

## Complexing Behaviour of 4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol

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### Abstract

A novel Schiff base ligand 4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3thiol [HETT] was derived by condensing 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol [AETT] with 3-(4-hydroxy-3-methoxyphenyl)prop-2-enal. Ag(I), Zn(II), Hg(II), Co(II) and Ni(II) complexes of HETT were prepared. The HETT and its metal complexes were characterised by various analytical methods. The HETT molecules are found to link to the metal ions, through thiol sulphur after deprotonation and the nitrogen of the azomethine group. The composition of the complexes are found to be ML where M= Ag, ML<sub>2</sub> where M= Zn, Hg and ML<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> where M= Co, Ni. Linear polymeric structure is proposed for Ag(I) complex, tetrahedral structure is proposed for Zn(II) and Hg(II) complexes, and octahedral structure is proposed for Co(II) and Ni(II) complexes.

**Keywords:** HETT, metal complexes, analytical studies, spectral analysis

### 1. Introduction

3-Substituted-4-amino-5-mercapto-1,2,4-triazoles have primary amine groups. They undergo condensation reactions with aldehydes and ketones to yield imine products known as Schiff bases [1]. Two ring nitrogen atoms at 1 and 2 in the triazole ring system, the tertiary nitrogen of the triazole ring, sulphur of mercapto group, and nitrogen of azomethine group are potential coordinating sites in the structure of Schiff base. Hence, Schiff bases readily form complexes with metal ions. Several complexes of transition metals with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4 triazoles have been synthesised and characterised [2-21]. By the literature survey, it was found that no work has been carried out for the synthesis and characterization of HETT and its metal complexes. The present work deals with the synthesis and characterization of complexes of Ag(I), Zn(II), Hg(II), Co(II) and Ni(II) with 4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol [HETT]. The structures of the ligand and metal complexes were determined by various methods like CHNS-O analysis, magnetic susceptibility measurements, thermal analysis, conductivity measurements and spectral analysis. Schiff bases and its complexes have a wide range of biological and non-biological applications.

### 2. Materials and Method

Analytical or chemically pure grade (Merck) reagents were used throughout the study. Carbon, hydrogen, nitrogen, sulphur and oxygen content of HETT and its complexes were analysed on microscale using Thermo Scientific (FLASH 2000)- CHNS-O Analyser. The magnetic susceptibilities of all the complexes were determined at room temperature using Gouy Balance. Thermogravimetric analysis of the complexes was carried on SDT Q600 V20.9 (Japan)-thermogravimetric analyser. The molar conductivities of the synthesised

complexes in  $1 \times 10^{-3}$  mol dm<sup>-3</sup> DMF solution were measured using Equiptronics: EQ-660A- Conductivity metre. The absorption spectra and infrared spectra of HETT and complexes were recorded on Jasco Model: V-360, ultraviolet visible spectrophotometer with quartz cell with a pathlength of 1 cm and Jasco Model: FT/IR 4100, fourier transform infrared spectrometer respectively.

#### 2.1 Synthesis of the ligand

The ligand was prepared by refluxing a mixture of 0.03 mol of 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol [AETT] and 0.03mol of 3-(4-hydroxy-3-methoxyphenyl)prop-2-enal in 50mL of absolute alcohol containing three drops of dilute HCl, for about three hours. Then the reaction mixture was cooled. The product was filtered and washed thoroughly with ether. Yellow crystals obtained was air dried and then recrystallised using ethanol containing 2-3 drops, dilute dil. HCl. Yellow crystals obtained were dried properly.

#### 2.2 Synthesis of 4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol)silver(I)

To a hot solution of ammoniacal AgNO<sub>3</sub> (2 mmol) in 60 mL water, a hot solution of HETT (2 mmol) in 30 mL of alcohol was added. The mixture was refluxed for an hour. The solution was cooled and filtered, washed with hot water, ethanol and finally with ether. The black coloured complex was dried at 100 °C.

#### 2.3 Synthesis of bis(4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol)zinc(II)

A solution of Zn(OOCCH<sub>3</sub>)<sub>2</sub> 2H<sub>2</sub>O (2 mmol) in 50 mL ethanol containing one drop of glacial acetic acid, was heated nearly to boiling and a hot solution of HETT (4 mmol) in 50 mL

ethanol was added dropwise. The solution was digested on a water bath for an hour. The yellow solid which slowly separated was filtered and repeatedly washed with hot water, ethanol and ether. The complex was dried at 110–120 °C.

#### 2.4 Synthesis of bis(4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol)mercury(II)

To a hot solution of HgCl<sub>2</sub> (2 mmol) in 50 mL of ethanol, a hot solution of HETT (4 mmol) in 50 mL ethanol was added and the mixture was refluxed for an hour. A grey solid separated on adding few drops of sodium acetate solution. Solid was filtered and repeatedly washed with hot water, ethanol and ether. The complex was dried in hot air oven.

