



## **SYNTHESIS, SPECTRAL AND STRUCTURAL STUDIES OF Ni (II) COMPLEXES OF BIS (2-AMINO-1,3,4-THIADIAZOLE)**

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### **ABSTRACT**

The, ligand bis (2-amino-1,3,4-thiadiazole) (L) has been synthesized by the reaction of oxalic acid with thiosemicarbazide. The ligand and Ni (II) complexes have been synthesized and its structures of these compounds have been determined by elemental analysis, spectrometric magnetic susceptibility and molar conductivity measurements. Coordination numbers of monomeric Ni (II) complex are six and four, respectively. From the elemental analysis and mass spectral data, the complexes were proposed to have the formula  $[\text{Ni}(\text{L})_2(\text{SO}_4)\text{H}_2\text{O}]\cdot 0.5\text{DMF}\cdot 2\text{H}_2\text{O}$ . Ni (II) complexes are paramagnetic and non-electrolytes.

**Key words:** Non-electrolytes Bis (2-amino-1,3,4-thiadiazole), Metal complexes, Spectrometric.

### **INTRODUCTION**

The poly functionally ring compounds and synthesis of their metal complexes which have various biological activities and include heteroatom, have been formed in organic synthesis and in coordination chemistry<sup>1-5</sup>.

1,3,4-thiadiazoles which have sulfonamide group act as a monodentate ligand through the thiadiazole N atom and behave as a bridge joining two metal ions *via* the N atom of thiadiazole ring and the N atom of the free sulfonamide group. These compounds are well known as inhibitors of carbonic anhydrase which catalyze the biological interconversion between  $\text{CO}_2$  and  $\text{HCO}_3^-$ . Therefore it has been consistently interesting bioinorganic subjects<sup>6</sup>.

In this work, we have synthesized bis(2-amino-1,3,4-thiadiazole) Ethane (L) by reaction of oxalic acid with thiosemicarbazide. Then Ni (II), complexes were synthesized by reaction of bis(2-amino-1,3,4-thiadiazole)-ethane and  $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$  and metal salts.

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## EXPERIMENTAL

Oxalic acid and thiosemicarbazide and metal salts were purchased from Aldrich  $\text{POCl}_3$ , DMF and methanol from Merck (Pure) and used without further purification.

Elemental analyses were carried out on Leco CHNS-O mode 1932 elemental analyzer. IR spectra were recorded Perkin-Elmer Precisely Spectrum one spectrometer on KBr discs in the wave number range of  $4000\text{-}400\text{ cm}^{-1}$ . Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. Molar conductivity was measured with a CMD WPA model 750 conductivity meter, using prepared solution of the complex in (DMSO/THF) and (DMF/DMSO) (1 : 1) ( $10^{-3}\text{ M}$ ).

### Synthesis of bis(2-amino-1,3,4-thiadiazole) (L)

A mixture of oxalic acid (0.04 mol), thiosemicarbazide (0.08 mol) and phosphorus oxychloride (0.08 mol) were heated at  $60^\circ\text{C}$  for 1 h and for an additional 3 h, temperature was raised to  $95^\circ\text{C}$ . The mixture was then poured into the least amount of crushed ice cooled to  $15^\circ\text{C}$  and the pH was adjusted to  $\approx 11$  using NaOH (10 M). The resulting solid washed again with hot absolute alcohol and the product was dried at room temperature<sup>7-8</sup>. Yield 1.26 g, 25%, m.p.  $325\text{-}326^\circ\text{C}$ , characteristic IR bands (KBr,  $\text{cm}^{-1}$ ): 3335, 3276 and  $1511\text{ v}(\text{NH})$  and  $\delta(\text{NH})$ ,  $1628\text{ v}(\text{C}=\text{N})$ ,  $1050\text{ v}(\text{=N-N=})$ ,  $683\text{ }\delta(\text{C-S-C})$ .

### Synthesis of Ni (II) complexes

The ligand, bis (2-amino-1,3,4-thiadiazole) (0.20 g, 1.00 mmol) was dissolved in 20 mL DMF in a 100 mL round-bottom flask. A solution of metal salts  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  : 0.14 g (0.50 mmol) ; in 5 mL MeOH was added dropwise in 15 min, periods with continuous stirring at room temperature and the solution was refluxed for 6 h. After the completion of the reaction, the precipitates was filtered off and washed with hot DMF and MeOH. The products were dried at  $80^\circ\text{C}$ . Decomposition temperature  $> 360^\circ\text{C}$ . Yield 0.23 g (72 %), 0.33 g (77 %), for Ni (II) complexes, respectively.

## RESULTS AND DISCUSSION

Bis(2-amino-1,3,4-thiadiazole) (L) was prepared using  $\text{POCl}_3$  as catalyst. The synthesis of ligand (L) by the nucleophilic addition reaction<sup>9</sup>. The characterization data of ligand and its complexes are given in Table 1.

**Table 1: Physico-chemical and elemental analyses of the ligand and its complexes**

Compd. (Colour)	m.w. (Yield, %)	Elemental analysis (%) Found (Calcd.)		$A_M$ ( $\Omega^{-1}\text{cm}^2$ $\text{mol}^{-1}$ )		$\mu_{\text{eff}}$ ( $\text{BM}^1$ )	
		C	H	N	S		
$\text{C}_4\text{H}_4\text{N}_6\text{S}_2$ (Yellow brown)	212 (25.0)	23.3 (24.0)	2.5 (2.0)	41.2 (42.0)	31.2 (32.0)	-	-
$[\text{Ni}(\text{L})_2\text{SO}_4\text{H}_2\text{O}] \cdot 0.5\text{DMF} \cdot 2\text{H}_2\text{O}$ (Light green)	645.69 (72.0)	17.0 (17.7)	2.9 (2.7)	26.6 (27.1)	24.0 (24.8)	4.4	3.82

### IR spectra

The IR spectral bands of the ligand and its complexes are listed in Table 2 together with assignments for most of the important peaks. The position and/or the intensities of these peaks are expected to be changed upon chelation.

