# MICROWAVE-ASSISTED SYNTHESIS OF A NOVEL LIGAND DERIVED FROM OXALIC ACID AND *M*-DIAMINE PHENYL AND ITS COMPLEXATION WITH SOME TRANSITION METALS

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***Abstract:*** *A novel macrocyclic ligand, 2,5,7,10-tetraaza-1,6(1,3)-dibenzenacyclodecaphane-3,4,8,9-tetraone (TF), was synthesized via solid-state microwave-assisted condensation of oxalic acid with* m-*phenylenediamine. Upon reaction with selected divalent transition metal ions, the ligand formed stable coordination complexes of the general formula* $[M(TF)_2Cl_2]$**,** *where M = Cu, Co, or Zn. The structures of the ligand and its complexes were comprehensively characterized by infrared (IR) and electronic (UV-Vis) spectroscopy,* $^1H$ *and* $^{13}C$ *NMR spectroscopy***,** *molar conductance measurements***,** *metal content analysis***,** *and magnetic susceptibility measurements***.** *Spectral and magnetic data support the formation of octahedral coordination geometries around the central metal ions in all synthesized complexes, with the TF ligand acting as a tetradentate donor.*
***Keywords:*** ***o****xalic acid, transition metalы (II), microwave irradiation, green macromolecules.*

## 1. Introduction

Green synthetic approaches to the preparation of various types of inorganic materials offer safer and more environmentally benign alternatives, particularly in terms of biocompatibility and reduced toxicity to living organisms [1-3]. To elucidate the coordination behavior of ligands within metal chelate structures, a combination of analytical techniques—elemental analysis**,** magnetic susceptibility measurements**,** conductometric studies**,** and various spectroscopic methods—can be employed. These methods provide comprehensive insights into the electronic structure, geometry, and bonding characteristics of the resulting metal complexes [4]. More than the efficient and friendly procedure for the synthesis, the reaction was conducted effortlessly in water, which is an economical, straightforward, sustainable, and non-harmful solvent at room temperature without the use of heating, microwaves, or ultrasound devices. Nearly all xylene-type hemicelluloses have hydrolyzed into C5 sugars after being liberated from the cell wall, as indicated. Enzymatic hydrolysis resulted in the conversion to 90% of the cellulose in the residual bagasse by enzymatic hydrolysis after pretreatment [5]. Among the commercial sugars that can be made from bagasse are d-glucose, d-xylose and l-arabinose [6-8].

The dynamics of vapor sorption, the mechanistic role of relative humidity (RH) at the model hemic material (salicylic acid)–urea interface, and associated surface reactions were investigated through *ab initio* thermodynamic calculations and Raman spectroscopy. Further studies are required to elucidate the influence of stabilizing structural features and the properties of urea-derived reaction products on organic moieties, in order to fully comprehend their implications for the global nitrogen cycle [9, 10]. Compared to unmodified urea, urea inclusion compounds (ICs) exhibited enhanced resistance to deliquescence, as indicated by an increase in their critical relative humidity [11]. In this work, we have synthesized novel types of complexes containing various donor atoms using a microwave-assisted approach.

## 2. Experimental part

**2.1. Materials.** BDH and Fluka companies provided all the chemicals needed for the experiment. We're using a FT.IR (Sh. Japan 400-4000 $cm^{-1}$). A model (Eu. Vactor. E A 3000) was utilized for CHN analysis. Elements of the ligand and its complexes are analyzed using the model (PY. UN-SP9). Conductivity use (M.M PI-700PC-Gondo-TAIWAN) and UV were recorded on (Sh-UV–1900), and magnetic susceptibility was measured (1H NMR, 13C NMR) at 25°C by (400 Mz (USA)) and (Va-In 500 Mz (USA)). The 9300 engineering is used for melting points, using a microwave oven-type (MO-R EM 820).

**2.2. Synthesis of TF.** The ligand (TF) synthesis was performed by the equation below, represented in Fig. 1. A solid oxalic acid (0.180 gm) was mixed with 0.60 gm of solid m-phenylenediamine and 0.003 gm of cerium-ammonium nitrate (CAN) as a catalyst. For 60 minutes, the solid mixture was exposed to 900 W of microwave radiation. 20 ml of ethylacetate was added once the liquid had cooled to room temperature, and it was swirled for almost an hour to dissolve the CAN, which was filtered out of the mixture, after being cleaned with ethanol and n-hexane, the gray precipitate was vacuum-dried for a few hours. A list of the physical attributes of prepared ligand may be found in Table 1.

