



# STUDIES ON SOME COMPLEXES OF 3-(4'-PYRIDYL)-4-PHENYL-1,2,4-TRIAZOLE-5-THIONE WITH Cr (III), Zr (IV), V (V), Nb (V) AND Ta (V) IONS

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## ABSTRACT

Complexes of 3- (4'-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (PpytTH) have been prepared with Cr (III), Zr (IV), V (V), Nb (V) and Ta (V) ions and the structures of the complexes have been investigated by physico-chemical methods. All these complexes are diamagnetic except the Cr (III) complexes, which has magnetic moment equal to 3.79 BM corresponding to octahedral  $sp^3d^2$  hybridization. In all the complexes, bonding to the metal ions has occurred through sulphur. This has resulted in the blue shifting of thio amide band I, band II and band III, splitting of band II and red shifting of the thio amide band IV from  $785\text{ cm}^{-1}$  in the ligand to  $770\text{-}750\text{ cm}^{-1}$  in the complexes. UV and visible spectra of complexes have been interpreted and crystal field calculations have been done for Cr (III) complexes only.

**Key words:** Complexes, Cr (III), Zr (IV), V(V), Nb (V), Ta (V)

## INTRODUCTION

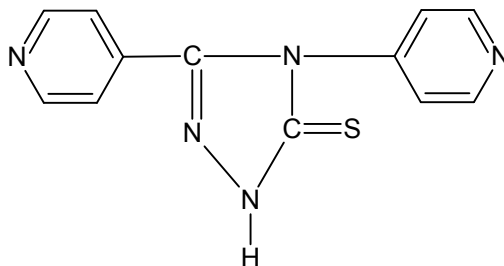
3-(4'-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (PpytTH) is an interesting ligand containing nitrogen and thiocarbonyl sulphur as donor atom (Fig. 1). Several of its complexes have been reported from this laboratory and it has been found that ligand coordinates through nitrogen, sulphur and simultaneously through nitrogen as well as sulphur<sup>1,2</sup>.

In view of its interesting coordination behaviour, its complexes with transition metal ions such as Cr (III), Zr (IV), V (V), Nb (V) and Ta (V) have been prepared and investigated. Cr (III) and V (V) ions are of particular importance because of their

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involvement in several biochemical reactions indicating glucose metabolism<sup>3</sup> and dinitrogen fixation<sup>4</sup> respectively.



**Fig. 1: PpytTH**

The present work is also significant because of the fact that V (V), Nb (V) and Ta (V) have formed cationic complexes, which are rare and also because of the fact that bonding in these complexes is only through sulphur in preference over bonding through nitrogen of the ligand.

## EXPERIMENTAL

All chemicals used in this work were of chemically pure grade. The ligand was prepared by the method reported by Dutta et al<sup>5</sup>. Carbon, hydrogen and nitrogen analysis were done at the micro analytical section of CDRI, Lucknow (India). The infrared spectra were recorded at CDRI, Lucknow on Perkin-Elmer 621 Spectrophotometer in the range of 4000-200  $\text{cm}^{-1}$ . Ultraviolet and visible spectra were recorded in DMF solution on Backmann and Carl Zeiss (Jenna) spectrophotometer. Complexes were reported by the following methods:

Cr (III), Zr (IV), V (V) and Ta (V) complexes were prepared by general method i.e. by refluxing ethanolic solution of corresponding salts with ligand (1 : 1 mmole) up to complexation. The pH of the solution was adjusted as desired, using NaOH and corresponding mineral acids. They are evaporated to dryness and dried over anhydrous  $\text{CaCl}_2$  in vacuum desiccator.

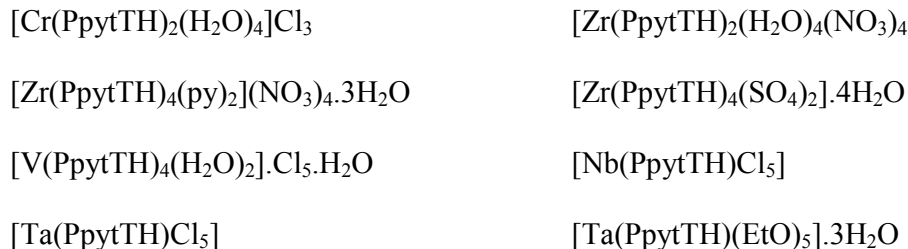
The Nb (V) complex was prepared by refluxing 1 mmole  $\text{NbCl}_5$  in 50 mL  $\text{CCl}_4$  and DMF (10 : 1) solutions with 1 m mole ligand in 50 mL.  $\text{CCl}_4$  solution at 65<sup>o</sup>C on magnetic stirrer up to evolution of HCl. It was cooled at room temperature and five drops of NaOH (2N) were added and shaken on magnetic stirrer for about 5 minutes. It was filtered, washed with  $\text{CCl}_4$  and dried over anhydrous  $\text{CaCl}_2$  in vacuum desiccator.

