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CHEMISTRY

Inorganic Chemistry

BILIGAND COPPER(II) COMPLEXES IN SOLUTION : Cu(II)-BIPYRIDINE-PURINE SYSTEMS

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The biligand complexes of Cu(II) with 2,2′-bipyridine as primary ligand and some purine derivatives as secondary ligands in aqueous medium have been studied by *p*H titration technique. The formation constants of biligand complexes (log K^{CuA}_{CuAL}) as well as of monoligand complexes (log K^{Cu}_{CuL}) were evaluated by an algebraic method.

The formation constants of biligand complexes obtained at 25° and $\mu = 0.1\ M KNO_3$ are as follows :

Adenine, 5.22 hypoxanthine, 4.93; xanthine, 3.84; guanosine, 4.81; xanthosine, 2.36.

For the above systems the difference, $\triangle \log K = \log K^{CuA}_{CuAL} - \log K^{Cu}_{CuL}$ is negative.

Keywords : Copper(II) Complexes; Copper(II)-bipyridine-purine Mixed Complexes; Biligand Complexes of Copper(II); Formation of Biligand Copper(II) Complexes in Solution.

INTRODUCTION

DERIVATIVES of purines occur in many living matters, viz., in nucleic acids, urine, milk, and various animal and vegetable materials, both in the free state or in the combined form. A number of important coenzyme systems also contain these derivatives. Metal complexes of the purines, therefore, offer interest.

Several binary metal complexes of the purine derivatives have been reported (Izatt *et al.*, 1971; Nayan & Dey, 1972; and Makar & Williams 1974), but biligand complexes have not received sufficient attention. For the study of biligand complexes of Cu(II) with purine derivatives, 2,2′-bipyridine (bipy) was chosen as a primary ligand. Though bipy forms hydroxo complexes stable over a limited *p*H range in aqueous solution, the hydroxo compounds do not disproportionate readily to the metal hydroxide and the 2 : 1 (ligand : metal) chelate (Heureux & Martell 1966). Therefore, it seems reasonable that they would also form stable biligand complexes in solution. Several papers (Chidambaram & Bhattacharya, 1970, 1971; Joshi *et al.*, 1973; Sharma & Tandon, 1972; Dwivedi *et al.*, 1977; Agrawal *et al.* 1978; and Beck, 1970) have appeared in literature on the biligand complexes of Cu(II) with 2,2′-bipyridine as a primary ligand (A), though biligand complexes with purine derivatives as secondary ligands (L) have not been described. *p*H-metric studies on the systems Cu(II)-bipy-purines using Bjerrum-Calvin titration technique as employed by

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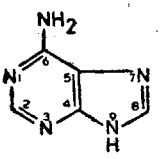
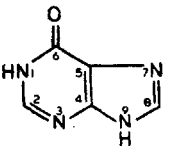
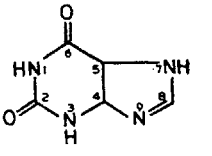
Goldberg (1962, 1963), are being described in this paper. The purine derivatives taken are adenine (ADN), hypoxanthine (HXNT), xanthine (XNT), guanosine (GNS), or xanthosine (XNS). The structures of these are shown below.



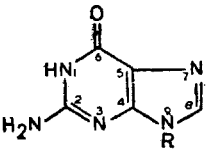
ADN



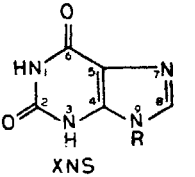
HXNT



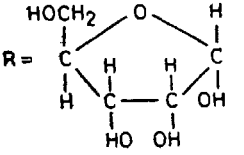
XNT



GNS



XNS



Ribose

EXPERIMENTAL

Materials

An aqueous copper(II) nitrate (BDH AnalaR) solution was prepared in water and was standardized as usual. An aqueous stock solution of bipy (E. Merck) was prepared by direct weighing. Fresh solutions of ADN (E. Merck), HXNT (Rearal, Budapest), XNT (Rearal, Budapest), GNS (E. Merck), XNS (E. Merck) were prepared in 0.02 M alkali. All chemicals used were of reagent grade.