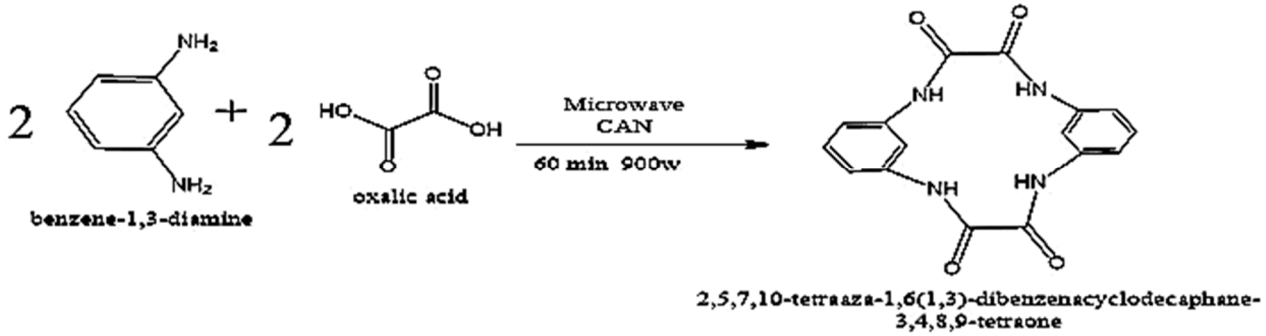



**Fig. 1.** (TF) Ligand preparation scheme

**2.3. Preparation of complexes [Cu $(TF)_2Cl_2$], [$Co(TF)_2Cl_2$], and [$Zn(TF)_2Cl_2$]:** The solution of the ligand (TF) (0.324 gm) in DMF (10 ml) with ethanol and (0.001 mole) of metal chloride [$CuCl_2.6H_2O$ (0.237 gm)]; [$CoCl_2.2H_2O$ (0.176 gm)]; and [$ZnCl_2$ (0.139.3 gm)] was stirred. For 2:15 hours, the mixture was refluxed [12-14].

