

Synthesis, Characterization and Thermal Properties of 2-Methoxy-6-[(thiazol-2-ylimino) Methyl] Phenol and Its Complexes With Co(II), Ni(II) And Cu(II)

Reyhan MURAT¹ and Sinan SAYDAM^{1*}

¹Firat University, Faculty of Science, Department of Chemistry, 23200 ELAZIĞ / TÜRKİYE

*Corresponding author: ssaydam@firat.edu.tr

Abstract

2-Methoxy-6-[(thiazole-2-yl-imino) methyl] phenol (LH), has been synthesized from 2-hydroxy-3-methoxy benzaldehyde and 2-aminothiazole in benzene. Metal complexes of the ligand (LH) were prepared from acetate salts of Co(II), Cu(II), Ni(II) and chloride in dry acetone. Characterization of the ligand and its complexes were made by microanalyses, FT-IR, ¹³C, ¹H NMR, and UV-Visible spectroscopy, magnetic susceptibility, thermogravimetric analysis. The structure of the complexes were suggested in the light of these results that two ligands coordinates to each metal atom by phenolic oxygen, imino nitrogen and two water molecule to form high spin octahedral complexes with Co(II), Ni(II) and Cu(II).

Keywords: 2-Methoxy-6-[(thiazole-2-yl-imino) methyl] phenol, 2-aminothiazole, 2-hydroxy-3-methoxy benzaldehyde, thiazole, Co(II), Ni(II), Cu(II), complex.

1. Introduction

It is well known that metal ions involve in biological processes of life and has been subject to interest. The modes of action of these metal ions are often complex but are believed to involve bonding to the hetero atoms of the heterocyclic residues of biological molecules, i.e, proteins, enzymes, nucleic acids, etc [1].

Schiff bases and their metal complexes, played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical [2] and biochemically relevant studies of metal complexes [3,4] and found wide range of applications. Thiazoles represent a very interesting class of compounds because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects, e.g. as antibacterial [5,6], fungicide [7,8], anti-inflammatory [9,10] antihelmintics, antitubercular [11], anti-HIV [12], Antidegenerative [13] and hypothermic [14] activities, herbicides [15]. In recent years thiazole based chemisensors have been investigated and showed to be successfully applicable in biological systems [16,17].

It is known that 2-aminothiazole is a biologically active compound with a broad range of activity and also it is an intermediate in the synthesis of antibiotics and dyes. Numerous thiazole derivative Schiff bases and their transition metal complexes have been investigated by various techniques [18,19,20].

From these points of view, it is interesting to study different types of transition metal complexes of these biologically active ligands. In this paper, the synthesis and characterization of the first row transition metal complexes of the type [ML₂] where M is Co(II), Ni(II) and Cu(II) metals, L is a deprotonated ligand (2-Methoxy-6-[(thiazole-2-yl-imino) methyl] phenol) have been studied.

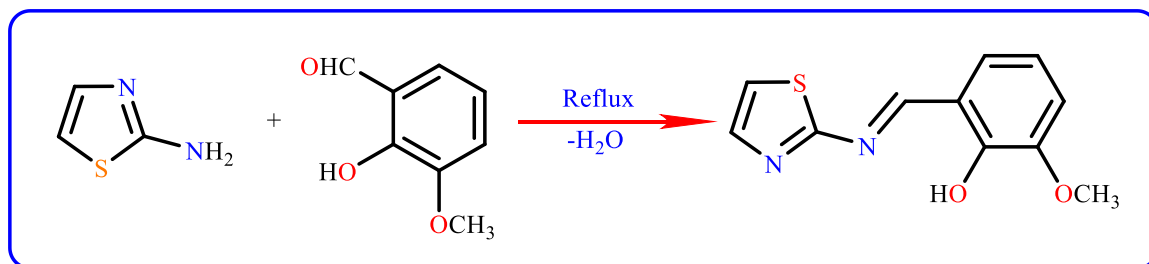
This study aimed to compare the amino acid compositions according to animal species by determining the amounts of essential and non-essential amino acids in egg white and yolk of organic and farm chicken, duck, quail and goose eggs.

