NaSTech
JOURNAL OF NATURAL SCIENCES AND TECHNOLOGIES
2022, 1(1), pp. 143-150, DOI: 10.5281/zenodo.7384181

SYNTHESIS OF PYRIDINE DERIVATIVE POLYMERIC COPPER COMPLEX WITH METAL-AZID BONDS

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ABSTRACT

In this study, pyridine-derived polymeric copper (II) complexes containing metal azide bonds were prepared. The characterization of the complexes given with the general formula, $[Cu(L)_2(N_3)_2Cl_2]n$ (L1: 3,5-dimethyl pyridine, L2: 3,4-dimethyl pyridine, L3: 2-amino-3-methyl pyridine, L4: 2,6-diamino pyridine) was performed by FT-IR, AAS and magnetic susceptibility analyzes. The intense peak observed at 2045-2167 cm-1 in the spectra corresponds to the asymmetric azide vibrations, $\upsilon as(N_3^-)$, which indicates that polymeric copper complexes are formed over azide bonds. Cu2+ amounts in the complexes were found in the range of 26.25%-33.61% from the AAS results. The thermal properties of polymeric copper complexes were investigated with the TG/DTA combined system. Unpaired electron numbers for copper complexes were found in the range of 0.89-1.45. Copper complexes are paramagnetic, and the number of unpaired electrons being different from the expected (n=1) value indicates that the geometry of the complex is distorted.

Keywords: Polymeric metal complexes, pyridine complexes, azide compounds.

1. INTRODUCTION

Metal coordination polymers (CPs) and their complexes are of interest to researchers due to their interesting structural properties. CPs are also defined as hybrid materials with metal ion-based, organic binders that bind vertices into 1D, 2D or 3D periodic configurations [1]. These materials have many properties such as luminescence [2] magnetism [3], nonlinear optics [4] and electrical conductivity [5]. Metal azide complexes have been used extensively recently for the development of new coordination polymers. Because azido ligand (N3-) is linear coordination linker. However, some forms of bi-cognate coordination are also possible [6]. Some of these can form porous metal-organic chains that can adsorb small molecules [7]. However, the chemical reactivity of a metal complex with a monodentate azido ligand was also studied. Such azido metal complexes give a [3 + 2] cycloaddition reaction with organic nitriles, isocyanides, isothiocyanides and alkynes and form complexes with a tetrazole or triazole-containing ligand [8]. Some other interesting reactivities of azido metal complexes have been reported in the literature [9]. On the other hand, the azide ion N3- can link two metal centers with end-to-end (EO) or end-to-end (EE) ends, yielding binuclear or multinuclear complexes [10]. Multinuclear metal azide complexes can be formed by the azide ligand binding two or more metal centers [11]. This versatility of azide ligands explains the spectral and magnetic properties of metal azido complexes and the diversity of their stereochemistry [10]. Recently, polymeric 1D cobalt(II) polymeric complexes of pyridine derivative ligands containing a single azide bond have been synthesized and their structures elucidated [12]. In addition, $[Cu(py)_3(N_3)](PF_6)$ polymeric complex containing three pyridine molecules was prepared. In addition, $[Cu(4\text{-ethylpyridine})(N_3)_2]_2$ polymeric complex was prepared and its structure was elucidated by spectroscopic, magnetic and crystallographic methods [13]. Azido metal complexes are thermally and photochemically reactive and can form some reactive intermediates [14]. Basolo et al. found that photolysis of the $[Ir(NH_3)_5(N_3)]^{2+}$ complex yielded N_2 with the higher reactivity $[Ir(NH_3)_5(NH)]^{3+}$ intermediate [15]. Higher reactivity nitrido complexes can be obtained by photolysis of azido complexes with tetradentate or five-dentate chelating ligands and azido complexes [16]. In addition, photolysis of the $[Cp^*Ir(PR_3)(N_3)_2]$ (Cp*=nu5-pentamethylcyclopentadienyl) complex results in the reductive cleavage of the azido ligand, resulting in the coordination-rich intermediate $Cp^*Ir(PR_3)$. The versatile behavior of the azido groups and the tendency of the cross-plane copper(II) complexes to coordinate two additional ligands at the apical position result in the formation of solid-state network structure. Whereas, most copper(II) compounds containing azido ligands in µ1,1-, and µ1,3- bridge modes have been frequently studied [17], examples of metal ions bound with azido groups in other coordination modes are scarce [18].