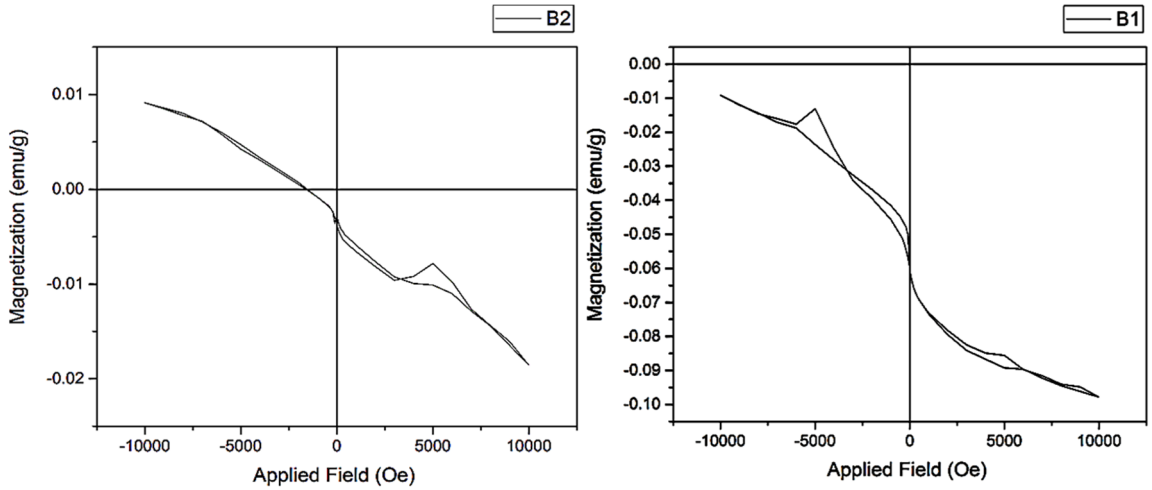



**Fig. 2.** Vibrating sample magnetometer (VSM) for [$Co(SU)Cl_2$] (*B1*), and for [$Cu(SU)_2Cl_2$] (*B2*)

**2.4. Vibrating sample magnetometer (VSM).** In Fig. 2 (B1), the vibrating sample magnetometer (VSM) showed the [$Co(SU)Cl_2$] detected an attribute S-shaped ring with a small zone. The magnetic field is between 0.10 kOe and 0.01 kOe. The saturation magnetization (Ms) was gauged at 3.3 emu $g^{-1}$, and the section field (Hc) and residual magnetization (Mr) showed the cobalt ion in it. After watching Ms values low, the magnetism decreases. But Fig. 2 (B2) showed the [$Cu(SU)_2Cl_2$]

saturation value is lower Ms (0.01 emu $g^{-1}$) The reason for the observed low magnetic copper ion is that it is paramagnetic [15, 16].

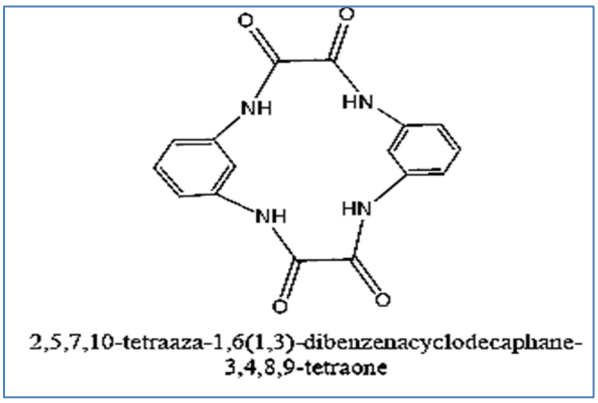
## 3. Results and Discussion

A combination of oxalic acid, m-phenylenediamine, and CAN catalyst was microwave-irradiated to produce a 93% yield of the ligand (TF), which is non-hydroscopic at room temperature and stable in air. The melting point, C.H.N. analyses, and other physical properties of the ligand are listed in Table 1. Physical characteristics of the compounds are reported in Table 1 and include stability, non-hydroscopicity, and high M.P.

TF is characterized by $^{1}$H-NMR and the data from the chemical shift are given in Table 2 and Fig. 4. Table 2 at δ (7.4 ppm) attributable to 2H (H-benzene ring) helped by the integration. For the (NH-benzene ring) group, the band at δ (8.96 ppm) was ascribed to 4H, while δ (7.9 ppm) was 2H (H-benzene ring) [17].

Table 3 and Fig. 5 contain $^{13}$C–NMR chemical shifts (160.1 ppm) for (HN-CO-CO-NH), (130 ppm) for (N-C-benzene ring), (55 ppm) for (149.1 ppm) for (N-C-benzene ring), and carbon for DMSO at (40 ppm) in Table 3, and Fig. 3 assists the structure of the ligand [18].

The complexes (1, 2, and 3) are nonelectrolytes based on the conductivity data (Table 1). TF's infrared spectrum data for (NH) stretching were shown in Table 4 at 3442 $cm^{-1}$, δ(NH) at 1340 $cm^{-1}$, and the frequency at 1741$cm^{-1}$ that was assigned to the δ(CO) band as medium intensity [19].




