

## Spectral studies on metal-chelates of titanium (III), iron (III) and cobalt (III) with 1-substituted tetrazoline-5-thione

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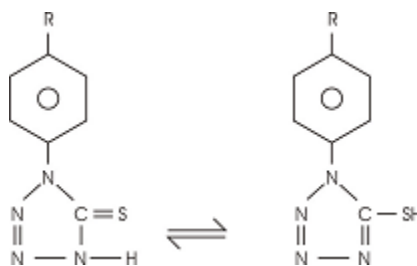
### ABSTRACT

Complexes of Metal (III) chelates with phenyl, Paratolyl, Para chlorophenyl and paramethoxy phenyl derivatives of 1-substituted tetrazoline – 5 – thione having general formula  $[ML_2A_2]Cl$  (M=Ti, Fe, W; LH = ligand ; A =  $H_2O/Py$ ) have been prepared and characterised using element analyses, magnetic moment, conductometric, IR, uv – vis,  $^1H$  NMR spectral data. The ligands act as bidnetate (N, S) and Trans – octahedral configuration to all complexes have been assigned.

**Key words :** Metal (III)-chelates, 1-substituted tetrazoline-5-thione, IR, UV-vis,  $^1H$  NMR spectral studies.

### INTRODUCTION

In continuation of our studies on the metal complexes of 1- substituted tetrazoline -5- thione<sup>1-3</sup>. we report here preparations, spectral characterisation and physico-chemical investigations of metal – chelates of Ti(III) Fe (III) and Co(III) with phenyl (IPT5TH), Paratolyl (IPTT5TH) and Para chlorophenyl (IPCIPT5TH) and Para methoxy Phenyl (PMPT5TH) derivatives of this ligand (I).



Scheme 1: (R = H,  $CH_3$ ,  $CH_3O$ , Cl)

### EXPERIMENTAL

All the chemicals used were either AnalaR or cp-grade. 1-phenyl tetrazoline -5-thione (MP =  $148^\circ C$ ), 1-Para tolyl-tetrazoline-5-thione (M.P. =  $157^\circ C$ ) and 1-para methoxy phenyltetrazoline-5-thione (M.P =  $160^\circ C$ ) were prepared by the method

reported by Lieber el.al.<sup>4</sup> The complexes were prepared by using a general method. Aqueous solution of hexammine cobaltic chloride/ferric acetate in dil HC/ (2N)/titanous chloride in ethylacetate were mixed with ethanolic solution of ligand such that the molar ratio of metal ion to the ligand is 1 : 2. The pH of solution was adjusted to desire between 8 to 9 using dil HC/(2N) and aq  $NH_3$  or Pyridine and refluxed on water bath for two hours. They were evaporated to ~ 15 ml on water bath and the different colour complexes obtained were further washed with ice-cold ethanol and dried over anhydrous  $CaCl_2$  in Vacuum desiccator.

Carbon, hydrogen and nitrogen analysis were done at the micro analytical section of CDRI, Lucknow (India). IR spectra of ligands and complexes were recorded with perkin Elmer model 577 spectrophotometer in the range of  $4000 - 200cm^{-1}$  as KBr pellets. The electronic spectra were recorded with Zeiss (Jena) model of automatic recording system. The  $^1H$  NMR spectra of ligands and complexes were recorded with 90 MHz NMR spectrometer in  $CDCl_3$  solution using TMS as the internal indicaor in the range of 0 to 10 PPM. Molar conductance of complexes were measured in  $DMF(10^{-3} M)$  using wiss – werkstatter weithein obb type LBR conductivity meter. Magnetic measurements were made on a gouy balance using

Hg[Co(SCN)<sub>4</sub>] as calibrant. The analytical and physical data of complexes are given in table 1.

## RESULTS AND DISCUSSION

Elemental analyses of the complexes correspond to [ML<sub>2</sub>A<sub>2</sub>] Cl (M = Ti, Fe, Co; LH = ligand, A = H<sub>2</sub>O/Py) stoichiometry. Molar conductance of the complexes in DMF(10<sup>-3</sup>M) were found to be 85.30 – 131.02 W<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> suggesting uni-univalent electrolyte<sup>5</sup> and chlorine is present in the outer sphere of the complexes. These complexes were shaken with aqueous Na<sub>2</sub>CO<sub>3</sub> solution thoroughly and the aqueous extract was filtered, acidified with dilute HNO<sub>3</sub> and when treated with AgNO<sub>3</sub> gave precipitation of total chlorine as AgCl. indicating the presence of ionic chlorine. Magnetic moment of Ti(III) complexes were found to be 1.65 – 1.87 BM corresponds to octahedral geometry.<sup>6</sup> All Fe (III) complexes have magnetic moment between 5.6 – 5.82 BM corresponding to five unpaired electrons for spin free octahedral complexes and <sup>6</sup>A<sub>1g</sub> ground term. All mononuclear high –spin complexes of iron (III) are expected to

show magnetic moment equal to 5.9 BM, which is independent of temperature.<sup>7</sup> The magnetic moment of cobalt (III) complexes were found to 0.32 – 0.62 BM due to the formation of Co(II) or due to second order zeeman effect<sup>8</sup>.