2. Experimental

2-Aminothiazole, and 2-hydroxy-3-methoxy benzaldehyde, were purchased from Aldrich and used without further purification. The ligand synthesized was dissolved in dichloromethane and precipitated from n-hexane and its purity checked by IR, NMR and elemental analysis. The elemental analyses were made by using a LECO-CHNS 932 microanalysis. IR spectrums were taken using Mattson 1000 FT-IR spectrophotometer as KBr pellets. ^1H and ^{13}C NMR spectrums were recorded on Jeol FX-90 spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance model MK1 at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_2]$ as a calibrant. Diamagnetic correction calculated from Pascal's constant. Thermogravimetric analyses were obtained from a Shimadzu TGA-50 Thermobalance. Melting points were determined on a Gallenkamp melting point apparatus. Electronic spectrums recorded on a Cecil CE 5502 Spectrophotometer in the quartz cell path length of 1.0 cm.

2.1 Synthesize of the ligand (LH)

10 mmol (1.522 g) of 2-hydroxy-3-methoxy benzaldehyde was dissolved in 25 ml benzene in 250 ml flask in hood and 10 mmol (1.004 g) of 2-aminothiazole dissolved in 25 ml benzene in the hood then added drop wise to flask at room temperature and two drop of concentrated sulfuric acid added as catalyst then the mixture was refluxed for 12 hours, then the temperature brought to room temperature and after the removal of the solvent in a rotary evaporator the mixture poured to cold water and precipitate was filtered and washed with water and ethyl alcohol-water mixture then it was dried at 60 °C temperature, yield 2.055 g (88 %).



2-Methoxy-6-[thiazol-2-yl-iminon)metil]phenol

The characteristic IR bands (KBr pellets, cm^{-1}) are given in Table 1. The ligand found to be soluble in CHCl_3 , THF, methanol, DMSO, DMF, acetone, ethyl acetate and insoluble in diethyl ether, n-hexane, and water, slightly soluble in ethanol. Characteristic ^1H NMR peaks are (CCl_4 TMS, δ ppm), 9.30 (s, $-\text{CH}=\text{N}$), 7.0-7.5 (m, $=\text{CH}-$ in thiazole ring). Aromatic protons appeared at about 7.8 - 8.0 as multiplets, 3.8 (s, $-\text{OCH}_3$), $-\text{OH}$ signal appeared at 11.3 ppm and disappeared upon addition of D_2O to the solution, indicating that it is an acidic proton. Anal. cal. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ (234.27): C, 56.39; H, 4.30; N, 11.96; S, 13.69; found: C 56.56, H 4.54, N 11.54, S 13.36.

2.2 General Procedures for the Synthesis of the complexes

1 mmol of LH dissolved in 15 ml of absolute acetone then 0.5 mmol of acetate salt of metals dissolved in 15 ml of absolute ethanol and added drop wise to the ligand solution while it was being stirred and refluxed for four hours. Then reaction was stopped and brought to room temperature, solvent was evaporated by rotary evaporator. After that the residue was dissolved in 5 ml of dichloromethane and precipitated in 100 ml of n-hexane then filtered off and dried at 60 °C. The complexes found to be soluble in DMSO, DMF, THF, CHCl₃, pyridine, dichloromethane, ethanol, ethyl acetate, slightly soluble in 1,4-dioxane, acetone, carbon tetrachloride, and insoluble in water, n-hexane, benzene, diethyl ether, petroleum ether.

The yield, color, melting point, and characteristic IR bands as KBr pellets, of the ligand and complexes are given in Table 1 and Table 2. Anal. cal. for C₁₁H₁₀N₂O₂S, Mol. Wt. 234.27 g/mol, C, 56.39; H, 4.30; N, 11.96; S, 13.69, found: C 56.06, H 4.06, N 11.96, S 13.46, for C₂₂H₂₆CoN₄O₈S₂, Mol. Wt.: 597.53, C, 44.22; H, 4.39; N, 9.38; S, 10.73, found: C 44.43, H 4.64, N 9.30, S 10.45, for C₂₂H₂₆NiN₄O₈S₂, Mol. Wt.: 597.29, C, 44.24; H, 4.39; N, 9.38; S, 10.74; found: C 44.21, H 3.95, N 9.16, S 10.99; and for C₂₂H₂₆CuN₄O₈S₂, Mol. Wt.: 602.14, C, 43.88; H, 4.35; N, 9.30; S, 10.65; found: C 44.16, H 4.53, N 9.20, S 10.51.

