

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and structural characterization of novel new Co (II) complexes of heteroatom bearing ligands

R Adiguzel*¹, M Sekerci², S Tascioglu³ and Z Ergin²

¹Tunceli University, Faculty of Engineering, Department of Chemical Engineering, 62000, Tunceli, Turkey

²Firat University, Faculty of Arts and Sciences, Department of Chemistry, 23169, Elazig, Turkey

³Gazi University, Faculty of Arts and Sciences, Chemistry Department 06500, Ankara, Turkey

ABSTRACT

In this study, the ligands of bis(2-amino-1,3,4-thiadiazole) (L_1), bis(2-amino-1,3,4-thiadiazolyl)methane (L_2) and bis(2-amino-1,3,4-thiadiazolyl)benzene (L_3) have been synthesized via the reactions of oxalic acid (1a), malonic acid (1b) and terephthalic acid (1c) with thiosemicarbazide. The structures of (L_1), (L_2) and (L_3) compounds have been elucidated, by elemental and spectroscopic analyses. Then, novel new Co (II) complexes of (L_1), (L_2) and (L_3) have been synthesized; and the structures of these complexes have been determined by elemental analysis, spectrometric and TGA/DTA methods and magnetic susceptibility and molar conductivity measurements. Coordination numbers of dimeric, L_1Co and L_2Co complexes and monomeric L_3Co complex are found to be six. From the elemental analyses and mass spectra data, the complexes were proposed to the formulas $[Co_2(L_1)(SO_4)_2(H_2O)_4]_2 \cdot 2.5H_2O$, $[Co_2(L_2)(SO_4)_2(H_2O)_4]_2 \cdot 2H_2O$ and $[Co_2(L_3)_2(SO_4)_2(H_2O)_2] \cdot 1.5H_2O$. All complexes were paramagnetic and proposed to be octahedral structure. Molar conductance data revealed that all complexes were non-electrolytes.

Key Words : Bis(2-amino-1,3,4-thiadiazole), bis(2-amino-1,3,4-thiadiazolyl)methane, bis(2-amino-1,3,4-thiadiazolyl)benzene and metal complexes

*Corresponding author

INTRODUCTION

The synthesis of heterocyclic sulphur and nitrogen containing compounds, 1, 3, 4-thiadiazoles are substances of great interest because of their widely use in medicine, agriculture and many technological applications. Some of these involve dyes, lubricants, optically active crystals, photographic materials, epoxy resins, etc. Thiadiazoles have been found to have, among other properties hypotensive and anticonvulsive activities [1].

There is much interest in synthesis and characterization of complexes with heterocyclic ligands with particular attention is focused on bioinorganic studies. It has been shown that the complexes with 1, 3, 4-thiadiazole derivatives are biologically active having fungicidal properties, inhibitory activity against carbonic anhydrase as well as antibacterial activity [2]. Thiadiazole ring is reported to display fungicidal property by virtue of $-N=C-S-$ linkage, which is a possible toxiphore in many pesticides [3]. Transitions metal complexes of 1,3,4-thiadiazoles derivatives are intriguing from both theoretical and practical viewpoints and are the subject of several industrial applications [4].

In our previous study it was discussed the synthesis of new Ni(II), Cu(II), Zn(II) and Cd(II) complexes of L_1 [5]. In the present work, we have synthesized L_1 , L_2 and L_3 by reaction of oxalic acid, malonic acid and terephthalic acid with thiosemicarbazide. Then, its novel new Co(II) complexes were synthesized by reaction of L_1 , L_2 and L_3 with $CoSO_4 \cdot 7H_2O$ salt.

EXPERIMENT

Reagents and Instrumentation

Bis(2-amino-1,3,4-thiadiazole) (L_1), bis(2-amino-1,3,4-thiadiazolyl)methane (L_2) and bis(2-amino-1,3,4-thiadiazolyl)benzene (L_3) were synthesized according to Scheme 1 by the procedure given by method. In the synthesis of ligand has been occurring nucleophilic addition reaction [6,7]. Oxalic acid, malonic acid, terephthalic acid, thiosemicarbazide and $CoSO_4 \cdot 7H_2O$ were obtained from Aldrich, $POCl_3$, DMF and methanol from Merck (pure) and used without further purification.

Elemental analyses (C, H, N, S) were carried out on a Leco CHNS-O model 932 elemental analyzer. 1H -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 $4000-400\text{ cm}^{-1}$. Molar conductivity was measured with a CMD WPA model 750 conductivity meter, using prepared solution of the complex in (THF/DMSO) (1:1) (10^{-3} M). 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 $20\text{ }^\circ\text{C}/\text{min}$. using Shimadzu TA-60WS thermal analyzer. LC/MS-API-ES mass spectra were recorded using AGILENT model 1100 MSD mass spectrometer.

General Synthesis Procedure for (L₁-L₃)

A mixture of acid (L₁-L₃) (0,04 mol) thiosemicarbazide (0.08 mol) and phosphorus oxychloride (0.08 mol) was warmed at 60 °C for 1 h, and temperature was raised to 95 °C for an additional 3 h. Then, the contents were poured onto crushed ice, cooled to 10 °C, pH adjusted to 10-11 with 10 M NaOH. Precipitate in alkaline media was filtered off, and washed with distilled water. The resulting solid washed again with hot absolute alcohol (for L₃ hot DMF), and the product was dried at room temperature [6,7].

