	−22.9	25	−14.3	−22.3	27	+18.3	−20.2	129
Ni(II)	−17.6	−23.7	20	−12.6	−22.7	34	+15.6	−19.5	118
Co(II)	−15.5	−22.9	25	−17.5	−22.2	16	+16.9	−18.9	120
Zn(II)	−7.6	−20.5	43						
Mn(II)	−8.9	−19.9	37	−6.6	−20.9	48	−14.1	−21.4	24
Mg(II)	+20.5	−17.1	126	+29.4	−15.4	150			
Ca(II)	+13.6	−16.3	100						

[†] The ΔH_f° values are accurate to ± 0.7 kJ mol^{-1} units and the ΔS_f° value to ± 3 J mol^{-1} K^{-1}.

dissociation from the N_3H group. In uridine, as the N_1 position is blocked by the presence of a ribose moiety, N_3 is the only proton ionization site. The enthalpy change for the dissociation of a proton from neutral uridine is more exothermic by 30.8 kJ mol^{-1} than thymine and 10.6 kJ mol^{-1} than uracil, respectively. The entropy is however more negative (87 and 30 J mol^{-1} K^{-1} than thymine and uracil, respectively). The exothermic enthalpy for the first dissociation of proton thus seems to be the contributing factor in making uridine less basic than uracil and thymine.

The stabilities of normal 1:1 metal-uridine complexes decrease in the order Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II) > Mg(II) > Ca(II) in accord with the Irving-Williams order. The stabilities of 1:1 metal-uridine complexes decrease with decreasing temperature. It is of interest to compare the stability constants of 1:1 metal-uridine species with those of uracil complexes[22]. Both uracil and uridine form metal complexes with the same binding site (N_3 of the pyrimidine ring). The weak basicity of uridine is reflected in the lower stability of its metal complexes than that of uracil. The enthalpy changes for the formation of the 1:1 metal-uridine complexes are endothermic and the entropy change values are positive in all the cases. The enthalpy and entropy values of these complexes are more positive than those of the corresponding metal-uracil and metal thymine species[23]. The entropy values decrease with increasing ionic radius of the metal ion. There is however no regular trend in the entropy values. The relatively small positive values of ΔH_1° compared with ΔS_1° (Table II) are contributing factors favouring the formation of the normal 1:1 complexes in solution.

The stability constants of the 1:2 metal-uridine complexes are lower than those of the corresponding 1:1 systems, as expected from statistical considerations. The Δ log K (log $K^{ML}_{ML_2}$ - log K^{M}_{ML}) values for the uridine complexes are negative (Table I). The enthalpy changes for 1:2 complex formation are less negative, *i.e.*, less exothermic, than the corresponding 1:1 complexes (Table II). The entropy values are however more positive for the 1:2 systems. This is the normal trend in neutral ligands where the enthalpy is more favourable for a 1:1 species (exothermic) as compared to a 1:2 species. The low enthalpy coupled with a higher positive entropy is responsible for the formation of 1:2 complexes.

It was shown earlier that the Δ log K values are all negative for 1:2 metal uridine complexes. Δ log K values often vary with temperature however, and the quantities of fundamental importance are the $\Delta\Delta$ H and $\Delta\Delta$ S ($\Delta\Delta H = \Delta H_2 - \Delta H_1$, where ΔH_2 and ΔH_1 are the ΔH_1° values for 1:2 and 1:1 metal-uridine systems, respectively and $\Delta\Delta S = \Delta S_2 - \Delta S_1$ where ΔS_2 and ΔS_1 are the entropies for 1:2 and 1:1 complexes, respectively). The $\Delta\Delta H$ values for the ML_2 complexes of uridine are all endothermic in the range of 0.2 - 7.4 kJ mol^{-1} (Table II). The values of $\Delta\Delta$ H may be roughly correlated to the extent of steric hindrance in the 1:2 complexes of uridine. The values of $\Delta\Delta$ S are however both positive and negative indicating that there are solvation differences in the 1:2 and 1:1 systems.

The stability constants for the mixed ligand complexes metal-bipyridyl-uridine and metal-o-phen-uridine-decrease in the order Ni(II) > Co(II) > Cu(II) > Zn(II) > Mn(II) > Ca(II). However, Ca(II) and Zn(II) do not form mixed ligand complexes in the latter system. For the above two ternary systems the Δ log K values are negative (Table IV). The lower stabilities of the mixed ligand ternary systems as compared to the corresponding binary complexes is in accord with statistical considerations. The stabilities of 1:1:1 metal-SSA-uridine ternary complexes decrease in the order Cu(II) > Ni(II) > Mn(II) > Co(II). The metal ions Zn(II), Mg(II) and Ca(II) do not form such ternary complexes (Table III). The Δ log K values are negative except for Mn(II) (Table V) and are also in accord with statistical considerations. By comparing the energetics of formation in the 1:1:1 ternary systems containing metal-bipyridyl-uridine, metal-o-phen uridine (Table IV), it is clear that the enthalpies and entropies do not follow regular trends. However, the entropies are less positive as compared to the

TABLE V
Δ log K values for the ternary complexes; $\mu = 0.10$ M (KNO_3).