Bu çalışmada, metal azid bağı içeren piridin türevli polimerik bakır (II) kompleksleri hazırlandı. $[Cu(L)_2(N_3)_2Cl_2]_n$ (L1: 3,5-dimetil piridin, L2: 3,4-dimetil piridin, L3: 2-amino-3-metil piridin, L4: 2,6-diamino piridin) genel formülü ile verilen komplekslerin karakterizasyonu FT-IR, AAS ve manyetik susseptibilite analizleriyle gerçekleştirildi. In addition, the thermal properties of the synthesized polymeric copper complexes were investigated with the TG/DTA combined system.

2. MATERIAL AND METHOD

The chemicals used for the synthesis were purchased commercially and used without further purification. 3,5-dimethyl pyridine, 3,4-dimethyl pyridine, 2-amino-3-methyl pyridine, 2,6-diamino pyridine, CuCl2.2H2O and NaN3 were obtained from Sigma-Aldrich.

FT-IR (PerkinElmer FRONTIER Model FT-IR (Mid-Far) Spectrometer) was used to elucidate the structures of the synthesized compounds. In addition, the magnetic properties of the complexes were carried out using Gouy balance, and thermal analysis studies were carried out using the Shimadzu TG-60 model combined DAT/TG system.

2.1. Synthesis of polymeric copper(II) complexes

Compounds were synthesized according to the method described in the literature [41]. 0.01 mol of CuCl2.2H2O was dissolved in 20 mL of ethyl alcohol and then a solution of NaN3 (0.02 mol) in 3 mL of water was added and heated in a magnetic stirrer for 30 minutes. To this solution, pyridine derivatives (3,5-dimethyl pyridine, 3,4-dimethyl pyridine, 2-amino-3-methyl pyridine, 2,6-diamino pyridine) (0.02 mol) were added and reacted for 1.5 hours under reflux. . The precipitate formed was filtered and dried in an oven. The general formula of the synthesized complexes is given in Figure 1.

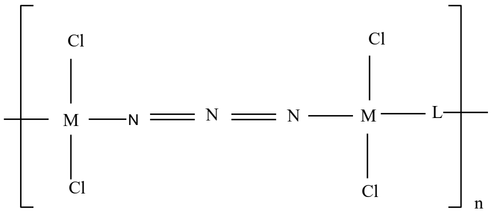

Figure 1. General formula of pyridine-derived polymeric copper (II) complexes containing metal azide bonds

3. RESULTS AND DISCUSSION

3.1. FT-IR studies

FT-IR spectrophotometer was used for structural characterization studies and important IR peaks are given in Table 1. Severe peak asymmetric azide vibrations observed at 2045-2167 cm-1 in the spectra, $\upsilon_{as}(N_3^-)$. The IR peaks observed at 1600-1657 cm^{-1} correspond to the vibrations of the C-N bond, υ(C=N). The peak observed at 455-483 cm^{-1} belongs to copper-nitrogen stretching vibrations (Cu-N), while 619-688 peaks belong to Cu-Cl vibrations. FT-IR results show that the proposed polymeric complex structures are formed.

Tablo 1. The selected important FT-IR peaks

Bileşik	**$\upsilon_{as}(N_3^-)$ (cm^{-1})**	**υ(C=N) (cm^{-1})**	**υ(M-N) (cm^{-1})**	**υ(M-Cl) (cm^{-1})**
$[Cu(L^1)_2(N_3)_2Cl_2]_n$	2081	1601	463	660, 688
$[Cu(L^2)_2(N_3)_2Cl_2]_n$	2047	1615	463	665, 680

$[Cu(L^3)_2(N_3)_2Cl_2]_n$	2046	1607	455	655, 683
$[Cu(L^4)_2(N_3)_2Cl_2]_n$	2059	1616	456	-

3.2. Atomic Absorption (AAS) Studies

Atomic absorption method was used for the determination of metal amounts in complex compounds and the results are given in Table 2. As a result of the AAS studies of the complex compounds, the metal amounts and % compositions in the compounds were calculated. Metal amounts were found in the range of 26.25%-33.61%.

