



GLOBAL JOURNAL OF SCIENCE FRONTIER RESEARCH

CHEMISTRY

Volume 12 Issue 5 Version 1.0 Year 2012

Type : Double Blind Peer Reviewed International Research Journal

Publisher: Global Journals Inc. (USA)

Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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**Keywords** : *Synthesis, Elemental analysis, Th(IV) complexes.*

**GJSFR-B Classification** : *FOR Code: 030699, 030505*



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# Synthesis and Spectral Characterization of Thorium(IV) Complexes with 3-Substituted-4-Amino-5-Mercapto-1,2,4-Triazole Schiff Bases

Mallikarjun S Yadawe <sup>α</sup> & Sangamesh A Patil <sup>σ</sup>

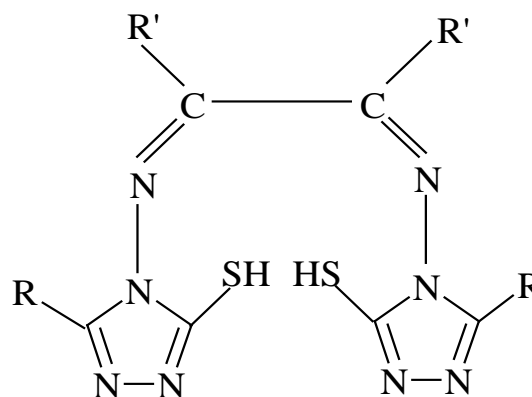
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## I. INTRODUCTION

In continuation of our earlier work on complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole<sup>1-5</sup>, we report Th(IV) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl. The metal complexes 1,2,4-triazole derivatives have been extensively investigated in previous reports<sup>6,7</sup>. Substituted triazoles are well known as bactericides<sup>8</sup>, pesticides<sup>9</sup>, insecticides<sup>10</sup> and potential fungicides<sup>11</sup>. In continuation of our work on metal complexes of triazoles and in our pursuit of a new ligand for metal complexes, we have synthesized 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl, as there is scant information on these complexes of the ligands. Therefore, it was thought worthwhile to study the synthesis and characterization of Th(IV) complexes with the following Schiff bases (fig.1).

Figure 1 : Structure of Schiff bases



Schiff base	R'	R
I	H	H
II	H	CH <sub>3</sub>
III	H	C <sub>2</sub> H <sub>5</sub>
IV	H	C <sub>3</sub> H <sub>7</sub>
V	CH <sub>3</sub>	H
VI	CH <sub>3</sub>	CH <sub>3</sub>
VII	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
VIII	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>
IX	C <sub>6</sub> H <sub>5</sub>	H
X	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
XI	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
XII	C <sub>6</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>

## II. EXPERIMENTAL

All the chemicals used were of reagent grade. 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared by the reported methods<sup>12,13</sup>.

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### III. SYNTHESIS OF 3-SUBSTITUTED-4-AMINO-5-MERCAPTO-1,2,4-TRIAZOLES

A mixture of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and lyoxal/biacetyl/benzyl in 1:1 molar proportions in EtOH was boiled under reflux for 4-5 h on a water bath. The reaction mixture was cooled at room temperature, within an hour the compound separated from the clear solution. It was filtered, washed and recrystallised from EtOH.

### IV. SYNTHESIS OF TH(IV) COMPLEX

Thorium(IV) nitrate (0.01 mol) was boiled under reflux with the ligand (0.01 mol) in alcohol for 3h. The

complex was ppted by adding distilled water containing liquor ammonia. The precipitated complex was filtered, washed thoroughly with distilled water, alcohol and dried under reduced pressure over fused  $\text{CaCl}_2$ .

### V. ANALYSIS

The thorium in the complex was determined by gravimetric method. Nitrogen was determined by Dumas method and sulphur was determined gravimetrically as  $\text{BaSO}_4$ <sup>14</sup>. The results of elemental analysis and molar conductance values are listed in the Table.1

**Table 1 :** Elemental Analysis and molar conductance (in DMF) of Thorium(IV) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases.