(L₁): Yield 1.26 g 25 %, mp 325-326 °C, IR bands (KBr pellets cm⁻¹): 3335, 3276, 3115 and 1511 ν(NH) and δ(NH), 1628 ν(C=N), 1050 ν(=N-N=), 683 δ(C-S-C). ¹H-NMR peaks (DMSO-d₆, δ ppm): 7.67 (-NH₂, 4H, s). ¹³C-NMR peaks (DMSO-d₆, δ ppm): 149 C₂, 169 C₁, and 40.0 DMSO [6,7].

(L₂): Yield 0.54 g 13 %, mp 251-252 °C, IR bands (KBr pellets cm⁻¹): 3369, 3266, 3102 and 1511 ν(NH) and δ(NH), 2927 ν(C-H, aliph.) 1635,1611 ν(C=N), 1058 ν(=N-N=), 655 δ(C-S-C). ¹H-NMR peaks (DMSO-d₆, δ ppm): 7.67 (-NH₂, 4H, s), 4.42 (-CH₂, 2H, s). ¹³C-NMR peaks (DMSO-d₆, δ ppm): 30.90 C₃, 154 C₂, 169 C₁, and 39.91 DMSO [6-8].

(L₃): Yield 1.46 g 22 %, mp 343-344 °C, IR bands (KBr pellets cm⁻¹): 3272 and 1511 ν(NH) and δ(NH), 3085 ν(C-H, ar.), 1627 ν(C=N), 1459 ν(C=C ar.), 1062 ν(=N-N=), 693 δ(C-S-C). ¹H-NMR peaks (DMSO-d₆, δ ppm): 7.52 (-NH₂, 4H, s), 7.83 (C₄H, 4H, s). ¹³C-NMR peaks (DMSO-d₆, δ ppm): 127 C₄, 132 C₃, 156 C₂, 169 C₁, 39.93 DMSO [6,7,9].

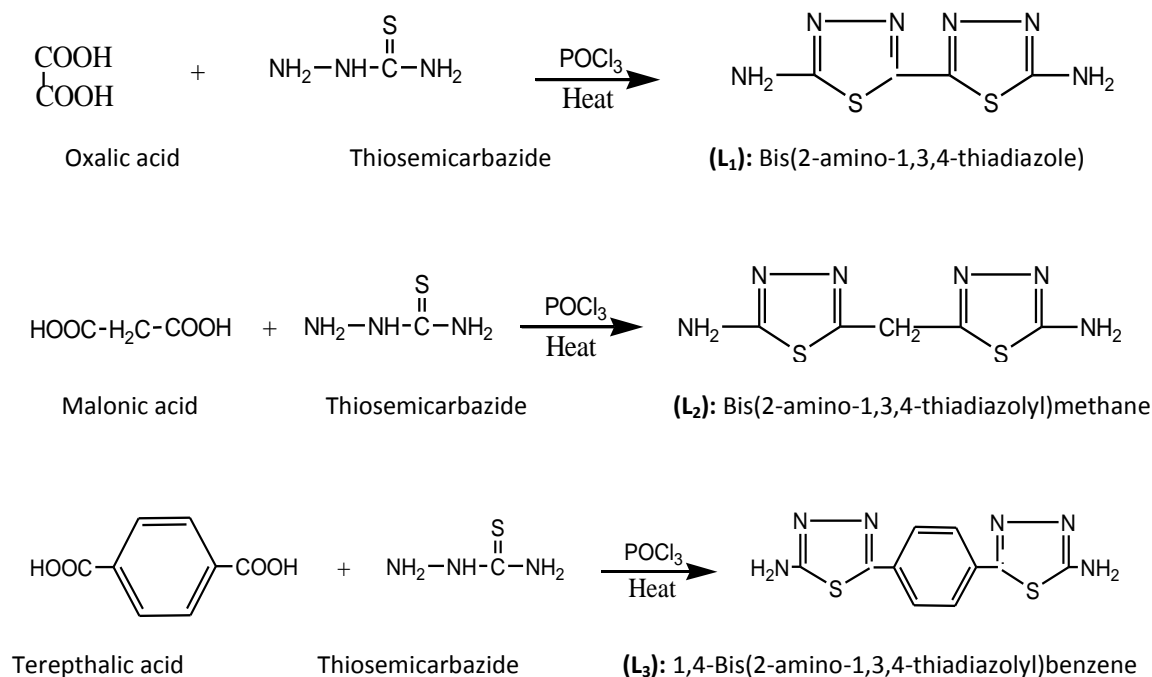
Synthesis of the novel Co(II) complexes of L₁, L₂ and L₃

The ligand (L₁) (0.22 g, 1.12 mmol) was dissolved in 20 mL DMF in a 100 mL round-bottom flask. A solution of 2.24 mmol of metal salt CoSO₄·7H₂O (0.63 g) in 5 mL MeOH and DMF was added dropwise in 15-minute periods with continuous stirring at room temperature. Brick colored mixture was refluxed for 2 h. The reaction mixture was then further stirred for 2 h at room temperature. The resulting precipitates was filtered off and washed with hot DMF and absolute ethanol. The product was dried in drying oven at 80 °C. Decomp. Temp.: > 360 °C. Yield 0.44 g (68 %) [7].

