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# Synthesis and Structural Characterization of Ni(II), Cu(II), Zn(II) and Cd(II) Complexes of *Bis*(2-amino-1,3,4-thiadiazole)

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In this study, the ligand *bis*(2-amino-1,3,4-thiadiazole) (L) has been synthesized by the reactions of oxalic acid with thiosemicarbazide. The ligand and Ni(II), Cu(II), Zn(II), Cd(II) complexes have been synthesized and its structures of these compounds have been deter-mined by elemental analysis, spectrometric and TGA/DTA, magnetic susceptibility and molar conductivity measurements. Coordination numbers of monomeric Ni(II) and Cd(II) complexes are six and four, respectively. The coordination numbers of dimeric Cu(II) and Zn(II) complexes are five and four. From the elemental analysis and mass spectral data, the complexes were proposed to have the formula $[Ni(L)_2(SO_4)H_2O]\cdot 0.5DMF\cdot 2H_2O$, $[Cu(L)(SO_4)H_2O]_2\cdot DMF\cdot 2H_2O$, $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ and $[Cd(L)_2]\cdot 2NO_3\cdot 1.5DMF\cdot H_2O$. Ni(II) and Cu(II) complexes are paramagnetic and non-electrolytes. The molar conductance data revealed that zinc(II) and cadmium(II) complexes are 1:2 electrolytes.

**Key Words: *Bis*(2-amino-1,3,4-thiadiazole), Metal complexes.**

## INTRODUCTION

Poly functionally ring compounds and synthesis of their metal complexes which have various biologicial activities and include heteroatom, have been formed in organic synthesis and in coordination chemistry[1-5]. The 1,3,4-thiadiazole ring is associated with diverse biological activities probably by virtue of incorporating a -N=C-S- linkage[6-8]. 2,5-disubstituted-1,3,4-thiadiazoles which caused N-donor atoms have shown various biological activities[9].

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 $CO_2$ and $HCO_3^-$. Therefore it has been consistently interesting bioinorganic subjects[10].

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In this work, we have synthesized *bis*(2-amino-1,3,4-thiadiazole)methane (L) by reaction of oxalic acid with thiosemicarbazide. Then, its Ni(II), Cu(II), Zn(II) and Cd(II) complexes were synthesized by reaction of *bis*(2-amino-1,3,4-thiadiazole)-methane and $NiSO_4\cdot7H_2O$, $CuSO_4\cdot5H_2O$, $Zn(NO_3)_2\cdot6H_2O$ and $Cd(NO_3)_2$ metal salts.

## EXPERIMENTAL

Oxalic acid and thiosemicarbazide and metal salts were purchased from Aldrich, $POCl_3$, DMF and methanol from Merck (pure) and used without further purification.

Elemental analyses were carried out on a Leco CHNS-O mode l 932 elemental analyzer. $^1$H NMR spectra were recorded using a model Bruker GmbH DPX-300 MHz FT spectrometer. IR spectra were recorded Perkin-Elmer Precisely Spectrum One spectrometer on KBr discs in the wave number range of 4000-400 cm$^{-1}$. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $Hg[Co(SCN)_4]$ as a calibrant. Thermal analyses (TGA and DTA) were carried out in nitrogen atmosphere with a heating rate of 15 °C/min. using Shimadzu TA-60 WS thermal analyzers. 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) ($10^{-3}$ M). LC/MS-API-ES mass spectra were recorded using a AGILENT model 1100 MSD mass spectrometer.

### General procedure

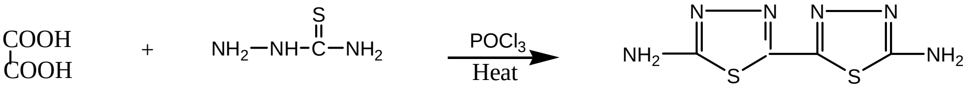
**Synthesis of for *bis*(2-amino-1,3,4-thiadiazole) (L):** A mixture of oxalic acid (0.04 mol) thiosemicarbazide (0.08 mol) and phosphorus oxychloride (0.08 mol) were heated at 60 ºC for 1 h and for an additional 3 h, temperature was raised to 95 ºC. The mixture was then poured into the least amount of crushed ice cooled to 15 °C and the pH was adjusted to ≈ 11 using NaOH (10 M). The resulting solid washed again with hot absolute alcohol and the product was dried at room temperature[11-12]. Yield 1.26 g, 25 %, m.p. 325-326 ºC, Characteristic IR bands (KBr, cm$^{-1}$): 3335, 3276 and 1511 ν(NH) and δ(NH), 1628 ν(C=N), 1050 ν(=N-N=), 683 δ(C-S-C). Characteristic $^1$H NMR peaks (DMSO-$d_6$, δ ppm): 7.67 ($-NH_2$, 4H, s). Characteristic $^{13}$C NMR peaks (DMSO-$d_6$, δ ppm): 149 $C_2$, 169 $C_1$, 40.0 DMSO.