Apparatus

*p*H measurements were done using an expanded scale *p*H-meter (Electronics Corpn. of India Ltd.) with a glass-calomel electrode assembly. The calibration was done with 0.05 M potassium hydrogen phthalate buffer (*p*H 4.0 at 25 °C), and was further checked with an alkaline buffer of *p*H 9.2.

Procedure

Six mixtures A, B, C, D, E, and F were prepared as below and were titrated separately against 0.2 N KOH (CO_2-free). In each case, the total volume was 50 ml, temperature maintained at 25 °C, and ionic strength at 0.1 M (KNO_3).

A. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + H_2O

B. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + bipy (0.01 M, 10.0 ml) + H_2O

C. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + bipy (0.01 M, 10.0 ml) + Cu^{2+}(0.01 M, 10.0) + H_2O

D. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + secondary ligand (0.01 M, 10.0 ml) + H_2O

E. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + bipy (0.01 M, 10.0 ml) + secondary ligand (0.01 M, 10.0 ml) + Cu^{2+}(0.01 M, 10.0 ml) H_2O

F. HNO_3(0.02 M, 10.0 ml) + KNO_3(1.0 M, 5.0 ml) + secondary ligand (0.01 M, 25.0 ml) + Cu^{2+}(0.01 M, 5.0 ml) + H_2O

The free acid in Cu(II) solution and the free alkali in the secondary ligand solution were taken into account in the calculations.

Results

It is observed from the titration curves obtained for the five sets of adenine as secondary ligand (Fig. 1) that Cu-bipy curve (C) diverges from the bipy (B) in the *p*H range 2–5.5 where a 1 : 1 complex is formed, the formation being complete around *p*H 5. The formation of hydroxo complexes of Cu-bipy occurs between *p*H 5.5 and 7.0. Though in a higher *p*H range the hydroxo complex formation takes place, but here $(Cu\ bipy)^{2+}$ (1 : 1) complex does not dissociate or disproportionate (Chidambaram & Bhattacharya, 1970, 1971).

In the case of mixed ligand titration, where the secondary ligand is also present (titration curve E) the curve E remains lower than C in the *p*H range 4.5 to 7. Proton from the secondary ligand gets liberated during titration which accounts for the lowering of the curve. After *p*H 7, the curve E coincides with C indicating thereby complete formation of mixed ligand complex. Therefore, in the *p*H range 4.5 to 7 the complex formation takes place as follows :

$$CuA + L \rightleftharpoons CuAL.$$

Similar titration curves (figs. omitted) were obtained with the other purine systems under reference with small variation in the *p*H range of biligand complex formation. Colour and *p*H range of mixed ligand complex formation for various systems are shown in Table I.

For the determination of protonation constants of secondary ligands, curve *D* was used and the average number of protons bound per free ligand molecule was calculated from Goldberg's approach (1962, 1963).

$$\bar{n}_H = \text{bound hydrogen ion/total ligand}$$

$$\begin{array}{lcccc} \text{bound} & & \text{total} & - \text{ reacted} & - \text{ dissociated} \\ \text{hydrogen} & = & \text{hydrogen} & - \text{ hydrogen} & - \text{ hydrogen} \\ & = & C_H & - C_{OH} & - ([H] - [OH]) \end{array}$$

