The OSCAR PUBLISHING Services
American Journal of Applied Science and Technology

VOLUME Vol.06 Issue 01 2026
PAGE NO. 73-79
DOI 10.37547/ajast/Volume06Issue01-15

Synthesis And Structural Study Of Coordination Complexes Of 5-Methyl-1,2,4-Triazole With Co(Ii), Ni(Ii), Cu(Ii)

R.X. Karimova
Student of the Faculty of General Medicine, Group 24-03, Uzbekistan

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

Received: 28 November 2025; **Accepted:** 18 December 2025; **Published:** 23 January 2026

Abstract: In this study, coordination compounds of 5-methyl-1H-1,2,4-triazole with Co(II), Ni(II), and Cu(II) acetates were synthesized and characterized. The 5-methyl-1,2,4-triazole ligand (L) was obtained via a cyclization route using acetamidine hydrochloride and formamide, yielding a pale crystalline product (m.p. 46°C) in 78% yield. Reaction of L with cobalt, nickel, and copper (II) acetates in ethanol produced the corresponding metal–ligand complexes in good yields (75–82%). These complexes are insoluble in nonpolar solvents but dissolve readily in water and ethanol. The composition and structures of the complexes were investigated using infrared (IR) spectroscopy, thermogravimetric analysis (TGA/DTG/DTA), and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis. IR spectral data revealed shifts in the triazole ring vibration bands upon complexation, indicating coordination of the ligand to the metal center via a ring nitrogen atom. SEM–EDS elemental analysis provided the C, H, N, O and metal percentages, consistent with empirical formulas of [ML2(CH_3COO)2] for M = Co, Ni, Cu. Thermal analysis showed multi-step decomposition for each complex, ultimately yielding metal oxide residues at high temperatures. Notably, the copper complex [CuL2(CH_3COO)2] displayed a major mass loss (~45%) around 680°C corresponding to the formation of CuO. The synthesized coordination compounds thus feature the triazole ligand coordinated through nitrogen donors, and their structures and stabilities have been confirmed by the combined physicochemical data.

Keywords: Co(II), Ni(II), Cu(II) acetates; ligand; 5-methyl-1H-1,2,4-triazole; complex compound; IR spectroscopy; thermal analysis; SEM.

INTRODUCTION:

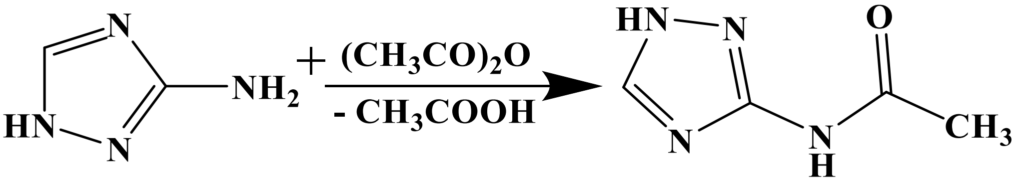
According to analyses of recent literature, the chemistry of metal complexes with heteroatom-containing ligands has advanced rapidly over the past decade. Complex compounds bearing azole-type ligands are especially important for understanding metal–biomolecule interactions, and they find applications in catalysis, pharmacology, analytical chemistry, and emerging areas of materials science. In particular, derivatives of 1,2,4-triazole have attracted considerable interest. Triazole compounds are widely utilized in medicine, agriculture, and chemical technology. Many 1,2,4-triazole derivatives exhibit diverse pharmacological properties, including antidepressant, antifungal, antibacterial, anti-inflammatory, and anticancer activities. For example, several systemic fungicides and antifungal drugs (e.g., **voriconazole**) owe their efficacy to the presence of a 1,2,4-triazole ring in their structure. Additionally, certain triazole derivatives are known as enzyme inhibitors and have analgesic (pain-relief) effects. In the pharmaceutical field, the 1,2,4-triazole scaffold is a key component of numerous therapeutic agents.

The development of metal-based complexes of such bioactive triazoles is considered important for enhancing drug pharmacodynamics and pharmacokinetics. Coordination complexes of triazole ligands have also been studied for potential use in catalysis and electronic materials, as triazoles can serve as ligands forming mono- or polynuclear metal structures.

