

## Formation constants of binary & ternary complexes of Cu(II) with substituted 1,2,4-triazoles & some O,O; O,N & N,N donors in aqueous medium

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The formation constants of 1 : 1 and 1 : 2 binary (Cu-A and Cu-A<sub>2</sub>) and 1 : 1 : 1 ternary (Cu-A-L) chelates [where A = 4-amino-5-mercapto-1,2,4-triazole (AMT) or 4-amino-5-mercapto-3-methyl-1,2,4-triazole (AMMT) and L = ethylenediamine (en); 1,10-phenanthroline (Phen); 2,2'-bipyridyl (Bipy), *o*-phenylenediamine (OPDA); glycine (Gly); *o*-aminophenol (*o*-AP); catechol (Cat); oxalic acid (Oxa) or thiodiacetic acid (TDA)] have been determined potentiometrically in aqueous medium. The ligands AMT and AMMT behave as primary ligands in presence of en, Gly, *o*-AP and Cat, while in presence of Phen, Bipy, NTA, IMDA and Oxa, they act as secondary ligands. They coordinate simultaneously in presence of OPDA and TDA. The overall stability constants, Log  $\beta_{CuAL}^{Cu}$ , are discussed in terms of the basicity of ligands, statistical aspects, electrostatic interaction, metal-ligand  $\pi$ -interaction, denticity, nature of donor sites and stereochemical aspects.

The chemistry of 4-amino-5-mercapto-3-alkyl/aryl-1,2,4-triazoles has gained importance due to

their analgesic and anti-inflammatory activities<sup>1-3</sup>. Some studies on the complex forming ability of these triazoles with various metal ions have been reported<sup>4,6</sup>. However, little work has been done on the solution equilibria and the formation constants of binary and ternary complexes of 4-amino-5-mercapto-3-alkyl/aryl-1,2,4-triazoles. Therefore, it was thought worthwhile to investigate the formation constants of binary and ternary complexes of AMT and AMMT with Cu(II) in presence of other chelating agents in aqueous medium at  $30 \pm 1^\circ\text{C}$ ,  $I = 0.1 \text{ M}$  (KNO<sub>3</sub>).

### Experimental

The ligands AMT and AMMT were synthesised by known procedures<sup>7-9</sup>. All the other chemicals used were of AR grade. The general experimental procedures were similar to those described earlier<sup>10</sup>.

The proton-ligand and metal-ligand formation constants in binary system have been determined potentiometrically in aqueous medium and the values of  $\bar{n}_H$ ,  $pK_1$ ,  $pK_2$ ,  $\bar{n}$ ,  $pL$ ,  $\log K_1$  and  $\log K_2$  were calculated by Irving-Rossotti titration technique<sup>11</sup>. The formation constants of ternary complexes were determined using the method of Santappa *et al.*<sup>12</sup>

### Results and discussion

The  $\bar{n}$  values ( $0.1 < \bar{n} < 1.9$ ) for [Cu-AMT] and [Cu-AMMT] systems indicate the formation of 1 : 1 and 1 : 2 complexes. The ligands AMT and AMMT start coordinating to Cu(II) at pH 2.50. The metal-ligand formation constants have been evaluated by various computational techniques like half-integral method, pointwise calculation and linear plots. The average  $\log K_n$  values along with the  $pK_a$  values of the ligands are presented in Table 1. The standard deviations for proton-ligand and metal-ligand formation constants are within  $\pm 0.06$  log units.

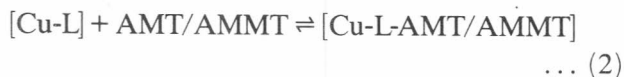
In the ternary systems studied, the mixed ligand curves closely follow those of the 1 : 1 [CuL] (where L = Phen, Bipy, IMDA, NTA and Oxa) binary curves in the lower pH region until the protons of primary ligands are neutralized, indicating the formation of binary [CuL] complexes in this region. The divergence of the ternary curves from the binary [CuL] systems above this region reveals the formation of ternary complexes of the type [Cu-L-AMT/AMMT] in two-step equilibria (Eqs 1 and 2) where AMT and AMMT act as secondary ligands (charges are omitted for clarity).



