

PREPARATION AND CHARACTERISATION OF Cu(I), Ag(I), Tl(I), Zn(II), Cd(II) AND Pb(II) COMPLEXES WITH 3-ETHYL-4-BENZYLIDENE-5-MERCAPTO-1, 2, 4-TRIAZOLE

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ABSTRACT

Complexes of 3-ethyl-4-benzylidene-5-mercapto-1,2,4-triazole with Cu(I), Ag(I), Tl(I), Zn(II), Cd(II) and Pb(II) are prepared. Based on analytical data, spectral studies, magnetic measurement and oxidation state study, the probable structures have been proposed. Cu(I), Tl(I), Ag(I) complexes seem to be linear polymeric, while Zn(II), Cd(II) and Pb(II) complexes appear to be tetrahedral chelates.

INTRODUCTION

SUBSTITUTED 1,2,4-Triazoles are good gravimetric reagents^{1,2}. This aroused our interest in elucidating the structures of some metal complexes of these ligands³. In this pursuit we synthesized 3-ethyl-4-benzylidene-5-mercapto 1,2,4-triazole (Fig. 1). This reagent showed good co-ordinating ability, since precipitated Ag(I) in aqueous solutions quantitatively⁴. Since the reagent readily formed well defined crystalline complexes with other metal ions also, the preparation and characterisation of those complexes were taken up. Complexes of Cu(I), Zn(II), Ag(I), Cd(II), Tl(I) and Pb(II) are reported here.

EXPERIMENTAL

All chemicals used were of AnalaR grade or were chemically pure.

Preparation of the Ligand

The ligand was prepared by refluxing a mixture of 28.0 g of 3-ethyl-4-amino-5-mercapto-1,2,4-triazole⁵ and 21.00 ml of benzaldehyde in 200 ml absolute alcohol containing 5 drops conc. HCl for six hours. The excess solvent was vaporized over a waterbath. The product was recrystallized from ethanol as colourless crystals (m.p. 160° C).

General method of preparation of the complexes

A hot alcoholic solution of the ligand in slight excess over the molar ratio was added to hot ammonical solutions of nitrates or sulphates of Ag(I), Tl(I), Cu(II), Zn(II) and Cd(II) and alcoholic solution of lead acetate containing a few drops of acetic acid. Pale yellow crystalline complexes of Tl(I), Zn(II), Pb(II) and white complex of Cd(II) so obtained were filtered, washed with hot water, sparingly with ethanol and finally with ether. These complexes were dried in vacuum over anhydrous CaCl₂. The light yellow complex of Cu(I) and the white complex of Ag(I) were digested on a waterbath for 1 h, centrifuged, washed with hot water, warm ethanol and ether. The complexes were dried in vacuum. The complexes of Cu(I), Ag(I) and Tl(I) are insoluble in alcohol, while those of Zn(II), Cd(II) and Pb(II) are moderately soluble in the solvent.

Analyses

The analyses of C, H and N were carried out at the National Chemical Laboratory, Poona. Sulphur was analysed by alkali fusion method³. Metals in the complexes were estimated by standard methods⁶ after destroying the ligand with conc. HNO₃ or aqua regia.

RESULTS AND DISCUSSION

Analytical data (Table I) show that Ag(I), Tl(I) and Cu(I) form 1 : 1 (metal : ligand) complexes while Zn(II), Pb(II) and Cd(II) form 1 : 2 complexes. Magnetic susceptibility and redox studies⁷ confirmed the +1 oxidation state of copper. It was found that 1 g atom of copper in the complex reduced 1.05 equivalents of iron as against the expected value of 1.00 equivalent.

I.R. Spectra

The ligand molecule exists in both thiol and thione forms due to tautomerism. A broad band around 3100 cm⁻¹ due to γ (N-H) indicates the thione form while a medium intensity band around 2550 cm⁻¹ due to γ (S-H) indicates the thiol form of the ligand.