#### 2.5 Synthesis of diaquabis(4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol)cobalt(II)

To a hot solution of CoCl<sub>2</sub> 6H<sub>2</sub>O (4 mmol) in 30 mL of water containing 1g NH<sub>4</sub>Cl and enough ammonium hydroxide to make the solution ammoniacal, a hot ethanolic solution of HETT (8 mmol) was added. The mixture was refluxed for an hour. The solution was cooled and stirred well. The coffee brown coloured complex was filtered, washed with hot water, ethanol and finally with ether and dried in hot air oven.

#### 2.6 Synthesis of diaquabis(4-[[3-(4-hydroxy-3-methoxyphenyl)prop-2-enalidene]-amino]-5-ethyl-4H-1,2,4-triazole-3-thiol)nickel(II)

To a hot solution of NiCl<sub>2</sub> 6H<sub>2</sub>O (4 mmol) in 30 mL of water containing 1g NH<sub>4</sub>Cl and enough ammonium hydroxide to make the solution ammoniacal, a hot ethanolic solution of

HETT (8 mmol) was added. The mixture was refluxed for an hour. The solution was cooled and stirred well. The coffee brown coloured complex was filtered, washed with hot water, ethanol and finally with ether and dried in hot air oven.

### 3. Results and discussion

#### 3.1 Nature and stoichiometry

The results of CHNS-O analysis are presented in Table 1. The analytical results show that Ag(I) forms ML type complexes while Zn(II) and Hg(II) form ML<sub>2</sub> type complexes. The Co(II) and Ni(II) complexes of HETT are of ML<sub>2</sub> type with two coordinated water molecules. The thermograms of Co(II) and Ni(II) complexes indicate a two-stage decomposition. The first stage around 200°C, corresponds to the weight loss due to coordinated water molecules. The second stage around 600 °C is sharp and which corresponds to the decomposition of organic matter and formation of metal oxides. The complexes exhibit molar conductance in the range 6.3–44.5 ohm<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>. The comparatively low values indicate that complexes are non-electrolytes and are neutral in nature.

#### 3.2 Magnetic susceptibility

The magnetic susceptibility studies showed that all complexes, except Co(II) Ni(II), are diamagnetic. The magnetic moment of the cobalt-HETT is 4.86 BM at room temperature. Since the orbital contribution of octahedral Co(II) is much more than that of tetrahedral complexes, octahedral Co(II) complexes have higher values of magnetic moments, as compared to that of tetrahedral complexes [22]. The magnetic moment of the Ni(II) complex of HETT at room temperature is 3.22 BM, which is in good agreement with those reported for octahedral nickel(II) complexes [23].

Table 1: Analytical data of HETT complexes

Complex	Found (Calculated) %					
	C	H	N	O	S	M
C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S (Ligand)	55.23 (55.26)	5.31 (5.26)	18.41 (18.42)	10.51 (10.53)	10.54 (10.53)	-
Ag(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S)	40.76 (40.78)	3.91 (3.88)	13.61 (13.59)	7.76 (7.80)	7.79 (7.77)	26.17 (26.18)
Zn(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub>	49.87 (49.93)	4.80 (4.75)	16.62 (16.64)	9.48 (9.51)	9.52 (9.51)	9.71 (9.66)
Hg(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub>	41.54 (41.50)	3.99 (3.95)	13.86 (13.83)	7.90 (7.92)	7.93 (7.90)	24.78 (24.90)
Co(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ·2H <sub>2</sub> O	47.79 (47.80)	5.15 (5.12)	15.95 (15.93)	13.62 (13.66)	9.12 (9.10)	8.37 (8.39)
Ni(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ·2H <sub>2</sub> O	47.81 (47.82)	5.15 (5.12)	15.92 (15.94)	13.65 (13.66)	9.13 (9.11)	8.34 (8.35)

#### 3.3 Electronic spectra

Electronic spectral band positions and assignments for the complexes of HETT are given in Table 2. For cobalt complexes, one can expect three bands corresponding to transitions, <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F); <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P). The ratio of the frequencies of the second (18 Dq) to the first transition (8 Dq) around 2.2 predicts octahedral structure [24] for Co(II) complex. For Nickel complexes, one can expect three bands corresponding to transitions, <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F); <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F)