The ligand (L₂) (0.15 g, 0.70 mmol) was dissolved in 20 mL DMF in a 100 mL round-bottom flask. A solution of 1.40 mmol of metal salt CoSO₄·7H₂O (0.40 g) in 5 mL MeOH and DMF was added dropwise in 15-minute periods with continuous stirring at room temperature. Brown mixture was refluxed for 2 h. The reaction mixture was then further stirred for 2 h at room temperature. The resulting precipitates was filtered off and washed with hot DMF and absolute ethanol. The product was dried in drying oven at 80 °C. Decomp. Temp.: > 360 °C. Yield 0.30 g (71 %) [7].

The ligand (L₃) (0.19 g, 0.69 mmol) was dissolved in 20 mL DMF in a 100 mL round-bottom flask. A solution of 0.69 mmol of metal salt CoSO₄·7H₂O (0.20 g) in 5 mL MeOH and DMF was added dropwise in 15-minute periods with continuous stirring at room temperature. Henna green mixture was refluxed for 2 h. The reaction mixture was then further stirred for 2 h

at room temperature. The resulting precipitates was filtered off and washed with hot DMF and absolute ethanol. The product was dried in drying oven at 80 °C. Decomp. Temp.: > 360 °C. Yield 0.21 g (67 %) [7].



Scheme 1. Synthesis scheme for the preparation of the ligands, (L₁, L₂ and L₃).

RESULTS AND DISCUSSION

Bis(2-amino-1,3,4-thiadiazole) (L₁), bis(2-amino-1,3,4-thiadiazolyl)methane (L₂) and bis(2-amino-1,3,4-thiadiazolyl)benzene (L₃) were prepared in one stage process as shown Scheme 1. In this reaction POCl₃ was used as catalyst where the ligand has been occurring nucleophilic addition reaction [6,7,10,11]. The structure of ligands was characterized by elemental analysis, IR, ¹H and ¹³C-NMR data. The results of ¹³C-NMR spectra for all ligands (L₁, L₂ and L₃) have been included firstly by our study to the literature. The novel complexes were characterized by elemental analysis, IR, mass spectra, magnetic susceptibility measurements, thermal analysis,. The corresponding data for the ligands and complexes were presented in Tables 1-5.

Table 1. The colors, formulas, formula weights, yields, molar conductivities, magnetic susceptibility and

Compounds	F.W., g/mol	Color	Yield, %	Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	M_{eff} (B.M.)	Elemental analyses, % found (calc.)			
						C	H	N	S
Ligand, (L ₁) C ₄ H ₄ N ₆ S ₂	200.24	Yellow Brown	25.0	—	—	23.6 (24.0)	2.3 (2.0)	41.6 (42.0)	31.8 (32.0)
[Co ₂ (L ₁)(SO ₄) ₂ (H ₂ O) ₄] ₂ ·2.5H ₂ O	1209.2 0	Brick-Red	68.0	7.5	2.74	8.2 (7.9)	2.2 (2.4)	13.4 (13.8)	21.5 (21.2)
Ligand, (L ₂) C ₅ H ₆ N ₆ S ₂	214.28	Brick-Red	13.0	—	—	27.6 (28.0)	3.0 (2.8)	38.7 (39.0)	29.5 (29.8)
[Co ₂ (L ₂)(SO ₄) ₂ (H ₂ O) ₄] ₂ ·2H ₂ O	1228.2 8	Brown	71.0	6.5	2.46	10.2 (9.8)	2.5 (2.6)	13.3 (13.6)	20.4 (20.8)
Ligand, (L ₃) C ₁₀ H ₈ N ₆ S ₂	276.34	Yellow Green	22.0	—	—	43.1 (43.4)	3.3 (2.9)	29.9 (30.3)	22.7 (23.1)
[Co ₂ (L ₃) ₂ (SO ₄) ₂ (H ₂ O) ₂] ₂ ·1.5H ₂ O	925.54	Henna Green	67.0	6.3	4.28	25.6 (25.9)	2.2 (2.4)	17.8 (18.2)	20.4 (20.7)

Elemental analysis results of the ligands and complexes

The ligands (L₁), (L₂) and (L₃) on interaction with Co(II) salt yields complex corresponding to the suggested formula [Co₂(L₃)₂(SO₄)₂(H₂O)₂]₂·1.5H₂O and for the novel dimeric Co(II) complexes the composition [Co₂(L₁)(SO₄)₂(H₂O)₄]₂·2.5H₂O and [Co₂(L₂)(SO₄)₂(H₂O)₄]₂·2H₂O were found.