Despite their significance, the coordination chemistry of simple 1,2,4-triazole derivatives—such as 5-methyl-1,2,4-triazole—remains relatively underexplored in the literature. Most studies focus on more functionalized triazoles (e.g. amino- or azolyl-substituted triazoles). Therefore, investigating the ability of 5-methyl-1,2,4-triazole to form stable complexes with transition metals is of both theoretical and practical interest. By examining such complexes, one can gain insight into the electronic and stereochemical effects of a small alkyl substituent on the triazole ring in coordination assembly.

Purpose of the study: The purpose of this work is to develop a synthesis method for coordination complexes of Co(II), Ni(II), and Cu(II) acetates with 5-methyl-1H-1,2,4-triazole (L), and to study the composition and structure of the obtained complexes using modern physicochemical techniques. The presence of a methyl substituent on the triazole ring could influence the ligand's coordination behavior and the properties of the resulting complexes. To explore this, synthesis reactions with selected 3d metal salts were carried out under various conditions.

The synthesis of N-(1H-1,2,4-triazol-3-yl)acetamide (L) was conducted according to the following scheme:



Scheme 1. Synthesis reaction of N-(1H-1,2,4-triazol-3-yl) acetamide

The 5-methyl-1,2,4-triazole ligand was prepared according to a known cyclization procedure (Scheme 1). In a round-bottom flask equipped with a reflux condenser, an equimolar mixture of formamide and acetamidine hydrochloride (which provides the –C(=NH)–CH_3 moiety) was heated to reflux for 6–8 hours. The reaction mixture was then cooled and neutralized with sodium hydroxide, inducing cyclization to form 5-methyl-1H-1,2,4-triazole. After concentration and cooling, the product was collected as pale white crystals, washed with cold water, and dried. The isolated yield of the ligand was 78%, with a melting point of 44–48°C, in agreement with literature data. The ligand is readily soluble in polar solvents (water, lower alcohols) due to its polar triazole ring, but it is only sparingly soluble in nonpolar solvents.

The synthesis of the Co(II), Ni(II), and Cu(II) coordination complexes with L was carried out by mixing hot aqueous–ethanolic solutions of the metal(II) acetate salts with a slight molar excess of the triazole ligand. For each reaction, -0.01 mol of $M(CH_3COO)_2\cdot xH_2O$ (M = Co, Ni, Cu) was combined with -0.02 mol of 5-methyl-1,2,4-triazole in 50 ml ethanol. The mixture was refluxed with stirring for 3 hours, then gradually cooled to room temperature. On standing, crystalline complexes precipitated from solution. These were filtered off, washed with cold ethanol, and dried in air. Yields of the isolated solid complexes were 75 % for Co(II), 82 % for Ni(II), and 80 % for Cu(II). The Co–L and Ni–L complexes yielded pink-purple and light green powders, respectively, while the Cu–L complex formed dark blue crystals. The melting (decomposition) points of the Co, Ni, and Cu complexes were observed at 92–93°C, 98–99°C, and 101–102°C, respectively. All three complexes are soluble in water and ethanol but insoluble in nonpolar organic solvents, indicating their ionic or polar nature (likely due to the presence of acetate anions and the polar triazole ligand).

Investigation of the obtained complexes by SEM. The elemental composition of the synthesized complexes (carbon, hydrogen, nitrogen, oxygen, and metal content) was examined using energy-dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy. SEM–EDS analysis (Figure 1) provided quantitative data on the percentage of each element present in the Co(II), Ni(II), and Cu(II) triazole complexes. These experimental elemental ratios were used to deduce the empirical formulas of the compounds. In all cases, the data were consistent with a metal-to-ligand ratio of 1:2 and the presence of two acetate groups per metal. Accordingly, the complexes are formulated as $[CoL_2(CH_3COO)_2]$, $[NiL_2(CH_3COO)_2]$, and $[CuL_2(CH_3COO)_2]$, where L = 5-methyl-1,2,4-triazole. This composition suggests that the metal ions are charge-balanced by two bidentate (or monodentate) acetate anions, and the neutral triazole ligands complete the coordination sphere. The microstructure of the complexes, as observed under SEM, appeared as agglomerated polycrystalline particles without distinct crystalline facets, indicating a somewhat amorphous or fine-grained nature for the coordination compounds. EDS mapping confirmed a uniform distribution of the constituent elements within each sample.

