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**Research Article**

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# Characterization by potentiometric procedures of metal binding properties of allopurinol in presence of ascorbic acid

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**ABSTRACT**

*The stability constant values of ternary complexation by transition metal ions such as Co (II), Ni(II),Cu(II),Zn(II) with allopurinol and ascorbic acid has been evaluated by potentiometric method. The ionic strength was maintained by $NaNO_3$ A computer based SCOG program is used to calculate stability constants. The trend in the stability constants varies for ternary complexes Co(II) > Zn (II) > Cu (II) > Ni(II).*

**Keywords:** Complexation; allopurinol ; ascorbic acid; stability constants

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## INTRODUCTION

Allopurinol is chemically known as 1,2-Dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one.It's molecular Formula: $C_5H_4N_4O$. Its structure is given is fig.1

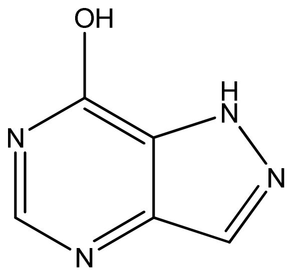


**Fig.1 structural formula of allopurinol**

This drug is used to control the uric acid production in the body. When complex formation is takes place, there may alteration in the production of such drugs. The study is also important from the point of view that will be helpful to know about the complexing nature of Allopurinol. Since it has atoms in the lone pair of electrons and transition metals are having empty d-orbitals to accumulate electrons denoted. In continuation of our earlier work with complexation of medicinal drug [1-6] we decided to undertake present investigation

## EXPERIMENTAL SECTION

**1 Materials:** NaOH, $NaNO_3$, $HNO_3$ & metal salts were of AR grade and was purchased from Sd fine chemical Ltd. The solutions used for the potentiometric titration were prepared in double distilled water. NaOH and $HNO_3$ solutions were standardized using known method before use. The metal salt solutions were also standardized using

EDTA titration. All the measurements were made at constant ionic strength of 0.1M $NaNO_3$.The thermostat model SL-131 (Adar Dutt and Co(India) Pvt. Ltd. Mumbai) was used to maintain the temperature constant. The pH measurement was made using a digital pH meter Elico L1-120 in Conjunction with a glass and reference calomel electrode (reading accuracy ± 0.01 pH units). The instrument was calibrated using buffer solutions of pH 4 and 9.18.

**2 Potentiometric procedures*:*** The proton ligand stability constants (protonation constant) of the primary and secondary chelating agents, and metal ligand stability constants (formation constants) of the complexes were determined by adopting the method suggested by Irving and Rossetti. For the determination of pK and logk values, six sets of the following solutions were titrated potentiometrically against carbonate free sodium hydroxide solution.

i. A: $HNO_3$ (0.2M) 5ml.
ii. $(A+L_1)$: $HNO_3$ (0.2M) 5ml+Allopurinol (0.01M) 5ml.
iii. $(A+L_2)$: $HNO_3$ (0.2M) 5ml+ ascorbic acid (0.01M)
iv. $(A+L_1 + M)$: $HNO_3$ (0.2M) 5ml + Allopurinol (0.01M) 5ml + metal (II) Nitrates (0.01 M) 5ml+ ascorbic acid (0.01M)
v. $(A+L_2 +M)$: $HNO_3$ (0.2M) 5ml+ ascorbic acid (0.01M)+ metal (II) Nitrates (0.01 M) 5ml
vi. $(A+L_1 +L_2+M)$: $HNO_3$ (0.2M) 5ml + Allopurinol (0.01M) 5ml+ ascorbic acid (0.01M) 5ml + metal (II) Nitrates (0.01 M)

All the systems were studied in 0.1M ($NaNO_3$) 5ml ionic strength at 298K temperature. The total volume of the test solution was raised to 50ml with double distilled water. The titrations were carried out in a 100ml beaker and stirred with magnetic stirrer. The reaction solution was potentiometrically titrated against the standard alkali of NaOH (0.2M) at 298K.