3. Results and Discussion

The synthesis of the ligand was given in Scheme 1. Authentication of the ligand was checked by FT-IR, ¹H NMR and elemental analysis. The coordination compounds of the ligand were synthesized in absolute ethanol in good yield (80-95%). The found and calculated element analyses (C, H, N and S) are in good agreement and confirm the proposed molecular formula of the isolated complexes. All the complexes have 1:2 ratio of metal to ligand and have an octahedral configuration with two moles of coordinated water.

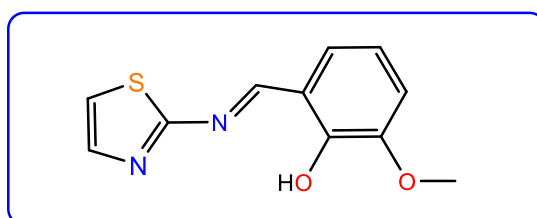


Figure 1. 2-methoxy-6-(thiazol-2-ylimino)methylphenol (LH)

3.1 IR spectra and mode of bonding

A detailed interpretation of IR bands of the ligand and the metal complexes are discussed. The IR spectra of the free ligand and metal complexes were carried out in the range of 4000 – 400 cm⁻¹ (Table 1). The IR spectra of the ligand show a broad band between 3200 - 3450 cm⁻¹, which can be attributed to phenolic OH group. This band disappear in all complexes after complexation, which can be attributed to involvement of phenolic OH in coordination. The involvement of deprotonated phenolic OH group in complexes are confirmed by the shift of ν(C-O) stretching band observed at 1202 cm⁻¹ in the free ligand to the lower frequency to the extent of 15 cm⁻¹ [21]. The IR spectrum of the ligand revealed a medium band at 1545 cm⁻¹ ν(C=N) thiazole ring, which is not changed after complexation indicate that it has not been affected upon coordination to metal ions. The unchanged band after complexation at 784 in the free ligand suggests non-involvement of the coordination to metal which was assigned as ν(C-S-C) [22]. In the

IR spectrum of all the complexes IR band observed between 556-560 cm^{-1} which is attributed to the $\nu(\text{M-N})$ stretching vibrations and the second band appeared between 420-432 cm^{-1} which is assigned to the phenolic oxygen to metal atoms stretching vibrations $\nu(\text{M-O})$.

Table 1 Characteristic IR bands of the ligand and its complexes as KBr pellets.

	Ligand (LH)	CoL ₂	NiL ₂	CuL ₂
$\nu(\text{O-H})$	3200-3450 br	----	----	----
$\nu(\text{C=N})_{\text{azomethine}}$	1617 w	1638 m	1637 m	1636 m
$\nu(\text{C=N})_{\text{thiazole}}$	1597 s	1608 s	1618 s	1612 s
$\nu(\text{C=C})_{\text{benzene}}$	1363 m	1356 w	1360 m	1360 w
$\nu(\text{C-O})$	1202 m	1187 m	1187 m	1187 m
$\nu(\text{C-S-C})$	780 w	782 w	784 w	782 w
$\nu(\text{M-N})$	-	558 w	556 w	560 w
$\nu(\text{M-O})$	-	420 w	421 w	421 w

Key: s (strong), m (medium), br (broad), w (weak).

3.2 UV-Visible Spectra and Magnetic Moments

The electronic spectrum of the Schiff base LH and its complexes were taken in THF. Two very strong bands at 350 nm and 240 nm were observed in the spectra of the ligand, which is attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the aromatic ring and C=N chromophore [23]. The cobalt complex have two bands one at 620 nm and the other at 430 nm which is assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions respectively. Calculated 10 Dq energy of the Co(II) complex is 16100 cm^{-1} and the Racah parameter is 700 cm^{-1} . From the position of the bands and the magnetic moment value of 4.62 B.M. the geometry of the cobalt complex suggested the geometry of the complex as octahedral. The observed d-d transition of the nickel complex at 650 nm and 470, corresponding to the transition of ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ in the octahedral field. Magnetic moment value of 2.78 BM supports the hexa coordinated configuration of the nickel complex. Calculated 10 Dq and the Racah parameters are 15400 and 575 cm^{-1} respectively.