Complex NO	Empirical formula	M%		N%		S%		Molar conductance $\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$
		Cald	Obtd	Cald	Obtd	Cald	Obtd	
1	$(\text{C}_6\text{H}_6\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	31.61	31.63	22.88	22.90	8.71	8.75	10.66
2	$(\text{C}_8\text{H}_{10}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	30.45	30.54	22.04	22.05	8.39	8.42	12.68
3	$(\text{C}_{10}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	29.38	29.32	21.32	21.30	8.14	8.12	10.73
4	$(\text{C}_{12}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	28.36	28.30	20.55	20.65	7.93	7.92	13.40
5	$(\text{C}_8\text{H}_{10}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	30.45	30.48	22.04	22.10	8.39	8.35	18.71
6	$(\text{C}_{10}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	29.48	29.45	21.21	21.31	8.06	8.00	15.05
7	$(\text{C}_{12}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	28.38	28.30	20.53	20.55	7.80	7.85	18.78
8	$(\text{C}_{14}\text{H}_{22}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	27.42	27.42	19.85	19.90	7.56	7.53	16.34
9	$(\text{C}_{18}\text{H}_{14}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	26.28	26.23	18.94	18.99	7.23	7.25	14.42
10	$(\text{C}_{20}\text{H}_{18}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	25.42	25.40	18.38	18.35	7.03	7.08	15.30
11	$(\text{C}_{22}\text{H}_{22}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	24.64	24.63	17.86	17.83	6.81	6.79	13.87
12	$(\text{C}_{24}\text{H}_{26}\text{N}_8\text{S}_2)\text{Th}(\text{NO}_3)_4$	23.95	23.96	17.38	17.35	6.61	6.59	12.84

### VI. RESULTS AND DISCUSSION

The thorium(IV) complexes 1-8 are light yellow in colour, whereas 9-12 are orange in colour. All the complexes are insoluble in common organic solvents. However, they are sparingly soluble in DMF and DMSO. The elemental analysis shown in Table.1 indicates that the complexes analysed for 1:1 stoichiometry of the type,  $\text{Th.LH}_2(\text{NO}_3)_4$ . Conductance measurements in DMF are too low to account for dissociation of these complexes in DMF at the concentration of the  $10^{-3}\text{M}$ . Hence the complexes may be regarded as nonelectrolytes. The molecular weight of the complexes could not be determined because of their insolubility in nitrobenzene.

### VII. INFRARED SPECTRA

The important IR frequencies which characterize the Schiff bases are discussed in the following texts (Table.2).

**Table 2 :** Important Infrared frequencies (in  $\text{cm}^{-1}$ ) of Thorium(IV) Complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl Schiff bases along with their Assignments.

Complex.No	(NH)	$\nu$ (SH)	$\nu$ (C=N)	$\nu$ (CS)	$\nu$ (M-N)
1	3275m	2400w	1620m	740m	540m
2	3260m	2385w	1615m	745m	450m
3	3255m	2390w	1620m	730m	460m
4	3240m	2405w	1615m	735m	480m
5	3265m	2410w	1620m	750m	495m
6	3180m	2400w	1615m	730m	535m
7	3200m	2385brw	1615m	740m	540m
8	3205m	2395brw	1620m	745m	530m
9	3245m	2405w	1615m	740m	490m
10	3255m	2410w	1615m	730m	465m
11	3100m	2405w	1615m	735m	470m
12	3255m	2400w	1620m	745m	495m

The present free ligands exist both in tautomeric thiol and thione forms. These ligands show a broad medium band in the region  $3280\text{-}3130\text{cm}^{-1}$  followed by a weak band around  $2400\text{cm}^{-1}$  due to  $\nu(\text{NH})$  and  $\nu(\text{SH})$  vibrations. Thus these ligands exhibit thiol thione tautomerism. The high intensity bands around  $1635 \pm 5\text{cm}^{-1}$  are assigned to  $\nu(\text{CN})$  in view of the previous assignments<sup>15</sup>. This observation renders proof for the presence of glyoxal, biacetyl and benzyl residue. These ligands also exhibit a medium intensity band around  $740\text{cm}^{-1}$  has been attributed to  $\nu(\text{C}=\text{S})$ <sup>16</sup>. These thorium(IV) complexes exhibit medium intensity bands in the region  $3275\text{-}3100\text{cm}^{-1}$  followed by weak band around  $2400\text{cm}^{-1}$  are attributed to  $\nu(\text{NH})$  and  $\nu(\text{SH})$  vibrations respectively. This indicates that, the ligands exhibit thiol thione tautomerism in the complexes. This supports the noninvolvement of the sulphur atom of the mercapto group in the coordination to the metal ion. Further, this is confirmed by the band due to  $\nu(\text{C}=\text{S})$  vibration appear around  $740\text{cm}^{-1}$ . The absence of shift in the  $\nu(\text{C}=\text{S})$  is suggestive of non-coordination of sulphur to the metal ion. Remarkable changes have occurred in the azomethine group of the ligands. The high intensity band around  $1640\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  of the ligands appears in the region  $1620\text{-}1615\text{cm}^{-1}$  in the complexes. The low frequency shift of the band relative to that of ligand provides support for the coordination of C=N groups to the metal ion through nitrogen.

