Synthesis, Crystal Structures and Properties of [Cu $(L1)_2$(ethylenediamine)] [HL1 = N-(5-ethyl-[1,3,4]–thiadiazole-2-yl)-naphthalenesulfonamide] and [$Cu(L2)_2$(ethylenediamine)] [HL2 = N-(5-thioethyl-[1,3,4]–thiadiazole-2-yl)-benzenesulfonamide]

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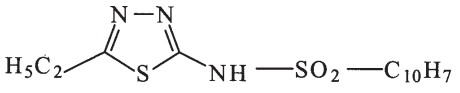
A series of new N-sulfonamide ligands and their cooper (II) complexes, [Cu(N-(5-ethyl- [1,3,4]-thiadiazole-2-yl)-naphthalenesulfonamidate)$_2$(ethylenediamine)] (1) and [Cu(N-(5-thioethyl-[1,3,4]-thiadiazole-2-yl)-benzenesulfonamidate)$_2$(ethylenediamine)] (2) have been synthesized and characterized. The X-ray crystal structures of the complexes (1) and (2) have been determined. In the both two complexes, the Cu(II) ion is four-coordinated, forming a CuN_4 chromophore. The ligands act as monodentate, coordinating the metal ion through a single $N_{thiadiazole}$ atom. The ethylenediamine molecule also participate to the coordination of Cu(II) as bidentate ligand. The both two complexes present a distortion of square-planar stereochemistry. The characterization of the complexes have been studied by FT-IR, electronic and EPR spectroscopic methods.

Keywords: Crystal Structures, Copper (II) complexes, Sulfonamides N-substituted

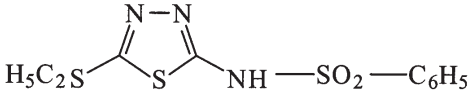
The synthesis of Cu(II) complexes with N-substituted heterocyclic sulfonamides greatly increased in the past twenty years due to the diversity of biological activity of the resulting compounds: antimicrobial, anti-inflammatory, mimetic SOD or nuclease activity. Studies have shown that Cu(II) complexes with different types of ligands can be used as potential "chemical nucleases" [1, 2].

As reported in literature, the ligands commonly used to form complexes with "nuclease activity" are quinolones, sulfonamides and flavonoids. The aromatic rings in the structure of N-substituted sulfonamides can be intercalated between the bases of the DNA chain. This interaction, along with the formation of ROS (due to the presence of Cu(II)), result in the cleavage of the DNA chain [3-5].

In the present paper we report the synthesis and the physico-chemical characterization of two news N-substituted heterocyclic sulfonamides: HL1= N-(5-ethyl-[1,3,4]–thiadiazole–2-yl)-naphthalenesulfonamide and HL2 = N-(5-thioethyl-[1,3,4]–thiadiazole–2-yl)-benzenesulfonamide (fig. 1). Two ternary complexes of these sulfonamido ligands with Cu(II) and ethylendiamine were prepared and their structures determined by X-ray diffraction. Their IR, ESR, electronic spectra and its magnetic susceptibility were determined and discussed, along with the structural and spectral comparisons with those of the analogous complexes.



N-(5-ethyl-[1,3,4]–thiadiazole–2-yl)-naphthalenesulfonamide **(HL1)**



N-(5-thioethyl-[1,3,4]–thiadiazole–2-yl)-benzenesulfonamide **(HL2)**

Fig. 1. Structural formulae of the HL1 and HL2

Experimental part

Materials and physical measurements

Cooper chloride dihydrate, benzenesulfonylchloride, naphthalenesulfonylchloride, 2-amino-5-ethyl-[1,3,4]–thiadiazole, 2-amino-5-thioethyl-[1,3,4]–thiadiazole and ethylenediamine were purchased from commercial sources. All reagents used were of analytical grade.

Elemental analysis (C, N, H, S) were performed on a Perkin-Elmer device, using the combustion technique. IR spectra were recorded with a Perkin–Elmer FT-IR 1730 spectrophotometer using powder samples in KBr disks, in the 4000-400 cm^{-1} range. Fast ion bombardment (FAB) mass spectra were obtained on a VG Autospec spectrometer in m-nitrobenzene as a solvent. Diffuse reflectance spectra (nujol mulls) were carried out on a Shimadzu UV-2101 PC spectrophotometer. Magnetic susceptibilities were measured at room temperature with the Faraday MSB-MKI balance. $Hg[Co(NCS)_4]$ was used as susceptibility standard. Electronic paramagnetic resonance (EPR) spectra were performed at room temperature with a Bruker ELEXSYS spectrometer operating at the X-band frequency.