## RESULTS AND DISCUSSION

Micro analytical results indicate that the complexes have the following stoichiometries:

- |  |   |
|--|---|
| (i) $\text{CrCl}_3 \cdot 4\text{H}_2\text{O} \cdot 2(\text{PpytTH})$                               | (ii) $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O} \cdot 2(\text{PpytTH})$                          |
| (iii) $\text{Zr}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O} \cdot 2\text{py} \cdot 4(\text{PpytTH})$ | (iv) $\text{Zr}(\text{SO}_4) \cdot 4\text{H}_2\text{O} \cdot 4(\text{PpytTH})$                            |
| (v) $\text{VCl}_5 \cdot 3\text{H}_2\text{O} \cdot 4(\text{PpytTH})$                                | (vi) $\text{NbCl}_5 \cdot (\text{PpytTH})$  |
| (vii) $\text{TaCl}_5 \cdot (\text{PpytTH})$  | (viii) $\text{Ta} \cdot (\text{C}_2\text{H}_5\text{O})_5 \cdot 3\text{H}_2\text{O} \cdot (\text{PpytTH})$ |

In  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O} \cdot 2(\text{PpytTH})$  and  $\text{VCl}_5 \cdot 3\text{H}_2\text{O} \cdot 4(\text{PpytTH})$ , all the chlorine and in  $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O} \cdot 2(\text{PpytTH})$  and  $\text{Zr}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O} \cdot 2\text{py} \cdot 4(\text{PpytTH})$  all nitrate groups were found to be ionic in nature. These were confirmed by appearance of positive test of  $\text{Na}_2\text{CO}_3$  extract of corresponding complexes. All other complexes were found to be neutral. Thus, the following formulation for these may be suggested:



### Magnetic moment

The magnetic moments of the complexes were measured using a Guoy balance and  $\text{Hg}[\text{Co}(\text{SCN})_4]$  was used as calibrant. All the complexes were found to be diamagnetic except  $[\text{Cr}(\text{PpytTH})_2(\text{H}_2\text{O})_4]\text{Cl}_3$ , which has a magnetic moment of 3.79 BM at  $27^\circ\text{C}$  corresponding to three unpaired electrons and  $sp^3d^2$  hybridization.

### Infrared spectra

The infrared spectra of the ligand and complexes are given in Table 2.

Table 1: Analytical and physical data of complexes

Compound (Colour)	pH of isolation	% Analysis- Found / (Calcd.)				M.P. (°C)	$\Delta$ (Ohm <sup>-1</sup> cm <sup>-2</sup> mol <sup>-1</sup> )
		N	C	H	M		
[Cr(PpytTH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>3</sub> (Yellowish green)	6	15.20 (15.10)	42.50 (42.20)	3.80 (3.70)	7.30 (7.00)	210	101.86
[Zr(PpytTH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>4</sub> (Light yellow)	4	18.10 (18.20)	33.60 (38.80)	3.70 (3.20)	9.80 (9.90)	150	115.89
[Zr(PpytTH) <sub>4</sub> (py) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> .3H <sub>2</sub> O (Brown)	6	19.60 (19.50)	47.30 (47.30)	3.80 (3.80)	5.80 (5.90)	250	118.03
[Zr(PpytTH) <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ].4H <sub>2</sub> O (Light yellow)	6	16.30 (16.20)	45.30 (45.20)	3.80 (3.70)	6.6. (6.70)	200	119.71
[V(PpytTH) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>5</sub> .H <sub>2</sub> O (Green)	6	15.10 (15.00)	48.10 (48.00)	3.60 (3.50)	3.30 (3.90)	230	140.34
[Nb(PpytTH)Cl <sub>5</sub> ] (White)	6	8.80 (8.90)	30.10 (29.80)	2.00 (1.90)	17.60 (17.80)	180	114.21
[Ta(PpytTH)Cl <sub>5</sub> ] (Broken white)	6	9.20 (9.10)	25.50 (25.40)	1.70 (1.80)	29.50 (29.40)	260	9.21
[Ta(PpytTH)(EtO) <sub>5</sub> ].3H <sub>2</sub> O (Yellowish green)	7	7.80 (7.80)	16.80 (16.70)	5.80 (5.90)	25.30 (25.30)	308	7.86