Infrared Spectra

In the IR spectrum of (L₁), the characteristic peaks are at 3335-3276, 1513 cm⁻¹ which are assigned to $\nu(\text{NH})$ and $\delta(\text{NH})$ and at 1628, 1050 and 683 cm⁻¹, which are assigned to the $\nu(\text{C}=\text{N})$, $\nu(\text{N}=\text{N}=\text{N})$ and $\delta(\text{C}-\text{S}-\text{C})$ group, respectively [6,7].

In the IR spectrum of (L₂), the characteristic peaks are at 3369-3266, 1511 cm⁻¹ which are assigned to $\nu(\text{NH})$ and $\delta(\text{NH})$ and at 2927, (1635 1611), 1058 and 655 cm⁻¹ which are assigned to the $\nu(\text{C}-\text{H}, \text{aliph.})$, $\nu(\text{C}=\text{N})$, $\nu(\text{N}=\text{N}=\text{N})$ and $\delta(\text{C}-\text{S}-\text{C})$ group, respectively [6-8].

In the IR spectrum of (L₃), the characteristic peaks are at 3272 and 1511 cm⁻¹ which are assigned to $\nu(\text{NH})$ and $\delta(\text{NH})$ and at 3085, 1627, 1459, 1062 and 693 cm⁻¹ which are assigned to the $\nu(\text{C}-\text{H}, \text{ar.})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C}, \text{ar.})$, $\nu(\text{N}=\text{N}=\text{N})$ and $\delta(\text{C}-\text{S}-\text{C})$ group, respectively [6,7,9,10]. Characteristic IR bands are given in the experimental section.

The metal to ligand ratio of the dimeric L₁Co and L₂Co complexes was found to be 1:2 and monomeric Co(II) complex of L₃ 1:1. Co(II) complexes of L₁, L₂ and L₃ have crystal water

molecule and Co(II) complex of L_2 has two additional crystal water molecules. However, Co(II) complexes of L_1 and L_3 have 2.5 and 1.5 moles crystal water molecules, respectively [12]. In Co(II) complex of L_1 , the $\nu(\text{C}=\text{N})$ absorption 1628 cm^{-1} of the metal-free ligand is shifted to the high wave number region and split into two absorptions at 1650 and 1613 cm^{-1} after complexation [13]. Other characteristic IR bands were observed of the ligand at 3369 – 3276 and 1513 cm^{-1} have been assigned to the $\nu(\text{NH})$ and $\delta(\text{NH})$ modes of vibrations, respectively. In the spectra of the complexes, these bands are shifted to the higher wave number region [14,15]. The shift of the N-H and C=N vibration to higher frequencies appear to be due to the coordination of 1,3,4-thiadiazole nitrogen atom and amino nitrogen atom to the metal ion [11,13,14].

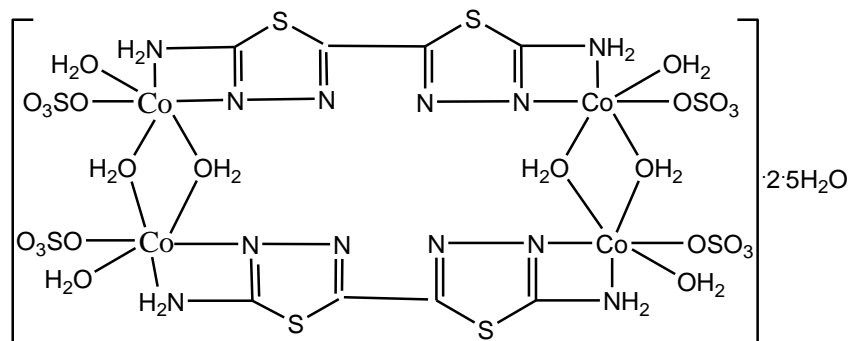


Figure 1. Suggested structure of the octahedral and dimeric Co(II) complex of the ligand, (L_1)

The IR spectra of octahedral sulfate complex of Co(II) were observed broad and strong peaks in the region of 1141 – 1102 cm^{-1} and intense and sharp band of 628 cm^{-1} , which split into three bands. Further, a medium intense peak was observed at 1017 cm^{-1} . These results suggest unidentate nature of sulfate group [15-18]. Thus sulfate group acts as monodentate ligand. In addition to in the lower frequency region, broad and medium intense band was appeared at 872 cm^{-1} for Co(II) complex, suggest to the coordination of H_2O [19,20]. New band was found in the spectra of the complexes in the 547 – 550 cm^{-1} region, which are assigned to $\nu(\text{M}-\text{O})$ stretching vibrations [20,21]

In Co(II) complex of L_2 , the $\nu(\text{C}=\text{N})$ absorption 1635 and 1611 cm^{-1} of the metal-free ligand shifted to the high wave number region and split into two absorptions at 1651 and 1620 cm^{-1} after complexation [13,22]. In the same time, the bands were observed at 3369 – 3269 and 1511 cm^{-1} in the free ligand. These bands were observed at 3395 – 3296 and 1518 cm^{-1} which are assigned to the $\nu(\text{NH})$ and $\delta(\text{NH})$ shifted to the higher wave number region after complexation.[11,14] The shift of the N-H and C=N vibration to higher frequencies appears to be due to the coordination of 1,3,4-thiadiazole nitrogen atom and amino nitrogen atom to the metal ion [14].

