

## Complexes of Cu(I), Ag(I), Tl(I), Zn(II) & Cd(II) with 3-Methyl & 3-Ethyl Derivatives of 4-Amino-5-mercapto-1,2,4-triazole

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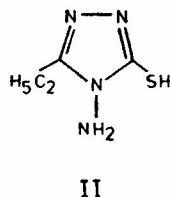
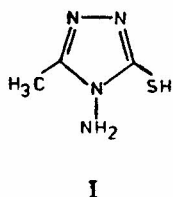
Complexes of Cu(I), Ag(I), Tl(I), Zn(II) and Cd(II) with 4-amino-3-methyl-5-mercapto-1,2,4-triazole and 4-amino-3-ethyl-5-mercapto-1,2,4-triazole have been prepared. Based on analytical data, spectral studies, magnetic susceptibility measurements and oxidation state studies, probable structures are suggested for these complexes. Cu(I), Ag(I) and Tl(I) complexes seem to be polymeric while Zn(II) and Cd(II) complexes appear to be tetrahedral chelates.

STRUCTURES of a number of metal complexes of mercapto derivatives of thiazoles have been reported in literature<sup>1-6</sup>. Besides, the ligands themselves are good analytical reagents<sup>7-12</sup> although they lack chelating ability. Mercapto derivatives of triazoles have great antiviral and anti-inflammatory activity<sup>13,14</sup>. 4-Amino-3-methyl-5-mercapto-1,2,4-triazole possesses chelating ability forming stable metal complexes. It has been used as an analytical reagent<sup>15,16</sup>. We report here the preparation and characterization of Cu(I), Ag(I), Tl(I), Zn(II) and Cd(II) complexes with 3-methyl and 3-ethyl derivatives of 4-amino-5-mercapto-1,2,4-triazole. These complexes can be expected to have great potentiality for industrial use.

### Materials and Methods

All the chemicals used were of AR or CP grade.

*Preparation of the ligands* — 4-Amino-3-methyl-5-mercapto-1,2,4-triazole (I) and 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (II) were prepared by the methods given in literature<sup>17,18</sup>. Ligand (I) is soluble in water while ligand (II) is soluble in ethanol.



*Complexes of Cu(I), Ag(I), Tl(I), Zn(II) and Cd(II) with ligand (I)* — Aqueous solutions of nitrates of Ag(I) and Tl(I) and sulphates of Cu(II), Cd(II) and Zn(II) were treated with 1:1 ammonia till there was a distinct smell of ammonia (1 g of solid ammonium chloride was added in the case of Zn(II) complex before the addition of ammonia to avoid possible hydrolysis). The clear solution

so obtained was heated nearly to boiling. To this, a hot aqueous solution of ligand (I) was added in slight excess over the molar ratio of 1:1 in the case of Ag(I) and Tl(I) and 1:2 in the case of the rest of the metal ions.

The Cu(I) and Ag(I) complexes precipitated immediately and settled down as amorphous mass on digesting over a water-bath for an hour. Zn(II) complex separated slowly in the form of colourless crystals on digesting over a water-bath. The Tl(I) complex separated in the form of colourless shining crystals while Cd(II) complex separated as colourless feather-like crystals on slow cooling. These complexes were separated by centrifugation, washed repeatedly with hot water, ethanol and ether and dried *in vacuo*.

*Preparation of complexes with ligand (II)* — The method of preparation was the same as described for ligand (I) except that an ethanolic solution of ligand (II) was used. The physical properties of the complexes with ligand (II) are identical to those with ligand (I).

The analysis of sulphur was carried out by fusing a known amount of the complex in a mixture of potassium hydroxide and potassium nitrate (8:1, w/w). The cooled melt was extracted with distilled water, acidified with appropriate mineral acid and the sulphate estimated as BaSO<sub>4</sub> (ref. 19).

Analysis of the metals in the complexes were carried out by dissolving a known amount of each complex in conc. HNO<sub>3</sub> or aqua regia followed by evaporation to dryness, extraction with distilled water and estimation of the metal ions<sup>19</sup>.

Carbon, hydrogen and nitrogen were analysed by the Microanalytical sections of the Central Drug Research Institute, Lucknow, and the National Chemical Laboratory, Poona.