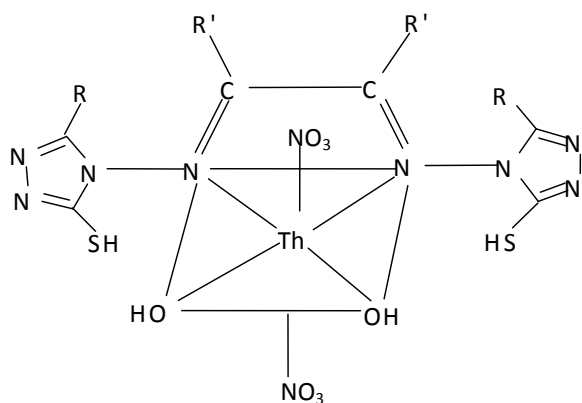
A strong band appeared in the region  $1260\text{-}1235\text{cm}^{-1}$  attributed to coordinated nitrate group. The assignments of the lower region are combroused as various skeletal vibrations of the ligands appear as high intensity bands and sometimes they are associated with metal in regard of these complexes are purely tentative and are founded on the previous reports. In these thorium(IV) complexes the  $\nu$  (M-N) bands have been assigned in the region  $540\text{-}450\text{cm}^{-1}$  in view of previous assignments<sup>18</sup>.

## VIII. PMR SPECTRUM

The PMR spectrum has been studied for only one representative complex viz., complex No.1. The PMR spectrum of corresponding ligand NO.1 exhibit resonance due to NH proton of 13.6ppm which is unaffected in the case of thorium(IV) comp. (around 13.6ppm). This suggests that, sulphur atom of SH group has not taken part in coordination as the ligand exists in thione form which is indicated by the signal appeared at 13.6 ppm in the present complex. There is a remarkable change in the position of resonance due to azomethine proton which is appeared at 9.14ppm in the thorium(IV) complex in relative to the corresponding ligand (8.2ppm). This downfield shift indicates the coordination of azomethine group to the metal ion through nitrogen. Another resonance due to proton of CH=N group of the triazole moiety appeared at 9.43 ppm. All these observations support IR inferences.

## IX. CONCLUSION

Analytical data indicates 1:1 stoichiometry for these complexes. IR and PMR spectral studies suggest the involvement of both C=N groups in the complex formation by keeping SH groups away from the coordination, considering all these observations, we propose the following structure, in which thorium exhibits coordination number of six.



17. K.Nakamoto, Infrared spectra of Inorganic and coordination compounds, Wiley, New York (1963).
18. H.M.Mohanta, K.C.Dash., J Indian.Chem.Soc., 54,166(1977).

## X. ACKNOWLEDGEMENTS

The authors are thankful to President B.L.D.E Association Bijapur, Principal, Head of chemistry S.B.Arts and K.C.P.Science college Bijapur. Special thanks to Dr.S.A.Patil Dept of Chemistry, Karnataka University Dharwad for valuable guidance.

## REFERENCES RÉFÉRENCES REFERENCIAS

1. S.A.Patil, B.M.Badiger, S.M.Kudari and V.H. Kulkarni., Transition Metal Chem.,8,238 (1983).
2. B.M.Badiger, S.A.Patil, S.M.Kudari and V.H.Kulkarni Rev, Roum, Chim.,31, 849 (1986).
3. A.Y.Naik, S.D.Angadi and V.H.Kulkarni, Oriental J.Chem., 10,23(1994).
4. M.S.Yadawe and S.A.Patil, Transition, Met.Chem., 22, 220 (1997).
5. M.S.Yadawe and S.A.Patil.,AJRC.03(2) 2010.
6. S.N.Dubey and B.Kaushik., Indian J.Chem., 24A 950 (1985).
7. J.P Corhnelissen, J.H Van Diemen.L.RGroeneveld, J.G.Haasnoot, A.L.Spek and J.Reedisk., Inorg. Chem,31 198 (1992).
8. A.K.Sengupta, O.P.Bajaj and U.Chandra., J.Indian. Chem.Soc, 55.962(1978)
9. H.Singh, L.D.S.Yadav and P.K.Bhattacharya., J.Indian Chem.Soc., 56, 1013(1979).
10. G.Tanara,Jpn, Kokai, 973, 7495(1974),Chem.Abs., 82,156320h( 1975).
11. S.Giri, H.Singh and L.D.S.Yadaw.,J.Indian. Chem.Soc., 55,168(1978).
12. L.F.Audriceth, E.S.Scott and P.S.Kipper,.. J.Org.Chem., 19, 733 (1954).
13. K.S.Dhaka, Jagamohan, V.K Chadha and H.K.Pujari., Indian J.Chem., 12,288(1974).
14. A.I.Vogel(1962) A Text Book of Quantitative Inorganic Analysis ELBS Longmans Green andCo.ltd.,London3<sup>rd</sup> edn.
15. P.R.Shukle, V.K .Singh and J.Bhargava, J.Indian Chem.Soc., 59,620(1082).
16. R.V.Gadag and M.R.Gajendragad,Talanta, 25,418(1978).