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Metal Ligand Stability Constant Of Antisuril And Some Metal Ions In Aqueos Media.

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Abstract: The PH-Metric stability constant of binary & ternary complexes of antisuril with bivalent metal & Adipic acid in aqueous solution has been determined. The ionic strength was kept constant by Sodium nitrate. The stability constant of ternary complexes have been quantitively compared with those of corresponding binary complexes in terms of the parameter ΔlogK.

In constitution of previous work (*).we hereby report coordination behavior of Allopurinol elements belonging to transition metal

Introduction.

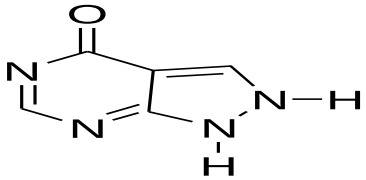
For the last few years the interest has been increased to study the interaction between metal ions and biologically active compounds. [(*)] This may due to the fact that some of the complexes shows different activities than the drug allopurinol itself.

Copper (II) complexes of fluroquinolone antimicrobial ciprofloxine synthesis x-ray structural characterization and potantiomtric study.

Antisuril.

Also known as lopurin, zyloprim ,allopurinol etc. molecular formula $C_5H_4N_4O$ .molecular wt.136.11146

A xanthyne oxidase inhibitor that decreases uric acid production .it also acts as an antimetabolite on some simple organisms.



It has 4- nitrogen hetro atoms in the ring system. Nitrogen contains lone pair electrons which can be used for the bonding purpose. Succinic acid possesses oxygen donor atom & can form complex with metal with mixed ligand complex formation of equilibria of cu (II) with glycylglycinate and gluanylurea.

In presence of antisuril there will be compititation for binary both of these ligands with metal ion.

At low PH metal coordinates with o-atom is replaced by deprotonated N-atom involving a structural equi-

librium this results in the formation of strong binary complexes.

Experimental

2.1 PH Titration.

All chemicals used were of analytical grade. Allopurinol was obtained from Dr.zahed Zahir (Associate.prof. Y. B. Chavan College of pharmacy, Aurangabad.) The ligands & metal nitrates were obtained from research laboratory. The potantiomtric PH titrations of ligands were performed at 39^0 c fresh solids were weighed out directly in to the reaction cell. The stock solution of analytically pure cobalt nitratrats was prepared and standardized volumetrically by titration with the disodium salt of EDTA in the presence of suitable indicator carbonate free NaOH was prepared & was standardized by titration with potassium hydrogen phthalate. The ionic strength was kept constant using 0.1M $NaNO_3$ as supporting electrolyte and relatively low concentration of ligands and metal ions (10^{-3}) M. An Elico digital PH meter fitted with a combined glass micro-electrode was used to determined hydrogen ion concentration. For determination of PH values below 3.5 & above 10.5.the system was calculated with standard HCl & NaOH solution respectively, each experiment was repeated at least three times.

2.2 Dissociation Constant.

The dissociation constant of ligands antisuril were determined by using the data from the experimental titration curve with help of computer program. The equilibria involved for the dissociation reaction are.

$$H_2L \xrightleftharpoons{K_1} HL + H^+$$

$$HL \xrightleftharpoons{K_2} H^+ + L$$

$$H_2L \xrightleftharpoons{K} 2H^+ + L$$

2.3 Stability Constant

To determine stability constant for 1:1 binary metal ligand complexes the following equation were used

$$M + L \rightleftharpoons ML$$

$$K^{L}_{(ML)} = \frac{[ML]}{[M][L]}$$

Table 1-Metal ligand stability constant of Antisuril

Allopurinol-	Pk_1	pK_2		
			$logK_1$	$logK_2$
Fe(II)	-	9.36	2.57	-
Co(II)	-	9.36	3.28	-
Ni(II)	-	9.36	3.13	-
Cu(II	-	9.36	3.10	-
Zn(II)	-	9.36	3.23	-

2-Metal ligand stability constant of Adipic Acid

Adipic Acid	Pk_1	pK_2		
			$logK_1$	$logK_2$
Fe(II)			3.46	
Co(II)		4.57	3.36	
Ni(II)			3.30	
Cu(II			3.62	
Zn(II)			3.54	

