The OSCAR PUBLISHING Services
American Journal of Applied Science and Technology

VOLUME Vol.05 Issue 05 2025
PAGE NO. 82-88
DOI 10.37547/ajast/Volume05Issue05-18

Synthesis and Investigation of Complex Compounds Of 3d-Metals With 3-Amino-1,2,4-Triazole

S.G. Usmonova
Teacher at Department of Medical and Biological Chemistry of Andijan Branch of Kokand University, Uzbekistan

Z.M. Chalaboyeva
Teacher at Department of Medical and Biological Chemistry of Andijan Branch of Kokand University, Uzbekistan

M.M. Mirzayeva
Teacher at Department of Medical and Biological Chemistry of Andijan Branch of Kokand University, Uzbekistan

Sh. A. Kadirova
Professor of the Faculty of Inorganic Chemistry at National University of Uzbekistan, Uzbekistan

Received: 24 March 2025; **Accepted:** 20 April 2025; **Published:** 22 May 2025

Abstract: The currently available scientific, technical, and patent literature contains a sufficient amount of general information on coordination compounds of biometals with various derivatives of triazole. However, this information is fragmented, and the complexation reactions have not been systematically studied. The present work is a scientific study focused on the systematic investigation of the structure and properties of previously unknown coordination compounds of Ni(II), Cu(II), and Zn(II) chlorides with 3-amino-1,2,4-triazole.

Keywords: Amitrole, IR spectroscopy, complex, solubility, ligand, quantum chemical calculation, geometry optimization, thermal analysis, scanning electron microscopy.

Introduction:

Research Objective: To develop a synthesis method for new complex compounds of Ni(II), Cu(II), and Zn(II) chlorides with 3-amino-1,2,4-triazole (L).

METHODOLOGY

Elemental analysis, SEM-EDTA, thermal analysis, IR spectroscopy, quantum chemical calculations.

Scientific Novelty: For the first time, complex compounds of some 3d-metals based on 3-amino-1,2,4-triazole have been synthesized. The composition and structure of the synthesized compounds were studied using elemental analysis, thermal analysis, and IR spectroscopy. Quantum chemical calculations were performed using the Biovia Accelrys Materials Studio software with the PM-6 method to determine the ligand's electronic structure, geometrical parameters, and energetic characteristics. The most probable coordination centers were identified based on charge distribution analysis.

Introduction: One of the rapidly developing areas of organic chemistry is the chemistry of heterocyclic compounds. Based on these, it is possible to synthesize new, low-toxic, and environmentally safe analogs of natural substances that can be used in medicine, agriculture, chemical technology, and analytical chemistry. The synthesis of new coordination compounds of transition metals based on heterocyclic compounds contributes to the expansion of the range of biologically active substances used as pharmaceuticals and chemical agents for protection against diseases, pests, and weeds, as well as plant growth regulators that are safe for humans and the environment. The study of

coordination compounds based on heterocyclic structures is important not only for expanding their practical application but also for addressing fundamental issues in coordination chemistry, such as the nature of chemical bonding, molecular structure, and properties.

In coordination chemistry of transition metals, nitrogen-containing heterocycles represent one of the most important classes of ligands, among which derivatives of 1,2,3-triazole, 3-amino-1,2,4-triazole, and others are widely studied [1–3].

It has been established that coordination compounds of 3-amino-1,2,4-triazole derivatives with metals also exhibit biologically active properties. Complexes of certain d-metals with aminotriazole derivatives have been synthesized and are widely used in medicine (e.g., antibacterial agents, cardiac stimulants) [4–5], in the production of inhibitors [6–8], herbicides [9–10], catalysts [11], and fungicides [12–13]. The study of the application areas of coordination compounds of 3-amino-1,2,4-triazole derivatives in medicine, agriculture, and industry holds great theoretical and practical significance. The aim of this research is the synthesis, structural investigation, and characterization of new complexes containing 3-amino-1,2,4-triazole derivatives as ligands.

Materials and Methods: Chlorides of Ni(II), Cu(II), and Zn(II) of analytical grade ("chemically pure") were used in the work. The organic reagents and solvents used were purified and dried by standard methods [14].