## RESULTS AND DISCUSSION

Allopurinol in complexation is used as one of the ligand, along with secondary ascorbic acids. The potentiometric Celvin Bjerrum method is used as discussed in the experimental section. The metal ligand stability constants for binary as well as ternary are determined .The protonation of allopurinol and ascorbic acid was determined by half integral method .It was found to be 9.36 for Allopurinol and 2.98 &7.08 for ascorbic acid.A binary system for Allopurinol with bivalent Metal ions has been already reported .[7] The binary system has ascorbic acid is shown in table1

**Table1. Protonation constant of Allopurinol**

| Metal | $pK_2$ | $logK_1$ |
|---|---|---|
| Co(II) | 9.36 | 3.29 |
| Ni(II) | 9.36 | 1.86 |
| Cu(II | 9.36 | 3.59 |
| Zn(II) | 9.36 | 3.51 |

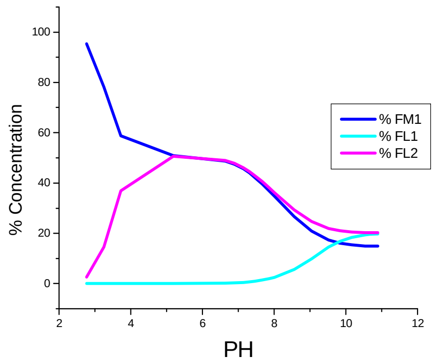
The table 2 shows stability constants for allopurinol, ascorbic acid, difference between the two stability constants and other complexing parameters. The theoretical ΔlogK value, for a square planner Copper(II) complex is – 0.6 the tendency to form ternary complexes was compared with this value, so that if Δlogk is greater than – 0.6, this should be taken to indicate that the ternary complex is favored. The ΔlogK value for ternary complexes are more positive than –0.6.

**2. Complexometric parameters of ternary complexes of Allopurinol and ascorbic acid**

| Metal | $Log\beta_L$ LogK1 (Logk2) | $Log\beta_R$ LogK1 (Logk2) | $Log\beta_{MLR}$ | ΔLogK | $KL_1$ | $KL_R$ | Kr |
|---|---|---|---|---|---|---|---|
| Fe(III) | 03.25 | 3.38 | | | | | |
| Co(II) | 03.28 | 3.29 (1.46) | 7.9936 | 2.4236 | 4.7136 | 4.7036 | 58.3277 |
| Ni(II) | 03.13 | 1.86 | 4.8800 | -0.26 | 1.6 | 3.02 | 18.6744 |
| Cu(II) | 03.10 | 3.59 | 6.3520 | -0.518 | 3.072 | 2.762 | 33.4780 |
| Zn(II) | 03.23 | 3.51 | 6.9904 | 0.2004 | 3.7104 | 3.4804 | 42.0757 |

When ascorbic acid is taken as ligand along with allopurinol nickel and copper shows negative ΔlogK values. Copper is having more negative values this indicates that the formation of ternary complex is not favored. in the case of Ni(II) &Cu(II), where as in Co(II) and Zn(II), ΔlogK values are positive. Co(II) is having more value indicating that ternary complexation is more favorable with Co ion. The trend in the stability constants of varies for ternary complexes Co(II) > Zn (II) > Cu (II) > Ni(II). In the fig1to fig 4 distribution of different species has been shown, which reflect the pH values at which complexation takesplace. . The equilibria can be ascertained as

| | | | |
|---|---|---|---|
| $H_2L_p$ | $\rightleftharpoons$ | $H_+ HL_S$ | $C_1$ |
| $HL_P$ | $\rightleftharpoons$ | $H_+ L_P$ | $C_2$ |
| $H_2L_S$ | $\rightleftharpoons$ | $H_+ HL_S$ | $C_3$ |
| $HL_S$ | $\rightleftharpoons$ | $H_+ L_S$ | $C_4$ |
| $M_+ L_P$ | $\rightleftharpoons$ | $ML_P$ | $C_5$ |
| $M_+ L_S$ | $\rightleftharpoons$ | $ML_S$ | $C_6$ |
| $M L_{S +} L_S$ | $\rightleftharpoons$ | $ML_{2s}$ | $C_7$ |
| $M_+ L_{P +} L_S$ | $\rightleftharpoons$ | $M L_P L_S$ | $C_8$ |



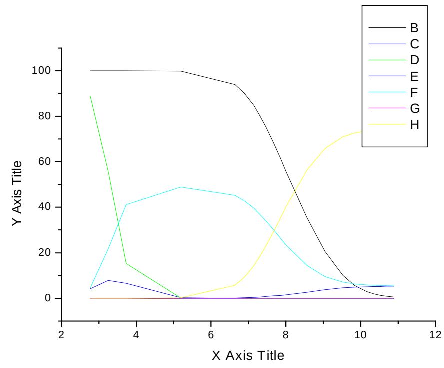
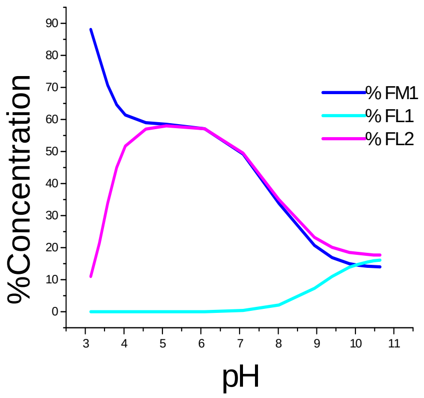




