

## Derivatographic and spectral studies of Ni(II) complexes with 4-salicyldimin-2,5-dimercapto-1,2,4-triazole

Minu Kumari<sup>1</sup>, K.N.Thakur<sup>1\*</sup>, Arnab Kashyap<sup>1</sup>, A.K.Jha<sup>2</sup>, Rakesh Roshan<sup>3</sup>, R.R.Jha<sup>2</sup>

<sup>1</sup>Department of Chemistry, Ranchi College, Ranchi, (INDIA)

<sup>2</sup>Department of Chemistry, Ranchi University, Ranchi, (INDIA)

<sup>3</sup>Department of Chemistry, Motihari College of Engineering, Motihari, (INDIA)

E-mail: drknthakur@gmail.com

### ABSTRACT

Pyridine adduct complexes of 4-Salicyldimino-2,5-dimercapto-1,2,4-triazole ( $H_2Saldmt$ ) of compositions  $PyH[Ni(Saldmt)Py]$  and  $[Ni(Saldmt)H_2O]$  were prepared and characterized by elemental analysis and spectral studies. The TGA and DTA analysis were performed between temperature ranges 40-650°C. The complexes were diamagnetic and possess four coordinated square planer structure. The IR spectra suggested coordination of ligand by deprotonation of thiol (-SH) and phenolic (-OH) as tridentate (O, N and S) donor molecule. The TG shows multistep decomposition of complexes with exothermic DTA maxima. © 2014 Trade Science Inc. - INDIA

### KEYWORDS

Nickel(II) 4-salicyldimino-2,5-dimercapto-1,2,4-triazole complexes;  
Derivatographic;  
Spectral studies.

### INTRODUCTION

Triazole, thiadiazole and thiazole ring system have medicinally active nuclei and a large number of their derivatives have been used as antibacterial and antitumoral medicines<sup>[1,2]</sup>. The triazole derivatives have been reported as nervous depressant<sup>[3]</sup>, analgesic<sup>[4]</sup>, herbicidal<sup>[5]</sup>, muscle relaxants<sup>[6]</sup>, anti-inflammatory<sup>[7]</sup>, antitumoral<sup>[8]</sup>, anti-tubercular and anti-hypertensive agent<sup>[9,10]</sup>. The complexing properties of a number of triazole derivatives have also been studied extensively<sup>[11,12]</sup>. In view of pharmacological activity of triazole and thiadiazole derivatives, we have been tempted to study the transition metal complexes of Schiff base of 4-aminotriazole derivative. In present paper we report preparation of 4-salicyldimin-2,5-dimercapto-1,2,4-triazole and its Nickel(II) complexes and their characterizations by elemental analysis and physi-

cal measurements.

### EXPERIMENTAL

The ligand 4-salicyldimino-2,5-dimercapto-1,2,4-triazole was prepared by condensing 4-amino-2,5-dimercapto-1,2,4-triazole<sup>[11]</sup> with salicylaldehyde in aqueous ethanol in presence of a few drops of acetic acid M.P. 249-251°C, Nitrogen found 24.06% required Nitrogen 23.14%. The metal salt and solvents used were obtained from B.D.H. The result of C,H,N and S were obtained from B.I.T. Mesra, Ranchi. The magnetic susceptibility was determined by Gouy method and T.G analysis were performed at B.I.T. mesra, Ranchi.

#### Preparation of complex $PyH[Ni(Saldmt)Py]$

About 0.01 mole of nickel(II) chloride was dis-

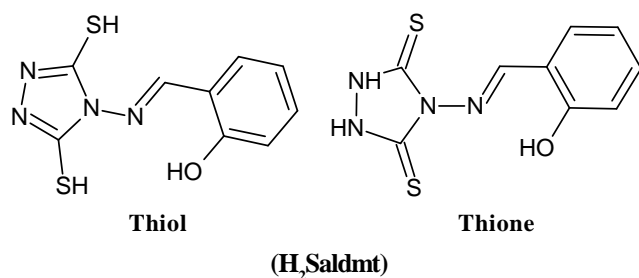
solved in 20 ml aqueous ethanol and 2 ml pyridine and added slowly with constant stirring to 0.01 mol of ( $H_2Saldmt$ ) dissolved in 25 ml ethanol and 2 ml pyridine. The resulting deep orange red solution was evaporated to syrupy mass and diluted with 25 ml cold water, stirred thoroughly to get crystalline orange yellow precipitate. The product was collected on filter, washed with few drops of methanol containing pyridine. The complex was dried in desiccators over  $CaCl_2$  yield 90 – 95%. On analysis it was found to contain Ni - 12.61%, C - 49.10%, H - 3.58%, N - 16.02%, S - 13.61%. The complexes  $PyH[Ni(Saldmt)Py]$  requires Ni - 12.56%, C - 48.82%, H - 3.42%, N - 17.99% and S - 13.70%