### Results and Discussion

Analytical data (Table 1) show that Ag(I), Tl(I) and Cu(I) form 1:1 (metal-ligand) complexes while Zn(II) and Cd(II) form 1:2 (metal-ligand) complexes. Magnetic moment and EPR studies

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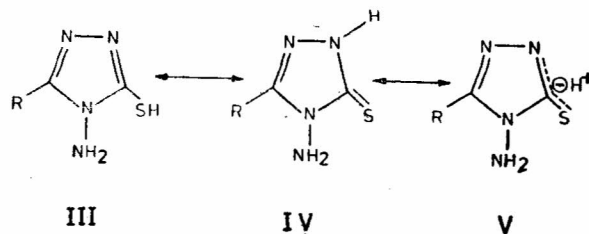
indicated the spin-paired diamagnetic nature of the copper complex. Redox studies<sup>20</sup> confirmed the +1 oxidation state of copper. It was found that 1 g atom of copper in complexes with (I) and (II) reduced 1.007 and 1.003 equivalents of iron against the expected value of 1.00.

The ligands can exist in the thiol or the thione forms (III-V). Since the ligand molecules contain an NCSH or HNCS group, thioamide bands are expected in the IR spectra of the ligands (I and II). In addition to confirming the existence of these bands the spectra also show bands around 2500 and 750  $\text{cm}^{-1}$  corresponding to  $\nu(\text{S}-\text{H})$  and  $\nu(\text{C}=\text{S})$  respectively, thus confirming the existence of tautomeric forms. In other words, the double bond in the thioamide group is delocalized as shown in (V).

The ligand molecules contain four donor sites, namely the two nitrogens in positions 1 and 2, the sulphur of thione (thiol) group and the nitrogen of the amino group. Coordination of metal ions through the nitrogen of the amino group and sulphur of the thione (thiol) group results in the formation of a five-membered ring and hence it is probably the most favoured arrangement. In addition to this further coordination at other positions cannot be ruled out.

A band around 2500  $\text{cm}^{-1}$  due to  $\nu(\text{S}-\text{H})$  in the spectra of the ligands is absent in the spectra of all the complexes indicating deprotonation of the thiol group and formation of metal-sulphur bond. Further, new bands around 350  $\text{cm}^{-1}$  appear in the spectra of the complexes confirming the formation of metal-sulphur bond.

*Structures of complexes of Cu(I), Ag(I) and Tl(I)*  
—If bonding occurs through the sulphur of the



thiol or thione group, the charge delocalized between N, C and S in the ligand molecules would get localized between N and C only as shown in VI. This would result in the shifting of the IR band due to  $\nu(\text{C}\cdots\text{N})$  towards higher wave numbers on complexation. The band due to  $\nu(\text{C}\cdots\text{S})$  would shift towards lower wavenumbers on complexation. Both these effects are actually observed since the thioamide band which has major contribution from  $\nu(\text{C}=\text{N})$  and minor contribution from  $\nu(\text{C}-\text{N})$ , appearing around 1295  $\text{cm}^{-1}$  in the spectra of the ligands, shifts by about 45  $\text{cm}^{-1}$  towards higher wavenumber side. The thioamide band around 750  $\text{cm}^{-1}$  in the ligands which is mostly due to  $\nu(\text{C}=\text{S})$ <sup>21</sup> shifts by about 70  $\text{cm}^{-1}$  towards lower wavenumber side on complexation.

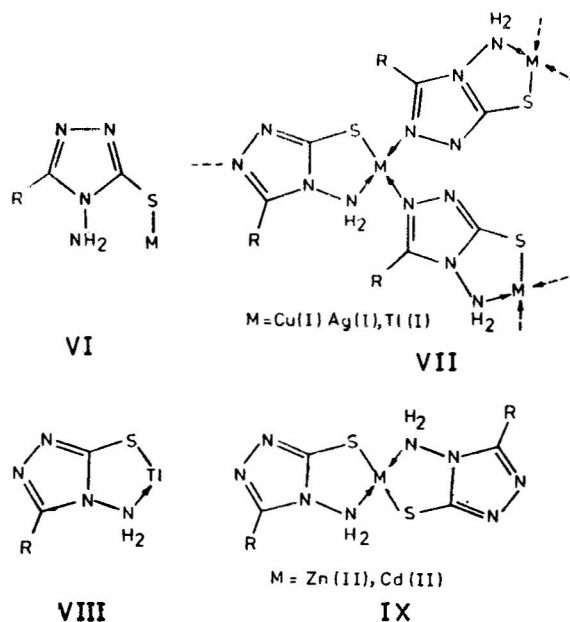
Besides, another new band appears in the spectra of the complexes around 400  $\text{cm}^{-1}$  indicating metal-nitrogen interaction.

