STUDIA UNIVERSITATIS BABEȘ-BOLYAI, CHEMIA, XLVII, 1-2, 2002

Dedicated to Professor Ionel Haiduc
on the occasion of his 65th birthday

SYNTHESIS AND STRUCTURAL STUDIES OF SOME METAL COORDINATION COMPOUNDS WITH [1,2,4]-TRIAZOLE DERIVATIVE AS LIGAND

L. OPREAN[1], L.DAVID[2], V. ZAHARIA[1], A.COMSA[1], R. OPREAN[1]

[1] *Faculty of Pharmacy, „Iuliu Hațieganu" University of Medicine and Pharmacy, Emil Isac 13, 3400 Cluj-Napoca, Romania*
[2] *Faculty of Physics, „Babeș-Bolyai" University, Kogălniceanu 1, 3400 Cluj-Napoca, Romania*

ABSTRACT. In this paper we report the synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II) complexes with ethyl-α-[(3-phenyl-[1,2,4]-triazol-5-yl)-thio]-acetoacetate as ligand (L). We have initiated studies of the behavior as ligand of named triazole derivative in methanol and dimethylformamide solutions in different metal-ligand molar ratio. Characterization of all complexes was accomplished by elemental analysis, IR, UV-Vis, ESR spectral studies and magnetic measurements. Correlations of the results obtained from physico-chemical investigations afford the assignment of the most probable structural formulae for the metal complexes. The new complexes are of the type $[ML_2(CH_3COO)_2]$, where M = Co(II), Ni(II) or $[CuL(CH_3COO)_2]$ and $[ZnLNH_3]$. The triazole derivative act as bidentate or tridentate ligand, the Co(II) and Ni(II) complexes have a octahedral geometry and the Cu(II) and Zn(II) complexes have a distorted tetrahedral local symmetry around the metals ions.

1. INTRODUCTION

The chemistry of [1,2,4]-triazole derivatives has been intensively investigated owing to their coordinating capability [1,2], their antibacterial and antifungal properties [3,4], anti-inflammatory activity [5] or others pharmacological activity [6,7]. They easily form chelate compounds with transition metals which also have stronger biological activities, so the coordination chemistry of [1,2,4]-triazole derivatives has been the subject of extensive studies. Taking into consideration these aspects, in this paper we report the synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II) complexes with ethyl-α-[(3-phenyl-[1,2,4]-triazole-5-yl)-thio]-acetoacetate as ligand (L).

2. EXPERIMENTAL

2.1. Materials and measurements

The ligand was prepared as described in the literature [8]. Metals acetates, zinc chloride and solvents were of chemical reagent grade or analytical grade.

The elemental chemical analysis of the complexes was performed by the classical method. The Ni(II) and Cu(II) ions are determined gravimetrically as $Cu(py)_2(SCN)_2$ and $Ni(dmg)_2$, where py = pyridine and dmg = dimethylglioxime.

The IR spectra were recorded with a FTIR Echinox 55 spectrophotometer in the 4000-400 cm^{-1} range, in KBr pellets.

The electronic absorption spectra in the UV-Vis region (190-900 nm) were recorded with a Perkin Elmer Lambda 15 instrument, in a homogenous suspension of nujol, on a filter paper support.

The polycrystalline powder ESR spectra of Cu(II) complex were obtained at room temperature in the X band (9,4 GHz) using a standard JEOL-JES-3B equipment.

Magnetic susceptibility measurements of Co(II), Ni(II) and Cu(II) complexes were recorded using a horizontal Weiss balance. The values of magnetic moments were determined from the plot of $1/\chi_M$ versus T values (70 – 300K).

