

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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Received 28.03.2025

Accepted 28.05.2025

Abstract: A novel macrocyclic ligand, 2,5,7,10-tetraaza-1,6(1,3)-dibenzeneclodecaphane-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: oxalic acid, transition metals (II), microwave irradiation, green macromolecules.

DOI: 10.65382/2221-8688-2026-2-262-268

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.

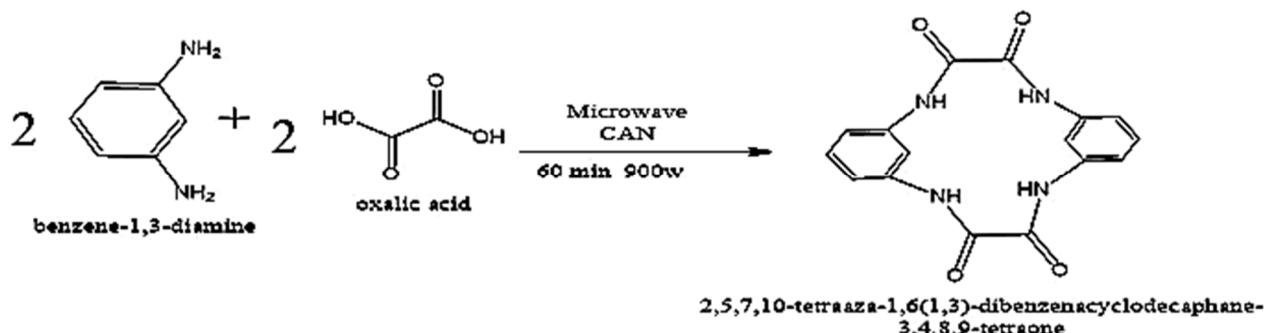


Fig. 1. (TF) Ligand preparation scheme

2.3. Preparation of complexes [Cu(TF)₂Cl₂], [Co(TF)₂Cl₂], and [Zn(TF)₂Cl₂]:

The solution of the ligand (TF) (0.324 gm) in DMF (10 ml) with ethanol and (0.001 mole) of

metal chloride [CuCl₂.6H₂O (0.237 gm)]; [CoCl₂.2H₂O (0.176 gm)]; and [ZnCl₂ (0.139.3 gm)] was stirred. For 2:15 hours, the mixture was refluxed [12-14].

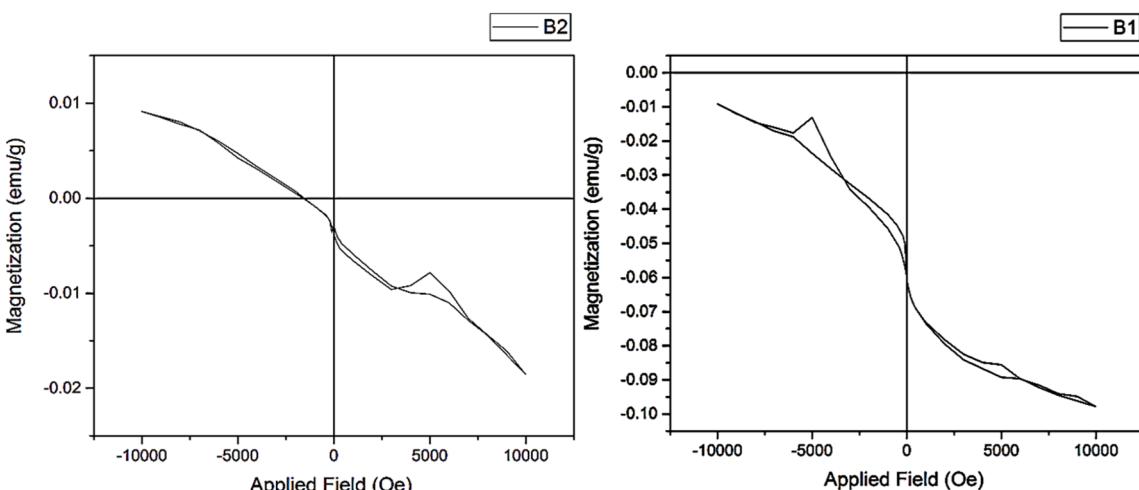


Fig. 2. Vibrating sample magnetometer (VSM) for [Co(SU)Cl₂] (B1), and for [Cu(SU)₂Cl₂] (B2)

2.4. Vibrating sample magnetometer (VSM). In Fig. 2 (B1), the vibrating sample magnetometer (VSM) showed the $[\text{Co}(\text{SU})\text{Cl}_2]$ 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 (M_s) was gauged at 3.3 emu g^{-1} , and the section field

(H_c) and residual magnetization (M_r) showed the cobalt ion in it. After watching M_s values low, the magnetism decreases. But Fig. 2 (B2) showed the $[\text{Cu}(\text{SU})_2\text{Cl}_2]$ saturation value is lower M_s (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 $^1\text{H-NMR}$ 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 $^{13}\text{C-NMR}$ 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} , $\delta(\text{NH})$ at 1340 cm^{-1} , and the frequency at 1741 cm^{-1} that was assigned to the $\delta(\text{CO})$ band as medium intensity [19].