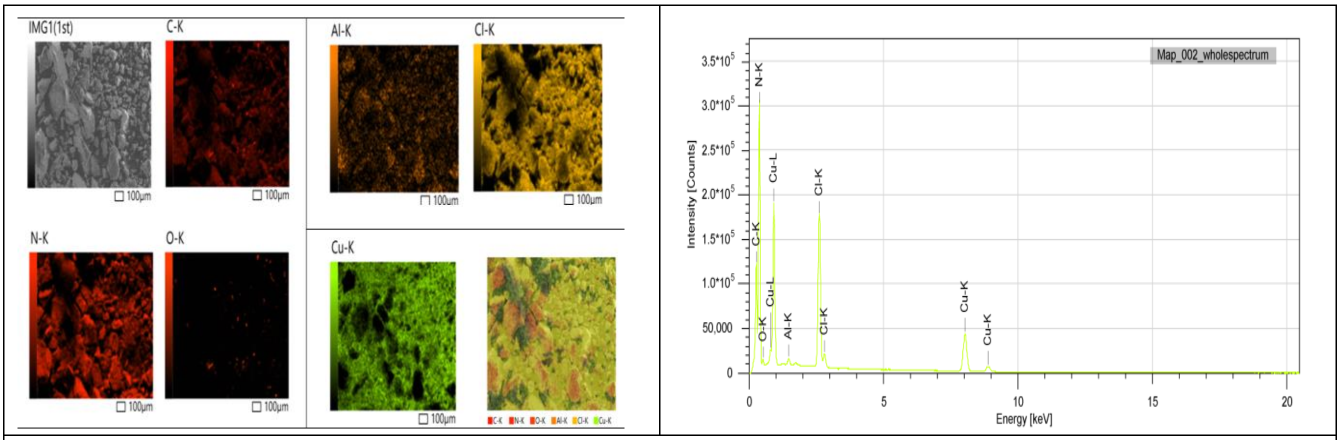


Figure 1. $[CuL_2(CH_3COO)_2]$ Microstructure of the Coordinated Complex Compound

METHODS

The composition and structure of the synthesized coordination compounds were further investigated by infrared spectroscopy and thermal analysis. In this work, the IR spectra of the free 5-methyl-1,2,4-triazole ligand and its Co(II), Ni(II), and Cu(II) acetate complexes were recorded in the range 4000–400 cm^{-1} (Figures 2 and 3). Comparison of the spectra of the complexes with that of the free ligand provides insight into the bonding mode of the ligand to the metal centers. Key absorption bands in the triazole ring and acetate groups were analyzed to determine which functional groups are involved in coordination.

In the IR spectrum of the free 5-methyl-1,2,4-triazole (L), several characteristic bands are observed. A moderate band at 3128 cm^{-1} is assigned to the stretching vibration of the ring N–H bond (the triazole N1–H, as 5-methyl-1,2,4-triazole exists in the 1H-tautomeric form). The aromatic C–H bonds on the triazole ring give rise to bands at 3097 and 3032 cm^{-1}. The ring stretching vibrations, which involve C=N and C–C bonds within the heterocycle, appear as strong absorptions in the 1550–1450 cm^{-1} region. For instance, the free ligand shows prominent bands near 1540 and 1490 cm^{-1}, which can be attributed to the C=N (azomethine) and C=C (olefinic) stretches of the triazole ring, respectively. A weaker band around 1410 cm^{-1} may be due to an N=N stretching vibration within the ring. Out-of-plane deformation modes of the ring C–H bonds appear as one or more bands in the region below 1000 cm^{-1} (commonly near 800–900 cm^{-1}). The free triazole ligand lacks other functional groups (such as C=O or N–H amide groups); thus, its IR spectrum is relatively simple, dominated by ring vibrations and a broad N–H band.