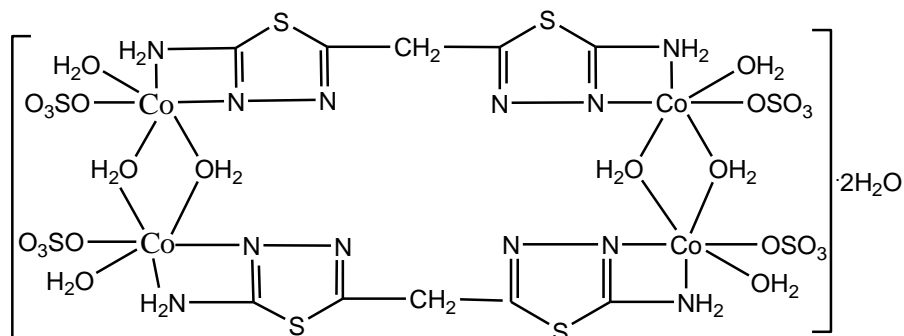


Figure 2. Suggested structure of the octahedral and dimeric Co(II) complex of the ligand, (L_2)

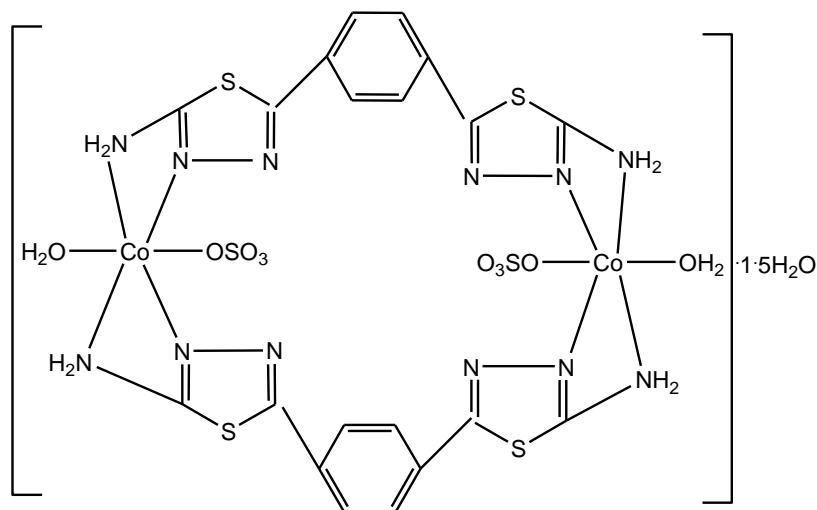


Figure 3. Suggested structure of the octahedral and monomeric Co(II) complex of the ligand, (L_3)

The IR spectra of octahedral sulfate complex of Co(II) were observed broad and strong peaks in the region of $1138\text{--}1100\text{ cm}^{-1}$ and medium intense broad band of 617 cm^{-1} which split into three bands. Further, a weak peak was observed at 979 cm^{-1} . These results suggest unidentate nature of sulfate group which indicated the sulfate group acts as monodentate ligand [16-18]. In addition to in the lower frequency region, medium intense band appeared at 873 cm^{-1} for Co(II) complex suggest to the coordination of H_2O [19,20].

Table 2. Characteristic IR bands (cm^{-1}) of the ligand and complexes as KBr pellets

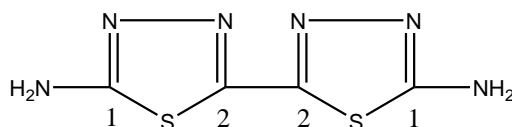
Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{NH}_2)$ and $\delta(\text{NH}_2)$	$\nu(\text{SO}_4)$	$\delta(\text{C-S-C})$	$\nu(\text{C=N})$	Others
Ligand, L_1 $\text{C}_4\text{H}_4\text{N}_6\text{S}_2$		3369, 3276; 1513		683	1628	$\nu(\text{N-N})=1050$
$[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2.5\text{H}_2\text{O}$	872	3390, 3282; 1506	1141-1102, 1017, 628		1650, 1613	$\nu(\text{M-O})$ 547
Ligand, (L_2) $\text{C}_5\text{H}_6\text{N}_6\text{S}_2$		3369, 3269; 1511		655	1635, 1611	$\nu(\text{C-H})_{\text{aliph.}}$ 2927
$[\text{Co}_2(\text{L}_2)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2\text{H}_2\text{O}$	873	3395, 3296; 1518	1138-1100, 979, 617		1651, 1620	$\nu(\text{C-H})_{\text{aliph.}}$ 2927
Ligand, (L_3) $\text{C}_{10}\text{H}_8\text{N}_6\text{S}_2$		3272, 1511		693	1627	$\nu(\text{C-H})_{\text{ar.}}$ 3085, $\nu(\text{C=C})_{\text{ar.}}$ 1459
$[\text{Co}_2(\text{L}_3)_2(\text{SO}_4)_2(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}$	836	3384, 3296, 1516	1130, 1102, 622		1657, 1604	