Tablo 2. AAS results

Complexes	**Cu^{2+} Amount (g)**	**Cu^{2+} Amount (%)**
$[Cu(L^1)_2(N_3)_2Cl_2]_n$	$7{,}71.10^{-3}$ g Cu^{2+}	31.74
$[Cu(L^2)_2(N_3)_2Cl_2]_n$	$8{,}394.10^{-3}$ g Cu^{2+}	26.25
$[Cu(L^3)_2(N_3)_2Cl_2]_n$	$9{,}052.10^{-3}$ g Cu^{2+}	28.91
$[Cu(L^4)_2(N_3)_2Cl_2]_n$	0,01042 g Cu^{2+}	33.61

3.3. Magnetic Susceptibility Studies

Magnetic susceptibility measurements are used to elucidate the structure of coordination compounds, and to determine the stereochemistry of the metal atom, the bond type, and the oxidation step. Magnetic susceptibility measurements of the synthesized polymeric complexes were made, μ (B.M.) values and unpaired electron numbers (n) were calculated. Unpaired electron numbers for copper complexes were found in the range of 0.89-1.45. Copper complexes are paramagnetic, and the number of unpaired electrons being different from the expected (n=1) value indicates that the geometry of the complex is distorted. In addition, the deviation from the expected value also proves the existence of polymeric complexes. The μ (B.M.) values and unpaired electron numbers (n) of the synthesized polymeric complexes are given in Table 3.

Tablo 3. Magnetic susceptibility results

Complexes	**μ (B.M.)**	**n**
$[Cu(L^1)_2(N_3)_2Cl_2]_n$	2.0533	1.28
$[Cu(L^2)_2(N_3)_2Cl_2]_n$	2.0764	1.30
$[Cu(L^3)_2(N_3)_2Cl_2]_n$	2.2387	1.45
$[Cu(L^4)_2(N_3)_2Cl_2]_n$	1.5969	0.89

3.4. Thermal Analysis Studies

Thermal analysis studies of the synthesized polymeric copper complex were carried out at a temperature range of 25-1000 oC and under nitrogen atmosphere. The heating rate was set as 10 oC/minute and the amount of substance in the range of 5-10 mg was studied. 10 mg of α-Al2O3 was used as reference material. It has been observed that complex compounds are stable up to about 200 °C and above this temperature they decompose very rapidly with great mass loss. The DTA peak positions of the decomposition reactions, the temperature ranges in which the decomposition is observed, the experimental mass losses and the leaving groups are given in Table.4.

Tablo 4. DTA peak positions, decomposition temperature ranges, experimental mass losses, and leaving groups

Complexes	**Decomposition step**	**DTA Peak/°C**	**TG temperature range/°C**	**Experimental mass loss/%**	**Leaving groups**
$[Cu(L^1)_2(N_3)_2Cl_2]_n$	I	212	100-221	84.52	Azide 3,5-dimethylpyridine
	II	-	221-492	10.209	
	Residue	-	492-1000	-	-
$[Cu(L^2)_2(N_3)_2Cl_2]_n$	I	220	100-226	52.61	Azide 3,4-dimethylpyridine
	II	-	226-326	8.50	
	III	-	326-1000	31.25	
	Residue	-	1000	7.64	Polymeric $CuCl_2$
$[Cu(L^3)_2(N_3)_2Cl_2]_n$	I	154	50-172	94.19	Azide 2-amino-3-methyl pyridine
	II	-	172-556	5.81	
	Residue	-	556-1000	-	-
$[Cu(L^4)_2(N_3)_2Cl_2]_n$	I	180	32-211	9.19	H_2O Azide 2,6-diamino pyridine
	II	369	211-455	44.89	
	III	-	455-620	18.67	
	IV	-	620-1000	11.56	
	Residue	-	1000	15.69	Polymeric $CuCl_2$

The TG/DTA curves of the $[Cu(L^1)_2(N_3)_2Cl_2]_n$ complex are given in Figure 2. It was determined from the TG curve that the compound decomposed in two steps. The mass loss of the first step is 84.52%. In this step, azide and 3,5-dimethylpyridine ligands are separated from the complex compound and pass into the gas phase. The remaining product is estimated as $CuCl_2$. $CuCl_2$ salt begins to sublime at temperatures above 350 °C [19].