Complexation with the metal acetates induces notable changes in the IR spectra. In the spectra of the Co(II), Ni(II), and Cu(II) complexes, the N–H stretching band of the triazole (originally at 3128 cm^{-1}) is slightly shifted to lower wavenumbers (around 3100 cm^{-1}) and often appears broadened. This shift ($\Delta \nu \approx 20–30$ cm^{-1}) suggests a change in the hydrogen-bonding environment or electronic distribution of the N–H group due to coordination of the adjacent ring nitrogen to the metal. More significantly, the intense ring stretching bands (C=N/C=C) of the triazole move to lower frequencies in the complexes compared to the free ligand. For example, the strong band at 1540 cm^{-1} in free L shifts to ~1530 cm^{-1} in the complexes. Such a shift of 5–10 cm^{-1} to lower energy is a clear indication that the triazole ring is involved in bonding, as coordination weakens the double-bond character of the C=N bond in the ring. New absorption bands appear in the spectra of the complexes that were absent for the free ligand. In particular, the acetate ions introduce characteristic vibrations: the asymmetric and symmetric stretching modes of the carboxylate (COO^-) groups are observed. The asymmetric $\nu_{as}(COO)$ typically emerges as a strong band around ~1560–1590 cm^{-1}, overlapping with ring vibrations, while the symmetric $\nu_s(COO)$ appears near ~1410–1440 cm^{-1}. Additionally, a unique band around 1300–1260 cm^{-1} (not present in the ligand) can be assigned to the δ(COO) deformation vibration of the acetate anion. The difference between the ν_{as} and ν_s of the acetate (~150–160 cm^{-1}) suggests that the acetate groups are coordinating in a monodentate fashion to the metal centers, although bridging or chelating modes cannot be ruled out without structural data.

Notably, in the far-IR region, new bands attributable to metal–ligand bonds are observed in the complex spectra. Weak bands in the 450–500 cm^{-1} range can be assigned to the M–N stretching vibrations, confirming that the metal is bonded to the triazole ring via a nitrogen donor. For instance, the Cu(II) complex shows a band near 470 cm^{-1} that is absent in the free ligand. In some complexes, a band around ~350–400 cm^{-1} may also appear, which could be attributed to M–O bonds (where the metal is bound to the oxygen of an acetate group in a unidentate coordination). The presence of these new low-frequency bands (M–N and M–O) substantiates the coordination of 5-methyl-1,2,4-triazole to the metal centers and involvement of acetate oxygen in the coordination sphere. Taken together, the IR spectral changes indicate that in all complexes the triazole ligand acts as a neutral monodentate ligand, binding through one of its ring nitrogens (most likely the N4 position, which is the ring nitrogen not bearing a hydrogen). The original N1–H of the triazole is not directly coordinated (as it remains present, though slightly shifted), suggesting the ligand coordinates in a **N(ring)** fashion without deprotonation.