2,5,7,10-tetraaza-1,6(1,3)-dibenzenacyclodecaphane-3,4,8,9-tetraone

**Fig. 3.** Structure of TF ligand

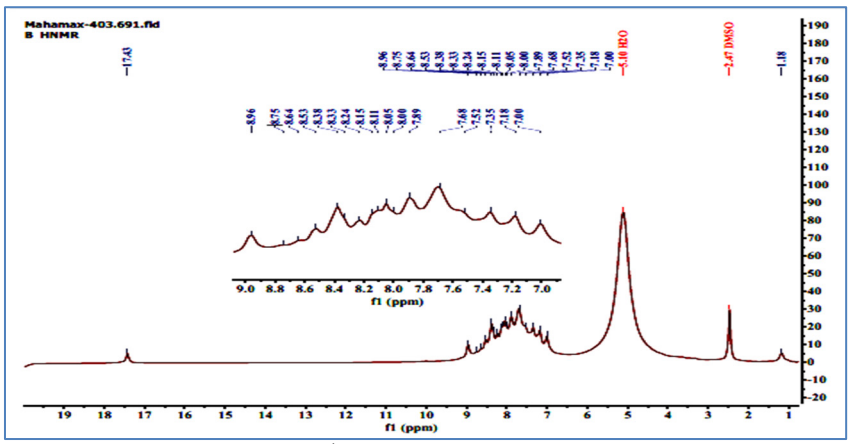



**Fig. 4.** $^{1}$H-NMR of ligand TF

As seen in Fig. 1, the reaction process for oxalic acid and m-phenylenediamine generates a hexaamide macrocycle. TF is confirmed by the IR spectra typical to δ(N-benzene), δ(CONHCO), and δ(CO) stretching frequencies. The coordination of two (NH) from the m-phenylenediamine group may be shown by the shifting of the stretching frequencies of δ(NH), δ(–NHCO), and δ(N-benzene)

to the lower frequency upon complication. Additional evidence for this coordination can be found in Fig. 1, where additional bands develop that are ascribed to δ (M-N) stretching at (433 - 516 $cm^{-1}$). Nevertheless, not all complexes have changed frequencies at the position of the δ (CO) stretching vibration [20]. The coordination of nitrogen atoms with metal ions may be demonstrated by new bands in the complexes' between (433 and 516 $cm^{-1}$) vibration of the δ (M-N) group in all complexes.

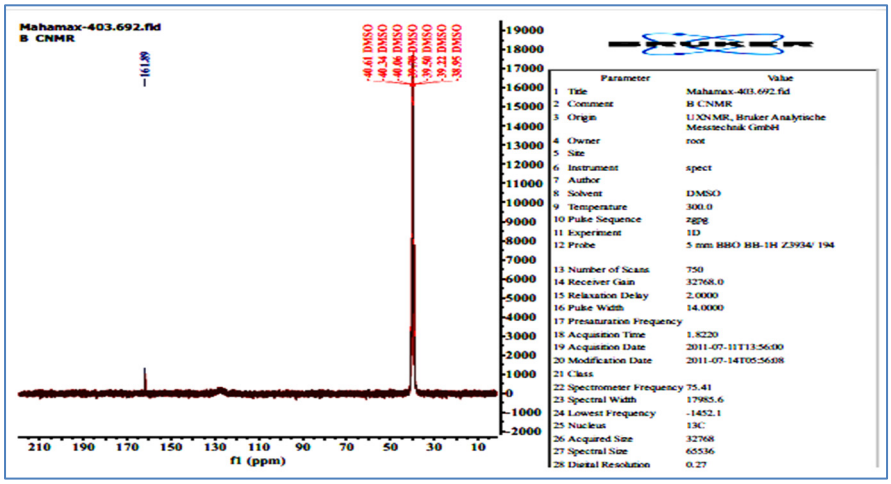



**Fig. 5.** $^{13}C$ –NMR for ligand TF

**3.1. Electronic Spectra and Magnetic Measurements.** The TF ligand's UV spectrum has bands at 33760 and 45871$cm^{-1}$, which are the n→π* and π→π* transitions, respectively (Table 4).

The magnetic moment values of the cobalt complex (1) are 3.30 B.M. Three unpaired electrons make the complex (1). Three bands are seen in the UV-visible spectrum at (9633 $cm^{-1}$), (14792 $cm^{-1}$), (37037 $cm^{-1}$) due to the transitions $^4T_1g(F)\rightarrow{}^4T_2g(F)\upsilon1$, $^4T_1g(F)\rightarrow{}^4A_2g(F)\upsilon2$, and $^4T_1g(F)\rightarrow{}^4T_1g(P)\upsilon3$, respectively and (33786 $cm^{-1}$) which is due to charge transfer. These data may be of complex number 1 attributed to octahedral structure [21, 22].

Three spin-allowed transitions $2E_2g(F)\rightarrow2T_2g$ are represented by (9633, 10344 $cm^{-1}$), (14679, 19047 $cm^{-1}$), and (23412, 32258) in the UV-visible for Cu (II) complex (2) and lie in the range (1.55 B.M) transition in a distorted octahedral environment [23].