The synthesis of complexes of 3-amino-1,2,4-triazole with chlorides of Cu(II), Zn(II), and Ni(II) was carried out by dissolving amitrole in 0.042 g of ethanol and stirring it on a magnetic stirrer. An aqueous (hot) solution of 0.034 g of copper(II) chloride, 0.035 g of zinc chloride, or 0.065 g of nickel(II) chloride was added dropwise while stirring. The mixture was stirred for 3 hours at room temperature using a magnetic stirrer. The solution was cooled to room temperature and filtered again (until a clear solution was obtained), then evaporated at room temperature under reduced pressure.

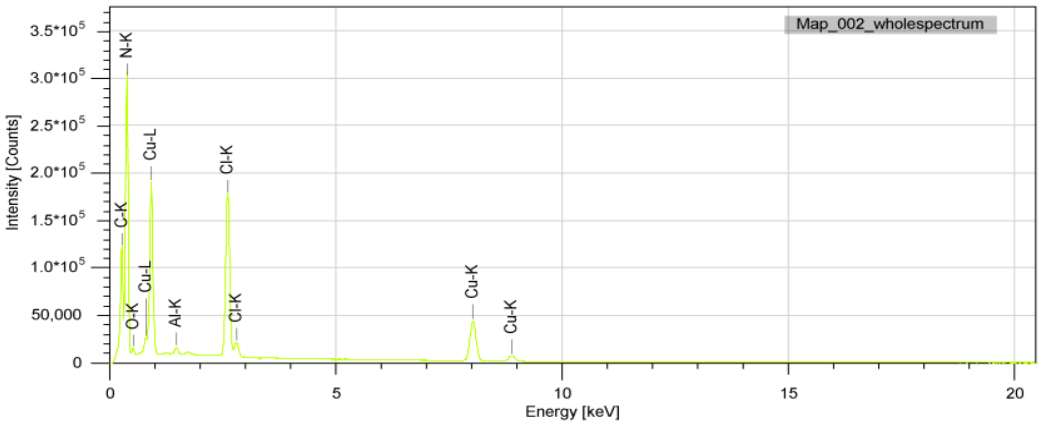
As a result of slow solvent evaporation over several days, green crystals with $CuCl_2$ and violet crystals with $NiCl_2$ were formed. The resulting crystals are stable in air, non-hygroscopic, and well soluble in organic solvents. The melting points are: $NiCl_2$ – 297°C, $CuCl_2$ – 295°C, and $ZnCl_2$ – 298°C.

The results of the synthesized compounds, their melting points, and elemental analysis data are presented in Table 1.

Table 1. Results of elemental analysis and selected properties of transition metal complexes with ligand L

№	Compound	Color	%	T пл, ^{0}C	Found (%)					Calculated (%)			
					C	H	N	M	Formula Brutto	C	H	N	M
1	L	White		157-159	28,6	4,76	33,3		$C_2N_4H_4$	29,1	4,26	32,9	
2	$Cu(C_2N_4H_4)_5Cl_2$	Green		294-295	21,6	3,60	50,5	11,5	$C_{10}N_{20}H_{20}Cl_2Cu$	20,9	3,45	49,8	10,9
3	$Ni(C_2N_4H_4)_5Cl_2(H_2O)_2$	Violet		296-297	20,5	4,09	47,8	10,1	$C_{10}N_{20}H_{24}Cl_2O_2Ni$	21,3	4,01	48,2	11,2
4	$Zn(C_2N_4H_4)_4Cl_2(H_2O)_4$	White		297-298	17,6	4,41	41,2	11,9	$C_8N_{16}H_{24}Cl_2O_4Zn$	18,6	4,49	41,9	11,1

The content of nitrogen, sulfur, and metal in the obtained metal complex compounds was determined using the SEM-EDTA method, on the basis of which, along with energy-dispersive analysis, it can be concluded that the complexation of metal ions with the organic ligand leads to changes in the microstructure of the latter. In particular, numerous metal peaks were recorded, which is confirmed in Table 2.



Element	Mass %	Atom %
C	18.87	0.01
N	61.11	0.04
O	1.35	0.01
Cl	7.03	0.01
Cu	11.41	0.02

Table 2. Microstructure of the metal complex compound $Cu(C_2N_4H_4)_5Cl_2$

As a result of studying the solubility of the metal complex compounds in various solvents, it was concluded that they are poorly or practically insoluble in benzene and DMF, but dissolve well in water, ethanol, and acetonitrile (Table 3).