**Synthesis of the Ni(II) and Cu(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 $NiSO_4\cdot7H_2O$: 0.14 g (0.50 mmol); $CuSO_4\cdot5H_2O$: 0.25 g (1.00 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 ºC. Decomposition temperature: > 360 ºC. Yield 0.23 g (72 %), 0.33 g (77 %), for Ni(II) and Cu(II) complexes, respectively.

**Synthesis of the Zn(II) and Cd(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 and a stoichiometric amount of an methanole solution of the appropriate nitrate $Zn(NO_3)_2{\cdot}6H_2O$: 0.30 g (1.00 mmol); $Cd(NO_3)_2$: 0.12 g (0.5 mmol) was added dropwise in 15 min periods with continuous stirring at room temperature. The mixture was refluxed for 6 h. A portion of the solvent was evaporated in water bath until concentrated solution was obtained. On the solution was added chloroform and resulting precipitate was filtered off and washed with chloroform. The products were dried at 80 ºC. Decomposition temperature: > 360 ºC, Yields, 0.31g (66 %), 0.25 g (66 %) Zn(II) and Cd(II) complexes, respectively.

## RESULTS AND DISCUSSION

*Bis*(2-amino-1,3,4-thiadiazole) (L) was prepared in one stage process as shown **Scheme-I**, using $POCl_3$ as catalyst. The synthesis of ligand (L) has been occurring according to the nucleophilic addition reaction[13]. The characterization data of ligand and its complexes are given in Table-1.



Oxalic acid Thiosemicarbazide (**L**): *Bis*(2-amino-1,3,4-thiadiazole)

**Scheme-I:** Synthesis scheme for the preparation of the ligand (L)

TABLE-1
PHYSICO-CHEMICAL AND ELEMENTAL ANALYSES OF THE LIGAND AND ITS COMPLEXES

| Compd. (colour) | m.w. (Yield, %) | Elemental analysis (%): Found (Calcd.) C | H | N | S | $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) | $\mu_{eff}$ (BM[1]) |
|---|---|---|---|---|---|---|---|
| $C_5H_4N_6S_2$ | 212 | 23.3 | 2.5 | 41.2 | 31.2 | – | – |
| (Yellow brown) | (25.0) | (24.0) | (2.0) | (42.0) | (32.0) | | |
| $[Ni(L)_2SO_4H_2O]{\cdot}0.5DMF{\cdot}2H_2O$ | 645.69 | 17.0 | 2.9 | 26.6 | 24.0 | 4.4 | 3.82 |
| (Light green) | (72.0) | (17.7) | (2.7) | (27.1) | (24.8) | | |
| $[Cu(L)(SO_4)H_2O]_2{\cdot}DMF{\cdot}2H_2O$ | 864.56 | 15.7 | 2.5 | 20.7 | 21.8 | 11 | 1.21 |
| (Henna green) | (77.0) | (15.3) | (2.2) | (21.1) | (22.2) | | |
| $[Zn(L)(NO_3)]_2{\cdot}2NO_3{\cdot}2DMF{\cdot}H_2O$ | 943.26 | 17.1 | 2.4 | 26.0 | 13.0 | 162 | Diamag. |
| (Yellow) | (66.0) | (17.8) | (2.5) | (26.7) | (13.6) | | |
| $[Cd(L)_2]{\cdot}2NO_3{\cdot}1.5DMF{\cdot}H_2O$ | 764.39 | 18.9 | 2.6 | 25.0 | 16.1 | 163 | Diamag. |
| (Yellow orange) | (66.0) | (19.6) | (2.7) | (25.6) | (16.7) | | |

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 cm$^{-1}$ which are assigned to ν(NH) and δ(NH), Further, the bands at 1628, 1050 and 683 cm$^{-1}$ which are assigned to the ν(C=N), ν(=N-N=) and δ(C-S-C) group, respectively[11].