Charge transfer may be the cause of $3A_2g(F)\rightarrow3T_1g(P)(\upsilon3)$, (35211,41025 $cm^{-1}$). The high spin configuration and the magnetic moment values (dia) are consistent and octahedral around Zn(II) ions. This could be because of charge transfer (35211, 41025 $cm^{-1}$) and indicated by the magnetic moment values (dia), which are consistent with the high spin configuration [24, 25]. Complexes are nonelectrolytes, according to molar conductance values, which also support an octahedral shape (Fig. 6).

**Table 1.** A few physical characteristics and elemental analysis information for every complex

| No. | Compounds | Color | M.P, (ºC) | $\mu_{eff}$, B.M(25 ºC) | CHN and Metals (%) | | | | Conductance Ω-1 $cm^2$.mol |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | Metal | |
| SU | $C_{16}H_{12}N_4O_4$ | Light Brown | 300 | ------ | 59.08 (59.88) | 3.73 (3.97) | 17.82 (18.34) | — | — |
| 1 | $[Co(TF)_2\ Cl_2]$ | Dark yellow | <400 | 3.30 | 50.68 (51.03) | 2.13 (2.24) | 14.78 (15.01) | 15.54 (15.33) | 21 |
| 2 | $[Cu(TF)_2Cl_2]$ | Deep brown | <400 | 1.95 | — | — | — | 16.56 (16.28) | 23.4 |
| 3 | $[Zn(TF)_2Cl_2]$ | Pal green | <400 | dia | — | — | — | 16.95 (16.77) | 20.3 |

**Table 2.** Chemical shift $^1H$-NMR for ligand TF

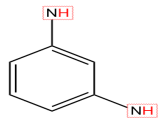
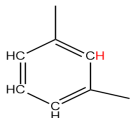
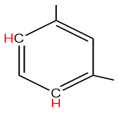
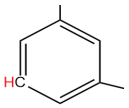
| Compound |  4H |  2H |  4H |  2H |
|---|---|---|---|---|
| TF | 8.96 | 7.4 | 7.6 | 7.9 |

**Table 3.** Chemical shift $^{13}C$ –NMR for ligand TF

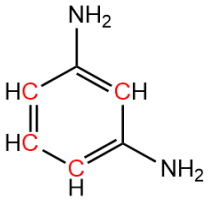
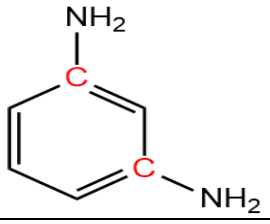
| |  | **HN-CO-CO-NH** |  |
|---|---|---|---|
| TF | 55 | 160.1 | 130 |

**Table 4.** I.R.($cm^{-1}$) assignment, and the complexes' UV-Visible

| No. | I.R. | | | | | UV-Vis. |
|---|---|---|---|---|---|---|
| | υ)N-H) | δ)N-H) | υ)C=O | υ) N-benzene) | υ(M-N) | ⅄ max ($cm^{-1}$) |
| TF | 3442 | 1340 | 1741 | 1546 | —— | 33760 , 45871 |
| 1 | 3022(w) | 1255(s) | 1736(m) | 1434 | 516(m) | 9633 , 14792,37037 |
| 2 | 3124(w) | 1262(m) | 1740(m) | 1437 | 495(m) | 10344, 19047 , 32258 |
| 3 | 3267(w) | 1280(w) | 1738(m) | 1454 | 433(w) | 30121 , 41025 |

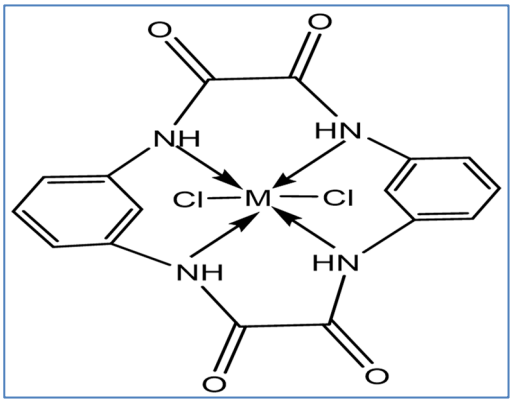



**Fig. 6.** Suggested new structures of three complexes (M= Co, Cu, and Zn).

## 4. Conclusion

A novel series of complexes was successfully synthesized using the ligand (TF) and selected transition metal ions—Co, Cu, and Zn. Based on the experimental data, the proposed structures for all synthesized complexes have been suggested. According to their molar conductance values, complexes behave as nonelectrolytes, which also supports the proposed octahedral geometry of these complexes.