### Preparation of aqua complex $[Ni(Saldmt)(H_2O)]H_2O$

The complex was obtained by boiling pyridine complex  $PyH[Ni(Saldmt)Py]$  in excess of water, neutralized with 2-3 ml dilute acetic acid. The product was cooled and collected on buckner funnel, washed with water and a few drop of methanol. The product was dried in a desiccator over  $CaCl_2$ . The complex was analyzed and found to contain Ni - 17.21%, C - 30.81%, H - 3.01%, N - 16.11% and S - 18.41%. The complex  $[Ni(Saldmt)(H_2O)]H_2O$  requires Ni - 17.01%, C - 31.30%, H - 2.89% N - 16.23% and S - 18.55%.

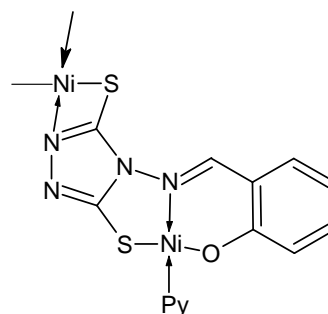
## RESULT AND DISCUSSION

The triazoleschiffs base 4-salicyldimino-2,5-dimercapto-1,2,4-triazole ( $H_2Saldmt$ ) is potent nitrogen, oxygen and sulphercontaining polydentate coordinating molecule. In solid the ligand usually exist in thione form<sup>[11]</sup>.

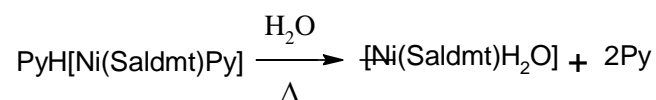


The ligand can exist in thiol tautomer in basic medium with two thiol(-SH) protons but only one thiol group is attached favorably to be deprotonated which

can form chelate ring with one metal atom. In presence of excess of metal in basic medium the second thiol (-SH) can also be utilized in bond formation forming polymeric complex. (Shown below)



The elemental analysis of nickel(II) complex correspond with composition  $PyH[Ni(Saldmt)Py]$  and  $[Ni(Saldmt)(H_2O)]H_2O$ . The complexes are stable in air but when the pyridinium salt of nickel(II) complex when boiled in aqueous medium in presence little acetic acid converted into aqua species  $[Ni(Saldmt)(H_2O)]H_2O$  with release of pyridine.



These complexes are almost insoluble in water and aqueous ethanol or methanol but dissolve appreciably in DMF. The DMF solution of complex shows strong electronic absorption band below 380 nm and a medium band at 417-420 nm. The electronic absorption band of complex is attributed to  ${}^1A_{1g} - {}^1B_{1g}$  transition in square planar field<sup>[14]</sup>. The complexes  $PyH[Ni(Saldmt)Py]$  and  $[Ni(Saldmt)(H_2O)]H_2O$  both are diamagnetic at room temperature. The diamagnetic character of complexes supported their square planar geometry. The IR spectrum of ligand  $H_2Saldmt$  display a broad band between 3260 – 2980  $cm^{-1}$  attributed from  ${}^2(OH)$ ,  ${}^2(NH)$  and  ${}^2(CH)$  of phenyl ring vibration. The azomethene ( $C=N$ ) stretching frequency of ligands was located at 1642  $cm^{-1}$ . The absence of band in between 2400 – 2700  $cm^{-1}$  in IR spectrum of ligand indicated thione tautomer of ligand molecule in solid state. The  $\delta(NH)$  of ligand was located at 1505  $cm^{-1}$  which is absent in complex  $PyH[Ni(Saldmt)Py]$  supporting deprotonation of thiol tautomer of the ligand. The  ${}^2(C=S)$  of free ligand was observed at 961  $cm^{-1}$  which shifts to lower frequency in complexes and ob-