Cu(II) complexes take a wide range of geometries, often with a low symmetry and in most geometries the electronic spectra exhibits a very broad band with maximum which contains all the expected transitions [24]. The UV-visible spectra of the Cu(II) complex, has a broad band at 720 nm, assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition with a tailing to higher wavelength which is well known for octahedral copper complex, [25,26]. The magnetic moment of 1.45 BM indicates some sort of molecular association that could be achieved through bridged ligand [27] or caused by spin orbit coupling.

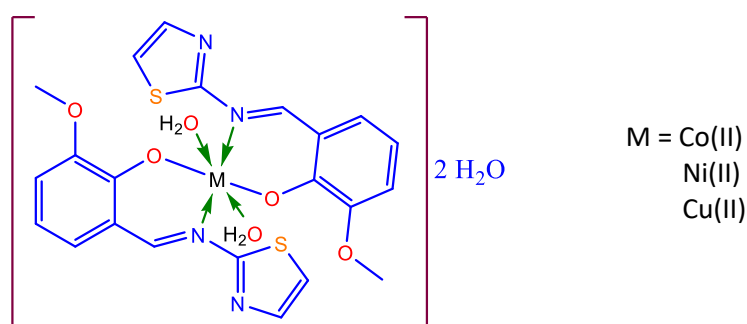


Figure 2. Suggested structure of the Co(II), Ni(II) and Cu(II) complexes.

Table 2. Formulas, formula weights, colors, melting points, yields, metal contents of the ligand and its complexes with transition metals of Cr(III), Co(II), Ni(II) and Cu(II).

Compounds	FW g/mole	μ_{eff} (B.M.)	Color	Mp (°C)	Yield %
LH C ₁₁ H ₁₀ N ₂ O ₂ S	234.27	---	Orange	114	88
[CoL₂ 2H₂O] 2H₂O C ₂₂ H ₂₆ N ₄ O ₈ S ₂ Co	597.53	4.62	Dark Orange	Dec >110	93
[NiL₂ 2H₂O] 2H₂O C ₂₂ H ₂₆ N ₄ O ₈ S ₂ Ni	597.29	2.78	Dark Orange	Dec >110	86
[CuL₂ 2H₂O] 2H₂O C ₂₂ H ₂₆ N ₄ O ₈ S ₂ Cu	602.14	1.45	Light Brown	Dec >120	80

The thermogram of the ligand shows that the weight loss begins at 130 °C and decomposes in two steps which are 130-220 °C, 480-750 °C leaving %9 residue. The first step which has %40 lost corresponds to 2-aminothiazole group (calculated %41), and the second decomposition step takes place between 480-750 °C with the complete decomposition of the ligand.

All the complexes have similar decomposition pattern in three steps. In first step %10-13 of weight loss between 110-160 °C corresponds to lost of four H₂O molecule (calculated \approx %12 for the all complexes). The loss of water at low temperature spanning to higher temperature suggest that some of these water molecules must be coordinated to metal ion. Therefore, to remove these molecules from the complex higher temperature needed. In the second step, complexes decompose with the weight loss of %45, which correspond to -CH-(C₆H₃OH(OCH₃)) group between 200-400 °C, and then they further decompose between 420-750 °C to yield corresponding metal oxide with the residue of %12.8, %11.2 and %12.1, corresponding to CoO (calculated % 11.0), NiO (calculated % 10.9) and CuO (calculated % 11.3) respectively.

4. Conclusions

Analysis of the synthesized complexes, show that the divalent metal ions surrounded by two ligand molecule which is coordinated to metal ions through imino nitrogen and phenolic oxygen atoms of the ligand. In addition, TGA analysis indicate that there are also two moles of water in coordination sphere of the complexes. UV-Vis spectra and magnetic moments measurements of the complexes together with microanalysis indicate that metal ions are octahedrally coordinated, with two moles of ligand and two moles of water (Figure 2).

Conflicting Interest

Authors declare that there is no conflicting interest

Acknowledgement

We would like to thank Firat University for financial support (FUBAP 306 and FUBAP 814).