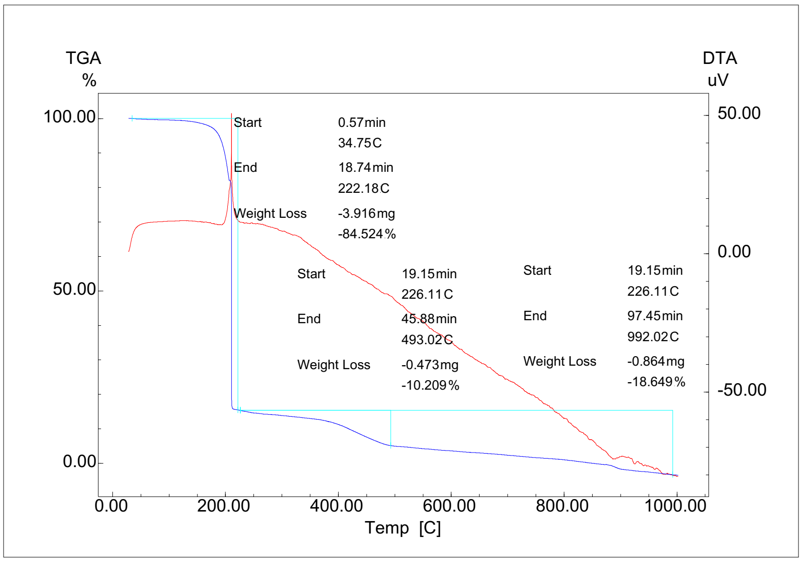

Figure 2. TG/DTA curves of $[Cu(L^1)_2(N_3)_2Cl_2]_n$ complex

The TG/DTA curves of the $[Cu(L^2)_2(N_3)_2Cl_2]_n$ complex are given in Figure 3. It has been determined from the TG curve that the compound decomposes in three steps. The mass loss of the first step is 52.61%, the mass loss observed in the second decomposition step is 8.5% and the third step is 31.25%. The % mass of the product remaining as a result of the decomposition reactions was determined as 7.64. In the first three steps, azide ligands and 3,4-dimethylpyridine ligands are separated from the complex and pass into the gas phase. It is speculated that the remaining product may be $CuCl_2$, which may be polymerized in itself with chloride ligands.