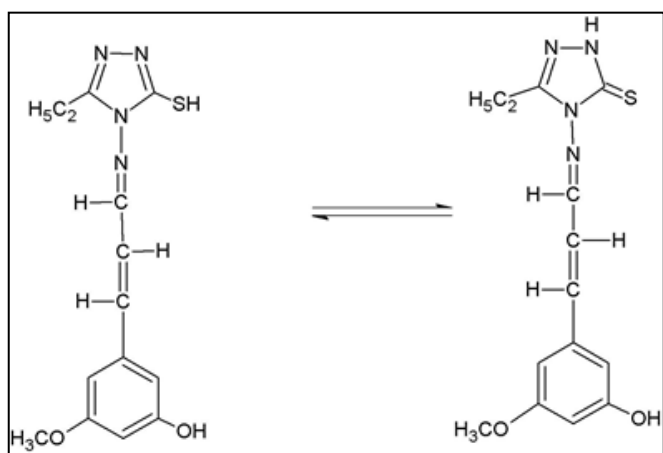
and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P). The ratio of the frequencies of the second (18 Dq) to the first transitions (10 Dq) around 1.8 predicts octahedral geometry [25] for Ni(II) complex. The value of Racah parameters ( $\bar{B}$ ) of both the complexes [26] are lower than the respective free-ion value i.e. 1117 cm<sup>-1</sup> in the case of Co(II) and 1082 cm<sup>-1</sup> in the case of Ni(II), indicate a high degree of covalent character in the metal-ligand bond in these complexes. The band position of the first transition in both complexes was calculated.

**Table 2.** Electronic Spectral Bands and their probable assignments of complexes

Complex	Band Positions (cm <sup>-1</sup> )	Assignment	10 Dq	$\bar{B}$	$\beta$
Co(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ·2H <sub>2</sub> O	7820 (Ca)	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)	9129	988	0.88
	16949	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)			
	21459	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)			
Ni(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> S) <sub>2</sub> ·2H <sub>2</sub> O	9216 (Ca)	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)	9216	781	0.72
	14837	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)			
	24510	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)			

### 3.4 Infrared Spectra

The ligand contains thioamide moiety (-N=C-S-H, H-N-C=S) and is expected to exist in tautomeric forms namely thiol and thione forms [Figure 1]. Simultaneous coordination of metal ions through nitrogen of the azomethine group and sulphur atom of the thiol (thione) group results in the formation of a five-membered chelate structure which probably may be most favoured arrangement.

**Fig 1:** Thiol-Thione form of HETT

The infrared spectrum of the ligand has the bands in the region 3283 cm<sup>-1</sup> due to  $\delta$ (N-H), in the region 2992 cm<sup>-1</sup> due to  $\nu$  (-C-H) and in the region 1978 cm<sup>-1</sup> due to  $\nu$  (=C-H). Thioamide band I has major contribution from  $\delta$ (N-H) and minor contributions from  $\nu$ (C=N) and  $\nu$ (C-H), is observed around 1559 cm<sup>-1</sup> in the spectrum of ligand. If the charge localisation occurs between C and N, this band would be expected to shift towards higher wave number side. However, contribution from  $\nu$ (C=N) being minor, such a shift would not be considerable. During complex formation deprotonation of the ligand takes place and  $\delta$ (N-H) disappears in the spectra of the complexes. As an overall effect Thioamide band I shifted slightly towards lower wave number side. Thioamide band II suffered a considerable shift towards higher wave number side. The thioamide band II at 1202 cm<sup>-1</sup> in the spectrum of ligands is shifted to around 1246 cm<sup>-1</sup> in complexes. Thioamide band III having a major contribution from  $\nu$ (C=N) and minor contribution from  $\nu$ (C=S), in the region around 932 cm<sup>-1</sup> in the spectrum of the ligand is found to be shifted slightly towards higher wave number side in the spectra of complexes. Thioamide band IV suffered a considerable shift towards lower wave number side. The thioamide band IV at 846 cm<sup>-1</sup> in the spectrum of ligand shifted to around 782 cm<sup>-1</sup> in spectra of complexes. The high intensity of the thioamide

band IV is due to the mixing of thioamide band IV with the band characteristic of phenyl ring. The band in the spectrum of the ligand at 1032 cm<sup>-1</sup>, due to  $\nu$  (N-N) of triazole is shifted towards the lower wave number side in the spectra of metal complexes. It indicates that the nitrogen of azomethine group forms the bond with the metal in the complex. Bands in the region around 3648 cm<sup>-1</sup> due to phenol group, in the region around 1077 cm<sup>-1</sup> due to ether group and in the region around 732 cm<sup>-1</sup> due to aromatic ring are observed in both ligand as well as complexes. New bands corresponding to  $\nu$ (-M-N) and  $\nu$ (-M-S) appeared around 520 cm<sup>-1</sup> and 454 cm<sup>-1</sup> respectively in the spectra of the complexes. In addition to these bands, additional bands around 3464 cm<sup>-1</sup> due to  $\nu$ (O-H) and around 902 cm<sup>-1</sup> characteristic of coordinated water, are also observed in the spectra of Co(II) and Ni(II) complexes. All these bands and shifts are presented in Table 3.