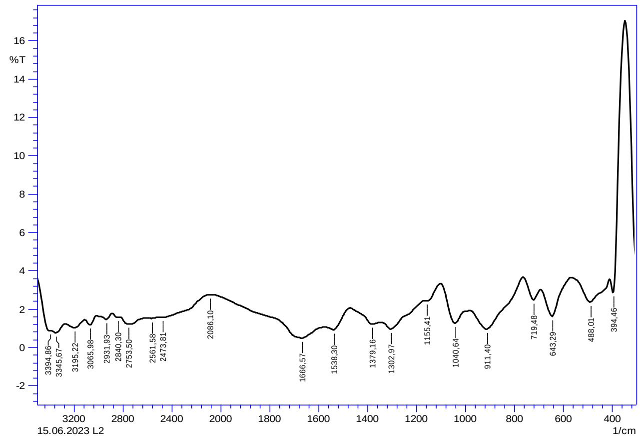


Figure 2. IR Spectrum of N-(1H-1,2,4-triazol-yl) acetamide

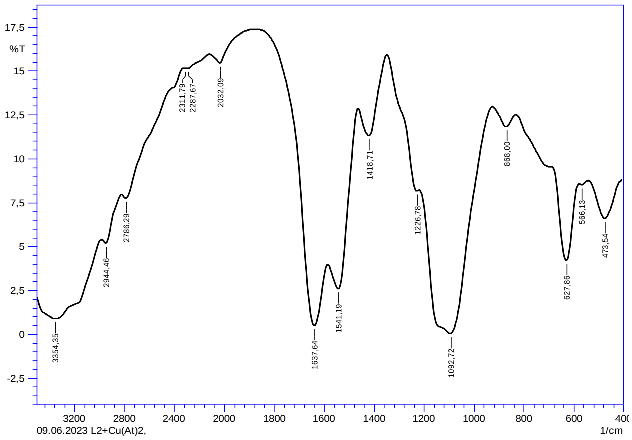


Figure 3. IR Spectrum of the Complex Compound $[CuL_2(CH_3COO)_2]$

To complement the spectroscopic analysis, thermal analysis was carried out to study the stability and decomposition behavior of the ligand and its complexes. Thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained for the free 5-methyl-1,2,4-triazole (L) and for each complex over the temperature range from room temperature up to 800–1000°C in air atmosphere (heating rate 10°C/min). The thermal analysis provides information on the presence of any solvent/water in the complexes, the sequence of decomposition events, and the thermal stability order of the compounds.

For the free 5-methyl-1,2,4-triazole ligand, the TG/DTA curves (Figure 4) showed that the compound has a relatively low melting point and boiling point, consistent with its small molecular size. An initial endothermic event was observed around 45–50°C on the DTA curve, corresponding to the melting of the crystalline triazole (in agreement with the measured m.p. of 46°C). No significant mass loss accompanied this melting, indicating the ligand is thermally stable as a solid up to its melting point. Upon further heating, a major mass loss step occurred between approximately 150°C and 220°C, accounting for essentially 100% of the sample's mass. This indicates that the ligand either volatilizes (sublimes/boils) or decomposes in this temperature range. Given the known boiling point of 5-methyl-1,2,4-triazole (≈233 C), it is likely that the compound evaporates upon heating, possibly with simultaneous decomposition. The DTA registered a broad endothermic process over this range, consistent with vaporization. By 250°C, no solid residue remained, and no further thermal events were observed up to 400°C, confirming that 5-methyl-1,2,4-triazole leaves no char or solid residue upon heating (it is fully volatilized or decomposed to gaseous products such as N_2, H_2O, etc.). This behavior (complete volatilization) is typical for low-molecular-weight, nitrogen-rich heterocycles.

In contrast, the coordination complexes exhibit much greater thermal stability, decomposing in multiple stages at higher temperatures (Figure 5). The Co(II), Ni(II), and Cu(II) acetate complexes of L show no weight loss up to about 100°C, indicating the absence of any unbound solvent or water in their lattice (i.e., they are anhydrous, as formulated). The first noticeable mass loss for each complex occurs in the 150–250°C range, which could correspond to the partial decomposition of the acetate ligands or the beginning of ligand degradation. For instance, a small endothermic peak around 180°C (with 5–8% mass loss) can be attributed to the loss of acetic acid or acetone (from acetate decomposition), or possibly the release of one triazole ligand if it is more loosely bound. The major decomposition step for all complexes occurs at higher temperatures, between roughly 300°C and 600°C, and is exothermic in nature (indicating oxidative degradation of the organic components). This step corresponds to the breakdown of the remaining organic ligands (triazole and acetate) and the formation of metal oxide residues. The copper complex, $[CuL_2(CH_3COO)_2]$, in particular, displays a prominent mass loss of about 44–46% centered around ~680°C. This significant mass loss is attributable to the final combustion of organic matter and the conversion of Cu(II) to copper(II) oxide (CuO). The residual mass observed at the end of the TGA run for the Cu complex (~23% of the original mass) is in good agreement with the theoretical yield of CuO expected from the complete decomposition of $[Cu(C_3H_5N_3)_2(C_2H_3O_2)_2]$. Similarly, the Co and Ni complexes leave behind final residues (CoO and NiO, respectively) whose masses correspond to the oxide products. The derivatograms (TG/DTG curves) for the complexes often show two to three distinct steps, reflecting the sequential loss of two L molecules and two acetate groups in overlapping stages. Above 700–800°C, no further mass change is observed, indicating that decomposition is complete and the metal oxides are the stable final products.