**Fig 1 (a)% concentration of free Cobalt(FM), Free Allopurinol ($FL_1$) and free ascorbic acid**
**(b) Species distribution curve for Cobalt(II)+ Allopurinol + ascorbic acid**



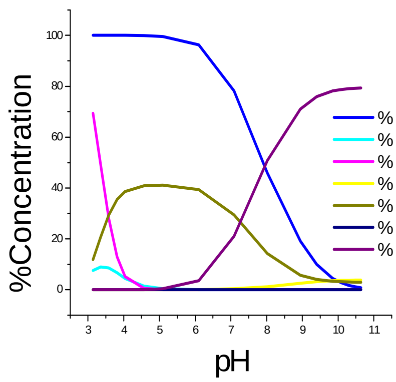
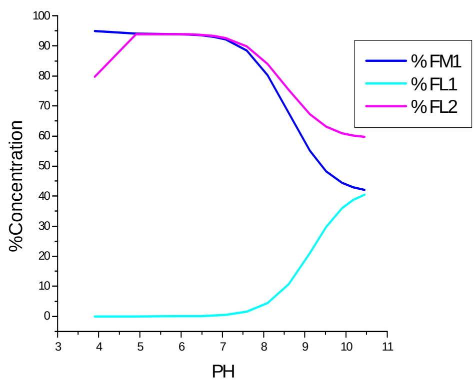




**Fig 2 (a)% concentration of free Copper (FM), Free Allopurinol ($FL_1$) and free ascorbic acid**
**(b) Species distribution curve for Copper (II)+ Allopurinol + ascorbic acid**



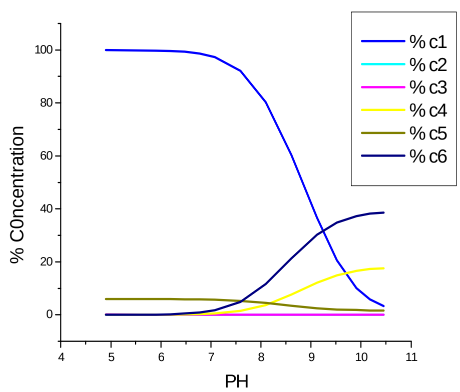




**Fig 3 (a)% concentration of free Nickel(FM), Free Allopurinol ($FL_1$) and free ascorbic acid**
**(b) Species distribution curve for Nickel(II)+ Allopurinol + ascorbic acid**

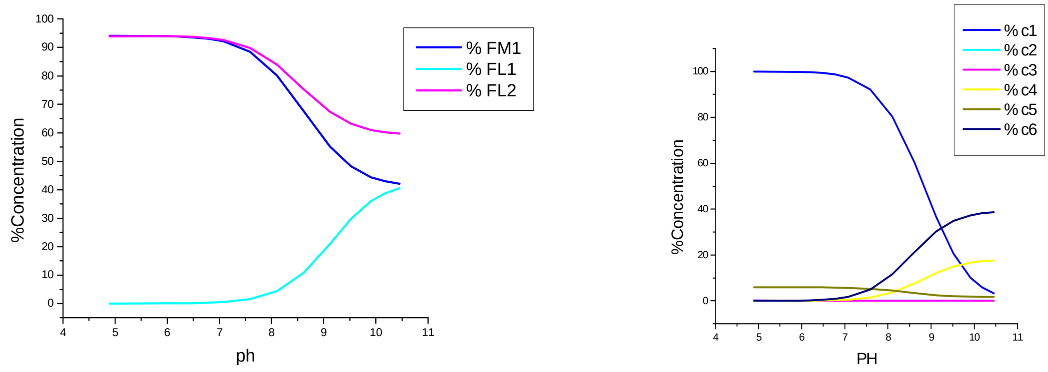



**Fig 4.(a)% concentration of free Zinc(FM), Free Allopurinol ($FL_1$) and free ascorbic acid (b) Species distribution curve for Zinc(II)+ Allopurinol + ascorbic acid**

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