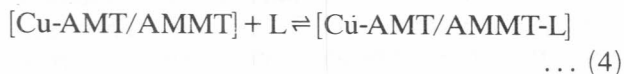
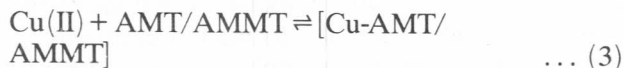
Table 1—Proton-ligand and metal-ligand stability constants of binary copper(II) complexes in aqueous medium

[ $I = 0.1 \text{ M}$  (KNO<sub>3</sub>); temp. =  $30 \pm 1^\circ\text{C}$ ]

Ligand	$pK_1$	$pK_2$	$\log K_{CuA/L}^{Cu}$	$\log K_{CuA_2/L_2}^{Cu}$
en	9.73	6.94	10.52	9.02
Phen	5.01	1.92	9.17	4.53
Bipy	4.48	1.51	8.07	5.51
OPDA	4.50	1.82	4.62	3.54
NTA	9.89	3.57	13.50	—
IMDA	9.12	3.21	10.63	6.05
Gly	9.54	2.45	8.32	6.54
<i>o</i> -AP	9.45	4.54	8.03	7.46
Cat	11.83	9.34	12.32	9.62
Oxa	3.78	1.29	4.82	3.22
TDA	4.22	2.96	4.52	2.92
AMT	7.47	—	7.42	6.44
AMMT	7.97	—	7.93	6.94



A similar consideration of pH titration curves suggests that in presence of en, *o*-AP, Gly and Cat, the ligands AMT and AMMT act as primary ligands. Thus, complex formation occurs according to Eqs 3 and 4



Either of the ligands, AMT or AMMT can undergo simultaneous coordination with Cu(II) (Eq. 5) in presence of ether TDA or OPDA. In these systems the ternary curves do not coincide either with [Cu-AMT/AMMT] curve or with [Cu-L] curve over the entire pH range and are well below the binary curves



The formation of ternary complexes is further supported by the non-superimposable nature of the

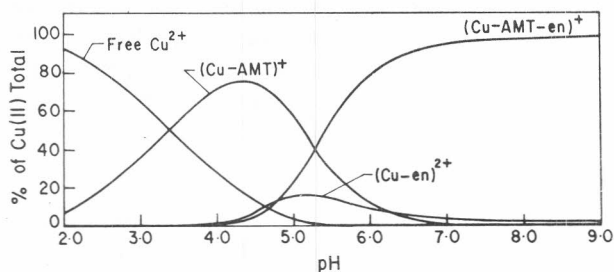


Fig. 1—Relative concentrations of binary and ternary complex species in [Cu-AMT-en]<sup>+</sup> systems (0.001 M each).

theoretical composit curves in the region of mixed ligand complex formation<sup>13</sup>. The stepwise formation and simultaneous formation of ternary complexes are confirmed by the plots of the concentrations of various species [as percentage of total Cu(II) present] against pH by the computer programme (BEST)<sup>14</sup>. A representative distribution diagram is presented in Fig. 1.

The order of formation constants of binary and ternary complexes with respect to AMT and AMMT is found to be AMMT > AMT. This is in accordance with their basicity order, because, for a series of similar ligands the higher the basicity of the ligand, the greater is the stability of the metal complex<sup>19</sup>.

In order to have uniformity and better correlation, stepwise formation constants have been converted into simultaneous formation constants (log β<sub>CuAL</sub><sup>Cu</sup> (Table 2) using the method of Sigel<sup>15</sup>. To discuss the order of log β<sub>CuAL</sub><sup>Cu</sup> values the ligands (L) are classified into several groups based on their donor sites, similarity in structure and denticity of the ligands.

In the case of Gly, IMDA and NTA, the observed stability order of the ternary complexes (NTA > IMDA > Gly) is in conformity with the denticities and basicities of these ligands. But the statistical values (Δ log K) are exactly in the reverse order (i.e. Gly > IMDA > NTA). This could have happened due to the availability of a lesser number of coordinating sites for the second ligand on the primary complex [Cu-L/A] compared to that on free Cu<sub>(aq)</sub><sup>2+</sup> ions<sup>16</sup> and charge neutralisation of the species during ternary complex formation.

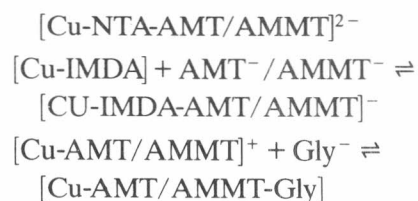


Table 2—Stability constants of ternary complexes of copper(II) complexes in aqueous medium

[I = 0.1 M (KNO<sub>3</sub>); temp. = 30 ± 1°C]

L	log K <sub>CuAL</sub> <sup>Cu</sup>	log K <sub>CuAL</sub> <sup>CuA</sup>	log K <sub>CuAL</sub> <sup>CuL</sup>	log β <sub>CuAL</sub> <sup>Cu</sup>	Δ log K	log K <sub>CuAL</sub> <sup>Cu</sup>	log K <sub>CuAL</sub> <sup>CuA</sup>	log K <sub>CuAL</sub> <sup>CuL</sup>	log β <sub>CuAL</sub> <sup>Cu</sup>	Δ log K
	A = 4-Amino-5-mercapto-1,2,4-triazole (AMT)					A = 4-Amino-5-mercapto-3-methyl-1,2,4-triazole (AMMT)				
en		9.39		16.81	-1.13		9.41		17.34	-1.11
Phen			6.44	15.61	-0.98			6.96	16.13	-0.97
Bipy			6.38	14.45	-1.04			6.90	14.97	-1.03
OPDA	10.46			10.46	-1.58	10.98			10.98	-1.57
NTA			5.35	18.85	-2.07			5.88	19.38	-2.05
IMDA			5.51	16.14	-1.91			6.03	16.66	-1.90
Gly		7.36		14.78	-0.96		7.37		15.30	-0.95
<i>o</i> -AP		7.34		14.76	-0.69		7.33		15.26	-0.70
Cat		12.63		20.05	+0.31		12.61		20.54	+0.29
Oxa			6.63	11.45	-0.79			7.13	11.95	-0.80
TDA	11.13			11.13	-0.81	11.62			11.62	-0.83