Table 2: Major infrared bands of the ligand and the complexes in  $\text{cm}^{-1}$ 

Complexes	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{NH}}$	$\nu_{\text{SH}}$	Thioamide band				$\nu_{\text{NO}_3}/\text{SO}_4$	Nature of metal ligand bond
				I	II	III	IV		
PpyrTH	-	3060 mb	2550 wb	1480 s	1290 s	1090 m	784 m	-	-
[Cr(PpyrTH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ][Cl <sub>3</sub> ] (Yellowish green)	3450 mb	3090 m	-	1510 s	1300 vs	1095 m	760 ws	-	Through sulphur
[Zr(PpyrTH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>4</sub> (Light yellow)	3600 mb	3070 m	-	1490 s	1295 s	1100 m	755 ws	1350 vs	Through sulphur
[Zr(PpyrTH) <sub>4</sub> (py) <sub>2</sub> ](NO <sub>3</sub> ) <sub>6</sub> ·3H <sub>2</sub> O (Brown)	3550 mb	3065 m	-	1445 s	1300 s	1095 m	65 w	1350 vs	Through sulphur
[Zr(PpyrTH) <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ].4H <sub>2</sub> O (Light yellow)	3525 ms	3075 m	-	1490 s	1295 s	1095 m	770 ws	1120 m	Through sulphur
[V(PpyrTH) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>5</sub> ·H <sub>2</sub> O (Green)	3450 mb	3070 m	-	1495 s	1300 s	1100 m	765 ws	970 m	Through sulphur
[Nb(PpyrTH)Cl <sub>5</sub> ] (White)	-	3065 m	-	1485 m	1295 s	1095 m	755 ws	605 s	Through sulphur
[Ta(PpyrTH)Cl <sub>5</sub> ] (Broken white)	-	3075 m	-	1485 s	1295 s	1095 m	750 ws	440 w	Through sulphur
[Ta(PpyrTH)(EtO) <sub>3</sub> ].3H <sub>2</sub> O (Yellowish green)	3525 ms	3065 m	-	1490 s	1300 s	1095 m	765 w	-	Through sulphur

A comparison of the infrared spectra of the ligand and the complexes indicate the following points:

- (i) There are medium and broad bands at 3450 and 3600  $\text{cm}^{-1}$  in the spectra of the Cr (III) & V (V) and  $[\text{Zr} (\text{PpytTH})_2 (\text{H}_2\text{O})_4](\text{NO}_3)_4$ , respectively. Free water gives absorption bands at 3560 and 3520  $\text{cm}^{-1}$  as a asymmetric and symmetric stretching mode of water molecules<sup>6,7</sup>. The above band in the complexes may be assigned to the presence of coordinated water molecule in these complexes. The broadness of band shows the involvement of water molecules in hydrogen bonding. But appearance of medium sharp bands at 3525  $\text{cm}^{-1}$  for  $[\text{Zr} (\text{PpytTH})_4 (\text{Py})_2]\text{SO}_4$  &  $[\text{Ta} (\text{PpytTH}) (\text{EtO})_5]3\text{H}_2\text{O}$  and at 3550  $\text{cm}^{-1}$   $[\text{Zr} (\text{PpytTH})_4 (\text{py})_2] (\text{NO}_3)_3.3\text{H}_2\text{O}$  may be assigned as lattice layer in coordinated water molecules<sup>8</sup> in these complexes.
- (ii) There is weak broad band at 2550  $\text{cm}^{-1}$  in the spectrum of ligand and it may be assigned as SH mode of vibrations<sup>9</sup>. This band is almost disappeared on complexation in all complexes. It may be due to the involvement of sulphur atom in bonding.
- (iii) The thio amide band IV in the infrared spectrum of ligand is observed at 785  $\text{cm}^{-1}$  as medium band. This band is shifted to 760 (ws)  $\text{cm}^{-1}$  in Cr (III), to 755-770 (ws) in Zr (IV), to 765 (ws) in V (V), to 755 (ws) in Nb (V) and to 750-765  $\text{cm}^{-1}$  to Ta (V) complexes. There is red shift of 15-35  $\text{cm}^{-1}$  in this band, which has main contribution from  $\nu\text{C}=\text{S}$ ; may be due to bonding of the ligand to the metal ions through sulphur<sup>10</sup> only.
- (iv) The thio amide band I of the ligand is observed at 1480  $\text{cm}^{-1}$  and this band is blue shifted (5 to 30  $\text{cm}^{-1}$ ) after complexation in all complexes. The thio amide band II appears at 1290 (s) and 1240 (m)  $\text{cm}^{-1}$  for ligand. This is splitted and slightly blue shifted on complexation. These results support the coordination through sulphur<sup>11</sup>.
- (v) If the bonding occurs through sulphur, then the thioamide band III is observed at higher frequencies<sup>12</sup>. The shifting pattern of the thioamide band III of the ligand on coordination to the metal ion in the present complexes is the same, which supported coordination through sulphur.
- (vi) The trans octahedral structures of Cr (III), Zr (IV) and V (V) complexes have been tentatively assigned on the basis of the comparatively less number of bands observed in their infrared spectra due to coordinated water, pyridine and sulphato groups.