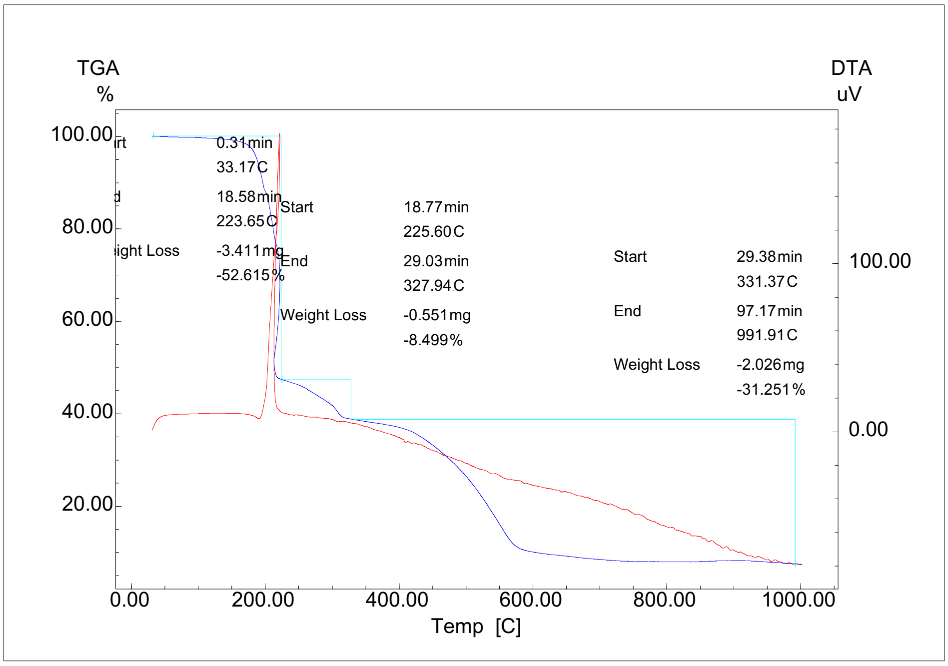

Figure 3. TG/DTA curves of $[Cu(L^2)_2(N_3)_2Cl_2]_n$ complex

The TG/DTA curves of the $[Cu(L^3)_2(N_3)_2Cl_2]_n$ complex are given in Figure 4. It was determined from the TG curve that the compound decomposed in two steps. The mass loss of the first step is 94.19%. In this step, azide and 2-amino-3-methyl pyridine are leaved from the complex and turn into the gas phase. The remaining product is estimated as $CuCl_2$.

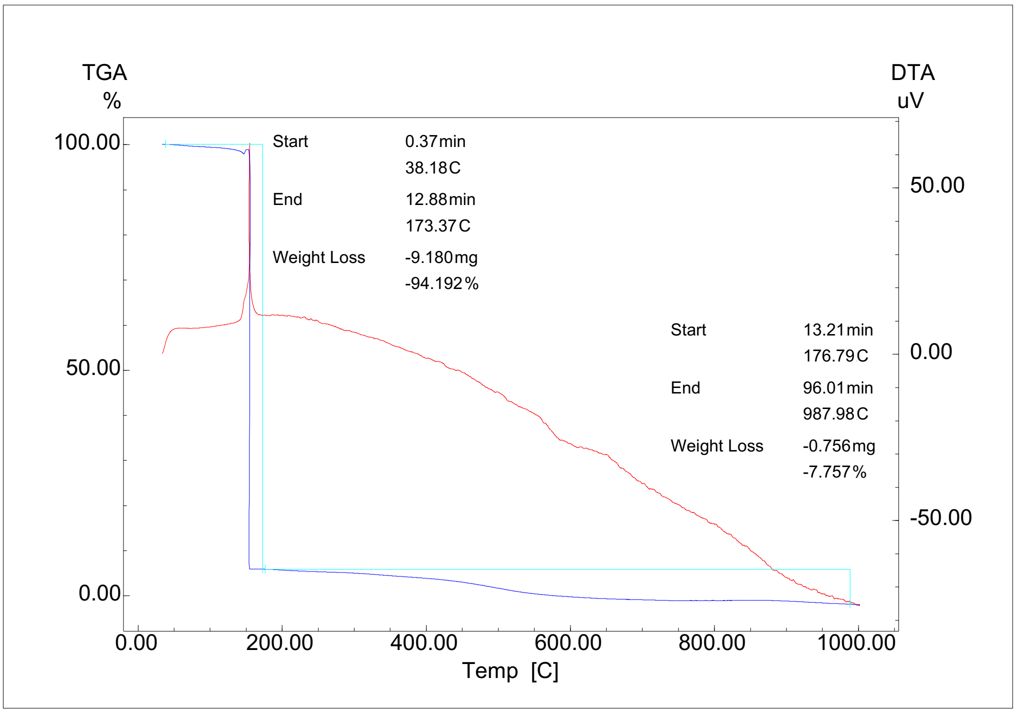

Figure 4. TG/DTA curves of $[Cu(L^3)_2(N_3)_2Cl_2]_n$ complex

The TG/DTA curves of the $[Cu(L^4)_2(N_3)_2Cl_2]_n$ complex are given in Figure 5. The complex decomposed in four steps. It is understood that the complex compound is hygroscopic and gives the moisture and crystal water in its body with a mass loss of 9.19% at temperatures between 32-211 °C. The second decomposition step takes place between 211-455 °C with a mass loss of 44.89%. Mass losses in the third and fourth steps were found to be 18.67% and 11.56%, respectively. In the decomposition steps, azide and 2,6-diamino pyridine are leaved from the complex as the gas phase. The remaining product is estimated to be polymeric $CuCl_2$ (15.69% by mass).