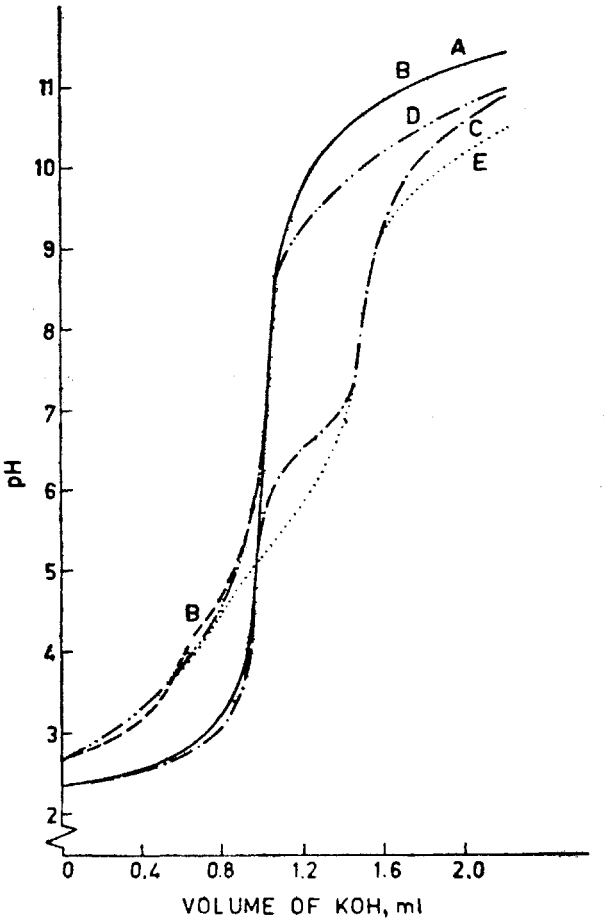


FIG. 1. Titration Curves Cu(II)-bipy-ADN System (25°, μ = 0.1 M KNO_3) A — Acid, B — Acid + bipy, C — Acid + bipy + Cu^{2+}, D — Acid+ADN, E — Acid + bipy + ADN+Cu^{2+}

TABLE I

Colour of biligand complexes formed

Systems	Colour
Cu(II)-bipy-ADN	Dark green
Cu(II)-bipy-HXNT	Green
Cu(II)-bipy-XNT	Yellow
Cu(II)-bipy-GNS	Blue
Cu(II)-bipy-XNS	Greenish blue

Therefore, $$\bar{n}_H = \frac{C_H - C_{OH} - [H] + [OH]}{C_{HL}} \quad \ldots(1)$$

C_{HL} is the initial concentration of the ligand L.

Formation curves were obtained by plotting n_H *vs.* pH, and at half integral values K_1^H and K_2^H were calculated (Beck 1970). In cases of HXNT, XNT, GNS and XNS, only one protonation constant was obtained and in case of ADN there were two protonation constants which are given in Table II.

TABLE II

Protonation constants of purine derivatives and the formation constants of complexes

(25°, $\mu = 0.1$)

Secondary ligand	$\log K_1^H$	$\log K_2^H$	$\log K_{CuL_1}^{Cu}$	$\log K_{CuAL}^{CuA}$	$\Delta \log K$
ADN	4.45	9.4	6.77	5.22	−1.55
HXNT	8.9	...	5.80	4.93	−0.87
XNT	7.51	...	...	3.84	...
GNS	9.70	...	5.82	4.81	−1.01
XNS	5.73	...	3.42	2.36	−1.06

The two equilibria with secondary ligand (L) can be represented as follows :

$$M + L \overset{K_{ML}^M}{\rightleftharpoons} ML \qquad ...(2)$$

$$MA + L \overset{K_{MAL}^{MA}}{\rightleftharpoons} MAL \qquad ...(3)$$

The values of the formation constants for equilibria (2) are available in literature (Izatt *et al.*, 1971; Nayan & Dey, 1972; and Makar & Williams 1974). In order to compare the values of K_{ML}^M and K_{MAL}^{MA}, K_{ML}^M were redetermined in the present work under identical experimental conditions using the graph obtained from the titration mixture *F* (curve *F* is omitted). The values agree with literature data.

To determine K_{MAL}^{MA} the free ligand concentration L was calculated from curve E using the expression (Goldberg, 1962)

$$[L] = \frac{C_H - C_{OH} - [H] + [OH]}{q_{H^1}[H] + 2q_{H^1}q_{H^2}[H]^2} \qquad ...(4)$$

where C_H is concentration of the hydrogen ion, C_{OH} is concentration of alkali at any point of the titration curve E

$$q_{H^1} = \frac{\bar{n}_H J_2' - \bar{n}_H' J_2}{J_1 J_2' - J_1' J_2} \qquad ...(5)$$

$$q_{H^2} = \frac{\bar{n}_H' J_1 - \bar{n}_H J_1'}{\bar{n}_H J_2' - \bar{n}_H' J_2} \qquad ...(6)$$

$$J_n = (1 - \bar{n}_H)[H] \qquad ...(7)$$

$$J'_n = (1 - \bar{n}'_H)\,[H] \qquad ...(8)$$

$\bar{n}_H$ and $\bar{n}'_H$ values were determined at 0.5 and 1.5.