In view of this discussion, tentative distorted octahedral structures may be assigned to Cr (III), Zr (IV), V (V), Nb (V) and Ta (V) complexes.

### Ultra-violet and visible spectra

The UV and visible spectrum of the ligand contains two broad bands at 310 and 330 nm, due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition. These bands shifted to (250-265) and (270-280) nm in all complexes of Cr (III), Zr (IV), V (V), Nb (V) and Ta (V) ions due to coordination of the ligand with the metal ion through sulphur. However, there is no absorption in the range of 1500-400 nm for Zr (IV), V (V), Nb (V) and Ta (V) indicating that these are in the form of  $Zr^{+4}$ ,  $V^{+5}$ ,  $Nb^{+5}$  and  $Ta^{+5}$  ion in complexes.

The octahedral structure of  $[Cr(PpytTH)_2(H_2O)_4]Cl_3$  complexes is also proved by UV and visible spectra. Following three bands are observed in its spectra:

- (i) 291 nm =  $34364\text{ cm}^{-1}$
- (ii) 392 nm =  $25510\text{ cm}^{-1}$  and
- (iii) 643 nm =  $15552\text{ cm}^{-1}$

However, as the concentration of the solution was not measured, molar extinction coefficient could not be calculated. Octahedral Cr (III) complexes<sup>15(a)</sup> generally gives rise to three bands in regions of 17000, 24000 and 37000  $\text{cm}^{-1}$ . Thus, three bands of  $[Cr(PpytTH)_2(H_2O)_4]Cl_3$  are in good agreement with positions generally observed for an octahedral Cr(III) complex. Thus, the following assignments are made.

- (i)  $15552\text{ cm}^{-1}$  band       ${}^4A_{2g}(F) \rightarrow {}^4A_{2g}(F)$
- (ii)  $25510\text{ cm}^{-1}$  band       ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
- (iii)  $34364\text{ cm}^{-1}$  band       ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$

and  $10 D_q$  value =  $15552\text{ cm}^{-1}$ . Thus, the 3-(pyridyl)-4-phenyl-1,2,4-triazole-5-thione is a weaker ligand than water vis-a-vis complexation to Cr (III) ion.

${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$  and  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$  bands are most sensitive. Their ratio:

$$\frac{{}^4A_{2g}(F) \rightarrow {}^4A_{2g}(F)}{{}^4A_{2g}(F) \rightarrow {}^4A_{2g}(F)} = 2.2$$

The best fit for this value in Tanabe and Sugano diagram<sup>15(b)</sup> for  $D_q/B'$  is 2.0

$$1555/B' = 2$$

$$\therefore B' = 1555/2 = 778 \text{ cm}^{-1}$$

The free ion value for  $\text{Cr}^{+3}$  ion,  $B = 1030 \text{ cm}^{-1}$

$$\therefore \beta' = B'/B = 778/1030 = 0.76$$

Thus, B is reduced to about 76% of the free ion value and the ligand is not acting as strong in the case.

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