Table 3. Solubility of the synthesized metal complex compounds based on ligand L

№	Compound	Water	Ethanol	Benzene	DMF	Acetonitrile
1	L	P.S.	S	I.S.	P.S.	S
2	$Cu(C_2N_4H_4)_5Cl_2$	S	S	P.S.	P.S.	S
3	$Ni(C_2N_4H_4)_5Cl_2(H_2O)_2$	S	S	P.S.	P.S.	S
4	$Zn(C_2N_4H_4)_4Cl_2(H_2O)_4$	S	S	P.S.	P.S.	S

Note: S – soluble, P.S. – poorly soluble, I.S. – insoluble

RESULTS AND DISCUSSION

The synthesized ligand is characterized by the presence of various functional groups containing multiple donor atoms. To enable the targeted synthesis of metal complexes, a quantum chemical calculation of the reactivity of the synthesized ligand was performed using the PM3 and MNDO quantum chemical methods in ChemOffice Ultra [15]. The nitrogen atoms in the amino group possess a higher negative effective charge compared to the nitrogen atoms located in the ring. Despite their significant negative effective charge, these donor atoms do not participate in the formation of coordination complexes.

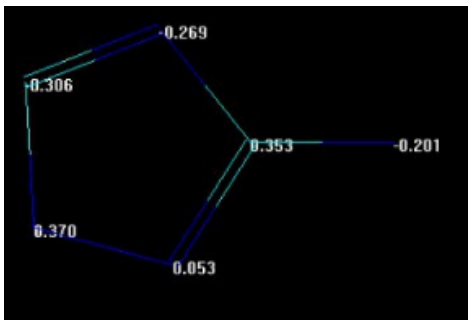


Figure 1 a

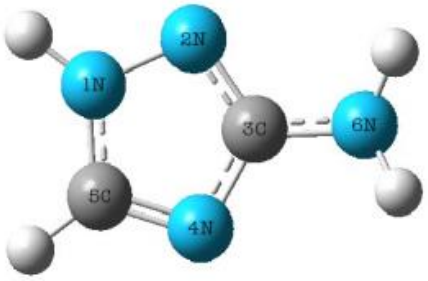


Figure 1 b

Figure 1 (a, b) – Diagram of electron density distribution of the 3-amino-1,2,4-triazole ligand calculated by the MNDO method

To determine the coordination center, IR spectra of the ligand and its corresponding complex were recorded (Fig. 2). An attempt was made to evaluate the electron–conformational changes upon complex formation using IR spectroscopy.

The ligand, amitrole, contains several functional groups. Intense asymmetric stretching vibrations of the C=N group are observed in the region of 1537–1560 cm^{-1}, while symmetric vibrations are found in the region of 729–828 cm^{-1}. Symmetric and asymmetric stretching and bending vibrations of the amino group are observed at 3331, 3414, 1271, 1373, and 1593 cm^{-1}, respectively. The stretching vibration of the C–N bond appears around 968 and 1425 cm^{-1}.

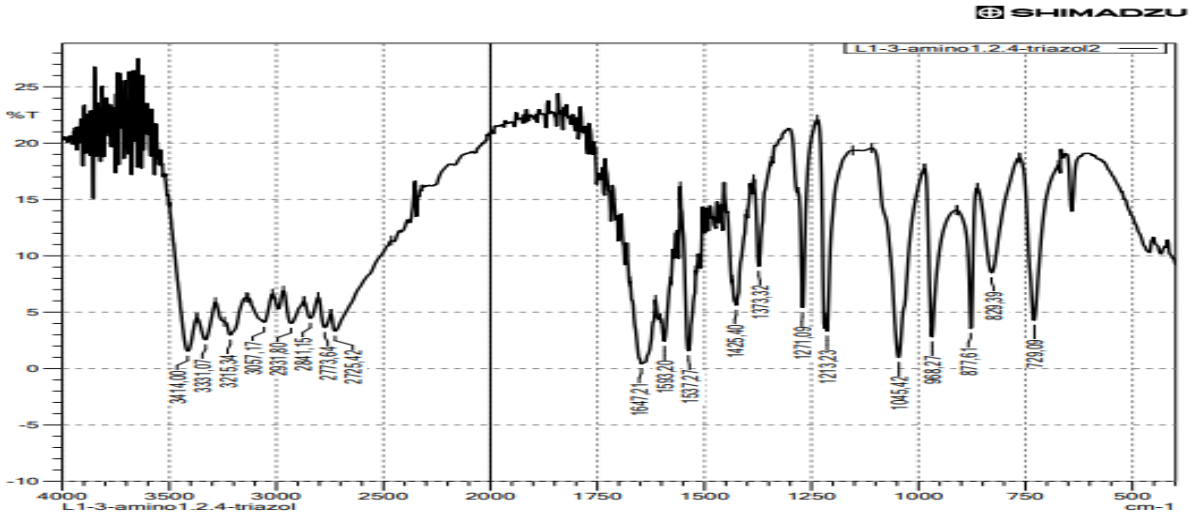
It is evident that in the IR spectra of the complexes of amitrole with zinc and copper chlorides, a shift in the frequencies of the asymmetric and symmetric stretching vibrations of the C=N group is observed by 6–11 and 26–32 cm^{-1}, respectively, compared to the ligand spectrum (Table 4).