2.2. PREPARATION OF COMPLEXES

Synthesis of $[CoL_2(CH_3COO)_2]$ *(C₁)*

10 ml methanolic solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) was added to 100 ml methanolic solution of the ligand (0.610 g, 2 mmoles) with continuous stirring at 60℃. After one hour, a pink precipitate was formed. The solid was isolated by filtration, washed with methanol and ethylic ether and dried until constant weight (0.462 g complex, η = 46%). (Found: C 49.27%; H 4.2%; N 9.87%; S 8.21; $C_{32}H_{36}N_6O_{10}S_2$ Co requires: C 48.79%; H 4.5%; N 10.67%; S 8.13%; Co 7.49%)

Synthesis of $[NiL_2(CH_3COO)_2]$ *(C_2)*

5 ml methanolic solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) was added to 100 ml methanolic solution of the ligand (0.610 g, 2 mmoles) with continuous stirring at 60℃. After 40 minutes, a yellow greenish precipitate was formed. The solid was isolated by filtration, washed with methanol and ethylic ether and dried until constant weight (0.401 g complex, η = 51%). (Found: C 48.56%; H 4.1%; N 10.3%; S 8.45%; Ni 8.21% $C_{32}H_{36}N_6O_{10}S_2$ Ni requires: C 48.79%; H 4.5%; N 10.67%; S 8.13%; Ni 7.49%)

Synthesis of $[CuL(CH_3COO)_2]$ *(C_3)*

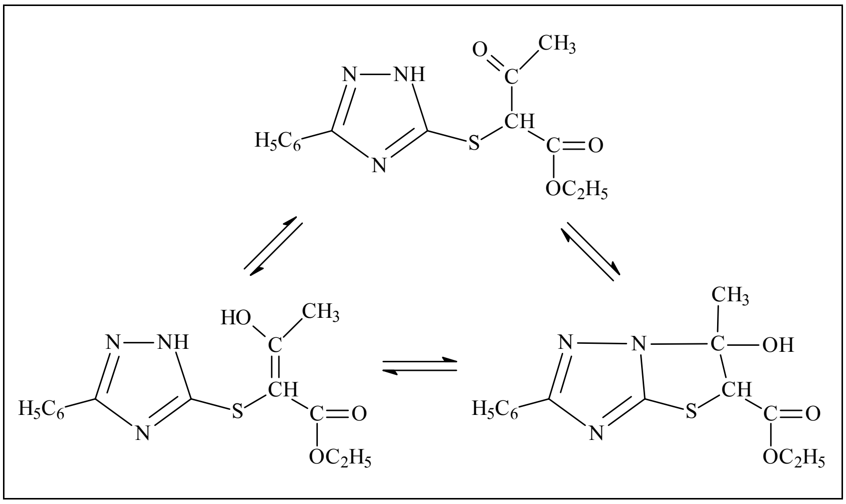
50 ml ethanolic (EtOH) solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.200 g, 1 mmol) was added to the solution of 0.305 g of the ligand (1 mmol) in 50 ml methanol with continuous stirring at 60 °C. After 30 minutes, a dark greenish precipitate was formed. The solid was isolated by filtration, washed with methanol and ethylic ether and dried until constant weight (0.379 g complex, η = 78 %) (Found: C 43.92%; H 4.2%; N 9.28%; S 7.21%; Cu 7.13%; $C_{18}H_{21}N_3OSCu$ requires: C 44.35%; H 4.3%; N 8.6%; S 6.5%; Cu 6.5%)

Synthesis of [ZnLNH$_3$](C$_4$)

0.138 g $ZnCl_2$ (1 mmol) was added with continuous stirring to the solution of 0.305 g of the ligand (1 mmol) in 60 ml methanol at 60℃. Then, 2 ml of concentrated ammonia was added. After two hours of stirring, solution was refluxed for 6 hours. The complex, white solid precipitated, was isolated by filtration, washed with methanol and ethylic ether and dried until constant weight (0.162 g complex, η = 42 %). **(**Found: C 46.81%; H 4.65%; N 14.83%; S 8.64; $C_{15}H_{17}N_4O_3SZn$ requires: C 46.63%; H 4.4%; N 14.5%; S 8.29%; Zn 16.8%).