	M-bipy-uridine				M-phen-uridine				M-SSA-uridine			
	Δ log K				Δ log K				Δ log K			
T(°C)	45°	35°	25°	15°	45°	35°	25°	15°	45°	35°	25°	15°
Cu(II)	−0.39	−0.26	−0.07	−0.07	−0.47	−0.35	−0.17	−0.03	−0.46	−0.50	−0.52	−0.58
Ni(II)	−0.09	+0.04	+0.20	+0.43	−0.29	−0.11	+0.03	+0.20	−0.45	−0.47	−0.53	−0.49
Co(II)	−0.09	+0.12	+0.22	+0.38	−0.21	−0.06	+0.10	+0.30	−0.42	−0.45	−0.48	+0.49
Zn(II)	−0.29	−0.26	−0.07	+0.06								
Mn(II)	−0.20	−0.09	+0.05	+0.17		+0.10	+0.23	+0.33	+0.02	+0.14	«0.31	+0.48
Mg(II)	−0.14	−0.13	−0.14	−0.18	−0.34	+0.41	+0.44	+0.54				
Ca(II)	−0.24	−0.21	−0.20	−0.17								

$\Delta \log K = (\log K^{M}_{MAL} - (\log K^{M}_{MA} + \log K^{M}_{ML}))$.

corresponding binary systems. The more negative and favourable enthalpy changes are responsible for the mixed ligand complex formation.

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REFERENCES

1. R.M. Izzatt, J.H. Christensen and J.J. Rytting, *Chem. Rev.*, **71,** 439 (1971).
2. H. Sigel (Ed.). In "Metal Ions in Biological Systems", Vol. 2, Chap. 2, Marcel Dekker, New York (1973).
3. R.B. Martin and Y.H. Mariam, In "Metal Ions in Biological Systems" (Edited by H. Sigel) Chap. 2, Marcel Dekker, New York (1979).
4. B. Taqui Khan, G. Narsa Goud and S. Vijaya Kumari, *Inorg. Chim. Acta,* **80,** 145 (1983).
5. B. Taqui Khan, A. Gaffuri and M.R. Somayajulu, *Ind. J. Chem.*, **20A,** 189, (1981).
6. L.G. Marzilli, B. de Castro and C. Solorzano, *J. Am. Chem. Soc.*, **104,** 461 (1982).
7. L. Pellerito, G. Ruisi, M.T. Logudice, J.D. Donaldson and S.M. Grimes, *Inorg. Chim. Acta,* **58,** 21-25 (1982).
8. M.J. McCarthy, *J. Gen. Physiol.*, **29,** 123 (1941).
9. J.P. Slater, I. Tamir, L.A. Loeb and A.S. Mildman, *J. Biol. Chem.*, **247,** 6784 (1972).
10. P. Ballard and H.G. Nathams-Ashman, *Nature (London),* **203,** 150 (1964).
11. C.C. Widnell and R.J. Tata, *Biochem. J.*, **92,** 313 (1964).
12. G.L. Eichhorn, In "Organic Biochemistry" (Edited by G.L. Eichhorn), Vol. 2, p. 1210, Elsevier, Amsterdam (1973).
13. M. Goodgame and K.W. Johns, *J. Chem. Soc., Dalton Trans.*, 1294 (1978).
14. B. Taqui Khan, A. Gaffuri, P. Nageshwara Rao and S.M. Zakeeruddin, *Polyhedron,* in press.
15. H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York (1950).
16. G. Schwarzenbach, "Complexometric titration", Interscience, New York, p. 77 (1957).
17. G. Schwarzenbach and R. Biedermann, *Helv. Chim. Acta,* **31,** 337 (1948).
18. M.M. Taqui Khan and A.E. Martell, *J. Am. Chem. Soc.*, **89,** 5585 (1967).
19. H.T. Miles, *Biochem. Biophys. Acta,* **22,** 247 (1956).
20. B.T. Schorukow, V.I. Polten and L. Blumenfeld, *Abh.-Deut. Akad., Wiss., Berlin, Kl. Med.*, 381 (1964).
21. M.M. Taqui Khan and S. Satyanarayana, *Ind. J. Chem.*, **20A,** 814 (1981).
22. M.M. Taqui Khan and C.R. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **36,** 711 (1974).
23. M.M. Taqui Khan and S. Satyanarayana, M.S. Jyothi and A. Purshotham Reddy, *Ind. J. Chem.*, **22A,** 357 (1983).