This indicates that the complexes are formed through the lone electron pairs of nitrogen in the heterocycle. Symmetric and asymmetric stretching vibrations of the amino group may also change, presumably due to electron redistribution during the formation of coordination compounds.

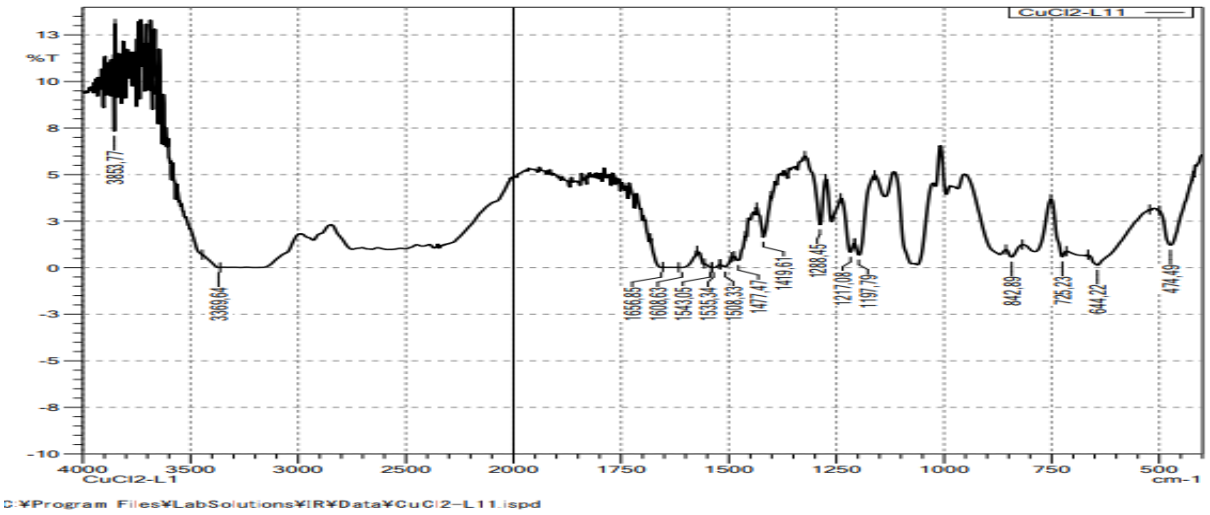
The absence of absorption line broadening in the 3000–3400 cm^{-1} region confirms the absence of moisture in the complexes. The appearance of new vibrational frequencies corresponding to M–N stretching vibrations in the region of 473–642 cm^{-1} provides evidence of complex formation [16].