3. RESULTS AND DISCUSSION

The present ligand L has the capacity of chelation (due to the existence of O, N, S donor atoms in the molecule) in relation to the nature of the metal ion and the anion and to the synthesis conditions (metal - ligand molar ratio, solvent, temperature, pH). In methanol and ethanol solutions the ligand presents a keto-enolic tautomerism peculiar to the structure of the acetoacetic ester, as well a ring-chain tautomerism [9]:



The elemental chemical analyses show that the complexes are of the type [$ML_2(CH_3COO)_2$], where M = Co(II) and Ni(II), or [$CuL(CH_3COO)_2$] and [$ZnLNH_3$]. The compounds are microcrystalline powders, sparingly soluble in methanol and ethanol, soluble in warm acetone, dimethyformamide and dimethylsulfoxide. They are air and light stable. The melting point of C_4 is 183 ^oC and the aspect of C_3 shows modifications above 178 ^oC. C_1 and C_2 complexes decompose above 300 ^oC.

3.1. IR Spectra

Information about the coordination mode of the ligands to the metals(II) ions was obtained by comparing the IR spectra of the metallic complexes with the IR spectra of the uncoordinated ligand L (Table 1) and those of the other similar metal complexes [2,4,9-11]. The involvement of the C=O esteric and cetonic group in coordination to the metallic ions is indicated by the shifts (to a lower frequency region, 1700 cm^{-1}, respectively in the 1640-1600 cm^{-1} region) and the shoulder form of the ν(CO) bands in the IR spectra of complexes compared to the ligand. The heterocyclic "C=N" moiety is not involved in the coordination of the metallic ions. This is sustained by the unchanged ν(C=N) triazole vibrations in the IR spectra of Co(II), Ni(II) and Cu(II) complexes compared to the IR spectra of the ligand.

The triazole ring coordinate the Zn(II) ion in C_4 complex through its ^{1}N nitrogen atom after deprotonation, which arises in the lowering of the ν(CN) endocyclic frequency and the increasing of the ν(NN) heterocyclic frequency. The news bands at 3440 cm^{-1} and 1100cm^{-1} in the IR spectra of Zn(II) C_4 complex corresponds to ν(NH) vibrations of the ammonia molecule and, respectively to ν(CO) enol form. These data suggests the enolization of the ligand and the reaction of the enol in deprotonated form [11]. The changes in the IR spectra of Zn(II) complex indicate that the ligand undergoes carbonyl enolization and then coordinate to metal ion through the enolic oxygen atom, triazole ^{1}N nitrogen atom and the ester oxygen atom.

The free acetate ion has characteristic bands at 1580 cm^{-1} (ν_{as}) and 1425 cm^{-1} (ν_s). The coordination of the acetate to the metallic ion is indicated by the complexes new IR bands (1430 - 1495 cm^{-1}).

Table 1

Some IR bands (cm^{-1}) of the ligand and their C_1 – C_4 complexes

Band	**L**	**C_1**	**C_2**	**C_3**	**C_4**
ν(NH) ammonia	-	-	-	-	3440 m
ν(CO) esteric	1730 s	1700 b	1700 b	1710 b	1700 b
ν(CO) cetonic	1630 s	1640 b	1640 b	1600 b	1620 b
ν(C=N) triazole	1580 w	1580 w	1580 m	1590 w	1560 w
ν(=NH) triazole	1520 w	1520 w	1520 m	1530 w	1500 w
ν(acetate)	-	1430 m 1490 m	1430 m 1490 m	1445 m 1495 m	-
ν(N-N) triazole	960 m	960 m	960 m	960 w	980 w

w – weak, m – medium, s – strong, b – broad

3.2. Electronic spectra

Information about geometry of complexes was obtained from electronic spectra [12, 13]. The assignment of the bands of the electronic spectra of C_1 – C_3 complexes are set out in Table 2.

