

# Synthesis and Characterization of Zirconium(IV) Complexes with 4-Amino-3-Ethyl-S-Triazole-5-Thione

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## Abstract

Metal chelates of 4-amino-3-ethyl-s-triazole-5-thione have been prepared with Zr(IV) salts at different pH and their structure are elucidated by various physico-chemical studies. Metal-ligand vibrations in far infrared spectra have been located and tentatively assigned. Octahedral configuration have been assigned for all Zr(IV) complexes.

**Keywords:** Synthesis, Characterization, Zirconium, Triazole, Complexes, Octahedral.

## Introduction

Schiff bases containing polyfunctional groups offer many practical advantage of unique environment for complexation<sup>1,2</sup>. Triazole derivatives have interesting ligational properties and have proved to be promising chelating against a number of transition elements<sup>3,4</sup>. The present studies deals the synthesis, spectral analysis and characterization of some mixed ligand complexes of tetravalent Zr ions with 4-amino-3-ethyl-s-triazole-5-thione (AESMTH) as primary ligand and pyridine as secondary ligand. Triazole contains active NH, C=S, H-N-C=S coordinating groups and has been shown that all three groups are involved in bond formation with transition metal ion in complexation.

## Review of The Literature

Triazole derivatives have shown various bonding scopes<sup>5-6</sup>. Various workers reported on metal triazole complexes<sup>7-8</sup>. Versatile uses of triazole derivatives attract workers to work with it.

## Objective of the study

The interaction of Zirconium(IV) with organic ligands are very interesting from structure and bonding point of view<sup>9</sup> and are reported with several oxygen donor<sup>10</sup>, nitrogen donor<sup>11</sup> Schiff base and many heterocyclic thioamides<sup>12</sup>. The present work reports this complexation study of Zirconium(IV) using 4-amino-3-ethyl-s-triazole-5-thione(AESMTH) as ligand at different pH values. The involvement of thione and thiol tautomeric form of ligand (Fig.1) is also studied. It would provide a biological study for some antifungal and many other drugs.

## Experimental

All chemicals used were C.P. grade and A.R. grade sample of metal salts of  $Zr(NO_3)_4 \cdot 5H_2O$ ,  $Zr(SO_4)_2 \cdot 4H_2O$  and  $ZrO(NO_3)_2 \cdot 2H_2O$ . The ligand was prepared by the method of Dutta et al<sup>13</sup>. All Zr(IV) complexes were prepared using a general method. Ethanolic metal salt and ligand were mixed in an appropriate molar ratio. The mixture was refluxed on a hot plate magnetic stirrer and its volume was reduced to 50 ml. pH of the mixture was adjusted as required using pyridine/NaOH and dilute mineral acid of corresponding metal salt. The complexes obtained with different metal ligand ratios were washed with ice cooled ethanol and dried in a vacuum desiccator over anhydrous  $CaCl_2$ . The analytical results are given in table-1.

The IR spectra of ligand and complexes were recorded on a Perkin-Elmer Modle-577 spectrophotometer in the range of 4000-200  $cm^{-1}$  as KBr pellets. The magnetic measurements were made on a Gouy balance and diamagnetic corrections for the ligand molecules were applied. The U.V. and visible spectra of the ligand and complexes were recorded on a Beckmann and Carl Zeiss(Jenna) spectrophotometer. The molar conductance of complexes( $10^{-3}M$ ) were measured in DMF using Wiss-Werkstatter Wertheim Obb type LBR conductivity meter.