**Table 3.** Infrared band positions and their probable assignments of HETT and its complexes (cm<sup>-1</sup>)

Ligand	Complexes		Assignments
	Ag(I), Zn(II), Hg(II)	Co(II), Ni(II)	
3648	3631 ± 10	3645 ± 05	Phenol group
-----	-----	3464	$\nu$ (O-H)
3283	-----	-----	$\nu$ (N-H)
2992	2954 ± 10	2969 ± 10	$\nu$ (C-H)
1978	1959 ± 10	1937 ± 10	$\nu$ (=C-H)
1629	1624 ± 05	1629 ± 05	$\nu$ (C=N)
1559	1548 ± 10	1539 ± 05	Thioamide band I
1202	1246 ± 10	1246 ± 10	Thioamide band II
1077	1070 ± 10	1075 ± 05	Ether group
1032	1032 ± 10	982 ± 10	$\nu$ (N-N) triazole
932	941 ± 10	941 ± 10	Thioamide band III
-----	-----	902	Coordinated water
846	782 ± 05	781 ± 05	Thioamide band IV
732	713 ± 10	713 ± 10	Aromatic ring
----	520 ± 10	520 ± 10	$\nu$ (M-N)
-----	454 ± 10	454 ± 10	$\nu$ (M-S)

### 4. Conclusion

On the basis of analytical, magnetic, thermal, molar conductance, electronic and infrared spectral data and keeping in view of the preferred geometries, Ag(I) complex has linear polymeric structure (Figure 2), tetrahedral structures are proposed for Zn(II) and Hg(II) complexes (Figure 3), while octahedral structures are proposed for Co(II) and Ni(II) complexes (Figure 4).

In conclusion, the ligand molecules link with metal ions, through thiol sulphur after deprotonation and the nitrogen of the azomethine group.

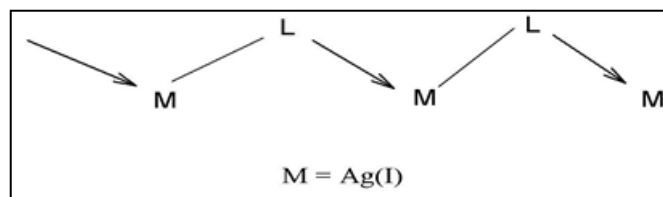


Fig 2: Structure (linear) of Ag(I) complex

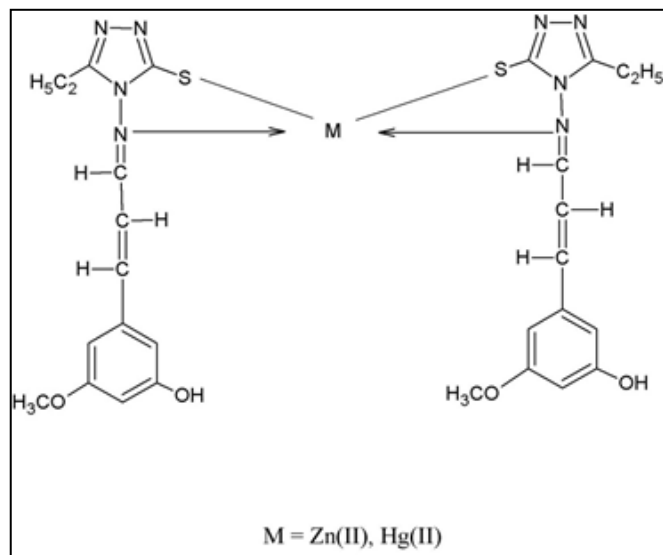


Fig 3: Structures (Td) of Zn (II) and Hg(II) complexes

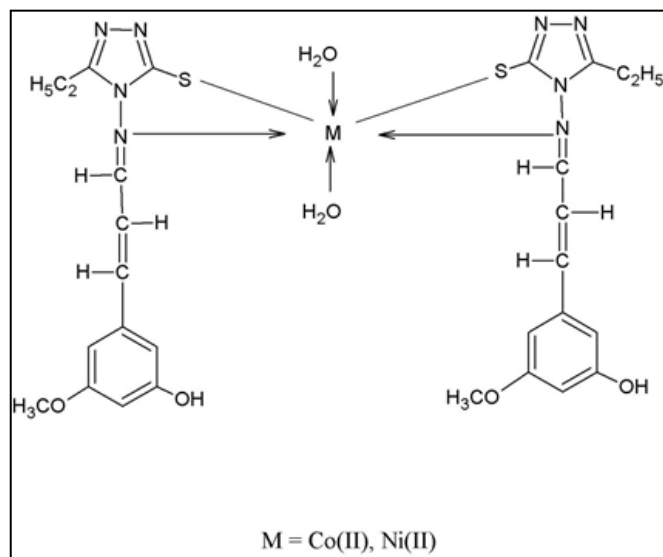


Fig 4: Structures (Oh) of Co(II) and Ni(II) complexes

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