On the basis of these facts and known preferences of Cu(I), Ag(I) and Tl(I) for tetrahedral structures<sup>22,23</sup>, the polymeric structures of type (VII) are proposed for these complexes.

Cu(I), Ag(I) and Tl(I) are all *b*-class metals and hence these would prefer to form bonds with easily polarizable sulphur<sup>24-27</sup> rather than nitrogen. This behaviour is particularly noticeable in the case of Tl(I) which has the highest *b*-class metal character and as a result the metal nitrogen bond should be quite feeble. At higher temperatures, monomeric chelates of type (VIII) can be formed in aqueous

TABLE 1 — ANALYTICAL DATA OF THE LIGANDS AND THE COMPLEXES

Compound	Calc. (Found), %				
	C	H	N	S	Metal
$\text{C}_3\text{H}_6\text{N}_4\text{S}$	27.69	4.62	43.08	24.62	—
Ligand (I)	(27.81)	(3.94)	(42.80)	(24.45)	—
$\text{Ag}(\text{C}_3\text{H}_5\text{N}_4\text{S})$	15.20	2.11	23.64	13.51	45.55
	(15.20)	(2.05)	(23.01)	(12.96)	(45.25)
$\text{Tl}(\text{C}_3\text{H}_5\text{N}_4\text{S})$	10.80	1.50	16.80	9.60	61.30
	(10.60)	(1.32)	(16.96)	(9.61)	(61.00)
$\text{Cu}(\text{C}_3\text{H}_5\text{N}_4\text{S})$	18.70	2.60	29.08	16.62	33.00
	(18.70)	(2.67)	(29.25)	(16.41)	(32.92)
$\text{Cd}(\text{C}_3\text{H}_5\text{N}_4\text{S})_2$	19.44	2.70	30.24	17.28	30.35
	(19.50)	(3.06)	(30.68)	(17.22)	(29.55)
$\text{Zn}(\text{C}_3\text{H}_5\text{N}_4\text{S})_2\text{H}_2\text{O}$	21.09	3.52	32.81	18.75	19.15
	(20.50)	(3.11)	(32.69)	(18.50)	(19.00)
$\text{C}_4\text{H}_8\text{N}_4\text{S}$	33.33	5.55	38.89	22.22	—
Ligand (II)	(32.57)	(5.87)	(38.57)	(22.08)	—
$\text{Ag}(\text{C}_4\text{H}_7\text{N}_4\text{S})$	19.13	2.79	22.32	12.75	43.00
	(19.16)	(3.44)	(21.92)	(12.45)	(42.35)
$\text{Tl}(\text{C}_4\text{H}_7\text{N}_4\text{S})$	13.82	2.02	16.12	9.21	58.84
	(13.95)	(2.08)	(15.99)	(9.02)	(58.41)
$\text{Cu}(\text{C}_4\text{H}_7\text{N}_4\text{S})$	23.24	3.39	27.11	15.49	30.76
	(23.39)	(3.06)	(27.07)	(15.81)	(30.16)
$\text{Cd}(\text{C}_4\text{H}_7\text{N}_4\text{S})_2$	24.09	3.51	28.11	16.06	28.21
	(23.89)	(3.37)	(27.03)	(16.09)	(28.17)
$\text{Zn}(\text{C}_4\text{H}_7\text{N}_4\text{S})_2$	27.32	3.98	31.87	18.21	18.61
	(27.21)	(4.10)	(31.72)	(18.08)	(18.25)



solution. This explains the solubility of Tl(I) complex in boiling water.

*Structures of complexes of Zn(II) and Cd(II)* — The IR spectra of these complexes also resemble those of Cu(I), Ag(I) and Tl(I). On the basis of 1:2 stoichiometry and known preference of Zn(II) and Cd(II) for tetrahedral geometry<sup>28</sup>, structures of type (IX) are proposed for these complexes.

The partial solubility of these complexes in boiling water can also be explained on the basis of monomeric nature of these complexes in contrast to polymeric nature of Cu(I), Ag(I) and Tl(I) complexes.

Since a band around 880 cm<sup>-1</sup>, characteristic of coordinated water, was not observed in the IR spectrum of the Zn(II) complex with ligand (I), it is assumed that the water molecule is lattice-held.

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