Average number of ligands L attached per central MA is

$$\bar{n} = \frac{C_{HL} - [L]\,(1 - q_{H^1}[H] - q_{H^1}\,q_{H^2}[H]^2)^2}{C_M} \qquad ...(9)$$

where C_M is the initial concentration of metal ion, C_{HL} is initial concentration of the ligand.

Knowing [L] and $\bar{n}$ values formation constants were calculated from the expression

$$K^{MA}_{MAL} = \frac{\bar{n}}{(1 - \bar{n})\,[L]} \qquad ...(10)$$

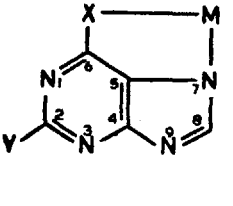
Values formation constants are given in Table II.

Further to ensure that K^{MA}_{MAL} value thus obtained is for 1 : 1 : 1 species the same experiment was carried out with different sets of metal-ligand concentrations. In all these sets of experiments same $\bar{n}$ values were found at same pH values which confirm the absence of any species other than 1 : 1 : 1.

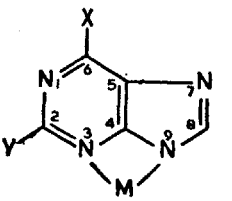
Discussion

In the case of ADN it has been indicated (Izatt *et al.*, 1971) that ionisation sites are $C_6—NH_3^+$ or $N_1—H^+$ and $N_9—H$ whereas in the cases of HXNT (Albert, 1953) and XNT (Ogston, 1935) it is reported that the possible ionisation site is 6-hydroxyl group (enol form). However, in case of GNS and XNS the presence of ribose group creates another possibility of ionisation from its own site through ribose hydroxyl groups. In case of adenosine (Izatt *et al.*, 1965, 1966), it has been established that for the dissociation of —OH group of ribose it is necessary to make the solution highly alkaline. In case of GNS and XNS, the ionisation takes place only in slightly alkaline medium indicating thereby that some other group is being ionized. It seems reasonable to consider the protonation of $N_1—H$ or $C_6—O$ and subsequent ionization at slightly alkaline medium.

The purine bases have two high electron density centres which are possible sites for metal ion chelation, viz., $C_6—NH_2$ or $C_6—O—N_7$(I) and $N_3—N_9$(II).



(I)



(II)

Chelation of Cu(II) by both sites has been suggested (Izatt *et al.*, 1971), though (II)

with a 4-membered ring is unlikely. In case of ADN both the modes of chelation would involve N/N donor complex. For the ligands HXNT, XNT, GNS, XNS it is assumed that chelation of type (I), i.e. through mixed donors, O/N, (X being O) occurs.

Generally, $(Cu\text{-}bipy)^{2+}$ binds with O-donor ligands more firmly than those with N donors and for mixed N/O ligands the binding is in between these two. (Sigel, 1973, 1979). This binding ability has been expressed by a parameter $\Delta \log K$ value which is the difference between $\log K^{CuA}_{CuAL}$ and $\log K^{Cu}_{CuL}$ values. For O/O donors generally it is positive and for N/N donors it is negative. For N/O donors values come in between.

From Table II, comparing the values of $\log K^{Cu}_{CuL}$ and $\log K^{CuA}_{CuAL}$ it may be seen that $\log K^{Cu}_{CuL}$ is greater than $\log K^{CuA}_{CuAL}$. The $\Delta \log K$ is negative in all cases except in case of xanthosine for it could not be determined due to hydrolysis.

The value of $\Delta \log K$ of ADN mixed complex is more negative (-1.55) than for other complexes (it is around -1). It appears from the magnitude of the values of $\Delta \log K$ that in case of ADN the complexation is through donors N/N and in the other cases it is O/N. Thus, complexation of type (I) is further substantiated in biligand complexes of Cu-bipy-purine systems.

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