

## Studies on Pd(0), Pt(0), Rh(I), Ni(II), Co(II) and Zr(IV) Complexes of 4-Amino-3-hydrazino-5-mercapto- 1,2,4-triazole

R.N. PANDEY\*, R.N. SHARMA, A.N. SAHAY, RITA ROY CHOUDHARY  
and J.N. DAS

*P.G. Centre of Chemistry (M.U.)  
College of Commerce  
Patna-800 020, India*

Complexes of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole(AH<sup>+</sup>Th) have been prepared with Pd(0), Pt(0), Rh(I), Ni(II), Co(II) and Zr(IV) and the structures of the complexes have been investigated by physico-chemical methods. Bonding of the ligand occurs through thione tautomeric form in Pd(0), Pt(0) and Zr(IV) but the ligand interacts with thiol form at pH 7 resulting in deprotonation of thiol hydrogen in Rh(I), Co(II), Ni(II) and few Zr(IV) complexes. Physico-chemical data suggest tetrahedral structure for Pd(0) and Pt(0), square planar for Rh(I) and octahedral configuration for Co(II), Ni(II) and Zr(IV) complexes.

### INTRODUCTION

Co-ordination complexes of substituted triazoles with a number of metal ions have been studied by several workers<sup>1-4</sup>. However, comparatively less amount of work has been done on Pd(0), Pt(0), Rh(I), and Zr(IV) ions with substituted triazoles having thioamide group. The present paper deals with the preparation and characterisation of complexes of these metal ions with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AH<sup>+</sup>TH) (Fig. 1) on the basis of various physico-chemical methods.

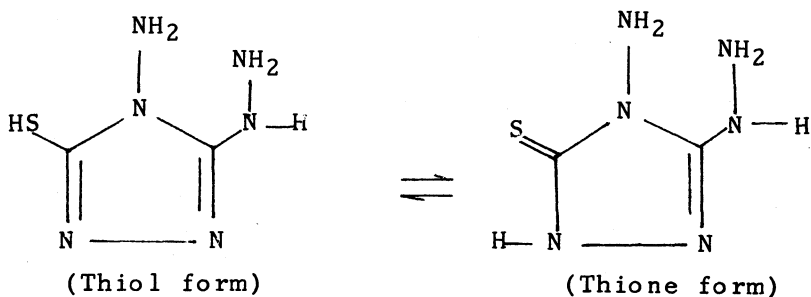


Fig. 1

## EXPERIMENTAL

All chemicals used were of AR/GR grade. The ligand was prepared by slightly modified method reported in literature<sup>5</sup>. All Zr(IV), Co(II) and Ni(II) complexes were prepared in methanolic media. Metal salts were dissolved in *ca.* 50 ml hot methanol and mixed with methanolic solution of ligand (M : L = 1 : 2 for Co(II) and Ni(II) and M : L = 1 : 4) for Zr(IV). The mixture was refluxed on water bath 2-3 hrs. and then pH of mixture was adjusted as desired using corresponding mineral acid of salt used and NaOH solution or pyridine. It was then evaporated on water bath to *ca.* 15 ml and cooled. The crystals of various complexes were separated out.

Pd(0) and Pt(0) complexes were prepared in benzene medium starting from Maletesta compounds<sup>6</sup> Pd(P $\emptyset$ <sub>3</sub>)<sub>4</sub> and Pt(P $\emptyset$ <sub>3</sub>)<sub>4</sub>. Rh(I) complexes were also prepared from Wilkinson *et al.* catalyst [Rh(P $\emptyset$ <sub>3</sub>)<sub>3</sub>Cl]<sup>7</sup> in benzene medium following the method of Singh *et al.*<sup>8</sup>

TABLE 1  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complexes	Colour	M.Pt. (°C)	pH of isola- tion	Analysis % Found (Calc.)	
				M	N
[Pd(P $\emptyset$ <sub>3</sub> ) <sub>3</sub> (AHfTH)]	Golden yellow	205	6	10.1 (10.2)	7.9 (8.1)
[Pt(P $\emptyset$ <sub>3</sub> ) <sub>3</sub> (AHfTH) <sub>3</sub> ]	Light yellow	137	6	21.9 (21.8)	28.0 (28.2)
[Rh(P $\emptyset$ <sub>3</sub> ) <sub>3</sub> (AHfT)(CS <sub>2</sub> ) <sub>2</sub> ]	Golden brown	>250	6	15.3 (15.5)	12.6 (12.7)
[Rh(P $\emptyset$ <sub>3</sub> ) <sub>3</sub> (AHfT)]	Golden yellow	250	7	10.0 (9.9)	8.3 (8.1)
[Co(AHfT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Pink	>250	7	15.4 (15.3)	43.9 (43.7)
[Ni(AHfT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Blue	205	7	7.8 (7.9)	47.4 (43.5)
[Zr(AHfTH) <sub>2</sub> (AHfT) <sub>4</sub> ]	Cream	226	7	10.0 (9.8)	52.2 (52.3)
[Zr(AHfT) <sub>3</sub> ]Cl	White	225	7	16.0 (16.2)	44.7 (44.9)
[Zr(AHfTH) <sub>4</sub> (Py) <sub>2</sub> ](SO <sub>4</sub> ) <sub>2</sub>	Royal ivory	>250	6	8.7 (8.9)	35.8 (35.5)
[ZrO(AHfTH) <sub>4</sub> (Py)]Cl <sub>2</sub> ·2H <sub>2</sub> O	Light yellow	227	6	10.1 (10.4)	39.6 (39.9)
[ZrO(AHfTH) <sub>4</sub> Cl]Cl	White	232	6	12.0 (11.9)	44.0 (44.1)
[ZrO(AHfTH) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	White	230	6	12.8 (12.9)	40.0 (39.7)