Table 1
CRYSTAL DATA AND REFINEMENT FOR [Cu $(L1)_2$(ETHYLENEDIAMINE)] **(1)** AND [Cu $(L2)_2$(ETHYLENEDIAMINE)] **(2)**

Complexes	**1**	**2**
Empirical formula	$C_{30}H_{32}CuN_8O_4S_4$	$C_{22}H_{28}CuN_8O_4S_6$
Formula weight	760.42	724.35
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 A
Crystal system, space group	monoclinic, P21/c	Monoclinic, P21/c
Unit cell dimensions	a = 18.5100(5)Å α = 90 (16)°	a = 13.6650(3) Å α = 90°
	b = 11.8940(5) Å β = 116.7680 (14)°	b = 15.2720(4) Å β = 105.7980(8) °
	c = 17.4690(8) Å γ= 90 (17)°	c = 15.4330(4) Å γ= 90°
Volume	3433.8(2) A^3	3099.09(15) A^3
Z	4	4
Calculated density	1.471 Mg/m^3	1.531 Mg/m^3
Absorption coefficient	0.927 mm^{-1}	1.024 mm^{-1}
F(000)	1572	1476
Crystal size	0.24 x 0.24 x 0.1 mm^3	0.15 x 0.15 x 0.15 mm
θ range for data collection	1.23 to 22.76°	1.91 to 27.53 °
Limiting indices	$-16 \le h \le 20, -12 \le k \le 2, -18 \le l \le 5$	$-17 \le h \le 7, -19 \le k \le 8, -20 \le l \le 20$
Reflections collected/unique	13026 / 4596 [R(int) = 0.0482]	12578 / 7059 [R(int) = 0.0400]
Completeness to θ = 22.76	99.4 %	99.0 %
Data/restraints/parameters	4596 / 1 / 424	7059 / 0 / 398
Goodness-of-fit on F^2	1.082	1.040
Final R indices [I>2σ(I)]	R1 = 0.0586, wR2 = 0.1725	R1 = 0.0510, wR2 = 0.1525
R indices (all data)	R1 = 0.1058, wR2 = 0.2217	R1 = 0.1076, wR2 = 0.2209
Largest diff. Peak and hole	0.525 and –0.811 $e^- Å^{-3}$	0.909 and –0.970 $e^- Å^{-3}$

Synthesis of the ligands

N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-naphthalenesulfonamide (**HL1**). A solution containing 1mmol of 2-amino-5-ethyl-[1,3,4]-thiadiazole and 0.9 mmoles of naphthalenesulfonylchloride in 6 mL of pyridine was heated at reflux for 1 h, at 60°C. The mixture was added to 10 mL water at 0°C and stirred for several minutes. The resulting solid was recrystallized from ethanol.

Data for **HL1** (yield 87%).

$C_{14}H_{13}N_3S_2O_2$ (319.4): C 52.77 (calc.52.64); H 3.67 (4.10); N 13.15 (13.16); S 20.08 (20.08)%. IR (KBr) (ν_{max} (cm^{-1})): 1545 (thiadiazole); 1308, 1147 $\nu(SO_2)$; 917 ν(S–N). Solid UV/Vis (λ_{max}) (nm): 314, 325 ($\pi \rightarrow \pi^*$). FAB: m/z 320 [M+H$^+$].

N-(5-thioethyl-[1,3,4]-thiadiazole-2-yl)-benzenesulfonamide (**HL2**). This ligand was obtained following the procedure described above. In this case, 1 mmol of 2-amino-5-thioethyl-[1,3,4]-thiadiazole and 0.9 mmoles of benzenesulfonylchloride were mixed.

Data for **HL2** (yield 72%).

$C_{10}H_{11}N_3S_3O_2$ (301.4): C 39.94 (calc. 39.85); H 3.60 (3.68); N 14.02 (13.95); S 31.97 (31.92) %. IR (KBr) (ν_{max} (cm^{-1})): 1566 (thiadiazole); 1317, 1153 $\nu(SO_2)$; 921 ν(S–N). Solid UV/Vis (λ_{max}) (nm): 313, 342 ($\pi \rightarrow \pi^*$). FAB: m/z 302 [M+H$^+$].