It is noteworthy that the decomposition onset temperatures follow the order Cu>Ni>Co, suggesting that the Cu(II) complex is thermally the most robust, while the Co(II) complex starts to decompose at slightly lower temperature. Such an order could be related to differences in bond strength or lattice energy: Cu(II) often forms slightly stronger bonds in this context (perhaps due to a Jahn–Teller distorted octahedral environment that stabilizes the complex), whereas Co(II) (a high-spin d^7 system) may form somewhat weaker bonds with the ligand. Overall, the thermal analysis confirms that these complexes are significantly more thermally stable than the free triazole ligand (which volatilizes below 250°C), and they decompose in a multi-step manner characteristic of coordinated organic ligands. The final formation of metal oxides aligns with expectations for metal–organic complexes heated in air.

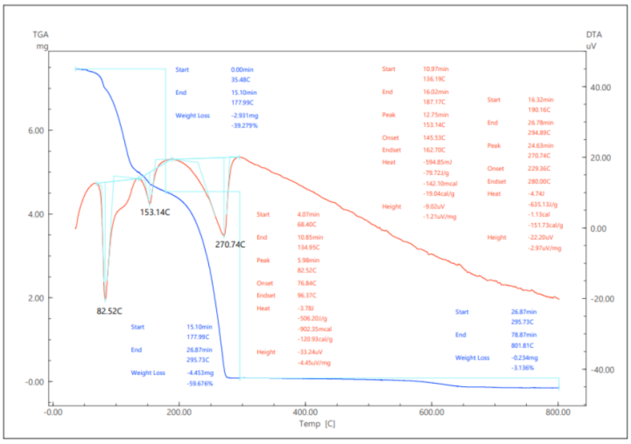


Figure 4. Thermogram of N-(1H-1,2,4-triazol-yl) acetamide

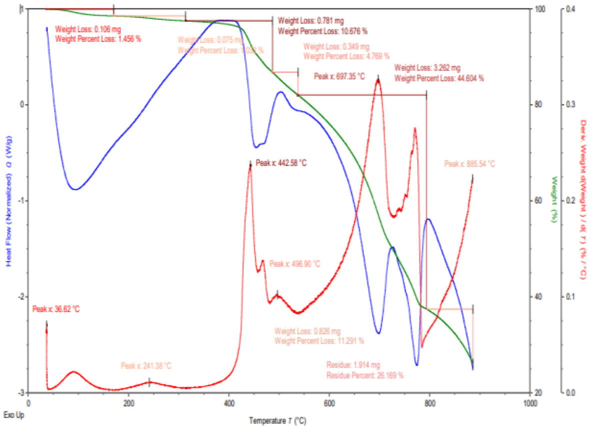
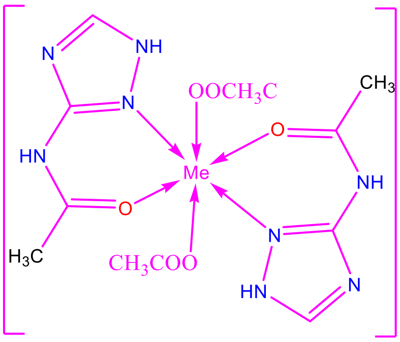