TABLE-2
CHARACTERISTIC IR BANDS ($cm^{-1}$) OF THE LIGAND AND COMPLEXES AS KBr PELLETS

| Compound | $\nu(H_2O)$ coord. | $\nu$(NH) and $\delta$(NH) | $\nu(SO_4)$/ $\nu(NO_3)$* | $\delta$(C-S-C) | $\nu$(C=N) | Others |
|---|---|---|---|---|---|---|
| $C_4H_4N_6S_2$ | – | 3335, 3276, 1511 | – | 683 | 1628 | $\nu$(=N-N=), 1050 |
| $[Ni(L)_2SO_4H_2O]\cdot 0.5DMF\cdot 2H_2O$ | | 3289, 3283, 1509 | 1148, 1111, 1078, 974, 648, 618 | | 1650<br>1616 | |
| $[Cu(L)(SO_4)H_2O]_2\cdot DMF\cdot 2H_2O$ | 776 | 3379, 3274, 1520 | 1166, 1094, 1064, 615 | – | 1650 | |
| $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ | | 3340, 3277, 1506 | 1383, 1248 | 671 | 1634 | $\nu$(M-O), 510 $\nu$(=N-N=), 1051 |
| $[Cd(L)_2]\cdot 2NO_3\cdot 1.5DMF\cdot H_2O$ | – | 3340, 3279, 1513 | 1380 | 666 | 1650, 1610 | $\nu$(=N-N=), 1055 |

The spectra of all the complexes exhibited intense broad 3505-3300 $cm^{-1}$ 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 $cm^{-1}$ is shifted to lower or higher frequencies for complexes Ni(II) and Cu(II). This phenomenon appears to be due to the coordination of 1,3,4-thiadiazole nitrogen atoms to the metal ion[14]. 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 Cu(II) and 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 $cm^{-1}$ and weak bands in the region of 648-618 $cm^{-1}$, which split into three bands. Further, a weak band observed at 974 $cm^{-1}$, these bands suggest the unidentate nature of sulfate group[15-18]. Therefore, sulfate group acts as monodentate ligand.

In the IR spectra of Cu(II) complex observed broad and strong bands in the region of 1094-1064 $cm^{-1}$ and weak bands in the region of 661-581 $cm^{-1}$ which split into three bands[15-18]. These results suggest the bidentate nature of sulfate group. Thus sulfate group acts as bridging bidentate ligand. In addition, a weak band appeared at 776 $cm^{-1}$ for Cu(II) complex, suggest that the coordination of $H_2O$[8].

In Zn(II) complex the $\delta$(C-S-C) absorption 683 $cm^{-1}$ of the metal-free ligand shifted to the lower wave number region and absorption at 671 $cm^{-1}$ after complexation, suggesting that sulphur atoms of the 1,3,4-thiadiazole groups are coordinated to the metal ions. The IR spectrum of Zn(II) complex give a sharp band at 1383 $cm^{-1}$ indicating both uncoordinated and coordinated nature of the nitrate group. However, a medium strong peak appeared at 1248 $cm^{-1}$ in the complex. Thus nitrate group acts as bridging bidentate ligand and a free ion[15,19-23]. Further, ν(M-O) band appeared at 510 $cm^{-1}$ in the complex[8,24].

In Cd(II) complex the δ(C-S-C) absorption 683 $cm^{-1}$ of the metal-free ligand shifted to the lower wavenumber region and absorption at 666 $cm^{-1}$ after complexation. This suggest that the coordination of 1,3,4-thiadiazole sulphur atoms to the metal ions. The IR spectrum of Cd(II) complex give a sharp and strong band at 1380 $cm^{-1}$ indicating uncoordinated nature of the nitrate group. Thus nitrate group acts as free ion[15,23-26]. In the spectra of Zn(II) and Cd(II) complexes ν(C=N) vibrations remain almost unchanged indicating, thereby, non-involvement of the C=N in the coordination.

**NMR spectra:** In the $^1H$ NMR spectrum of (L) peaks occur at 7.67 ppm ($-NH_2$) as singlet. This peak ($-NH_2$) disappeared upon addition of $D_2O$[13,27]. In a addition, in the $^{13}C$ NMR spectrum (DMSO-$d_6$, δ ppm) of (L), the all of carbon atoms have single resonance 149 $C_2$, 169 $C_1$, 40.0 DMSO[27]. Since Ni(II), Cu(II) complexes are paramagnetic and Zn(II) and Cd(II) complexes are soluble only in (DMF/DMSO) system, their $^1H$ NMR spectra could not be obtained.