## Full Paper

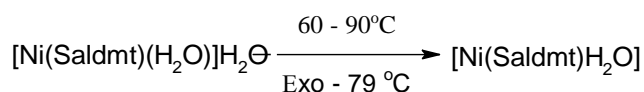
served near 722 and 716  $\text{cm}^{-1}$  in complexes,  $\text{PyH}[\text{Ni}(\text{Saldmt})\text{Py}]$  and  $[\text{Ni}(\text{Saldmt})(\text{H}_2\text{O})]\text{H}_2\text{O}$  respectively. The pyridine adduct complex show a strong band at 1590  $\text{cm}^{-1}$  and pyridine ring breathing mode of vibration at 1025  $\text{cm}^{-1}$  suggesting bonding of pyridine ring (CN) nitrogen to metal atom<sup>[15,16]</sup>. The salicylidimineazo (C=N) stretch located at 1642  $\text{cm}^{-1}$  shift to lower frequency and observed at 1608 and 1604  $\text{cm}^{-1}$  supporting the coordination of salicylidimino (C=N) nitrogen to metal atom. Thus these IR shift and IR vibrations unambiguously suggest the bonding of  $\text{H}_2\text{Saldmt}$  through deprotonated phenolic oxygen, thiol sulphur and aldimine (C=N) nitrogen with metal atom, as tridentate molecule<sup>[17,18]</sup>. The broad band near 3340-3040  $\text{cm}^{-1}$  in aqua complex and weak broad band near 670 – 680  $\text{cm}^{-1}$  assignable to rocking  $\rho_w(\text{H}_2\text{O})$ , confirms the coordination of water molecule in aqua complex  $[\text{Ni}(\text{Saldmt})(\text{H}_2\text{O})]\text{H}_2\text{O}$ .

### T.G.studies

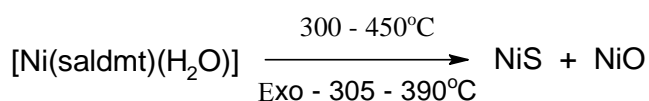
The thermogravimetric analysis of  $\text{PyH}[\text{Ni}(\text{Saldmt})\text{Py}]$  and  $[\text{Ni}(\text{Saldmt})(\text{H}_2\text{O})]\text{H}_2\text{O}$  were made between temperature range 40 - 650°C with heating rate 10° per minute. The complex  $\text{PyH}[\text{Ni}(\text{Saldmt})\text{Py}]$  started losing weight at 90°C gradually with DTG maxima at 135°C and exothermic DTA peak at 136°C and loss continued upto 230°C giving  $[\text{Ni}(\text{Saldmt})]$ . The loss expected for elimination of two Py was 38.28% and the loss incurred for the first step of elimination of two Py molecules was 37.62%. The compound formed was stable till 260-265°C and after that it started decomposition in two continuous steps giving DTG maxima at 290 and 385°C and showing exothermic peak at 295 and 390°C. The loss in first step appears to be decomposition of Schiff base and second step due to decomposition of triazole ring. The loss in weight continued up to 460°C with formation of  $\text{NiS} + \text{NiO}$ . The weight of residue at 650°C was 18.10% and expected loss for formation of  $\text{NiS}$  was 19.43% while expected weight of  $\text{NiO}$  was 16.02%. The residual weight indicated the formation of  $\text{NiS} + \text{NiO}$  in TG analysis. The TG Study of aqua complex  $[\text{Ni}(\text{Saldmt})(\text{H}_2\text{O})]\text{H}_2\text{O}$  showed loss of a water molecule between 60-90°C with DTG maxima at 80° and exothermic DTA peak at 79°C. The loss occurred during loss of  $\text{H}_2\text{O}$  was 6.2% and expected loss for

one  $\text{H}_2\text{O}$  is 5.52%. The compound  $[\text{Ni}(\text{Saldmt})\text{H}_2\text{O}]$  formed was stable upto 300°C and on further heated started decomposition with two step decomposition showing exothermic DTA maxima at 310°C and 390°C showing exothermic DTA maxima at 305 and 390°C. The loss incurred in these steps indicated the formation of  $\text{NiO} + \text{NiS}$ . The expected weight of residue for formation of  $\text{NiS}$  is 27.01% and weight of residue found was 26% which indicated the formation of a mixture of  $\text{NiS} + \text{NiO}$ . The TGA scheme can be presented as given below.

