Mixed Ligand Complexes of Uranyl ion with 4-amino-2,6-dimethylpyrimidine and some Selected Ligands

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During recent years there has been an upsurge of interest in the interaction of various mono- and di- substituted purines with bivalent metal ions [1,2]. The metal complexes of pyrimidines and nucleotides play a dominant role in many biochemical systems. Although considerable work has been carried out on the complexes of substituted purines and pyrimidine with a number of metal ions in solid state [3] and also in aqueous media [4,5], very little chemistry is known for the interaction of these ligands with metal uranium. It was therefore considered important to investigate the metal complexes of substituted pyrimidines with uranyl ion in aqueous solution.

EXPERIMENTAL

Each ligand was titrated with standard sodium hydroxide solution in the absence and presence of uranyl ion. The titration solution contains relatively low concentration of ligand and metal ion and the ionic strength of the solution was maintained at 0.10 M with KNO_3. The temperature was maintained at 35 $\pm$ 0.1° C. Pre-saturated nitrogen was passed through the solution throughout the course of the titration. A Beckman model G pH meter with glass and calomel electrode was used to determine the hydrogen ion concentration. The electrode system was calibrated by direct titration with acetic acid and the observed pH meter reading was compared with the actual hydrogen ion concentration as calculated from the data tabulated by Harned and Owen [6]. The pH regions below 3.5 and above 10.5 were calibrated by direct measurement of the hydrogen ion concentration in hydrochloric acid and sodium hydroxide solution respectively. The pH meter readings were plotted against 'a' (moles of base added per mole of ligand) or 'm' (moles of base added per mole of metal ion).

The acid dissociation constants of the ligands - 4-amino-2,6-dimethylpyrimidine (ADMP), ethylenediamine (en), o-phenylenediamine (oPDA) and o-aminophenol (oAP) - were calculated from potentiometric data using the computer program PKAS [7a]. All the binary and ternary stability constants were computed by using the computer program BEST [7b]. The equilibrium constants reported in this investigation correspond to the reference state of infinitely dilute reacting species in a medium of 0.10 M KNO_3.

RESULTS AND DISCUSSION

Potentiometric titration of the ligand 4-amino-2,6-dimethylpyrimidine in the diprotonated form shows that the two protons undergo dissociation in separate steps. The first dissociation probably involves the removal of a proton from NH_3^+ group on the fourth carbon atom of the pyrimidine. The second dissociation is obviously due to the dissociation of a proton from the NH^+ on the third member of the pyrimidine ring. The dissociation constants were calculated in the buffer region of a = 0 to 1 and a = 1 to 2.

Titration curve for the system containing 4-amino-2,6-dimethylpyrimidine and uranyl ion in 1:1 molar ratio shows inflection at m = 2 indicating the release of two protons simultaneously upon coordination. Calculations for the normal complexes were computed in the region m = 0 to 2.

Potentiometric titration curves for ternary systems containing 4-amino-2,6-dimethylpyrimidine, uranyl ion and the ethylenediamine (en) / o-aminophenol (oAP) / o-phenylenediamine (oPDA) in 1:1:1 molar ratio exhibit feeble inflection at

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m = 4. Calculation shows that ternary complexes are formed in all these systems. The ternary stability constants for the ternary metal complexes are listed in Table 1.

Table 1

Formation Constants of Ternary Uranyl Complexes

Primary ligand (A): 4-amino-2,6-dimethyl pyrimidine

Secondary ligands (L): en / oAP / oPDA

T = 35° C ; μ = 0.1 M (KNO_3), aqueous medium

Ligand	ADMP	en	oAP	oPDA
pK_1	2.75	6.87	4.59	4.53
pK_2	6.97	9.60	9.35	-
$\log K^{M}_{MA/L}$	6.55	10.45	10.30	4.86
$\log K^{ML}_{MAL}$	-	4.65	5.15	4.75
$\log K^{MA}_{MAL}$	-	8.55	8.90	3.06
$\log K^{M}_{MAL}$	-	15.10	15.45	9.61
Δlog K	-	-1.90	-1.40	-1.80

The relative stabilities of the ternary complexes compared to the corresponding binary complexes can be quantitatively expressed in many different ways. We have expressed the relative stabilities in terms of Δ log K which is defined as

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

The advantage of using Δlog K for comparison of the stability of binary and ternary complexes has been reviewed [8]. The Δ log K values obtained in the present investigation are also tabulated in Table 1.

The formation constants of the ternary metal complexes are quite large indicating that the ligands L have considerable affinity for the binary [M-A] complex and form stable ternary complexes by replacing the coordinated water molecule of the binary complex. Comparison of the ability of the ligands L to bind the binary complex MA [K^{MA}_{MAL}] relative to the aquo metal ion [K^{M}_{ML}] in terms of the parameter Δlog K shows that the ligands L prefer to bind the aquo metal ion. This is expected on statistical grounds since there are more coordinating positions available on the aquo metal ion.

From a comparison of the Δ log K values, the order of stability in terms of ligands [L] is found to be oAP > oPDA > en. This trend could be explained in terms of electrostatic attractions. More electrostatic attraction is expected between mononegative [oAP]- and neutral [M-ADMP] complex than that between neutral [oPDA]/ [en] and [M-ADMP] complexes. Further Sigel [9] and Bhattacharya [10] have observed that in the case of ternary complexes with N,N donor like bipyridyl and 1,10-phenanthroline as primary ligands, the Δlog K values are positive if secondary ligands are O,O-donors, negative if the secondary ligands are N,N donors and midway between the two if the secondary ligands are N,O donors. In the present study the ligand ADMP is N,N donor, other ligands such as en, oPDA are N,N donors whereas the oAP is N,O donor. Similar argument could be extended for the ternary complexes containing ADMP (N,N donor) and the oAP (N,O donor) which show less negative value than other ternary complexes. Hence this trend in terms of donor atoms: NN,NO > NN is justified.

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