Figure 5. Thermogram of the $[CuL_2(CH_3COO)_2]$ complex compound

CONCLUSION

A series of new coordination complexes of Co(II), Ni(II), and Cu(II) with 5-methyl-1,2,4-triazole has been synthesized successfully, and their structure and properties have been elucidated. A convenient solution-based method was developed to obtain the complexes in good yield and purity, and the resulting compounds are stable, water-soluble solids. Based on the results of elemental analysis (SEM–EDS), IR spectroscopy, and thermal analysis, it is established that in these complexes the metal ion coordinates with the triazole ligand through a ring nitrogen atom (presumably the N4 position of the triazole ring). The neutral ligand L is bound in a monodentate fashion, and the overall composition of the complexes corresponds to the empirical formulas $[ML_2(CH_3COO)_2]$ (M = Co, Ni, Cu). These formulas and the accompanying physicochemical data suggest an octahedral coordination environment around each metal center, where two triazole ligands and two bidentate acetate groups satisfy the coordination sphere (though polymeric structures via bridging acetate or triazole are possible). The combination of IR shifts and the appearance of new M–N bands confirms the metal–ligand binding via triazole nitrogen, while thermal gravimetry confirms the presence of strongly bound acetates and the production of metal oxides upon decomposition.

The synthesized coordination compounds demonstrate predictable bonding modes and appreciable thermal stability relative to the free organic ligand. Their good solubility in polar solvents points to potential processability in solution. Structural elucidation through the applied physicochemical techniques has provided a consistent picture: the metal ions are coordinated by triazole nitrogen donors and acetate oxygens, leading to stable chelated structures. These findings enrich our understanding of simple 1,2,4-triazole-based ligands in coordination chemistry and could inform the design of related complexes for practical applications. By comparing this 5-methyl-substituted triazole ligand to other functionalized triazoles, we contribute valuable data on how small substituents affect coordination and stability. Future work may include crystallographic analysis of these complexes to confirm the proposed structures and exploring their reactivity or biological activity given the known importance of triazole compounds.



Here: M is replaced by Co(II), Ni(II), and Cu(II).

REFERENCES

1. Romain Noel, Xinyi Song, Rong Jiang, Michael J. Chalmers, Patrick R. Griffin, and Theodore M. Kamenecka. Efficient Methodology for the Synthesis of 3-amino-1,2,4–triazoles. // J.Org.Chem. 2009,74,19,7595-7597.
2. Иванова Ю.С., Цаплин Г.В., Попков С.В. Метод получения N^1-замещенных – 4–(1,2,4–триазол–1–илметил)–1,2,3–триазолов и изучение их фунгицидной активности. // Успехи в химии и химической технологии. Том XXXIV.2020. №8.
3. Khadir A., Verreault J., Averill DA., Inhibition of antioxidants and hyperthermia enhance bleomycin – induced cytotoxicity and lipid peroxidation in Chinese hamster ovary cells. // Arch Biochem Biophys., 1999 Oct; 370(2):163-75.
4. MacCabe AP, Miro P, Ventura L, Ramon D. Glucose uptake in germinating Aspergillus nidulans conidia: involvement of the creA and sorA genes. // Microbiology 149:2129-2136.
5. Fauchere JL, Boutin JA. Исследования субстратной специфичности и ингибирования серотонин-N-ацетилтрансферазы человека. // J. Biol. Chem. 2000. 275 (12): 8794–805.
6. Lowe RF, Nelson J, Dang TN, Crowe PD, Paxuja A, McCarthy JR, Grigoriadis DE, Conlon P, Saunders J, Chen C, Szabo T, Chen TK, Bozigian. Rational design, synthesis, and structure–activity relationships of aryltriazoles as novel corticotropin-releasing factor-1 receptor antagonists. // HJ Med. Kimyo 2005; 48: 1540–1549. [PubMed: 15743196].
7. Marino JP, Fisher PW, Hofmann GA, Kirkpatrick RB, Janson CA, Jonson RK, Ma C, Mattern M, Meek TD, Rayan MD, Schulz C, Smit WW, Tew DG, Tomazek TA, Veber DF, Xiong WC, Yamamoto Y , Yamashita K, Yang G, Tompson SK. Highly potent inhibitors of methionine aminopeptidase-2 based on a 1,2,4- triazole pharmacophore. // J. Med. Kimyo 2007;50:3777–3785. [PubMed: 17636946].
8. А. В. Васильев, Е. В. Гриненко, А. О. Щукин, Т. Г. Федулина Инфракрасная спектроскопия органических и природных соединений. Санкт-Петербург 2007. Ст-16.
9. Шаталова Т.Б., Шляхтин О.А., Веряева Е. Методы термического анализа. - Москва: 2011