Result & Discussion:

The protonation constant of allopurinol was determined by using following equation.

$$n^{-} = \frac{(v_3 - v_2)}{(v_0 + v_2)} \frac{(N + \varepsilon^0)}{n^{-}_A T^0_M}$$

3. Stability constant of ternary complexes

Allopurinol-adipic acid	$\log\beta_L$		$\log\beta_R$		$\log\beta_{MLR}$	$\Delta\log K$	KL_L	KL_R	Kr
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$					
Fe(II)	03.25		03.46						
Co(II)	03.28		03.36		7.1403	0.5003	3.8603	3.7803	44.3439
Ni(II)	03.13		03.30		8.4309	2.0009	5.3009	5.1309	64.6501
Cu(II	03.10		03.62		7.8752	1.1552	4.7752	4.2552	55.2988
Zn(II)	03.23		03.54		7.7712	1.0012	4.5412	4.2312	53.6216

Graph 1.for Antisuril**+adipic acid Co(II)**

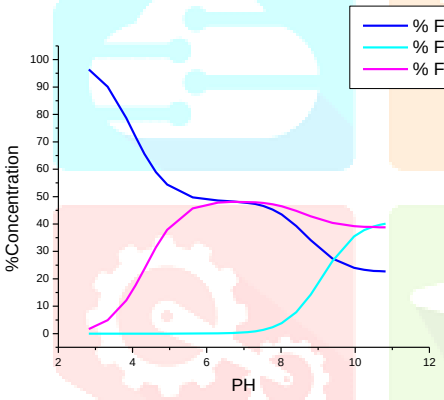


Fig. 1. Antisuril + adipic Acid-Co (II)(111)

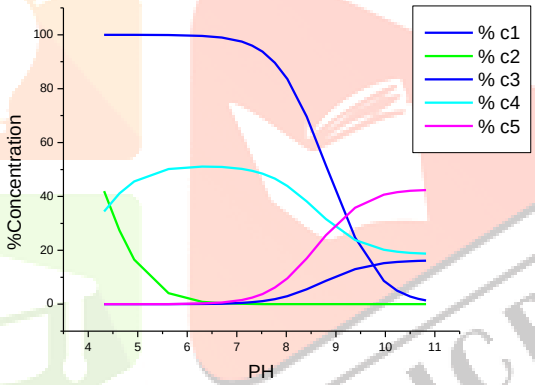
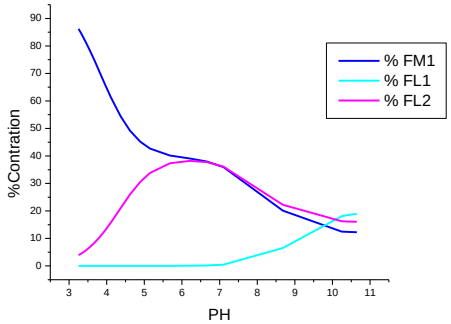
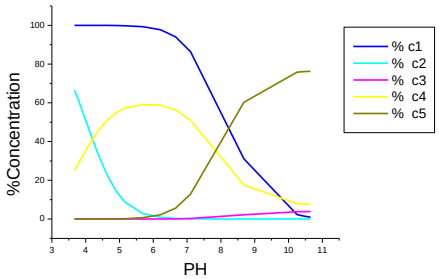


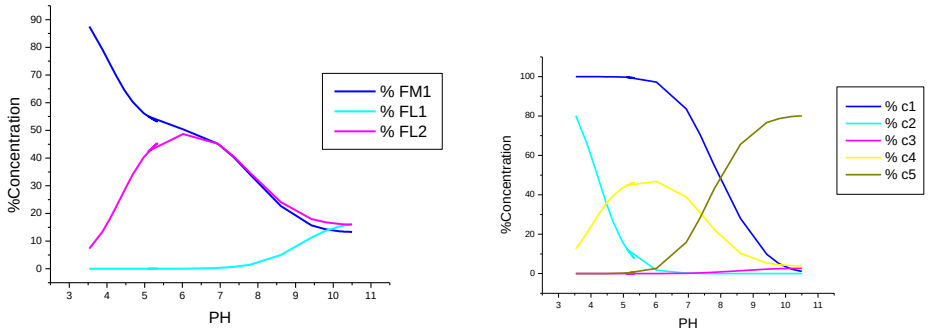
Fig.2: % conc. of free metal and free ligands