**Magnetic and conductivity studies:** The Ni(II) and Cu(II) complexes are paramagnetic and their magnetic susceptibility values are 3.82 and 1.21 BM, respectively. The Zn(II) and Cd(II) complexes are diamagnetic. The low moment could be attributed interaction between copper(II) centers, occurring through either Cu-Cu bonding or through a bridging ligand[28]. According to the above results, octahedral geometry for Ni(II) complex[29] and square pyramidal geometry for Cu(II) complex are proposed[28] (Table-1).

The complexes Ni(II) and Cu(II) are non-electrolytes, as shown by their molar measurements in (THF/DMSO) (1:1), which are in the range 4.4-11.0 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. For the reference solution was used $1 \times 10^{-3}$ M $CaCl_2$ and was measured 236 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. However, Zn(II) and Cd(II) complexes behave as 1:2 electrolytes in (DMF: DMSO) (1:1) solution, which are in the range 162-163 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. Therefore, these complexes have been included free $NO_3^-$ ions[20].

**Mass spectra:** The mass spectra of the metal complexes peaks attributable to the molecular ions and in response to isotopes of the metals m/z: 556.20 $[Ni(L)_2(SO_4) + H]^+$, m/z: 759.56 $[[Cu(L)(SO_4)(H_2O)]_2 + 4H]^+$, m/z: 945.26 $[[Zn(L)(NO_3)]_2[NO_3]_2 \cdot 2DMF \cdot H_2O + 2H]^+$, m/z: 638.89 $[Cd(L)_2(NO_3)_2 + 2H]^+$[19]. The mass spectra data of the complexes was shown in Table-3.

**Thermal studies:** The thermal stability of the complexes was investigated by a combination of TGA and DTA. The TGA and DTA curves were obtained at a heating rate of 15 °C/min. The thermogravimetric data for the studied ligand and its complexes are listed in Table-4. The results obtained are in good agreement with the theoretical formula suggested from the elemental analyses.

TABLE-3
MASS SPECTRA DATA OF THE COMPLEXES

| Compound (m.w.) | Isotopes | MS/EI | Assignment |
|---|---|---|---|
| $[Ni(L)_2SO_4H_2O]\cdot 0.5DMF\cdot 2H_2O$<br>(645.69) | $^{60}$Ni: 60.35 | 556.20 | $[Ni(L)_2(SO_4)+H]^+$ |
| $[Cu(L)(SO_4)H_2O]_2\cdot DMF\cdot 2H_2O$<br>(864.56) | $^{65}$Cu: 130.35 | 759.56 | $[[Cu(L)(SO_4)(H_2O)]_2+4H]^+$ |
| $Zn(L)(NO_3)]_2[NO_3]_2\cdot 2DMF\cdot H_2O$<br>(943.26) | $^{64}$Zn: 64.05,<br>two Zn: 129.0 | 945.26 | $[[Zn(L)(NO_3)]_2(NO_3)_2\cdot 2DMF\cdot H_2O+2H]^+$ |
| $[Cd(L)_2][NO_3]_2\cdot 1.5DMF\cdot H_2O$<br>(764.39) | $^{114}$Cd or<br>$^{116}$Cd: 115.95 | 638.89 | $[Cd(L)_2(NO_3)_2+2H]^+$ |

TABLE-4
TGA DATA OF THE SYNTHESIZED COMPLEXES

| Compound | Step-I (ºC) leave group | Step-II (ºC) leave group | Step-III (ºC) leave group | Total weight loss (%): found (calcd.) |
|---|---|---|---|---|
| $[Ni(L)_2(SO_4)H2O]\cdot 0.5DMF\cdot 2H_2O$ | 35.0-120.0<br>$2H_2O$ | 120.0-258.0<br>$H_2O$+0.5DMF | – | 13.96 (14.02) |
| $[Cu(L)(SO_4)H_2O]_2\cdot DMF\cdot 2H_2O$ | 40.0-117.0<br>$2H_2O$ | 117.0-270.0<br>$2H_2O$+DMF | – | 16.55 (16.76) |
| $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ | 38.0-120.0<br>$H_2O$ | 150.0-390.0<br>2DMF+$2NO_3$ | – | 29.23 (30.53) |
| $[Cd(L)_2]\cdot 2NO_3\cdot 1.5DMF\cdot H_2O$ | 36.0-123.0<br>$H_2O$ | 170.0-220.0<br>1.5DMF | 220.0-328.0<br>$2NO_3$ | 33.84 (32.90) |

The decomposition curve of $[Ni(L)_2SO_4H_2O]\cdot 0.5DMF\cdot 2H_2O$ begins by a step 50-100 ºC displaying 5.83 % weight loss corresponding to the removal $H_2O$ (5.64 %). The second weight loss stage at 100-258 °C refers to the removal of the one mole coordinated water molecule and 0.5 mole DMF with a weight loss 13.96 % (14.02 %)[29-32].