Synthesis of the complexes [Cu(N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-naphthalenesulfonamidate)$_2$(ethylenediamine)] ***1*** *and [Cu(N-(5-thioethyl-[1,3,4]-thiadiazole-2-yl)-benzenesulfonamidate)$_2$(ethylenediamine)]* ***2***

1 mmol of the ligand (HL1 or HL2) is dissolved in 40 mL of methanol. To this solution is added 1 mmol of $CuCl_2 \cdot 2H_2O$ and the mixture is stirred until the cooper salt is completely dissolved, forming a green solution. 0.5 mmol of ethylenediamine are added dropwise. The solution turns to blue, forming a violet precipitate (Cu(II)-ethylenediamine complex). The mixture is stirred at room temperature for three hours. The precipitate is then filtered. The filtrate is kept at room temperature in a crystallizer. After six respectively two weeks by the slow evaporation of the solvent, dark-green crystals (compound 1) and dark-blue crystals (compound 2) suitable for X-ray diffraction were obtained.

Data for complex **1** (yield 68%).

$C_{30}H_{32}CuN_8S_4O_4$ (760.44): C 47.36 (calc. 47.38); H 4.21 (4.24); N 14.73 (14.74); S 16.84 (16.87)%. IR (KBr) (ν_{max} (cm^{-1})): 1495 (thiadiazole); 1297, 1123 $\nu(SO_2)$; 955 ν(S–N). Solid UV/Vis (λ_{max}) (nm): 396 (LMCT), 621 (d-d).

Data for complex **2** (yield 78%).

$C_{22}H_{28}CuN_8S_6O_4$ (724.45): C 36.47 (calc. 36.47); H 3.94 (3.90); N 15.29 (15.47); S 26.39 (26.56)%. IR (KBr) (ν_{max} (cm^{-1})): 1476 (thiadiazole); 1297, 1142 $\nu(SO_2)$; 930 ν(S–N). Solid UV/Vis (λ_{max}) (nm): 407(LMCT), 607 (d-d).

X-ray structure determination

Data collection of [Cu(L1)$_2$(ethylenediamine)] ***(1).*** A dark-green crystal, size 0.1 x 0.24 x 0.26 mm^3, monoclinic, space group P21/c (determined from the systematic absences) was used. Data collection was performed at 293 K on a Nonius Kappa-CCD single crystal diffractometer, using Mo Kα radiation (λ = 0.7173 Å). Crystal-detector distance was fixed at 45 mm, and a total of 293 images were collected using the oscillation method, with scan angle per frame 1.30° oscillation and 45s exposure time per image.

Data collection of [Cu (L2)$_2$(ethylenediamine)] ***(2).*** A dark-blue crystal, size 0.15 x 0.15 x 0.15 mm^3, monoclinic, space group P2/n (determined from the systematic absences) was used. Data collection was performed at 293K on a Nonius Kappa-CCD single crystal diffractometer, using Mo Kα radiation (λ = 0.7173Å). Crystal-detector distance was fixed at 30 mm, and a total of 135 images were collected using the oscillation method, with scan angle per frame 2° oscillation and 30s exposure time per image.

Data collection strategy was calculated with the program Collect [6]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [7].Crystal structure was solved by direct methods, using the program SIR-97 [8]. Anisotropic least-squares refinement was carried out with SHELXL-97 [9]. Geometrical calculations were made with PARST [10, 11]. The crystallographic plots were made with ORTEP [12]. A

Table 2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR COMPOUNDS **(1)** AND **(2)**