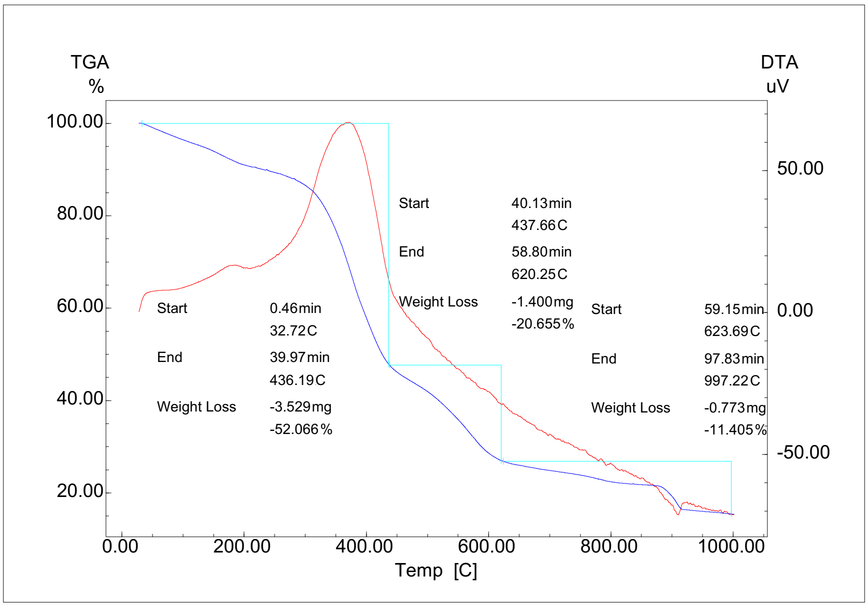

Figure 5. TG/DTA curves of $[Cu(L^4)_2(N_3)_2Cl_2]_n$ complex

4. CONCLUSION

In present study, pyridine-derived polymeric copper (II) complexes containing metal azide bonds were prepared and characterized via FT-IR, AAS and magnetic susceptibility techniques. FT-IR spectra of $[Cu(L)_2(N_3)_2Cl_2]n$ (L1: 3,5-dimethyl pyridine, L2: 3,4-dimethyl pyridine, L3: 2-amino-3-methyl pyridine, L4: 2,6-diamino pyridine) complexes showed intense peaks observed at 2045-2167 cm^{-1} attributed to the asymmetric azide vibrations, υ_{as} (N_3^-), which indicates that polymeric copper complexes are formed over azide bonds. Copper complexes are paramagnetic, and the number of unpaired electrons being different from the expected (n=1) value Unpaired electron numbers for copper complexes were found in the range of 0.89-1.45 which were different from the expected (n=1) value. These indicate that the complexes geometry is distorted tetrahdral. The findings obtained in this study indicate that polynuclear polymeric pyridine-derived copper chloride complexes can be obtained via azide bonds. These complexes may have magnetism, nonlinear optics and electrical conductivity properties and have the potential to be used in these fields.

REFERENCES

[1] Amo-Ochoa. P., Zamora, F. Coordination polymers with nucleobases: From structural aspects to potential applications. Coordination Chemistry Reviews 2014. 276. pp. 34–58.

[2] Cui, Y., Yue, Y., Qian, G., Chen, B. Luminescent Functional Metal–Organic Frameworks. Chemical Reviews. 2012. 112. pp. 1126–1162.

[3] Kurmoo, M. Magnetic metal–organic frameworks. Chemcal Society Reviews. 2009. 38. Pp. 1353–1379.

[4] Wang, C., Zhang, T., Lin, W., Rational Synthesis of Noncentrosymmetric Metal–Organic Frameworks for Second-Order Nonlinear Optics. Chemical Reviews. 2011. 112. pp. 1084–1104.

[5] Givaja, G., Amo-Ochoa, P., Gómez-García, C.J., Zamora, F. Electrical conductive coordination polymers. Chemical Society Reviews. 2011. 41. pp. 115–147.

[6] Yang, Q., Zhao, J. P., Hu, B. W., Zhang, X. F., Bu, X. H. New Manganese (II) azido coordination polymers with nicotinic/isonicotinic acids as coligands: Synthesis, structure, and magnetic properties. Inorganic Chemistry. 2010. 49(8). pp. 3746-3751.