In the IR spectrum of L, the characteristic bands are at 3335-3276, 1511  $\text{cm}^{-1}$  which are assigned to  $\nu$  (NH) and  $\delta$  (NH), Further, the bands at 1628, 1050 and 683  $\text{cm}^{-1}$  which are assigned to the  $\nu$  (C = N),  $\nu$  (=N-N=) and  $\delta$  (C-S-C) group, respectively.

**Table 2: Characteristic IR bands ( $\text{cm}^{-1}$ ) of the ligand and complexes as KBr pellets**

Compound	$\nu(\text{H}_2\text{O})$ Coord.	$\nu(\text{NH})$ and $\delta$ (NH)	$\nu(\text{SO}_4)/$ $\nu(\text{NO}_3)^*$	$\delta$ (C-S-C)	$\nu$ (C=N)	Others
$\text{C}_4\text{H}_4\text{N}_6\text{S}_2$	-	3335, 3276, 1511	-	683	1628	$\nu$ (=N-N=), 1050
$[\text{Ni}(\text{L}_2)(\text{SO}_4)$ $\text{H}_2\text{O}] \cdot 0.5\text{DMF} \cdot 2\text{H}_2\text{O}$		3289, 3283, 1509	1148, 1111, 1078, 974, 648, 618		1650 1616	

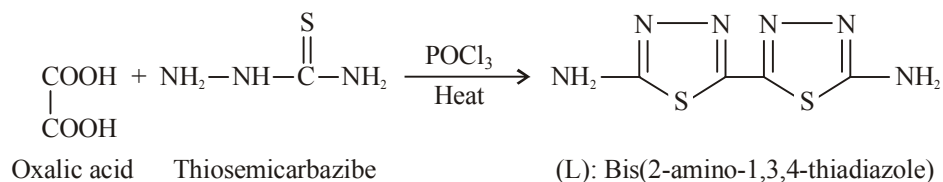
The spectra of the complexes exhibited intense broad 3505-3300  $\text{cm}^{-1}$  due to  $\nu$  (OH) of hydrate and coordinated water. The presence of hydrate or/and coordinated water molecules are also confirmed by elemental analyses and thermogravimetric analyses.

The IR spectra of the complexes compared with the ligand, indicate that the C=N band 1629  $\text{cm}^{-1}$  is shifted to lower or higher frequencies for complexes Ni (II). This phenomenon appears to be due to the coordination of 1,3,4-thiadiazole nitrogen atoms to the metal ion<sup>10</sup>. The bands due to  $\nu$  (NH) and  $\delta$  (NH) in the spectra of the ligand were observed

the same positions in the spectra of the Ni (II) complexes did not participate in complex formation.

The IR spectra of Ni (II) complex observed broad and strong bands in the region of 1148-1078  $\text{cm}^{-1}$  and weak bands in the region of 648-618  $\text{cm}^{-1}$ , which split into three bands. Further, a weak band observed at 974  $\text{cm}^{-1}$ , these bands suggest the unidentate nature of sulfate group<sup>11-14</sup>. Therefore, sulphate group acts as monodentate ligand.

Thus, according to the elemental analyses, IR and magnetic susceptibility results, the structures of complexes are suggested to be shown below.

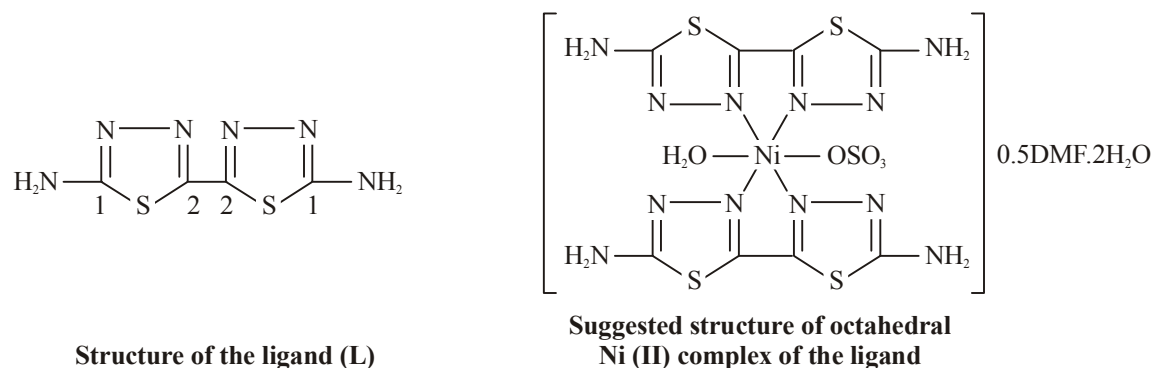


### Magnetic and conductivity studies

The Ni (II) complexes are paramagnetic and their magnetic susceptibility values are 3.82 and 1.21 BM, respectively. According to the above results, octahedral geometry for Ni (II) complex are proposed<sup>15</sup> (Table 1).

The complexes Ni (II) are non-electrolytes, as shown by their molar measurements in (THF/DMSO) (1 : 1), which are the range 4.4-11.0  $\Omega^{-1} \text{cm}^2 \text{molar mol}^{-1}$  For the reference solution was used  $1 \times 10^{-3} \text{ M CaCl}_2$  and was measured 236  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Therefore, these complexes have been included free  $\text{NO}_3^-$  ions.

Thus, according to the elemental analyses, IR and magnetic susceptibility results, the structures of complexes are suggested to be as shown below.



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