Table 2

Electronic spectral data for C_1 – C_3 complexes in nujol suspension (RD)

Complex	ν_{max} [cm^{-1}]	
C_1	ν_1 = 9740	ν_3 = 17880
C_2	ν_1 = 9170	ν_2 = 16950
C_3	ν = 16100	

The reflectance spectrum of Co(II) complex, C_1 shows two bands at 9740 cm^{-1} and 17880 cm^{-1} and a shoulder at about 19260 cm^{-1}. These may arise from $^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1) and $^4T_{2g} \leftarrow {}^4T_{2g}$ (ν_2) transitions and suggest an octahedral environment around the Co(II) ion.

The RD spectra of Ni(II) complex, C_2, shows two bands at 9170 cm^{-1} and 16950 cm^{-1} assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1) and $^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2) transitions of the Ni(II) ion an octahedral stereochemistry. The band corresponding to $^3T_{1g} \leftarrow {}^3A_{2g}$ transition (ν_3 = 19000 – 27000 cm^{-1}) is overlapped with the more intense charge transfer and ligand – to - ligand transitions.

The spectrum of the copper complex displays a broad d – d band at 16100 cm^{-1}. The intense band at 25340 cm^{-1} is assigned to a charge transfer. This data suggest that C_3 has a distorted tetrahedral geometry around the central Cu(II) ion .

3.3. ESR Spectra and magnetic susceptibility measurements

Powder ESR spectrum of the C_3 complex, obtained in the X band at room temperature, contains a broad signal at g = 2.124. The obtained spectra (Fig. 1) are in agreement with a distorted tetrahedral symmetry and a CuO_4 chromophore [12]. For obtaining more information on this system and about the possible interactions between the copper (II) ions, the complex was studies by means of magnetic measurements. The magnetic susceptibility data have been determined for the Co(II) and Ni(II) complexes, the Zn(II) complex are diamagnetic, due to the 3d^{10} electronic configuration of Zn(II).

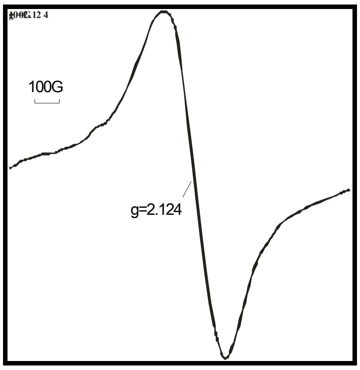


Fig.1 *ESR spectra of theCu(II) C_3 complex*

The magnetic moment of μ_{eff} = 1.94 BM for C_3 indicates the presence of monomeric species and the lack of any interactions between the Cu(II) ions from neighboring molecules (Fig.2) [13].

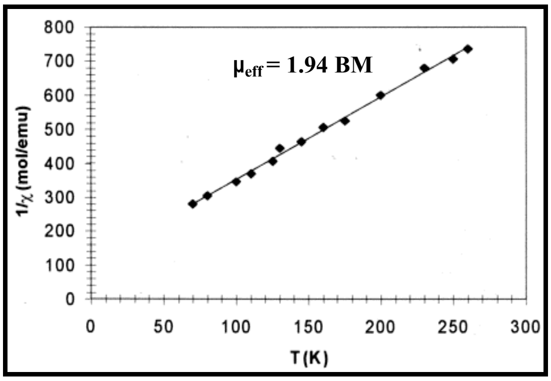
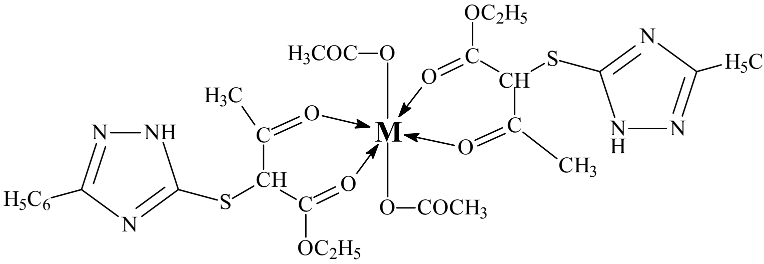


Fig.2 *Temperature dependence of the inverse of the magnetic susceptibility for the C_3 Cu(II) complex*

The magnetic moments obtained for C_1 (μ_{eff} = 4.81 BM) and C_2 (μ_{eff} = 3.20 BM) indicate a octahedral coordination around the Ni(II) ion and, respectively, Co(II) ion [14].