The standard deviation is between ± 0.02 and ± 0.07.



The stability order of ternary complexes formed by Phen, Bipy and OPDA is in accordance with the increasing order of their basicities and also depends on the conjugation in the ligand system (Phen & Bipy). This leads to  $d\pi - p\pi^*$  interaction between metal-ion and ligand. Hence, the  $\log \beta_{\text{CuAL}}^{\text{Cu}}$  order is Phen > Bipy > OPDA. This is also supported by the statistical data (i.e.  $\Delta \log K$  values).

Catechol, *o*-aminophenol and *o*-phenylenediamine have great similarity in structure with  $\text{O}^-$ ,  $\text{O}^-$ ;  $\text{O}^-$ , N and N, N donor sites. The observed stability constants ( $\log \beta_{\text{CuAL}}^{\text{Cu}}$ ) and  $\Delta \log K$  values of ternary complexes of these ligands are in the order Cat > *o*-AP > OPDA. This is primarily in conformity with the relative basicity values of the ligands. Further, in heterocyclic ligand systems like AMT and AMMT, metal  $\rightarrow$  ligand (A)  $\pi$ -back bonding is expected due to availability of vacant 'd' orbitals of sulphur atom present in AMT and AMMT. As a result of this, electron density on copper atoms of  $[\text{Cu-A}]^+$  primary complex is reduced. This enables the secondary ligand to donate lone pairs of electrons more efficiently. As has been pointed out by Bhattacharya *et al.*<sup>17</sup>, such  $[\text{M} \leftarrow \text{L}]$  charge-transfer interactions are maximum in  $\text{O}^-$ ,  $\text{O}^-$  donors like Cat<sup>18</sup>, minimum in N,N donors like OPDA and intermediate in  $\text{O}^-$ , N donors like *o*-AP. Hence the observed order is justified.

Oxalic acid, glycine and ethylenediamine are aliphatic bidentate ligands. They have  $\text{O}^-$ ,  $\text{O}^-$ ;  $\text{O}^-$ , N and N, N donor sites like Cat, *o*-AP and OPDA. The observed order of  $\log \beta_{\text{CuAL}}^{\text{Cu}}$  values (en > Gly > Oxa) is in accordance with their basicities and flexibilities, whereas the statistical ( $\Delta \log K$ ) values are found to be in the reverse order (i.e. Oxa > Gly > en). The observed order may be due to the greater interaction of oxalic acid and lesser interaction of ethylenediamine with Cu(II) ion. The said interaction is caused by lowering of electron density on Cu(II) ion due to back bonding from Cu(II) ion to AMT/AMMT<sup>19</sup> as explained in the case of Cat, *o*-AP and OPDA.

Iminodiacetic acid and thiodiacetic acid are tridentate ligands forming two-, five-membered chelate rings with Cu(II) ion. The ternary complex of IMDA has greater stability constant value than that of TDA system. This may be due to higher basicity of IMDA. However, a reversal in the  $\Delta \log K$  values

can be explained in the light of  $d\pi - d\pi$  back bonding between  $\text{Cu}^{2+}$  ion and the sulphur atom of TDA.

The stabilities of ternary complexes formed by glycine and ethylenediamine are greater than those of *o*-aminophenol, and *o*-phenylenediamine systems respectively. This may be due to greater basicities of glycine and ethylenediamine and greater flexibility of aliphatic glycine and ethylenediamine molecules when compared to aromatic analogs *o*-aminophenol and *o*-phenylenediamine respectively.

It can be seen that the binary complexes are more stable than the ternary complexes, resulting in negative  $\Delta \log K$  values for  $[\text{Cu(II)-AMT/AMMT-L}]$  systems (where L=en, Phen, Bipy, OPDA, NTA, IMDA, Gly, *o*-AP, Oxa and TDA). Such a lowering of stabilities of ternary complexes compared to that of binary chelates may be due to the greater destabilisation effect<sup>13,15</sup> caused by the ligand repulsion in the mixed ligand complexes than that in the binary systems, coupled with the availability of lesser number of coordinating sites for the second ligand on the primary complex  $[\text{Cu-A/L}]$  compared to free  $\text{Cu}_{(\text{aq})}^{2+}$  ions<sup>16</sup>.

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