## RESULTS AND DISCUSSION

All Pd(0), Pt(0) and Rh(I) complexes were air stable and soluble in most of common organic solvents. They decolourised violet solution of iodine in  $\text{CCl}_4$ . Oxidation states of metal in Pd(0), Pt(0) and Rh(I)-complexes were determined iodometrically<sup>9</sup>. The diamagnetic nature of these complexes suggested  $d^{10}$  for Pd(0) & Pt(0) and  $d^8$ -configuration for Rh(I). However, the magnetic moment of  $[\text{Co}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  were found to be 4.72 and 3.08 BM suggesting the presence of three and two unpaired electrons respectively in outer orbital octahedral configuration<sup>10</sup>. Molar conductance in DMF of  $[\text{ZrO}(\text{AHtTH})_4\text{Cl}]\text{Cl}$ ,  $\text{ZrO}(\text{AHtTH})_4(\text{Py})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Zr}(\text{AHtT})_3]\text{Cl}$  and  $[\text{Zr}(\text{AHtTH})_4(\text{Py})_2](\text{SO}_4)_2$  indicated the presence of ionic chloride and sulphate. The presence of ionic chloride and sulphate was further supported by the qualitative analysis of sodium carbonate extract solution of these complexes. All hydrated Zr(IV) complexes lose their associated water molecules below  $120^\circ\text{C}$ . However, no loss in weight in Co(II) and Ni(II) complexes was observed and water molecules in these complexes are most probably present in the inner sphere of complex coordinated to these divalent ions.

Electronic spectra of Pd(0), Pt(0), Rh(I) and Zr(IV) display very strong absorption band in the range of  $27,778\text{--}29,990\text{ cm}^{-1}$  assigned to charge transfer band<sup>11</sup>. However, no absorption has been observed above  $25,000\text{ cm}^{-1}$  in Zr(IV) complexes indicating  $d^0$ -configuration<sup>12</sup>. Bands at 38,314, 18,629 and  $14,706\text{ cm}^{-1}$  in  $[\text{Co}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  are assigned to charge transfer ( $M \rightarrow L$  or  $L \rightarrow M$ ),  $4T_{1g}(\text{F}) \rightarrow 4T_{2g}(\text{P})$ ,  $4T_{1g}(\text{F}) \rightarrow 4A_{2g}(\text{F})$  transitions<sup>13</sup> and at 36,231, 28,253 and  $20,661\text{ cm}^{-1}$  in  $[\text{Ni}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  are assigned to charge transfer,  $3A_{2g}(\text{F}) \rightarrow 3T_{1g}(\text{P})$ ,  $3A_{2g}(\text{F}) \rightarrow T_{1g}(\text{F})$  transitions<sup>14</sup> respectively. The ligand field parameters for Co(II) and Ni(II) complexes were calculated and  $\beta$  values were found to be 0.76 and 0.69 respectively which puts the ligand towards the strong end of nephelauxetic series. However, corresponding low  $\beta'$  value ( $857\text{ cm}^{-1}$  for Co(II) and  $669\text{ cm}^{-1}$  for Ni(II)) most probably due to coupling with high intensity of absorption band or due to coordination of ligand through sulphur<sup>15</sup>. Thus, octahedral probable structure may be assigned to Co(II) and Ni(II) complexes.

There are four medium bands at 3230, 3190, 3070 and  $3010\text{ cm}^{-1}$  in the infrared spectrum of the ligand due to the interaction between  $\text{NH}_2$  group and  $-\text{NH}-\text{NH}_2$  group of stretching modes of vibration<sup>16</sup>. Almost the same pattern of multiplet bands are observed in all Pd(0), Pt(0), Rh(I) and Zr(IV) complexes except in  $[\text{Co}(\text{AHtT})_2(\text{H}_2\text{O})_2]$ ,  $[\text{Ni}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  and  $[\text{Zr}(\text{AHtT})_3]\text{Cl}$ . There is slight shift of these bands towards higher wave number which suggests deprotonation of  $\text{NH}_2$  and  $-\text{NH}-\text{NH}_2$  group of ligand may not have occurred<sup>17</sup>. However, slight red shifting ( $10\text{--}15\text{ cm}^{-1}$ ) of these bands of ligand in  $[\text{Zr}(\text{AHtT})_3]\text{Cl}$ ,  $[\text{Co}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  and in  $[\text{Ni}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  complexes have occurred probably

bonding through thione form of the ligand and deprotonation of imino nitrogen atom which cause reduction in splitting due to less availability of H-atoms for tautomerisation. These results are further supported by the considerable reduction of intensities of ligand bands at 1630 ( $\delta_{\text{NH}}$ ), 980 ( $\rho_{\text{NH}_2}$ ) and 680 ( $\tau_{\text{NH}_2}$ )  $\text{cm}^{-1}$  and disappearance of  $\nu_{\text{SH}}$  band (2350  $\text{cm}^{-1}$ ) on complexation.