## Electronic spectra

A weak and broad band centred at 21300 – 21980 cm<sup>-1</sup> in all Ti(III) complexes in agreement with the octahedral geometry<sup>9</sup> for transition <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>. The broad nature of Spectral band is probably due to Jahn – Teller distortion.

The visible spectra of cobalt (III) complexes display shoulder at 23530cm<sup>-1</sup> assigned to <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> transition<sup>10</sup> with other spin allowed <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> band masked by the intense charge transfer band occurring at 32786-27778cm<sup>-1</sup> and octahedral structure of all Co(III) complexes was assumed following previous observations<sup>10-11</sup>.

The electronic spectra of Fe(III) complexes exhibit three bands at 15885 – 16700 cm<sup>-1</sup>, 17550 – 20000 cm<sup>-1</sup> and 26300 – 29000 cm<sup>-1</sup> assignable

Table 1 : Analytical and physical data of complexes

S. No.	Complex/ (Colour)	Mol. Cond. (W <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	μ <sub>eff</sub> (BM)	Analyses % Found/(Calcd)			
				C	H	N	Metal
1.	[Ti(IPT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Cl]2H <sub>2</sub> O (Light yellow)	87.20	1.65	33.1 (32.9)	3.6 (3.5)	21.9 (21.8)	9.8 (9.7)
2.	[Ti(IPTT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Cl (yellow)	89.10	1.66	38.5 (38.1)	3.8 (3.6)	22.5 (22.3)	10.1 (9.9)
3.	[Ti(IPC/PT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Cl (Yellow)	82.15	1.65	31.1 (30.9)	2.4 (2.2)	20.6 (20.5)	10.0 (9.2)
4.	[Ti(PMT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl (Yellow)	89.10	1.82	36.1 (35.9)	3.5 (3.4)	20.8 (20.9)	10.0 (9.4)
5.	[Ti (IPC/PT5T) <sub>2</sub> (Py) <sub>2</sub> ]Cl (Redish yellow )	85.30	1.87	43.4 (43.2)	2.6 (2.7)	21.2 (21.0)	8.0 (7.5)
6.	[Fe(IPT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Cl (Yellow)	95.60	5.82	35.0 (34.9)	3.1 (2.9)	23.5 (23.3)	12.0 (11.6)
7.	[Fe (IPTT5T) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Cl (Yellow)	98.20	5.71	37.8 (37.7)	3.6 (3.5)	22.1 (22.0)	11.1 (11.0)
8.	[Fe (PMT5T) <sub>2</sub> (Py) <sub>2</sub> ]Cl (Yellowish brown)	97.30	5.60	47.2 (47.0)	3.7 (3.6)	17.1 (16.9)	8.8 (8.4)
9.	[Co (IPT5T) <sub>2</sub> (py) <sub>2</sub> ] Cl (pink)	130.2	0.70	48.1 (47.5)	3.4 (3.3)	22.9 (23.0)	10.2 (9.7)
10.	[Co(IPCIPT5T) <sub>2</sub> (Py) <sub>2</sub> ] Cl (Dull grey)	130.6	0.34	43.1 (42.7)	2.7 (2.6)	20.8 (20.7)	8.8 (8.7)
11.	[Co(PMT5T) <sub>2</sub> (Py) <sub>2</sub> ] Cl (Dull grey)	131.02	0.32	47.1 (46.8)	3.6 (3.6)	21.2 (21.0)	9.1 (8.8)

to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}$  transitions respectively for octahedral stereochemistry are in consistent with<sup>12</sup> Ball hausen and Balt *et al*<sup>13</sup>. The value of Dq, B' and  $n_3$  have been calculated to be 1034, 795 and  $30200\text{ cm}^{-1}$  respectively. This value  $n_3$  differs by  $1200\text{ cm}^{-1}$  from the observed value of the broad band in the range  $26300 - 29000\text{ cm}^{-1}$ . The difference may be attributed to departure from the octahedral symmetry.

### IR spectra

All derivatives of 1-substituted tetrazoline -5-thione display two distinct broad absorption bands around  $3120-3180\text{ cm}^{-1}$  and  $3050\text{ cm}^{-1}$  are assigned to superimposed bands of  $\nu_{\text{NH}}$  and  $\nu_{\text{CH}}$  vibrations. Rao *et al.*,<sup>14</sup> on examining the spectra of tetrazoles (pKa = 4.89) in very dilute solution observed  $\nu_{\text{NH}}$  frequency at  $\sim 3145\text{ cm}^{-1}$ . This band is absent in the spectra of the complexes. So the NH moiety was deprotonated due to complex formation. Further evidence in support of this comes from systematic shifts<sup>15-16</sup> in thioamide band positions in the infrared spectra of the complexes as compared with those for the ligands.

The formation of simultaneous metal -S and metal-N bond blue shift thioamide band II ( $20 - 30\text{ cm}^{-1}$ ), red shifts thioamide band I ( $20-35\text{ cm}^{-1}$ ), band III ( $25- 40\text{ cm}^{-1}$ ) and band IV ( $35-60\text{ cm}^{-1}$ ) of ligands due to increase in CN bond order and decreases in CS bond order<sup>17-19</sup>.