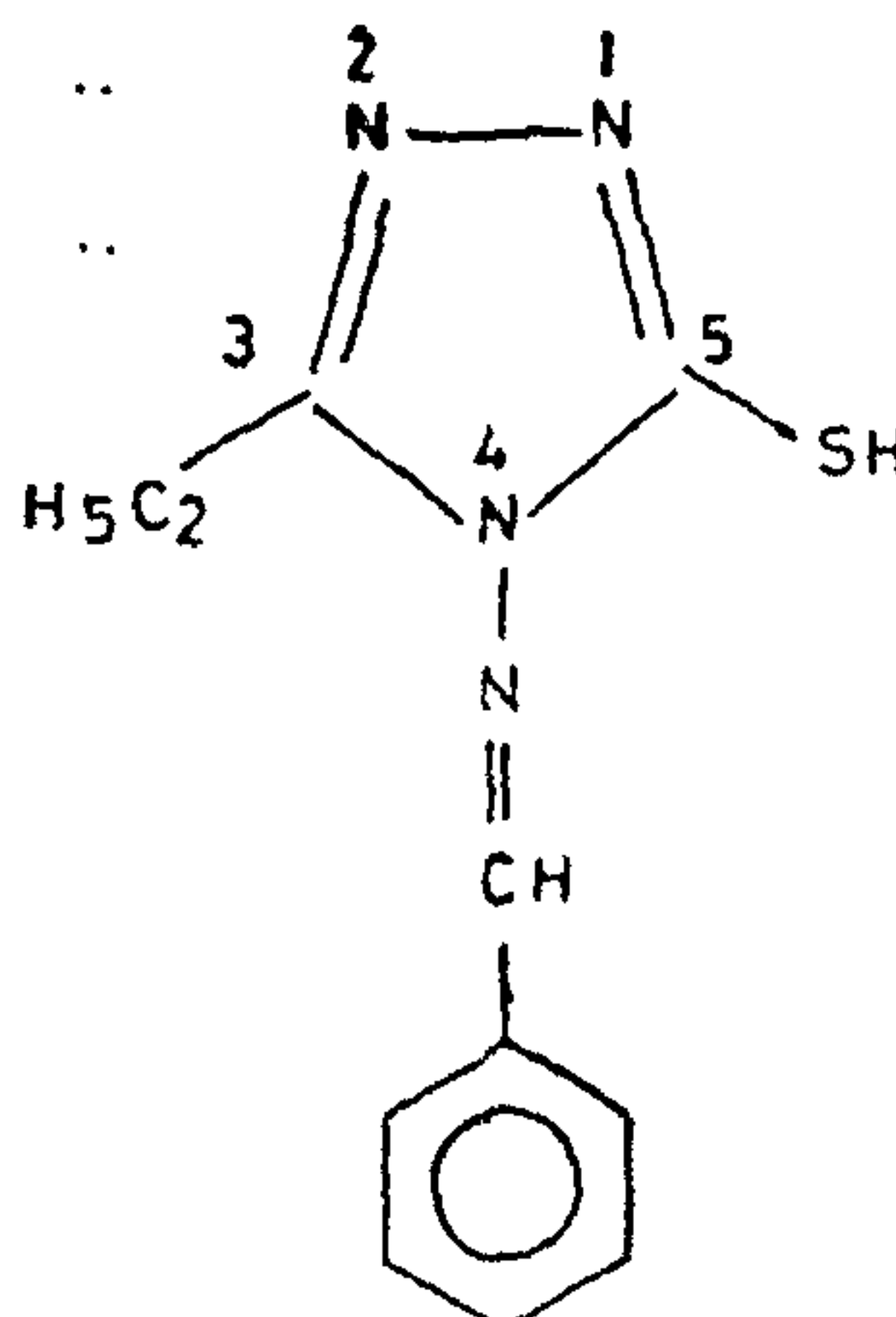


FIG. 1. 3-Ethyl-4-benzylidene-5-mercapto-1,2,4-triazole.

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TABLE I
Analytical data of the reagent and its complexes

Compound	C	H	N	S	M
	as percentages				
C ₁₁ H ₁₂ N ₄ S	56.87 (56.79)	5.21 (5.28)	24.12 (24.12)	13.80 (13.65)
Cu(C ₁₁ H ₁₁ N ₄ S)	44.81 (44.86)	3.76 (3.88)	19.00 (19.24)	10.87 (10.77)	21.55 (21.44)
Ag(C ₁₁ H ₁₁ N ₄ S)	38.96 (38.88)	3.27 (3.31)	16.52 (16.48)	9.45 (9.38)	31.80 (31.67)
Tl(C ₁₁ H ₁₁ N ₄ S)	30.32 (30.41)	2.54 (2.45)	12.86 (12.91)	7.36 (7.05)	46.91 (46.70)
Zn(C ₁₁ H ₁₁ N ₄ S) ₂	50.05 (50.17)	4.20 (4.38)	21.22 (21.34)	12.14 (11.98)	12.38 (12.23)
Cd(C ₁₁ H ₁₁ N ₄ S) ₂	45.96 (45.94)	3.85 (3.76)	19.49 (19.23)	11.15 (11.01)	19.55 (19.31)
Pb(C ₁₁ H ₁₁ N ₄ S) ₂	39.45 (39.35)	3.31 (3.67)	16.73 (16.81)	9.57 (9.73)*	30.94 (30.44)

* Found by difference. Values in parenthesis are the experimental and the others are calculated.