Table 4. IR spectroscopic analysis of the complexes

Type of vibration.	**ν_aC=ν_{as}C=N N**	ν_s NH_2	δ NH_2	νC-N	ν_sC=N	ν_{as} NH_2	νM→N
L	1537,1560	1271,1373	1593	968,1425	729,878	3331,3414	-
CuL	1508	1261,1288	1632	1063,1477	725,870	3298	473
NiL	1508	1248	1629,1641	1058	988	2776,3630	642
ZnL	1527,1566	1307	1610,1639	1020,1425	743,881	3385	486



A



B

Figure 2: (A, B) IR spectra of the ligand (A) and its complexes (B)

Thermogravimetric analysis of the complexes was carried out in the temperature range of 20–1000°C. On the TG curve of the complex compound $[Cu(L)_5]Cl_2$, an exothermic effect is observed in the region of 250–335°C, accompanied by a mass loss of 75.9% of the total weight. Based on this, it can be assumed that the remaining mass corresponds to the composition $C_{10}N_{20}H_{20}Cl_2Cu$, i.e., it matches the formula $Cu(C_2N_4H_4)_5Cl_2$ (Figure 3).

On the TG curve of the complex compound $[Ni(L)_4]Cl_2(H_2O)_2$, an exothermic effect is observed in the region of 420–780°C, along with a mass loss of 74.9% of the total weight. Based on this, it can be assumed that the remaining mass corresponds to the composition $C_{10}N_{20}H_{24}Cl_2O_2Ni$, which corresponds to the formula $Ni(C_2N_4H_4)_5Cl_2(H_2O)_2$ [17,18].

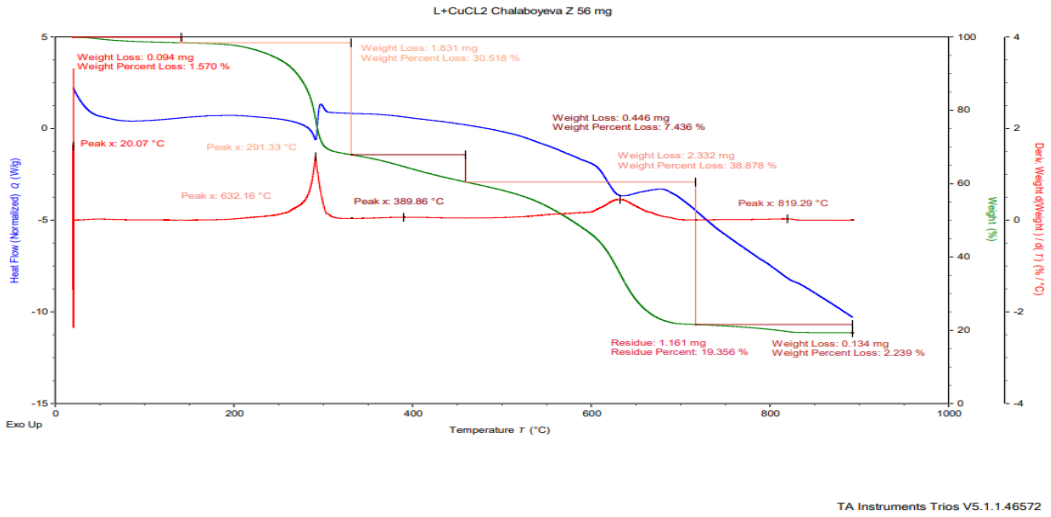


Figure 3. Thermogram of the complex compound $[CuL_5]Cl_2$

CONCLUSION

A method for the synthesis of complexes of 3-amino-1,2,4-triazole with copper(II) and nickel(II) chlorides has been developed, and the corresponding complex compounds have been synthesized. These complexes are well soluble in fresh water. The composition and structure of the synthesized complexes were studied using physicochemical methods. It was established that the metal complexes of 3-amino-1,2,4-triazole with copper(II) and nickel(II) chlorides in a metal-to-ligand ratio of 1:5 are thermally more stable than the ligand itself and possess a unique crystal lattice. Based on IR spectroscopic analysis, the geometry of the synthesized complexes depends on the nature of the metal and corresponds to monodentate coordination.

REFERENCES

Кадирова Ш.А., Парпиев Н.А., Ишанходжаева М.М., Каримов З., Тожибоев А., Ташходжаев Б. Пятикоординационный комплекс хлорида меди с 2-амино-5-этил-1,3,4-тиадиазолом// Журнал общей химии.-Санкт-Петербург, 2007- №10 – С. 1734-1737.

Кадирова Ш.А., Турсунова М.Р., Парпиев Н.А., Ишанходжаева М.М., Каримов З., Тожибоев А., Ташходжаев Б. Синтез и структура комплексов ацетата Co(II) и хлорида Zn(II) с 2-аминобензотиазолом// Журнал общей химии. - Санкт-Петербург, 2007. №10.-С. 1743–1747.