## Results and Discussion

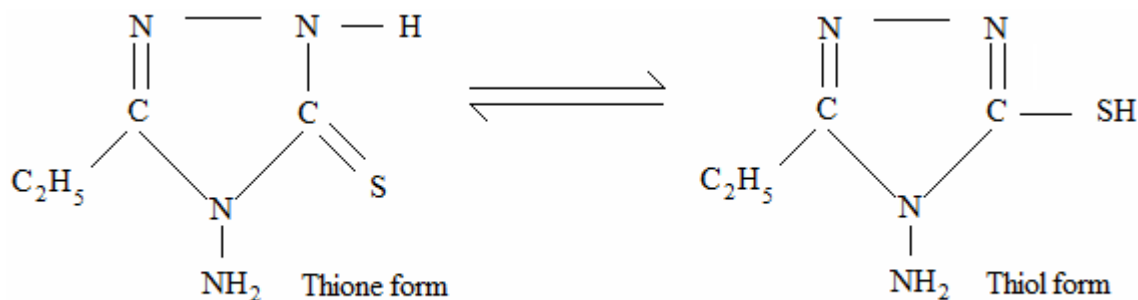


Fig. 1. 4-Amino-3-Ethyl-S-Triazole-5-Thione

Stoichiometries of the isolated compounds have been established on the basis of elemental analysis (Table-1). The compounds are fairly soluble in DMF and insoluble in non polar solvents. The electrical conductance measurement in DMF ( $10^{-3}\text{M}$ ) indicate that zirconoxy complexes are 1:2 electrolyte and non-oxy zirconium nitrate complexes are 1:4 electrolyte and others are non-electrolytic in nature<sup>14</sup>. All the nitrate complexes are thermally stable up to  $200^\circ\text{C}$  but all sulphato complexes lose their weight on heating up to  $200^\circ\text{C}$  due to presence of lattice layer water in these sulphato complexes. All reported complexes are diamagnetic as expected for  $d^0$  configuration.

Electronic spectral band of AESMTH observed at 255 nm is blue shifted ( $\sim 20\text{-}25$ ) in all Zr(IV) complexes and assigned as charge transfer bands<sup>15</sup>.

## Infrared Spectra

Some IR spectral bands of interest of ligand (AESMTH) and complexes are shown in Table-02. The  $\nu\text{SH}$  band at  $2450\text{ cm}^{-1}$  of ligand (AESMTH) is disappeared in all complexes indicates the involvement of sulphur atom in coordination<sup>16</sup>. The appearance of  $\nu\text{Py}$  vibrational bands<sup>17</sup> at  $1605\text{ cm}^{-1}$  and  $635\text{ cm}^{-1}$  in all pyridyl complexes indicates the presence of pyridine as secondary ligand. The four bands at region of  $3260\text{-}3065\text{ cm}^{-1}$  in the spectrum of AESMTH have contribution from  $\nu\text{NH}$  mode of vibration<sup>18-19</sup>. The thio amide bands are either blue shifted ( $\sim 5\text{-}10\text{ cm}^{-1}$ ) or identical after complexation indicates the intactness of  $\text{NH}_2$  and  $\text{NH}$  groups in coordination. This observation is further supported by either blue shifting ( $\sim 5\text{-}10\text{ cm}^{-1}$ ) or unperturbed in

position with higher intensity of thio amide band I, II and III indicating the absence of bonding neither through amino nor through imino nitrogen. Thio amide band I of ligand has mixed contributions from  $\delta\text{NH} + \delta\text{CH}$  and  $\delta\text{CN}$  modes<sup>20</sup> and observed at  $1570\text{ cm}^{-1}$  in AESMTH. Thio amide band IV observed at  $785\text{ cm}^{-1}$  for ligand and have major contribution from  $\delta\text{C}=\text{S}$  mode<sup>21-22</sup>. On complexation band IV is shifted to lower frequency about  $15\text{-}25\text{ cm}^{-1}$  due to bonding through thione sulphur due to increase of CN bond order and decrease of CS bond order on coordination<sup>22</sup>. The non ligand bands at  $3480$ ,  $1610$  and  $830\text{ cm}^{-1}$  in all aqua complexes are assigned to  $\nu\text{H}_2\text{O}$ ,  $\delta\text{H}_2\text{O}$  and  $\pi\text{H}_2\text{O}$  mode of vibrations respectively for all aqua Zr(IV) complexes<sup>23-24</sup>.

The presence of ionic nitrate is indicated by the appearance of very strong band at  $1340\text{ cm}^{-1}$ - $1350\text{ cm}^{-1}$  and a medium band at  $825\text{-}830\text{ cm}^{-1}$  in all nitrate complexes<sup>25</sup>. The appearance of fundamental mode of vibration  $\nu_3$ ,  $\nu_4$  of sulphato group are observed at  $1150$  and  $610\text{ cm}^{-1}$  respectively indicates the presence of ionic sulphate in all reported sulphato complexes<sup>26</sup>.

Some new bands are observed in far IR spectra of complexes. Three  $\nu\text{Zr-S}$  ( $410\text{-}400$ ,  $370\text{-}365$  and  $330\text{-}320\text{ cm}^{-1}$ ) and two  $\nu\text{Zr-O}$  ( $540$  and  $520\text{-}510\text{ cm}^{-1}$ ) stretching modes in complexes has shown a good agreement in normal coordinated analysis of  $\text{MX}_4\text{Z}_2$ ,  $\text{MX}_2\text{Y}_2\text{Z}_2$ ,  $\text{MX}_4\text{YZ}$  and  $\text{MX}_3\text{YZ}_2$  type of molecules.