TABLE II

The positions in cm⁻¹ and assignments of major infrared bands in the spectra of the ligand and its complexes

Ligand	Ag(I), Tl(I), Cu(I) complexes	Zn(II), Cd(II), Pb(II) complexes	Assignment
3075-3120 (broad and split)	γ (N-H)
2560 ms	γ (S-H)
1585 Ss	1555 ± 5 ms	1560 ± 5 ms	Thioamide band I ^a
1300 Ss	1385 ± 5 Ss	1380 ± 10 Ss	Thioamide band II ^b
1028 m	975 ± 5 ms	972 ± 5 ms	Thioamide band III ^c
778 Ss	690 ± 2 Ss	695 ± 2 Ss	Thioamide band IV ^d
..	380 ± 5 ws	360 ± 10 w	γ (M-S)

(a) Due to γ (N-H) (major contribution) + γ (C=N) (minor contribution).

(b) Due to γ (C=N) (major contribution) + γ (C-N) (minor contribution).

(c) Due to γ (C-N) (major contribution) + γ (C=S) (minor contribution).

(d) Due to γ (C=S).

S = strong, s = sharp, m = medium, w = weak.

The ligand, being an acid, undergoes deprotonation resulting in charge delocalization between -N-C-S of the thioamide group. The metal ions can form complexes with the ligand by bonding at N or S and

of the deprotonated ligand molecule according as they are hard or soft acids considered from the 'Hard Soft Acid Base' theory⁸⁻¹⁰.

The ligand molecule contains a thioamide moiety $\text{H}-\overset{\text{I}}{\text{N}}-\overset{\text{I}}{\text{C}}=\text{S}$ or $\overset{\text{I}}{\text{N}}=\overset{\text{I}}{\text{C}}-\text{SH}$ and hence gives rise to four characteristic 'thioamide bands' in the i.r. spectrum of the ligand. Because of redistribution of the electron cloud as a result of complex formation, one can expect systematic shifts in the positions of these thioamide bands in the i.r. spectra of the complexes as compared to those of the ligand (Table II).

Bonding of the metal with ligand through thiol sulphur would localise the double bond between N and C of the thioamide group. This would result in the blue shift of the band due to γ (CN) and red shift of the band due to γ (CS), disappearance of the band due to γ (S-H) and appearance of a new band due to γ (M-S) in the spectra of the metal complexes¹¹⁻¹³. All these changes are observed (Table II).

Ag(I), Tl(I) and Cu(I) being soft acids show preference for bonding with sulphur — a soft base. Keeping this and their preferred geometries in view, linear polymeric structures are proposed for these complexes. Insolubility of these metal complexes in common non-coordinating solvents lends further support to the structures as proposed.

Metal ions like Zn(II), Cd(II) and Pb(II) have intermediate polarizabilities and so they can bond with 'a-class' bases like N or 'b-class' bases like S according as situation demands. Besides, they prefer to form tetrahedral complexes. Therefore they can bond with S of the thiolate group and co-ordinate with N of the benzylidene group of different ligand molecules simultaneously to form stable five membered chelates.

This is in conformity with charge balance too. Hence monomeric complexes of these metals seem to be a distinct possibility. The solubility of the metal complexes in alcohol lends further support to the structures as proposed.

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ON THE OCCURRENCE OF ABNORMAL STOMATA IN PLANTS

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ABSTRACT

A number of different types of unusual and abnormal stomata are described along with examples of taxa in which they have been reported. As the abnormalities are more common in mature leaves it is suggested that they are due to an interaction of factors responsible for stomatal differentiation and leaf maturation and may belong to the last generation of meristemoids.

INTRODUCTION

ALTHOUGH extensive information is available on abnormalities of different plant organs, relatively little is known of similar occurrences in the stomata. However, from time to time there have been scanty reports or passing remarks of unusual or abnormal

stomata in the literature. An exhaustive account of these is presented hereunder.

The term "stoma" (pl. stomata) is defined as a pore in the epidermis, bounded by two lenticular sister cells, called guard cells. The guard cells are normally elongated, their long axes being parallel to the pore. In *Azolla*, the guard cells are broader than long and the pore is directed at right angles to the polar axis. In *Hamelia patens** a stoma with two

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