4. CONCLUSION

A correlation of the results obtained from chemical analysis and spectral data afford the assignment of the most probable structural formulae. The ligand L act as tridentate ligand in the Zn(II) complexes, that seams to have a tetrahedral geometry. In the Co(II), Ni(II) and Cu(II) complexes the ligand act as bidentate, with a octahedral geometry around Co(II) and Ni(II) ions and a distorted tetrahedral geometry around the Cu(II) ion. The proposed structures of the complexes are presented in Fig. 4.



C_1: M = Co(II)
C_2: M = Ni(II)

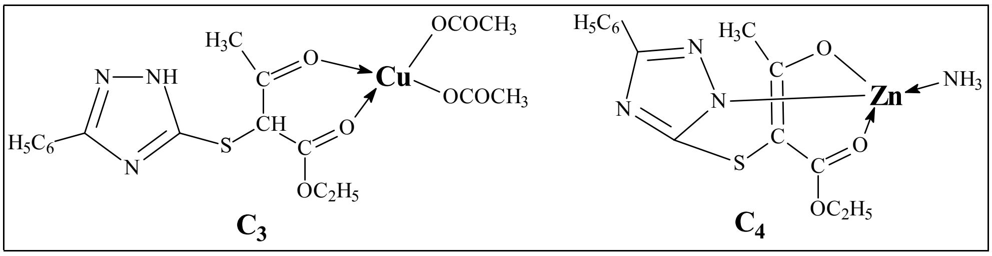


Fig.4 *Proposed structures of the complexes C_1 – C_4*

REFERENCES

1. A.K. Sen, S.N. Dubey and P.J. Squattrito, *Acta Cryst.*, 52, 865 – 868, **1996.**
2. J. G. Haasnoo, *Coord. Chem. Rev.*, **200,** 131 – 185, **2000.**
3. E.Ilhan, N. Ergenc, M. Uzun, D. Kaya, *Arch. Pharm. (Weinheim),* **327,** 825-826, **1994.**
4. A.S. Orabi, M.A. Moneim, E. El–Din Salem and Abd El Fattah *Polish. J. Chem.,* **74,** 1675 – 1683, **1994.**
5. I.H. Hall, R. Simlot, R.A. Izydore, *Arch. Pharm. (Weinheim),***328**, 5 - 10, **1995.**
6. V. Darias, S. Abdala, D. Martin-Herrera, M. Luisa-Tello, S.Vega, *Pharm.,* **53**, 7, 477-481, **1998.**
7. A. Mureşan, M. Palage, *Chimie terapeutică – medicamente utilizate în afecțiuni cardiovasculare,* Ed. Accent, Cluj-Napoca, **2000.**
8. I. Simiti, V. Zaharia, M. Coman, H. Demian, *Arch. Pharm. (Weinheim),* **324,** 49-51, **1991.**
9. I. Simiti, V. Zaharia, H. Demian, and S. Mager, *Studia Univ. Babeş-Bolyai*, XXXIV, **1**, 53-59, **1989.**
10. Nakamoto, *Infrared and Raman Spectra of Inorganic Coordination Compounds*, 3rd, Ed. Wiley, New York **1978.**
11. S. Jayasree and K. K. Aravindakshan, *Polyhedron,* **12**, 1187-1192, **1993.**
12. B.J. Hathaway, in "*Comprehensive Coordination Chemistry*", G. Wilkinson, R. Gillard, J. McCleverty Eds., Pergamon Press, Oxford, **1987.**
13. A.B.P. Lever, in "*Inorganic Electronic Spectroscopy*", Elsevier, New York, **1984.**
14. Drago, S. Russell, *Physical Methods in Chemistry*, W.B. Saunders Company, **1977.**