## Conclusion

Thus on the basis of aforesaid discussion octahedral structure is tentatively assigned for all reported complexes as given below:

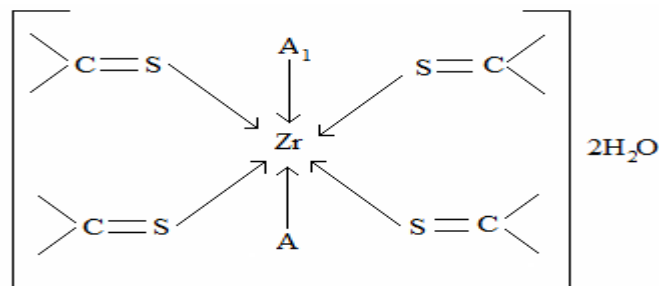


Table-1: Physical and analytical data of Zr(IV) complexes.

S.N.	Complexes/(Colour)	M.P. (in °C)	pH of isolation	Molar conductance (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Analytical data(%) : Cal./(Found)			
					C	H	N	Zr
1.	[ZrO(AESMTH) <sub>4</sub> (H <sub>2</sub> O)](NO <sub>3</sub> ) <sub>2</sub> (Yellow)	215	6	54.14	23.25 (22.79)	4.11 (3.93)	30.52 (30.18)	11.04 (10.71)
2.	[ZrO(AESMTH) <sub>4</sub> (Py)](NO <sub>3</sub> ) <sub>2</sub> (White)	210	7	57.12	32.33 (32.11)	4.74 (4.31)	32.33 (31.93)	11.74 (11.09)
3.	[Zr(AESMTH) <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ].2H <sub>2</sub> O (Yellow)	196	5	5.31	21.43 (20.12)	4.01 (3.79)	25.01 (24.56)	10.18 (10.01)
4.	[Zr(AESMTH) <sub>3</sub> (Py) (SO <sub>4</sub> ) <sub>2</sub> ]. 2H <sub>2</sub> O (Brownish yellow)	159	7	6.12	24.56 (24.13)	3.97 (3.56)	21.91 (21.26)	10.98 (10.13)
5.	[Zr(AESMTH) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> (Golden brown)	227	7	104.51	20.18 (19.71)	3.78 (3.46)	29.43 (29.19)	9.59 (9.03)
6.	[Zr(AESMTH) <sub>2</sub> (Py) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> (Brownish yellow)	204	6	106.10	26.26 (25.99)	3.64 (3.13)	23.83 (23.29)	11.09 (10.81)

Table-02: Vibrational data of Zr(IV) Complexes

S.N	Complexes	Electronic data(nm)	νNH	νSH	νNO <sub>3</sub>	νSO <sub>4</sub>	Thio amide band			
							I	II	III	IV
1.	AESMTH	255	3260 3210 3110 3050	2450	—	—	1570	1390	1090	785
2.	[ZrO(AESMTH) <sub>4</sub> (H <sub>2</sub> O)] (NO <sub>3</sub> ) <sub>2</sub>	230	3270 3240 3120 3065	—	1340 825	—	1580	1395	1095	760
3.	[ZrO(AESMTH) <sub>4</sub> (Py)]( NO <sub>3</sub> ) <sub>2</sub>	230	3270 3240 3110 3065	—	1350 830	—	1585	1395	1095	765
4.	[Zr(AESMTH) <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ]. 2H <sub>2</sub> O	232	3265 3215 3120 3060	—	—	1150 610	1580	1390	1095	765
5.	[Zr(AESMTH) <sub>3</sub> (Py) (SO <sub>4</sub> ) <sub>2</sub> ]. 2H <sub>2</sub> O	233	3270 3240 3110 3060	—	—	1150 610	1585	1390	1090	770
6.	[Zr(AESMTH) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]( NO <sub>3</sub> ) <sub>4</sub>	235	3280 3230 3120 3060	—	1340 825	—	1590	1390	1095	765
7.	[Zr(AESMTH) <sub>2</sub> (Py) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub>	230	3275 3220 3120 3060	—	1350 830	—	1575	1395	1095	760

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