1		**2**	
Cu(1)–N(2B)	1.982 (6)	Cu(1)–N(2B)	1.996 (4)
Cu(1)–N(2)	2.008 (5)	Cu(1)–N(2)	1.992 (4)
Cu(1)–N(1)	2.031 (5)	Cu(1)–N(1)	2.022 (4)
Cu(1)–N(1A)	2.054 (5)	Cu(1)–N(1A)	2.050 (4)
N(2B)–Cu(1)–N(2)	173.9 (2)	N(2B)–Cu(1)–N(2)	176.43 (16)
N(2B)–Cu(1)–N(1)	95.6 (2)	N(2B)–Cu(1)–N(1)	95.63 (16)
N(2)–Cu(1)–N(1)	83.1 (2)	N(2)–Cu(1)–N(1)	83.53 (17)
N(2B)–Cu(1)–N(1A)	92.2 (2)	N(2B)–Cu(1)–N(1A)	92.14 (15)
N(2)–Cu(1)–N(1A)	86.1 (2)	N(2)–Cu(1)–N(1A)	87.21 (16)
N(1)–Cu(1)–N(1A)	149.2 (2)	N(1)–Cu(1)–N(1A)	154.55 (17)

summary of the crystal data, experimental details and refinement results is listed in table1.

Results and discussion

*Crystal structure of [Cu (L1)$_2$(ethylenediamine)] (**1**) and [Cu (L2)$_2$(ethylenediamine)] (**2**)*

Relevant bond distances and angles for the complexes **1** and **2** are collected in table 2.

Figures 2 and 3 show molecular structures with the atom numbering scheme of the complexes **1** and **2** respectively.

In the both complexes the Cu(II) ion is four-coordinated. The cromophore type for these complexes is CuN_4. The both two complexes present a square-planar geometry. The Cu(II) ion is surrounded by two nitrogen atoms $N_{ethylynediamine}$ of the ethylenediamine molecule which is a bidentate ligand, [Cu(1)-N(2)= 2.008(5)Å and Cu(1)-N(1)= 2.031(5) Å] for complex **1** and [Cu(1)-N(2)= 1.992(4)Å and Cu(1)-N(1)= 2.022(4) Å] for complex **2**, and by other two nitrogen atoms $N_{thiadiazole}$ of the thiadiazole moiety, corresponding to two molecules of the ligand, [Cu(1)-N(2B)= 1.982(6)Å and Cu(1)-N(1A)= 2.054(5)Å] for complex **1** and [Cu(1)-N(2B)= 1.996(4)Å and Cu(1)-N(1a)= 2.050(4)Å] for complex **2**. The sulfonamide