In Co(II) complex of L_3 , the $\nu(\text{C=N})$ absorption 1627 cm^{-1} of the metal-free ligand is shifted to the high wave number region and split into two absorptions at 1657 and 1604 cm^{-1} after complexation [13,22]. In the same time, the bands were observed at 3272 and 1511 cm^{-1} in the free ligand. These bands were observed at 3384 - 3296 and 1516 cm^{-1} assigned to the $\nu(\text{NH})$ and $\delta(\text{NH})$ shifted to the higher wave number region after complexation [14]. The shift of the N-H and C=N vibration to higher frequencies appears to be due to the coordination of 1,3,4-thiadiazole nitrogen atom and amino nitrogen atom to the metal ion [14].

The IR spectra of octahedral sulfate complex of Co(II) were observed broad and strong peaks in the region of 1130 - 1102 cm^{-1} and medium intense broad band of 622 cm^{-1} which split into three bands that suggest unidentate nature of sulfate group [17,18]. Thus sulfate group acts as monodentate ligand. In addition to in the lower frequency region, weak and broad band was appeared at 836 cm^{-1} supporting to the coordination of Co(II) to the H_2O [13,22].

$^1\text{H-NMR}$ Spectrum

The characteristic ^1H and ^{13}C NMR spectral results were obtained for (L_1) in (DMSO-d_6) , together the assignments, were given in Experimental Section. In the $^1\text{H-NMR}$ spectrum of (L_1) ($-\text{NH}_2$) observed at 7.67 ppm as singlet peak. This peak ($-\text{NH}_2$) was disappeared upon addition of D_2O [5-7]. In an addition, in the $^{13}\text{C-NMR}$ spectrum (DMSO-d_6 , $\delta \text{ ppm}$) of (L_1) , the all of carbon atoms have single resonance 149 C_2 , 169 C_1 , 40.0 DMSO [5,7,23].


Figure 4. The structure of the ligand, (L_1)

The characteristic ^1H and ^{13}C NMR spectral results were obtained for (L_2) in (DMSO-d_6) , together the assignments, are given in Experimental Section. In the $^1\text{H-NMR}$ spectrum of (L_2)

peaks occur at 7.67 ppm (-NH₂) as singlet. This peak (-NH₂) disappeared upon addition of D₂O. Observation of the (-CH₂) peak occurs at 4.42 ppm as singlet [6,7]. In a addition, in the ¹³C-NMR spectrum (DMSO-d₆, δ ppm) of (L₂), the all of carbon atoms have single resonance 30.90 C₃, 154 C₂, 169 C₁, 39.91 DMSO [7,23]. According to the elemental analysis, IR, ¹H and ¹³C-NMR results, the structure of ligand was determined to be as shown in Figure 5.

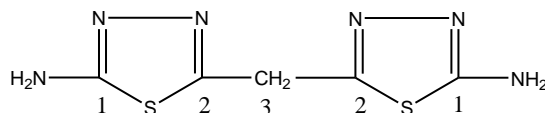


Figure 5. The structure of the ligand, (L₂)

The characteristic ¹H and ¹³C NMR spectral results obtained for (L₃) in (DMSO-d₆), together the assignments, are given in Experimental Section. In the ¹H-NMR spectrum of (L₃) peaks occur at 7.52 ppm (-NH₂) as singlet. This peak (-NH₂) disappeared upon addition of D₂O. Observation of the (C₄H) peak occurs at 7.83 ppm as singlet [6,7]. In a addition, in the ¹³C-NMR spectrum (DMSO-d₆, δ ppm) of (L₃), the all of carbon atoms have single resonance 127 C₄, 132 C₃, 156 C₂, 169 C₁, 39.93 (DMSO) [7,23]. According to the elemental analysis, IR, ¹H and ¹³C-NMR results, the structure of ligand was determined to be as shown in Figure 6.

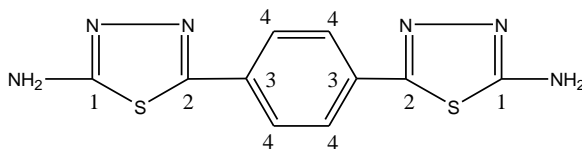


Figure 6. The structure of the ligand, (L₃)

Magnetic and Conductivity studies

Octahedral Co(II) complexes of the ligands (L₁ and L₂) are paramagnetic, and their magnetic susceptibility values are 2.74 and 2.46 B.M, respectively. The observed low magnetic moment values indicate equilibrium between high and low spin states [7,24].

Magnetic susceptibility value for octahedral Co(II) complex of the ligand (L₃) measured 4.28 BM. This observed value is in the range expected for octahedral Co(II) high spin complexes with only a small orbital contribution (the spin only value for three unpaired electrons is 3.89 B.M. [24-26]. Analytical data for the complexes are given in the Tables 1-4. The suggested structure of the complexes is shown in Figure 1-3.