The curves obtained for $[Cu(L)(SO_4)H_2O]_2\cdot DMF\cdot 2H_2O$ complex shows decompositions step within the temperature 40-270 ºC. The first (40-100 °C) is due to removal of two water molecules with a weight loss of 4.16 % (4.08 %). The second (117-270 °C) with 12.52 % (12.39 %) weight loss is associated with the removal of DMFand two mole of coordination water molecules.

The thermogram of $[Cd(L)_2]\cdot 2NO_3\cdot 1.5DMF\cdot H_2O$ shows stability up to 100 °C, displaying 2.35 % (2.35 %) weight loss corresponding to removal of the $H_2O$. The second weight loss stage at 170-220 °C refers to the removal of the 1.5 DMF with weight loss 14.32 % (14.57 %)[29,30]. The third weight loss stage at 225-328 °C refers to the removal of the 2 mole $NO_3$ with weight loss 16.32 % (16.57 %).

The decomposition curve of $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ begins by a step 100-125 ºC displaying 1.92 % weight loss corresponding to the removal $H_2O$ (1.76 %). In the decomposition process of the $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ complex, the mass losses corresponded to $H_2O$ leaving in the first stage of the decomposition

1.92 % (1.33 %). The TG curve of the $[Zn(L)(NO_3)]_2\cdot 2NO_3\cdot 2DMF\cdot H_2O$ presents a second step 150-390 ºC where the loss of the DMF molecules and $2NO_3$ molecule takes place at the same time 28.62 % (27.60 %).

Thus, according to the elemental analyses, IR, magnetic susceptibility, mass spectra and thermogravimetric analyses results, the structures of complexes are suggested to be as shown in Figs. 1-5.

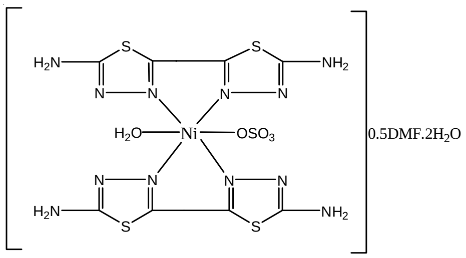


Fig. 1. Suggested structure of the octahedral Ni(II) complex of the ligand

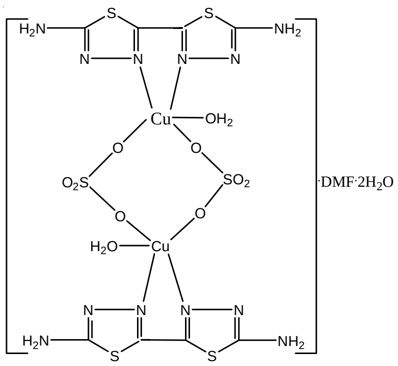


Fig. 2. Suggested structure of the square pyramidal pyramidal Cu(II) complex of the ligand

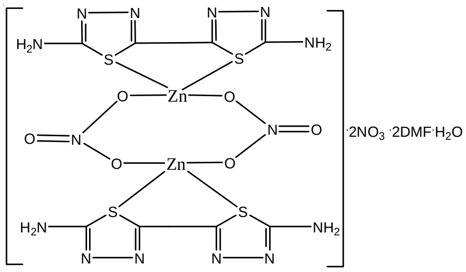


Fig. 3. Suggested structure of the four coordinated Zn(II) complex of the ligand

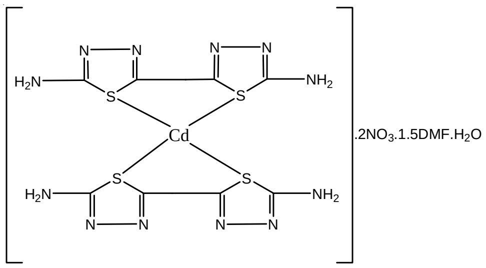


Fig. 4. Suggested structure of the four coordinated Cd(II) complex of the ligand

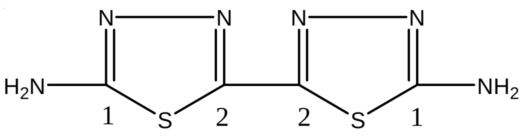


Fig. 5. Structure of the ligand (L)

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