## References

1. Fakhree F.M., Dawood S.K. Synthesis and characterization of novel metal complexes with new ligand derived from glutaric acid by using microwave irradiation technique. *InAIP Conference Proceedings,* 2022, **Vol. 2386(1),** 030015. DOI:10.1063/5.0066862.
2. Karipcin F., Dede B., Caglar Y., Hür D., Ilican S., Caglar M., Şahin Y. A new dioxime ligand and its trinuclear copper (II) complex: Synthesis, characterization and optical properties. *Opt. Commun.* 2007, **Vol. 272(1)**, p. 131-137. DOI:10.1016/j.optcom.2006.10.079.
3. Mosallanezhad A., Kiyani H. Green synthesis of 3-substituted-4-arylmethylideneisoxazol-5 (4H)-one derivatives catalyzed by salicylic acid. *Cur Organocatalysis*. 2019, **Vol. 6(1)**, p. 28-35. DOI:10.2174/2213337206666190214161332.
4. Silva M., Barcauskaite K., Drapanauskaite D., Tian H., Bučko T., Baltrusaitis J. Relative humidity facilitated urea particle reaction with salicylic acid: a combined in situ spectroscopy and DFT study. *ACS Earth Space Chem*. 2020, **Vol. 4(7)**, p. 1018-1028. DOI:10.1021/acsearthspacechem.0c00051.
5. Hu X., Xiao Y., Niu K., Zhao Y., Zhang B., Hu B. Functional ionic liquids for hydrolysis of lignocellulose. *Carbohydr. Polym*. 2013, **Vol. 97(1)**, p. 172-176. DOI:10.1016/j.carbpol.2013.04.061.
6. Liu Y., Guo L., Wang L., Zhan W., Zhou H. Irradiation pretreatment facilitates the achievement of high total sugars concentration from lignocellulose biomass. *Bioresour. Technol*. 2017, **Vol. 232**, p. 270-277. DOI:10.1016/j.biortech.2017.01.061.
7. Zhang M.S., He Z. Enzymatic conversion of lignocellulose into sugars. *Prog Chem*. 2009, **Vol. 21(05)**, p. 1070-1074.
8. Yan Y., Zhang C., Lin Q., Wang X., Cheng B., Li H., Ren J. Microwave-assisted oxalic acid pretreatment for the enhancing of enzyme hydrolysis in the production of xylose and arabinose from bagasse. *Molecules,* 2018, **Vol. 23(4)**, 862. DOI:10.3390/molecules23040862.
9. Fakhree M.F., Dawood S.K. Preparation and Characterization of some Transition Metal Complexes with Two Mixed Ligands Macrocyclic and Ligands PPh3. *Raf. J. Sci.* 2019, **Vol. 28(5)**, p. 29-37. DOI:10.33899/rjs.2019.163294.
10. Neerja G., Ruby N. CAN promoted synthesis of amid derivatives green technology for pharmaceuticals. *Int. J. Pharma and Bio. Sci*. 2010, **Vol. 1(3)**, p. 1-7.
11. Ali E.M., Iqbal A., Ibrahim M.N., Alheety M.A., Ahmed N.M., Yanto D.H., Zainul R. Magnetic attapulgite synthesized via Sonochemistry: an innovative strategy for efficient solid phase extraction of As3+ from simulated and unrefined crude oil samples. *J. Porous Mater*. 2024, **Vol. 31(4)**, p. 1183-1195. DOI:10.1007/s10934-024-01581-0.
12. Eshankulov K.N., Turaev K.K., Geldiev Y.A., Nomozov A.K., Eshankulov S.S., Musaev C.A., Yuldasheva S.G. Studying of metal containing acrylic copolymers and sulfur modified bitumen BH 90/30. *Chemical Problems,* 2025, **Vol. 23(2)**, p. 202-213. DOI: 10.32737/2221-8688-2025-2-202-213.
13. Al-Obedi A.D., Al-Nama K.S. Computational binding studies and bioactivity evaluation for certain Schiff base metal-complexes transformed from ciprofloxacin. *Chemical Problems,* 2025, **Vol. 23(3)**, p. 449-461. DOI: 10.32737/2221-8688-2025-3-449-461.
14. Mohammed E.H., AlSultan M., Alasalli S.M., Sabah A.A. Syntheses, characterization and thermal stability study of new Co (II), Cu (II) and Zn (II) complexes deviates from Schiff base 4-(dimethylamino) benzaldehyde. *Chemical Problems,* 2025, **Vol. 23(3)**, p. 395-406. DOI:10.32737/2221-8688-2025-3-395-387.
15. Liu X., Ma Z., Xing J., Liu H. Preparation and characterization of amino–silane modified superparamagnetic silica nanospheres. *J. Magn. Magn. Mater*. 2004, **Vol. 270(1-2)**, p. 1-6.
16. Maurice P.A. Applications of atomic-force microscopy in environmental colloid and surface chemistry. *Colloids Surf. A: Physicochem. Eng. Asp*. 1996, **Vol. 107**, p. 57-75. DOI:10.1016/0927-7757(95)03372-6.