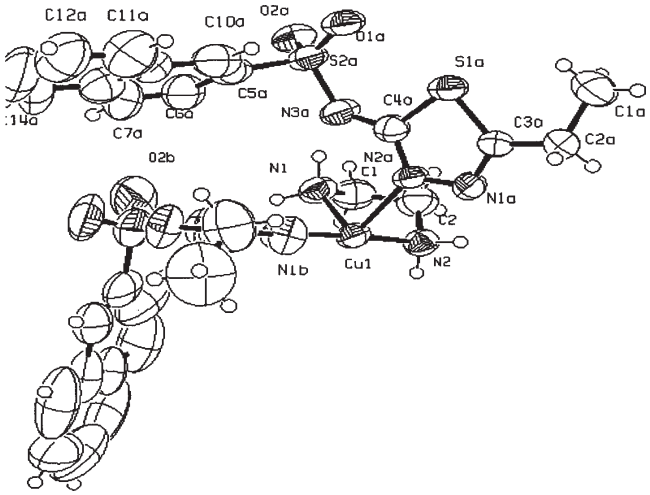


Fig. 2. ORTEP drawing of the [Cu(L1)$_2$(ethylenediamine)] (**1**) complex

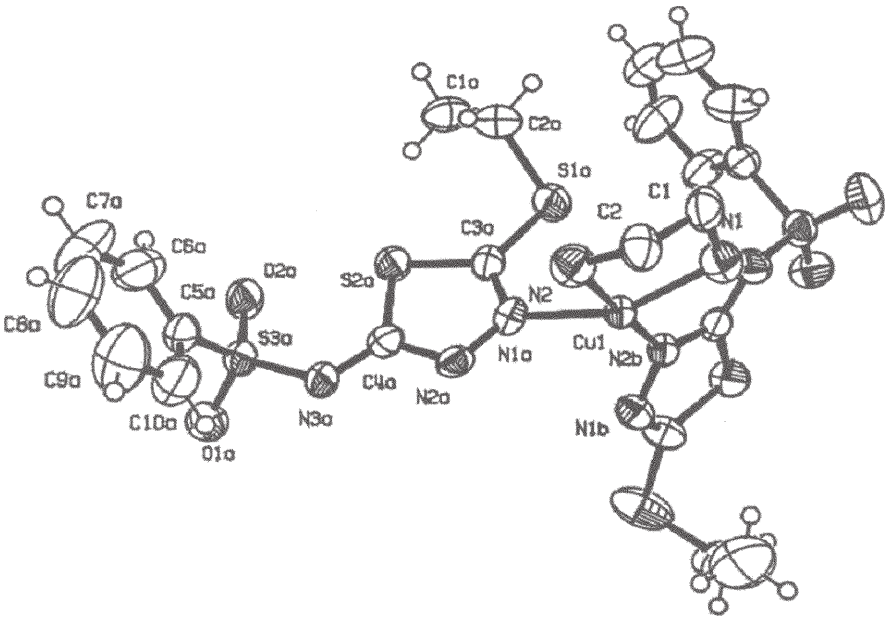


Fig. 3. ORTEP drawing of the [Cu(L2)$_2$(ethylenediamine)] (**2**) complex

ligands (HL1 and HL2) coordinate the Cu(II) ion upon the deprotonation of the –NH-SO2- moiety. The N-Cu-N angles that describe the polyhedron of coordination range from 83.1(2)° to 95.6(2)° for complex **1** and 85.53(17)° to 95.63(16)° for complex **2**. The diagonal angles N(1) – Cu(1) – N(1A) and N(2B) – Cu(1) – N(2) are 149.2(2)° and 173.90(2)° in complex **1,** respectively 154.55(17)° and 176.43(16)° in complex **2**. The distances between the Cu(II) ion and the the four nitrogen atoms and the angles that describe the polyhedron of coordination are similar to those reported in literature for CuN_4 cromophores [13-15]. The distorsion of the square-planar geometry (commonly known as tetrahedrality) can be determined by the dihedral angle between the two planes described by the atoms N2-Cu1-N1 and N1a-Cu1-N2b respectively. In the case of complex **1** and **2** the dihedral angle values of 48.3° and 39.0° indicates a highly distorted square-planar geometry around copper(II).This distortion could be explained on the basis of the participation in the coordination of the metallic ion of ethylenediamine as a bidentate ligand *(N, N* –donor), situated in the same plane together with other two rather bulky ligand molecules [16].

The complex **1** is stabilized through moderate and weak hydrogen bonds between the $N_{ethylenediamine}$ and the $N_{sulfonamidato}$ [N(1)-N(3B) 2.866Å; N(1)-H(1A)-N(3B) 134.34° and N(1)-N(3A) 2.953 Å; N(1)-H(1B)-N(3A) 139.11°] and between the $N_{ethylenediamine}$ and the $N_{thiadiazol}$ [N(1)-N(2B) 2.973Å; N(1)-H(1A)-N(2B) 82.88° and N(2)-N(2A) 3.083 Å; N(2)-H(2A)-N(2A) 90.90°]. The complex **2** is stabilized through moderate and weak hydrogen bonds between the $N_{ethylenediamine}$ and the $N_{sulfonamidato}$ [N(1)-N(3B) 2.872Å; N(1)-H(1B)-N(3B) 130.92°] and between the $N_{ethylenediamine}$ and the $N_{thiadiazol}$ [N(1)-N(2B) 2.978 Å; N(1)-H(1B)-N(2B) 82.32°].

Spectroscopic and magnetic properties

The IR spectra of both complexes present a similar pattern. The most remarkable difference occurs in the band corresponding to the stretching vibration of the thiadiazole ring, which is shifted from 1545 cm^{-1} (HL1) and 1566 cm^{-1} (HL2) in the free ligands to 1495 cm^{-1} (complex **1**) and 1476 cm^{-1} (complex **2**) in the complexes. The characteristic band corresponding to the ν(S-N) appears at 955 cm^{-1} (1) and 930 cm^{-1} (**2**) shifted to higher frequencies with respect to those of the uncoordinated ligands. These modifications in the thiadiazole heterocycle and in the sulfonamide group are attributed to the involvement to the $N_{thiadiazole}$ atom in coodination of Cu(II) and to the deprotonation of the sulfonamido moiety [17, 18]. This deprotonation will also lead to an electron delocalization involving the atoms of the sulfonamide moiety and the atoms from the thiadiazole ring [19].There are also modifications of the values of the symmetrical and asymmetrical valence vibrations [$\nu_s(SO_2)$ and $\nu_{as}(SO_2)$] for the S=O bond of the sulfonamide moiety, as they too shift to lower frequencies in the complex's IR spectrum (1123 and 1297 cm^{-1} (complex **1**) respectively 1142 and 1297 cm^{-1} (complex **2**)). The IR spectrum of the complexes shows an overlap of some other bands on the bands corresponding to the ligands, which makes them difficult to interpret. Thus, the characteristic bands of the -NH_2 group of ethylenediamine (2900 cm^{-1}, 1600 cm^{-1} and 1460 cm^{-1}) cannot be distinguished from the sulfonamide ligand bands [20, 21].