The Co(II) complexes are nonelectrolytes, as shown by their molar conductivity (Λ_M) measurements in (THF/DMSO) (1:1), which are in the range 6.3-7.5 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. For the

reference solution 1×10^{-3} M CaCl_2 was used and measured $236 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Therefore, these complexes haven't been including free SO_4^{2-} ion [7].

Mass Spectra

The mass spectra of the $\text{L}_1\text{Co(II)}$, $\text{L}_2\text{Co(II)}$ and $\text{L}_3\text{Co(II)}$ complexes peaks attributable to the molecular ions m/z : 1208.20 $[\text{M}-\text{H}]^+$, m/z : 1229.29 $[\text{M}+\text{H}]^+$ and m/z : 921.54 $[\text{M}-4\text{H}]^+$ respectively. The peak of the each free ligand was observed m/z : 201.24 $[\text{L}_1+\text{H}]^+$, m/z : 215.28 $[\text{L}_2+\text{H}]^+$ and 277.34 $[\text{L}_3+\text{H}]^+$ in every spectra [27]. Besides, the isotopic distribution for each metal ion and other peaks with related to cationic complexes were given. The mass spectra data of the complexes was shown in Table 3. The values in the table which have high abundance were reported.

Compound Formula weight	Isotopes	MS/EI	Assignment
$[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2.5\text{H}_2\text{O}$ 1209.20	^{58}Co : 230.95* ^{59}Co : 235.60* ^{60}Co : 239.74*	1208.20 912.20 866.20 783.20 581.10 543.10 201.24	$[\text{M}-\text{H}]^+$ $[\text{Co}_4(\text{L}_1)_2(\text{SO}_4)_2(\text{H}_2\text{O})_5-6\text{H}]^+$ $[\text{Co}_4(\text{L}_1)_2(\text{SO}_4)_2(\text{H}_2\text{O})_4+2\text{H}]^+$ $[\text{Co}_4(\text{L}_1)_2(\text{H}_2\text{O})_8+3\text{H}]^+$ $[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_4-\text{H}]^+$ $[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_2-3\text{H}]^+$ $[\text{L}+\text{H}]^+$
$[\text{Co}_2(\text{L}_2)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2\text{H}_2\text{O}$ 1228.28	^{58}Co : 231.30* ^{60}Co : 242.35*	1229.28 910.28 658.42 543.14 215.28	$[\text{M}+\text{H}]^+$ $[\text{Co}_4(\text{L}_2)_2(\text{SO}_4)_2(\text{H}_2\text{O})_3]^+$ $[[\text{Co}_2(\text{L}_2)_2(\text{H}_2\text{O})_6]+4\text{H}]^+$ $[[\text{Co}_2(\text{L}_2)(\text{SO}_4)_2(\text{H}_2\text{O})]+\text{H}]^+$ $[\text{L}+\text{H}]^+$
$[\text{Co}_2(\text{L}_3)_2(\text{SO}_4)_2(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}$ 925.54	^{59}Co : 117.86*	921.54 543.27 447.27 277.34	$[\text{M}-4\text{H}]^+$ $[\text{Co}_2(\text{L}_3)(\text{SO}_4)_2(\text{H}_2\text{O})_2]-2\text{H}]^+$ $[\text{Co}(\text{L}_3)(\text{SO}_4)(\text{H}_2\text{O})]-2\text{H}]^+$ $[\text{L}+\text{H}]^+$

(* This peak is observed value in mass spectra.)

Table 3. Mass spectra data of the complexes

TGA Studies

TGA/DTA studies were carried out from 30 to 800 °C. TGA results of the complexes were shown in Table 4. Decomposition of Co(II) complexes have been explained in two stages. The TGA of L_1 , L_2 and L_3 complexes show weight loss in the first step 2.5, 2.0 and 1.5 moles H_2O , respectively. Weight loss of these complexes at the temperature range between 68.0-100.0 °C was indicated water molecules and not bound to metal as a ligand [27,28] The decomposition of Co(II) complexes in the second stage, weight loss which was correspond to 8 moles of coordinated water for $[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2.5\text{H}_2\text{O}$ and $[\text{Co}_2(\text{L}_2)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2\text{H}_2\text{O}$ occurs at

the temperature range between 100.0-318.0 °C and 100.0-190.0 °C. Total weight loss for two complexes was found 15.39 % (15.63 %) and 14.62 % (14.65 %), respectively.

Furthermore, the weight loss of $[\text{Co}_2(\text{L}_3)_2(\text{SO}_4)_2(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}$ complex which corresponding to 2 moles of coordinated water molecules occurs at the temperature range between 100.0-320.0 °C. Total weight loss for this complex was established 7.17 % (6.81 %) [19,29-31]. In addition to the weight loss, which occurs at the temperature range between 120.0-130.0 °C, it can be explained with H- bond in the complexes. [32]

Compound	I. Step (°C) Leave Group	II. Step (°C) Leave Group	Total Weight Loss %
$[\text{Co}_2(\text{L}_1)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2.5\text{H}_2\text{O}$	84.0-100.0 2.5H ₂ O	100.0-318.0 8H ₂ O (coord.)	15.39, (15.63)
$[\text{Co}_2(\text{L}_2)(\text{SO}_4)_2(\text{H}_2\text{O})_4]_2 \cdot 2\text{H}_2\text{O}$	68.0-100.0 2H ₂ O	100.0-190.0 8H ₂ O (coord.)	14.62, (14.65)
$[\text{Co}_2(\text{L}_3)_2(\text{SO}_4)_2(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}$	81.0-100.0 1.5H ₂ O	100.0-320.0 2H ₂ O (coord.)	7.17, (6.81)

Table 4. TGA data of the complexes

ACKNOWLEDGEMENTS

The support Scientific and Technology Research Laboratory Inonu University and Ankara Test and Analysis Laboratory (TUBITAK-ATAL) is gratefully acknowledged.