17. Elmali F.T. Synthesis, characterization and DNA binding properties of Schiff base derivatives and Ru (II) complexes. *Journal of Molecular Structure*. 2022, **Vol. 1261**, 132900. DOI:10.1016/j.molstruc.2022.132900.
18. Pilkington N.H., Robson R. Complexes of binucleating ligands. III. Novel complexes of a macrocyclic binucleating ligand. *Aust. J. Chem*. 1970, **Vol. 23(11)**, p. 2225-2236. DOI:10.1071/CH9702225.
19. Srimurugan S., Suresh P., Pati H.N. Microwave assisted synthesis of 72-membered chiral hexanuclear [6+ 6] macrocyclic Schiff base. *J. Incl. Phenom. Macrocycl. Chem*. 2007, **Vol. 59(3)**, p. 383-388. DOI:10.1007/s10847-007-9341-0.
20. Shakir M., Varkey S.P., Nasman O.S. Transition metal complexes of 20–22-membered octaazamacrocycles: synthesis and characterization. *Polyhedron*. 1995, **Vol. 14(10)**, p. 1283-1288. DOI:10.1016/0277-5387(94)00395-U.
21. Chandra S., Gupta L.K. Electronic, EPR, magnetic and mass spectral studies of mono and homo-binuclear Co (II) and Cu (II) complexes with a novel macrocyclic ligand. *Spectrochimica Acta - A: Mol. Biomol.* 2005, **Vol. 62(4-5),** p. 1102-1106. DOI:10.1016/j.saa.2005.04.007.
22. Chandra S., Gupta L.K. Spectroscopic characterization of tetradentate macrocyclic ligand: it's transition metal complexes. *Spectrochimica Acta - A: Mol. Biomol*. 2004, **Vol. 60(12)**, p. 2767-2774. DOI:10.1016/j.saa.2004.01.015.
23. Jackman L.M., Sternhell S. *Applications of nuclear magnetic resonance in organic chemistry*. Pergamon Press. Oxford. 1969. 2nd edition. DOI:10.1002/jps.2600560902.
24. Siddiqi Z.A., Shadab S.M. Novel 16-membered [N 6] macrocycles bearing hexaamide functions and their metal-encapsulated compounds. *Indian J. Chem*. 2004, **Vol. 43(A)**, p. 2274-2280.
25. Zhang Z., Gao W.Y., Wojtas L., Ma S., Eddaoudi M., Zaworotko M.J. Post-Synthetic Modification of Porphyrin-Encapsulating Metal–Organic Materials by Cooperative Addition of Inorganic Salts to Enhance CO2/CH4 Selectivity. *Angew. Chem*. Int. Ed. 2012, **Vol. 51(37)**, p. 9330-9334. DOI:10.1002/anie.201203594.