The solid electronic spectra of the both complexes display a band near 400 nm (396 nm for complex **1** and 407 nm for complex **2**) assigned to a LMCT transition. The complex **1** exhibits a d-d band at 621 nm and the complex **2** show a d-d band at 607 nm. The presence of ethylenediamine in the complexes leads to a stronger separation between the e_g-t_{2g} orbitals of the Cu(II) ion, leading to a shift towards lower wavelenghts for the electron transitions of the metallic ion [22]. This pattern, characteristic for distorted square-planar cooper (II) complexes, agrees well with the crystallographic data [23].

The polycrystalline X-band EPR spectra of the both complexes are axial. The EPR parameters, obtained by simulation [24] are $g_{||}$ = 2.135, $g\perp$ = 2.075 and $A_{||}$ = 190 x 10^{-4} cm^{-1} for complex **1** (fig. 4) and $g_{||}$ = 2.14, $g\perp$ = 2.09 and $A_{||}$ = 200 x 10^{-4} cm^{-1} for complex **2.** According to the Bertini's classification, the values of $A_{||}$ for complex **1** and **2** can be correlated with the structure of the complex [25]. Thus, values between 160 and 200 x 10^{-4} cm^{-1} correspond to a square-planar geometry. As $g|| > g\perp$ in the complexes, the unpaired electron must be in the $d_{x^2-y^2}$ (or d_{xy}) orbital [26].

The room temperature magnetic moments of complex **1** (μ_{eff} = 1.72 MB) and for complex **2** (μ_{eff} = 1.77 MB) are consistent with the presence of a single unpaired electron.

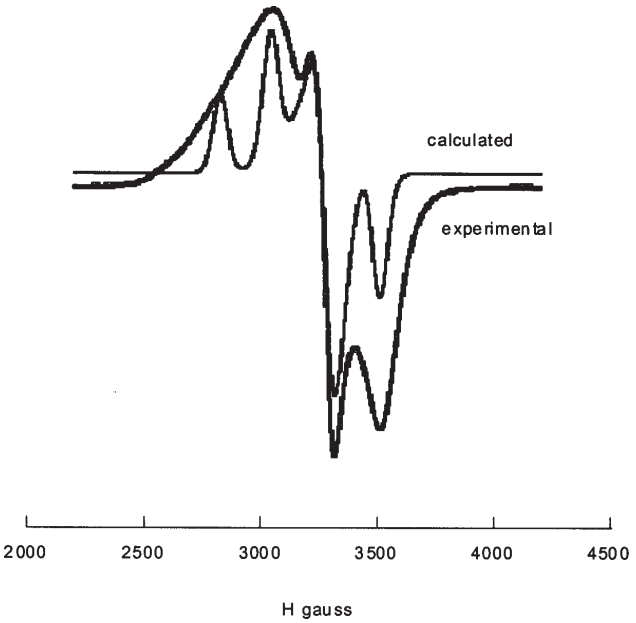


Fig. 4. X Band EPR of the compound **1**

Conclusions

Two new sulfonamide ligands were synthezised: N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-naphthalenesulfonamide (HL1) and N-(5-thioethyl-[1,3,4]-thiadiazol-2-il)-benzenesulfonamide (HL2); they were used as ligands for the synthesis of two cooper complexes: [$Cu(L1)_2$ (ethylenediamine)] and [$Cu(L2)_2$ (ethylenediamine)]. The crystalline structures for the complexes were attributed using X-ray diffraction and were confirmed by the data obtained from elemental analysis, spectral (IR, UV-Vis, EPR) and magnetic determinations.

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Manuscript received: 14.01.2009