The non-ligand bands at 3410, 1605 and  $810\text{ cm}^{-1}$  in aquo-complexes assigned to  $\pi_{\text{H}_2\text{O}}$ ,  $\delta\text{H}_2\text{O}$  and  $\pi\text{H}_2\text{O}$  of coordinated water molecules in the

complexes<sup>20</sup>. The presence of coordinated Pyridine molecules are indicated by its characteristic ir absorption frequency. The Pyridine ring vibrations in the high frequencies region are not shifted appreciably but in - plane-ring deformation ( $604\text{ cm}^{-1}$ ) and out - of - plane - ring deformation ( $405\text{ cm}^{-1}$ ) are shifts to higher frequencies  $15-20\text{ cm}^{-1}$  and  $20-25\text{ cm}^{-1}$  respectively.<sup>21</sup> The metal-Pyridine stretching mode is observed at  $265\text{ cm}^{-1}$ (Fe-Py)  $260-270\text{ cm}^{-1}$  (Co-Py) and  $275-280\text{ cm}^{-1}$ (Ti-Py). The presence of single metal - Pyridine stretching mode indicates two Pyridine molecules are at trans in octahedral structure of the complexes. A new single metal-oxygen stretching mode at  $480-500\text{ cm}^{-1}$  in Ti(III) complexes<sup>22</sup> at  $500-510\text{ cm}^{-1}$  in Co (III) complexes<sup>23</sup> and at  $490-510\text{ cm}^{-1}$  in Fe(III) - complexes<sup>24</sup> indicate trans-configuration for  $[\text{ML}_2(\text{H}_2\text{O})_2]$  complexes.

### <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectra of some complexes are presented in table - 2 to substantiate further metal - ligand bonding. The chemical shift values of the main groups associated with derivatives of 1-substituted tetrazoline - 5- thione reveal that there is bonding of metal ions through thione sulphur after deprotonation of imino nitrogen of the ligands. The resonances in the region 7.72, 8.07 and 8.81 PPM assignable to the protons of the Pyridine ligand along with the resonances due to aromatic protons. The Pyridine proton resonances exhibited down field ( Sl no. 5,6,9 & 12) as compared to that in free ligand indicate the complexation of Pyridine nitrogen atom with metal centre<sup>25</sup>. All complexes display broad multiplet in the region  $\nu 7.41$  to 7.72 PPM

**Table 2 : Prton chemical shift (dPPM) of some important groups of complexes**

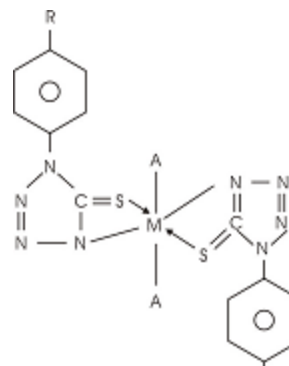
Complex/ S. No.	Phenyl Proton	Py-ring Protons $\alpha, \beta, \gamma$	Methoxy Protons	Methyl Protons	H <sub>2</sub> O Protons
1.	7.61 (bs)	-	-	-	1.2 & 2.1
2.	7.48 (bs)	-	-	3.71	1.3
3.	7.8 (bs)	-	-	-	1.43
4.	7.45(bs)	-	3.77	-	1.2 & 2.0
5.	7.46(bs)	(7.76, 8.10, 8.82)	-	-	1.2 & 2.1
8.	7.46 (bs)	(7.78, 8.30, 8.86)	3.78	-	-
9.	7.61 (bs)	(7.78, 8.30, 8.86)	-	-	-
10.	7.72 (bs)	(7.77, 8.26, 8.85)	-	-	-
11.	7.44(bs)	(7.76, 8.12, 8.78)	3.77	-	-

a = Sl. no represents complexes of Table 1;

bs = broad signal

due to Phenyl protons of Phenyl and substituted phenyl tetrazoline – 5- thione in complexes. The broad nature of Peak may be due to large quadrupole resonance broadening effect of tetrazole nitrogen atoms. The signal due to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton. However, a peak observed at  $\nu$ 1.25 PPM in the ligands is absent in the spectra of complexes suggesting the formation of metal – N bond and deprotonation of N – H group on complexation. All aquo complexes exhibit singlet signal at  $\nu$ 1.31 PPM which corresponds to two protons and another multiplet at  $\nu$ 2.1 PPM corresponding to two protons. This is due to 4-protons of the two coordinated water molecules<sup>26</sup> which are in two different magnetic environment. The methoxy protons observed as sharp singlet at  $\nu$ 3.76 PPM in complexes coincides with that of methoxy group protons in literature<sup>27</sup>.

Thus, on the basis of aforesaid observations octahedral structure of all complexes may be assigned.



**Trans – Oh. Structure**  
 (M = Ti, Fe, Co; A = H<sub>2</sub>O/Py  
 R = H/CH<sub>3</sub>/Cl/CH<sub>3</sub>-O)

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