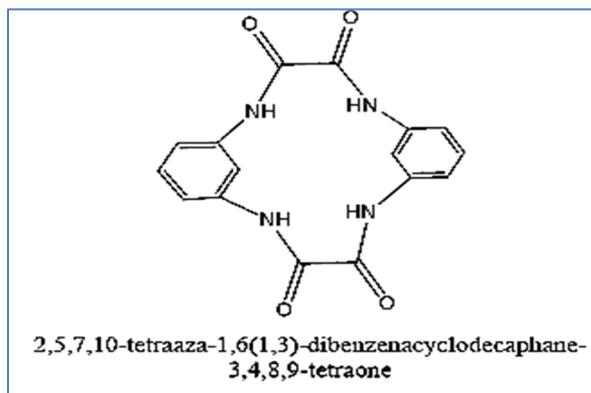


Fig. 3. Structure of TF ligand

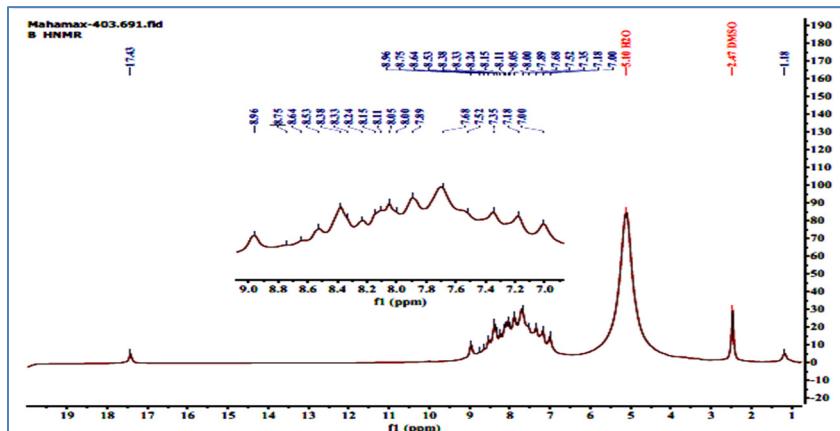


Fig. 4. $^1\text{H-NMR}$ of ligand TF

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.

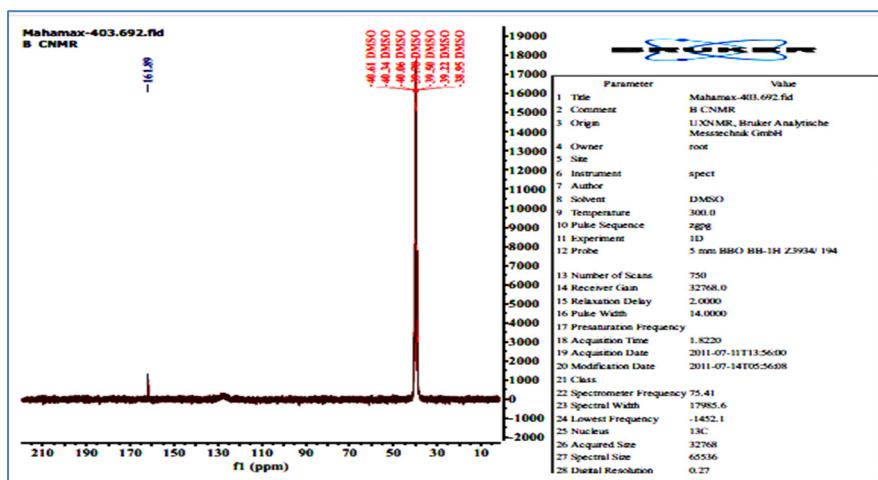


Fig. 5. ^{13}C -NMR for ligand TF

3.1. Electronic Spectra and Magnetic Measurements. The TF ligand's UV spectrum has bands at 33760 and 45871 cm^{-1} , which are the $\text{n}\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ 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 $^4\text{T}_{1g}(\text{F})\rightarrow^4\text{T}_{2g}(\text{F})\nu_1$, $^4\text{T}_{1g}(\text{F})\rightarrow^4\text{A}_{2g}(\text{F})\nu_2$, and $^4\text{T}_{1g}(\text{F})\rightarrow^4\text{T}_{1g}(\text{P})\nu_3$, 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 $2\text{E}_{2g}(\text{F})\rightarrow 2\text{T}_{2g}$ 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 $3\text{A}_{2g}(\text{F})\rightarrow 3\text{T}_{1g}(\text{P})(\nu_3)$, (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, (°C)	μ_{eff} , B.M (25 °C)	CHN and Metals (%)				Conductance $\Omega^{-1} \text{cm}^2 \cdot \text{mol}$
					C	H	N	Metal	
SU	$\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_4$	Light Brown	300	-----	59.08 (59.88)	3.73 (3.97)	17.82 (18.34)	—	—
1	$[\text{Co}(\text{TF})_2 \text{Cl}_2]$	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) ₂ Cl ₂]	Deep brown	<400	1.95	—	—	—	16.56 (16.28)	23.4
3	[Zn(TF) ₂ Cl ₂]	Pal green	<400	dia	—	—	—	16.95 (16.77)	20.3

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

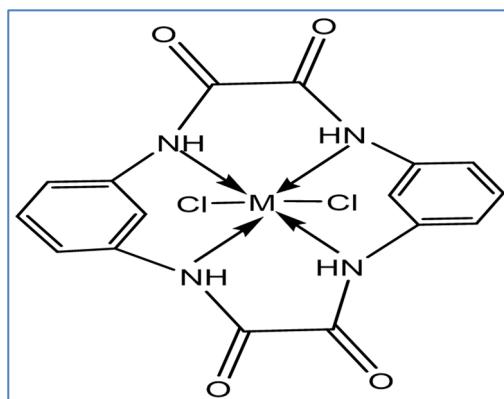
Compound				
TF	4H	2H	4H	2H

Table 3. Chemical shift ¹³C-NMR for ligand TF

TF	55	160.1	130

Table 4. I.R.(cm⁻¹) assignment, and the complexes' UV-Visible

No.	I.R.						UV-Vis. λ _{max} (cm ⁻¹)
	ν)N-H	δ)N-H	ν)C=O	ν) N-benzene)	ν(M-N)		
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.

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