References

- [1] Erwin B. and Omoshile C., *J. Chem. Soc. Perkin Trans. 2*, 1333 (1995).
- [2] Luo X.F., Hu X., Zhao X.Y., Goh S.H. and Li X.D., *Polymer*, 44, 5285 (2003).
- [3] Murthy A. S. N. and Reddy A.R., *Proceedings of the Indian Academy of Sciences-Chemical Sciences*, 90, 519 (1981).
- [4] V. Ambike, S. Adsule, F. Ahmed, Z. Wang, Z. Afrasiabi, E. Sinn, F. Sarkar, S., *J. Inorg. Biochem.*, 101 (2007), pp. 1517-1524
- [5] Agarwal N., Kumar S., Srivastava A. K., Sarkar K.P.C., *Ind. J. Het. Chem.*, 6, 291-294 (1997).
- [6] Dan Qiao, Qidong Tang, Wei Ruan, Zhouling Xie, Jiaojiao Guo, Wufu Zhu, *European Journal of Medicinal Chemistry*, Volume 259, 2023, 115689,
- [7] Sup R. C., Sukp R.Y., Bang C. W., *Korean J. Med. Chem.*, 5, 72 (1995).
- [8] Buristrov S. I., and Bobashko Z. A., USSR. Pat. No: 154861, (1964). (*Chem Abstr.* 60, 5508c, (1964))
- [9] Hadjipavlou-Litina J. D., Geronikaki A., *Arz. Forsch./Drug Res.* 46, 805 (1996).
- [10] Seyedmohammad Hosseiniyehzad, Ali Ramazani, *Arabian Journal of Chemistry*, Volume 16, Issue 11, 2023, 105234.
- [11] Tsuruoka M. and Seikutsugaka I., *Med. Biol.*, 10, 296 (1947).
- [12] Maass G., Immendoerfer U., Koenig B., Leser U., Mueller B., Goody R., Pfatt B., *Antimicrob. Agents. Chemotter.*, 37, 2612 (1993).
- [13] Anna M. P., Athina G., Remi M., Venera C., Barbara G. and Irini D., *Bioorganic & Medicinal Chemistry*, 11, 2983 (2003).
- [14] Kapoor R. P., Rastogi M. K., Khanna R. and Garg C. P., *Indian J. Chem.*, 23B, 390 (1984)
- [15] Metzger J. V., Katritzky A. R., Rees W., Potts K. T., (Eds.). *Comprehensive Heterocyclic Chemistry*, (Pergamon Oxford, 1984; Vol. 6)
- [16] Hosseini A. K, Tadjarodi A. *J Nanotechnol Nanomaterials.* 2024;5(1):1-6.
- [17] Kumar Virendra, Sony Simran, Kaur Navpreet, Mobin Shaikh M., Kaur Paramjit, Singh Kamaljit, *Analytica Chimica Acta*, 2022, Volume 1206, 339776.
- [18] Eynde Vanden J. J. and Fromont D., *Bull. Soc. Chim. Belg.*, 106, 393 (1997).
- [19] Sitkowski J., Stefaniak T. Dziembowska, E., Grech E., Jagodzinska G. A., Webb J., *Molecular Structure*, 381, 177 (1996).
- [20] Castro R., Garcia-Vazquez J. A., Romero J. and Sousa A., *Polyhedron*, 12, 2241 (1993).
- [21] Omar M. M. Mohamed G. G., *Spectrochimica Acta Part A*, 61, 929-936 (2005)
- [22] Castro R., Garcia-Vazquez J.A., Romero J. and Sousa A., *Polyhedron*, 12, 47 (1993).
- [23] Williams D. H. and Fleming I., *Spectroscopic Methods in Organic Chemistry*, 4th Edition, (McGraw-Hill, London, 1989).
- [24] Drago R. S., *Physical Methods for Chemists*, (Sounders College Publishing, New York, 1992).
- [25] Gul A. and Bekaroglu O. *J. Chem. Soc. Dalton Trans.*, 2537 (1983).
- [26] Greenwood N. N. and Earnshaw A., *Chemistry of the Elements*, (Pergamon Press, Oxford, 1984).
- [27] El Sonbati A. Z., El-Bindary A. A., Mabrouk E. M., *Transition Metal Chemistry*, 17, 66 (1992).