REFERENCES

- [1] Coyanis EM, Boese R , Autino JC, Romano RM and Della Vedova CO. J Phys Org Chem 2003; 16: 1-8.
- [2] Olar R, Badea M, Stanica N, Cristurean E and Marinescu D. J Therm Anal Cal 2005; 82: 417-422.
- [3] Nath M, Goyal S, Eng G and Whalen D. Bull Chem Soc Jpn 1996; 69: 605-612.

- [4] Shen XQ, Yang R, Yao H-C, Zhang H-Y, Li G, Zhang H-Q, Chen P-K and Hou H-W. *Coord J Chem* 2006; 59: 2031-2038.
- [5] Adiguzel R, Ergin Z and Sekerci M. *Asian J Chem* 2010; 22(5): 3895-3902.
- [6] Muglu H, Firat University Institute of Science and Technology Ph.D. Thesis, Elazığ, Turkey, 2003.
- [7] Adiguzel R, Gazi University Institute of Science and Technology Ph.D. Thesis, Ankara, Turkey, 2008.
- [8] Temel H, Cakir U, Ugras HI and Sekerci M. *J Coord Chem* 2003; 56(11): 943-951
- [9] Ilhan S, Temel H, Ziyadanogullari R and Sekerci M. *Transition Metal Chemistry* 2007; 32: 584-590.
- [10] Cetin A, Firat University Institute of Science and Technology Ph.D. Thesis, Elazig, Turkey, 2003.
- [11] Koparir M, Cansiz A, Cetin A and Kazaz C, *Chemistry and Natural Compound*, 2004; 41(5): 569-571.
- [12] Turan N, Firat University Institute of Science and Technology Ph.D. Thesis, Elazig Turkey, 2008.
- [13] Franski R and Gierczyk B. *International J Mass Spectroscopy* 2005; 246: 74-79.
- [14] Emara Adel AA, El-Sayed B A and El-Sayed AE. *Spectrochim. Acta Part A*, 2008; 69(3): 757-769.
- [15] Ahsen V, Gokceli F and Bekaroglu O. *J Chem Soc Dalton Trans* 1987; 1827.
- [16] Sekerci M. *Synth React Inorg Met-Org Chem* 2000; 30(1): 117-127.
- [17] Nakamoto K, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; A Wiley Interscience Publication, 1998; 79-88.
- [18] Mishra L and Said MK. *J Indian Chem Soc* 1993; 70: 981-985.
- [19] Refat M, El-Deen S, Ibrahim IM and K. El-Ghool HS. *Spectrochim Acta Part A* 2006; 65:1191-1203.
- [20] Sharaby MC and Mohamed GG. *Spectrochim Acta Part A* 2006; 1-10.
- [21] Chandra S, Lokesh K and Gupta S. *Spectrochim. Acta Part A* 2005; 62: 453-460.
- [22] Maekawa M, Munakata M, Kuroda- Sowa T, Suenega Y and Sugimoto K. *Inorganica Chimica Acta* 1999; 290: 153-158.
- [23] Erdik E, *Spectroscopic Methods at Organic Chemistry*. Ankara University Press: Ankara, Turkey, 1993; 344- 354.
- [24] El-Boraey HA, Donia AM and El-Samalehy MF. *Anal J Appl Pyrolysis* 2005; 73: 204-211.
- [25] Nicholls D, *Complexes and First Row Transition Elements*, 1st ed.: Macmillan, London, 1974; 237.
- [26] Temel H and Sekerci M. *Synth React Inorg Met-Org Chem* 2001; 31(5): 849-857.
- [27] Ilhan S, Temel H, Yilmaz I and Sekerci M. *Polyhedron* 2007; 26: 2795- 2802.
- [28] Kopel P, Travniczek Z, Kvitek L, Cernosek Z, Wrzeszcz G and Marek J. *J Coord Chem* 2003; 56(1): 1-11.
- [29] Sadeek AS. *Journal Mol Structure* 2005; 7531-7542.
- [30] Borra's E, Alzuet G, Borra's J, Server- Carrio J and Alfonso C. *Polyhedron* 2000; 19: 1859-1866.
- [31] Olmez H, Arslan F and Icbudak H. *J Therm Anal Colorimetry* 2004; 76: 793-800.
- [32] Shen XQ, Zhong HJ, Zheng H, Zhang HY and Zhao GH. *Polyhedron*, 2004; 23, 1851- 1857.