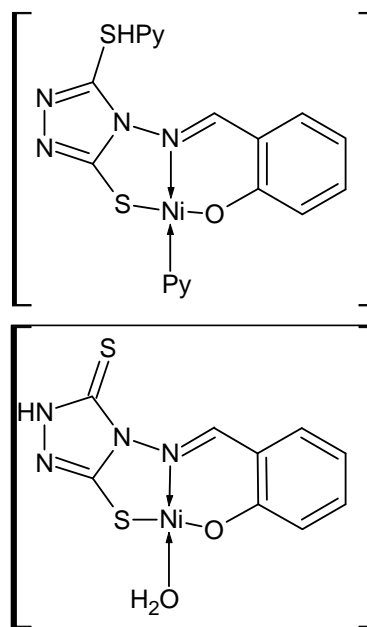
1<sup>st</sup> step



2<sup>nd</sup> step



Thus from elemental analysis, magnetic susceptibility measurement spectroscopic studies, the planar structure shown below is suggested for complexes  $(\text{PyH})[\text{Ni}(\text{Saldmt})\text{Py}]$  and  $[\text{Ni}(\text{Saldmt})\text{H}_2\text{O}]$ .



### ACKNOWLEDGEMENT

Thanks are due to Head of Chemistry Dept. Ranchi

University, Ranchi for magnetic susceptibility Measurements and authority of BIT, Mesra for UV, IR and TGA Analysis.

### REFERENCES

- [1] P.P.Deohate; J.Indian Chem.Soc., **59**, 253 (2012).
- [2] K.Tsukamoto, M.Suno, K.Igarashi, Y.Kozai, Y.Sugino; Cancer Res., **35**, 263 (1975).
- [3] J.Millard, M.Vincont, R.Morin, M.Benard; French Patent, M-379, Chem.Abst., **57**, 1525 (1962).
- [4] H.Nager, R.Giudecelli, C.Moraland, M.Menin; Bull Chem.Soc., **75**, 153 (1966).
- [5] D.A.Kennedy, L.A.Summers; J.Het.Chem., **18**, 409 (1981).
- [6] H.I.Yale, K.Losee; Med.Chem., **9**, 78 (1996).
- [7] M.Amir, K.Shikha; Eur.J.Chem., **34**, 535 (2004).
- [8] N.Demirbas, S.AIpay Karaoglu, A.Demirbas, K.Sancak; Eur.J.med.Chem., **30**, 793 (2004).
- [9] N.Demirbas, R.Ugurluoglu, A.Demirbas; Bioorg. Med.Chem., **10**, 3717 (2002).
- [10] F.Malbec, R.Milcent, P.Vcart, A.M.Bure; J.Het. Chem., **21**, 1769 (1984).
- [11] B.K.Sinha, R.Singh, J.P.Srivastva, L.K.Mishra; J.Inorg.Nuel.Chem., **30**, 1797 (1977).
- [12] B.N.Figgis, J.Lewis; Modern Coordination Chemistry, Interscience, New York, (1960).
- [13] S.Yamada; Coord.Chem.Rev., **1**, 415 (1966).
- [14] A.B.P.Lever; Inorganic Electronic Spectroscopy, Elsevier Amsterdam, (1968).
- [15] K.Nakamoto; Infrared and Raman Spectra of Inorganic and Complex Compounds, John Wiley, New York, 5<sup>th</sup> Edition, (1997).
- [16] V.K.P.Unny, D.G.Vartak; Indian J.Chem., Sec A, **21**, 493 (1982).
- [17] M.K.Das, M.Nath, Zuucermann; Inorg.Chem.Acta, **21**, 49 (1983).
- [18] R.D.Beraman, D.M.Baird, J.Bordner, J.Dorfman; J.Polyhedron., **2**, 25 (1983).