Graph 2. For Antisuril **-adipic acid Cu (II)**

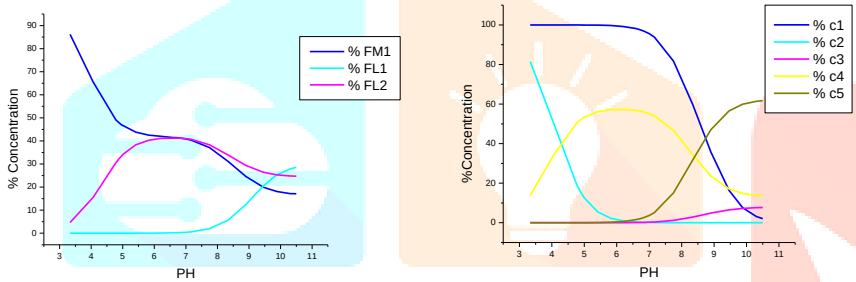




Graph 3. For Antisuril **+-adipic acid Ni (II)**



Graph 4. For Antisuril -adipic acid Zn (II)



The pka values of antisuril were found to be 9. 36.&that of Succinic acid was found to be 2.62 & 3.89, this is due to presence of –NH-group the values are different than secondary imines because in the present situation nitrogen is part of hexagonal and pentagonal rings. The metal ligand stability constant was determined by using following equation.

$$n^{-}_{A} = \gamma - \frac{(v_2 - v_1)(N + \varepsilon^0)}{(v_0 + v_1)T^0 L}$$

To insure the nature of species present in the solution when stiachometry is in doubt several Titrations were performed. It was observed that in 1:1 ratio the predominant species is ML. Though other species

Are also observed. Analysis of complexing ligands curve (not shown) indicates that addition metal ion-ns to the free ligands solution shifts the buffer region towards lower PH value hence complexation proc-

eeds by release of protons from horizontal displacement of complex curve. It can be inferred that complex

is strong[2]. mixed ligand complex formation of equilibria of cu (II) with glycylglycinate and gluanylurea.

The present study shows that 1:1 metal to ligand types of species are important .the titration curve (not shown) shows two inflections. After the addition of NaOH this suggests the dissociation of two protons from Adipic

acid in stepwise manner while in case of allopurinol single step is observed. These equilibria can be represented as.

$M+HL \leftrightarrow ML+H$

$\text{Log } K^{M}_{ML} = \log k\,(ML) - (\log [M] + \log [L])$

$ML+HL \leftrightarrow ML_2+H$

$\text{Log}k^{M}_{ML2} = \log [ML_2] - (\log [ML] + \log [[L])$

Similarly for allopurinol (L^1)

$\text{Log}k^{M}_{ML1} = \log [ML^1] - (\log [M] + \log [L^1])$

$\text{Log}k^{M}_{ML^1{}_2} = \log [ML^1{}_2] - (\log [ML^1] + \log [L^1])$

$\{\text{Log}\beta = \log k^{M}_{ML} + \log k ML_2 ML\}$.

The binary stability constant for antisuril is observed to be Fe(II)< Cu(II)< Ni(II)< Zn(II)< Co(II) for Adipic acid the trend observed is Ni(II)< Co(II)< Fe(II)< Zn(II)<Cu(II).The difference in trend was observed due to different nature of donor atoms. The sterichindrece is more in heterocyclic antisuril. In the ternary the trend observed was Co (II) < Zn (II) < Cu (II) < Ni (II).

ΔlogK values are found to be positive which indicate that the ternary complexation is more favorable than binary.

Conclusion:

Antisuril and Adipic acid both forms ternary complexes with transition metal ions.

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