[7] Yu, Q., Zeng, Y. F., Zhao, J. P., Yang, Q., Hu, B. W., Chang, Z., Bu, X. H. Three-dimensional porous metal−organic frameworks exhibiting metamagnetic behaviors: synthesis, structure, adsorption, and magnetic properties. Inorganic Chemistry. 2010. 49(9). pp. 4301-4306.

[8] Mukhopadhyay, S., Mukhopadhyay, B. G., Silva, M. F. C. G. D., Lasri, J., Charmier, M. A. J., Pombeiro, A. J. PtII-promoted [2+ 3] cycloaddition of azide to cyanopyridines: convenient tool toward heterometallic structures. Inorganic Chemistry. 2008. 47(23). pp. 11334-11341.

[9] Nagao, H., Kikuchi, T., Inukai, M., Ueda, A., Oi, T., Suzuki, N., Yamasaki, M. Formation of a Methyleneimine Moiety by Reaction of a RuII-Coordinated Azide Ion with Methyl Iodide. Angewandte Chemie International Edition. 2006. 45(19). pp. 3131-3133.

[10] Goher, M. A. S., Escuer, A., Mautner, F. A., Al-Salem, N. A. Synthesis, spectral, magnetic and crystal structural characterization of two new copper (II) azido complexes: catena-[μ (N3) Cu (pyridine) 3] n (PF6) n and dimeric [Cu (4-ethylpyridine)(N3) 2] 2. Polyhedron. 2001. 20(24-25). pp. 2971-2977.

[11] Peisach, J., Blumberg, W. E. Structural implications derived from the analysis of electron paramagnetic resonance spectra of natural and artificial copper proteins. Archives of Biochemistry and Biophysics. 1974. 165(2). pp. 691-708.

[12] Goher, M. A., Mautner, F. A. Synthesis and characterization of a new series of 1D cobalt (II) complexes of pyridine derivative ligands with a single azido bridge and X-ray crystal structure of catena-(μ-N3)[Co (4-methylpyridine) 4](PF6). Polyhedron. 1999. 18(18). pp. 2339-2344.

[13] Goher, M. A. S., Escuer, A., Mautner, F. A., Al-Salem, N. A. Synthesis, spectral, magnetic and crystal structural characterization of two new copper (II) azido complexes: catena-[μ (N3) Cu (pyridine) 3] n (PF6) n and dimeric [Cu (4-ethylpyridine)(N3) 2] 2. Polyhedron. 2001. 20(24-25). pp. 2971-2977.

[14] Šima, J. Photochemistry of azide-moiety containing inorganic compounds. Coordination chemistry reviews. 2006. 250(17-18). pp. 2325-2334.

[15] Gafney, H. D., Reed, J. L., Basolo, F. Photochemical reaction of the azidopentaammineiridium (III) ion. Coordinated nitrene intermediate. Journal of the American Chemical Society. 1973. 95(24). pp. 7998-8005.

[16] Du Bois, J., Tomooka, C. S., Hong, J., Carreira, E. M. Nitridomanganese (V) complexes: Design, preparation, and use as nitrogen atom-transfer reagents. Accounts of Chemical Research. 1997. 30(9). pp. 364-372.

[17] Mukherjee, P. S., Maji, T. K., Escuer, A., Vicente, R., Ribas, J., Rosair, G., Mautner, F.A., Chaudhuri, N. R. Three Novel End-to-End Single Azido-Bridged Ferromagnetic Copper (II) Chains: Synthesis, Crystal Structure, and Magnetic Behavior. European Journal of Inorganic Chemistry. 2002. 4. pp. 943-949.

[18] Zhang, L., Tang, L. F., Wang, Z. H., Du, M., Julve, M., Lloret, F., Wang, J. T. Ferromagnetic coupling in a one-dimensional molecular railroad copper (II) azido compound containing a defective double cubane motif. Inorganic Chemistry. 2001. 40(14). pp. 3619-3622.

[19] Wehrmeier, A., Lenoir, D., Sidhu, S. S., Taylor, P. H., Rubey, W. A., Kettrup, A., Dellinger, B. Role of copper species in chlorination and condensation reactions of acetylene. Environmental Science & Technology. 1998. 32(18). pp. 2741-2748.