Кадирова Ш.А., Торамбетов Б.С., Парпиев Н.А., Хушвактов Ж. Квантово-химическая оценка реакционной способности фенилпиколинамида – лиганда в реакциях комплексообразования// Научный журнал ''Globus'', - Санкт-Петербург, 2018. 08 январъ. – С. 40-46.

J.Mehla, J.H.Caufield, N.Sakhawalkar, P.Uetz., Chapter Seventeen A Comparison of Two-Hybrid Approaches for Detecting Protein-Protein Interactions., Methods in Enzymology., 2017, Pages 333-358.

Guy Landau, Vamsik. Kodali, Jyoti D. Malhotra, Randal J. Kaufman., Chapter Fourteen-Detection of Oxidative Damage in Response to Protein Misfolding in the Endoplasmic Reticulum., Methods in Enzymology., 2013, Pages 231-258.

Matija Dreze, Dario Monachello, Cloire Lurin, Michael E, Cusick, David E, Hill, Mare Vidal, Pascal Braun., Chapter 12-High-Quality Binary Interactome Mapping., Methods in Enzymology., 2010, Pages 281-315.

Бреннан MB, Struhl K (1980).«Механизмы увеличения экспрессии дрожжевого гена в Escherichia coli».J. Mol.Биол.136(3): 333–8.DOI:10.1016 / 0022-2836 (80) 90377-0.PMID 6990004.

Joung Ю.К., Рамм Е.И., Pabo CO (2000).«Бактериальная двухгибридная селекционная система для изучения взаимодействий белок-ДНК и белок-белок». Proc. Natl. Акад.Sci.США.97(13): 7382–7.DOI: 10.1073 / pnas.110149297. PMC 16554. PMID 10852947.

GrahamF. Smith., Designing Drugs to Avoid Toxicity., Progress in Medicinal Chemistry., 2011, Pages 1-47.

«Интерпретация критериев одобрения действующих веществ в предлагаемых правилах ЕС по защите растений». Шведское химическое агентство (KemI).2008-09-23. Архивировано из оригинала на 1 января 2009 года. Проверено 14 января 2009.

"Yeastgenome.org". Архивировано из оригинала на 2006-05-05. Проверено 1декабря 2006.

Lauren Makuch., Chapter Three-Yeast Two-Hybrid

Screen., Methods in Enzymology., 2014, Pages 31-51.

Anureolha Vivekanandan-Giri, Jaeman Byun, Subrama naim Pennathur., Chapter five-Quantitative Analysis of Amino Acid Oxidation Markers by Tandem Mass spectrometry., Methods in Enzymology., 2011, Pages 73-89.

Титце Л., АйхерТ. Препаративная органическая химия.-М.: Мир, 2017. -704 с

Rumyana Yankova, Lachezar Radev. Density Functional Theory Calculations of [Me(3-Amino-1,2,4-Triazole)2] 2+ Complex Ions (Me =Zn,Cu, Co, Ni and Cd) in Water Phase. International Journal of Materials and Chemistry 2015, 5(2): 25-30 DOI: 10.5923/j.ijmc.20150502.01.

Накамото К. ИК-спектры неорганических и координационных соединений. - М . : Мир, 1996. - 204 с. 17. Топор Н.Д., Огородова Л.П., Мельчакова Л.В. Термический анализ минералов и неорганических соединений. - М.: Изд-во МГУ, –1987. –190 с.

Кукушкин Ю.Н., Ходжаев О.Ф., Буданова В.Ф., Парпиев Н.А. Термолиз координационных соединений. -Тошкент: Фан, –1986. – 198 с.

Калмыков К.Б., Дмитриева Н.Е. Сканирующая электронная микроскопия и рентгено-спектральный анализ неорганических материалов. Методическое пособие. Москва, –2017. –С.54.

Кадирова Ш.А., Раззокова С.Р., Садуллаева Г.Б. Синтез и спектроскопическое исследование комплексов Co(II), Ni(II) и Zn(II) с 5-(3-гидроксифенил)-1,3,4-оксадиазолин-2-тионом// – ТерГУ, 24-26 апреля, –2020. – С. 317-320.