The mixed thioamide band-I<sup>18-20</sup> ( $\delta_{\text{NH}} + \nu_{\text{C-N}}$ ) red shifted (10–20  $\text{cm}^{-1}$ ) in  $[\text{Zr}(\text{AHtT})_3]\text{Cl}$ ,  $[\text{Co}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{AHtT})_2(\text{H}_2\text{O})_2]$  suggesting bonding through deprotonated imino nitrogen atom of the ligand. However, this band is either identical or blue shifted (10–40  $\text{cm}^{-1}$ ) in other complexes indicating the intactness of imino nitrogen atom of the ligand. Thioamide band-II ( $\nu_{\text{C-S}} + \nu_{\text{CN}} + \delta_{\text{NH}}$ ), -III ( $\nu_{\text{CN}} + \nu_{\text{CS}} + \nu_{\text{C-C}}$ ), -IV ( $\nu_{\text{C-S}}$ ) of the ligand observed at 1330, 1090 and 715  $\text{cm}^{-1}$  are also red shifted supporting coordination through sulphur due to increase of CN and decrease of CS bond order<sup>21-23</sup>. But thioamide band-IV is observed almost identical in Co(II) and Ni(II) with reduction in intensities. Most probably blue shifting of thioamide band-IV due to formation of metal-nitrogen bond is compensated by its red shifting due to formation of metal-sulphur bond.

Weak absorption bands near 1580, 1435, 1070, 1040, 695  $\text{cm}^{-1}$  in the spectra of Pd(0), Pt(0) and Rh(I) complexes suggest the presence of coordinated  $\text{P}\emptyset_3$  group<sup>24</sup> strong band at 1515  $\text{cm}^{-1}$  in  $[\text{Rh}(\text{P}\emptyset_3)(\text{AHtT})(\text{CS}_2)_2]$  are assigned to  $\nu_{\text{CS}_2}$  of  $\sigma$ -bonded  $\text{CS}_2$  group through sulphur following Wilkinson *et al.*<sup>25</sup> and others<sup>26-28</sup>. In oxozirconium complexes  $\nu_{\text{Zr-O}}$  is observed at *ca.* 995  $\text{cm}^{-1}$ . Four coordinated Pd(0)<sup>29, 30</sup> and Pt(0)<sup>31, 32</sup> complexes, having four monodentate ligands, are generally tetrahedral. In far infrared spectra two  $\nu_{\text{Pd-P}}$  (430 and 420  $\text{cm}^{-1}$ ) and one  $\nu_{(\text{Pd-S})}$  (360  $\text{cm}^{-1}$ ) in  $\text{Pd}(\text{P}\emptyset_3)_3(\text{AHtTH})$ , two  $\nu_{\text{Pt-S}}$  (340 and 325  $\text{cm}^{-1}$ ) and one  $\nu_{\text{Pt-P}}$  (425  $\text{cm}^{-1}$ ) in  $[\text{Pt}(\text{P}\emptyset_3)(\text{AHtTH})_3]$  supports tetrahedral configuration ( $\text{C}_{3v}$  point group). In  $[\text{Rh}(\text{P}\emptyset_3)_3(\text{AHtT})]$ , two  $\nu_{\text{Rh-P}}$  (380 and 343  $\text{cm}^{-1}$ ) and one  $\nu_{\text{Rh-S}}$  (310  $\text{cm}^{-1}$ ) have been observed which suggest two  $\text{P}\emptyset_3$  group at *cis* positions in most probable tentative planar structure. In  $\text{Zr}(\text{AHtTH})_4(\text{Py})_2(\text{SO}_4)_2$ , one  $\nu_{\text{Zr-Py}}$  (260  $\text{cm}^{-1}$ ) and one  $\nu_{\text{Zr-S}}$  (410  $\text{cm}^{-1}$ ) are observed suggesting *trans*-octahedral configuration<sup>33</sup>. Moreover, in Co(II) and Ni(II) the ligand forms inner type  $\text{O}_h$ -complex in which bonding occurs through deprotonated imino nitrogen and thione sulphur and most probably the metal ions and the plane of the ligand molecules are in one plane and the water molecules are coordinated perpendicularly above and below this plane.

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(Received: 11 January 1992; Accepted: 15 October 1992)

AJC-500