Synthesis, Characterization, Electrochemical Behavior and Antimicrobial Evaluation of 3-Cyanoformazanate Coordination Complexes

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Abstract :

Metal complexes where ligands are bound via the N = N and C = N functionalities have received a lot of interest due to their highly π-accepting properties and the presence of redox-active components that result in interesting properties. Herein, we report the synthesis of cobalt (Co), Nickel (Ni), and copper (Cu) metal complexes from a newly designed 1,5-bis(4-bromophenyl)-3-cyanoformazan ligand. The characterization of metal complexes were carried out using UV-Vis spectroscopy, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), cyclic voltammetry (CV) with their electrochemical redox activity and Thermo gravimetric-differential thermal analysis (TG-DTA) to analyze their morphology, thermal properties and evaluation of their antimicrobial activities. Comprehensively, the study highlights that 1,5-bis(4-bromophenyl)-3-cyanoformazan ligand act as effective bi-dentate donors for the synthesis of thermally stable transition metal complexes. Additionally, they demonstrate significant antimicrobial activity, which is attributed to gram positive (S. aureus ,Bacillus) and gram negative (E. coli, Salmonella) bacteria.

Key words : formazonate metal complex, antimicrobial activity ,electrochemical properties.

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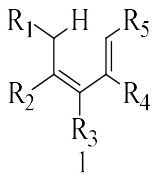
Introduction:

The most important classes of spectator ligands are chelating anionic, π-conjugated N-donors. Such is the case for this ligand architecture, which is highly efficient and versatile synthetic scalability as well as the ability to finely tune the electronic and steric properties of the generated metal complexes. The modulation is usually carried out by specific substitution at co-ordinating nitrogen atoms or at other sites, which is facilitated by the conjugated π system.



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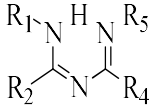

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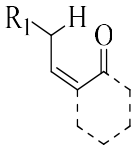

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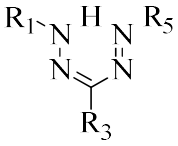
In the past decade, however, β-diketiminates (1) have proven to be probably the most versatile of the related conjugated polyamido frameworks, which include amidinates [1-3], aminotroponiminates[4], radical anions of diiminopyridines[5,11], and diazabutadienes[6-10]. By systematic variation of steric bulk and electronic density at theR_1 and R_5positions (and to a smaller extent at theR_2, R_3 andR_4backbone positions), β-diketiminates have emerged as a core class of ligands in within modern coordination chemistry.



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The β-diketiminate skeleton is also seen to be structurally useful, as it is used to evolve into derivative ligand platforms such as 1,3,5-triazapentadiene [12-17] (2) and β-ketimines (3). The other class of compounds that is entirely isostructural with the β-diketiminate framework are the formazans [18-21] (4). Although formazan derivatives are known to be synthesized, there is no readily available synthetic pathway to formazan derivatives.

Synthetic approaches to formazan derivatives were developed more than 50 years ago, with over 1000 of the variants reported [22], but their coordination chemistry has been poorly developed. Past decade researchers reported the synthesis and it's characterization of a series of boron complexes using 1,3,5-triarylformazanates[23]. In addition to this, until the last quarter of the 1940s[24-31], only sporadic literature describing transition metal-formazan complexes has appeared. As a result, there are only a few systematic investigations[32-35] and many of the previously reported coordination complexes were not fully characterized analytically.

While the vast majority of chemistry involving β-diketiminate scaffolds has involved those with the classic "nacnac" substitution group (R2 = R4 = Me, R3 = H), many other examples have also been reported. However, a number of studies are known to show complexes of **1** with substituents at the R_3 position that are highly electron withdrawing such as cyano groups[36-41]. The electron-withdrawing properties and catalytic reactivity of the electron-withdrawing substituents at the R_3 backbone position can significantly influence the electronic properties and catalytic activity [42-46] of the resulting coordination complexes.

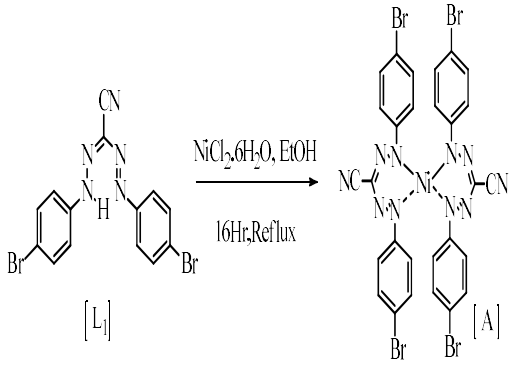
In contrast, the coordination chemistry of 3-cyanoformazans [47-51] & 3-substitutid formazans [52, 53] has been studied little more than briefly in the solution state by spectroscopic methods. The lack of structure did not prevent these ligands from being used as chromophoric dyes, and the many bathochromic shifts occurring on complexation have been exploited as the basis for metal-sensing [30, 54-58] colorimetric reagents.

Given the unique reactivity properties noted in related electronic deficient β-diketiminate complexes, and our recently developed high-yielding synthetic routes to 3-cyanoformazans with a variety of N-aryl substituents [59], we are focused on extending the coordination chemistry of such entities. In this work we report the synthesis, structural elucidation and spectroscopic characterization of a family of complexes of first-row transition metal ions derived from the 3-cyanoformazans, mainly to afford the determination of the coordination mode, structure and electronic structure of the complexes. Further antimicrobial activity of the complex is tested against the selected Gram-positive and Gram-negative bacterial strains[61].

Material and Methodology:

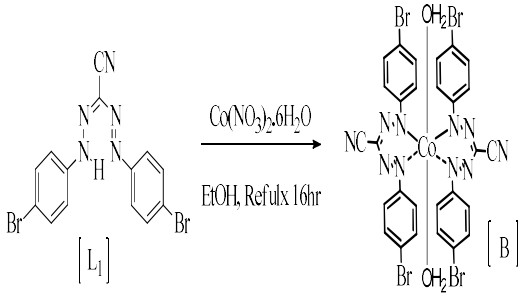
Cobalt(II) nitrate hexahydrate $Co(NO_3)_2.6(H_2O)$., (M.W. 192.03 g/mol), nickel(II) chloride hexahydrate $NiCl_2.6(H_2O)$ (M.W. 237.69 g/mol), and copper(II) chloride dihydrate $CuCl_2.2(H_2O)$ (M.W. 170.48 g/mol),DCM, ethanol, methanol this all the reagent and solvent's used analytical gread without further purification. ligand 1,5-bis(4-bromophenyl)-3-cyanoformazan [60] (L_1) was prepared in the lab through the use of the standard literature procedures and recrystallized to purify.

Scheme 1. Synthesis of Bis(4-bromophenyl-cyanoformazanate) nickel(II)complex



3.1a) Synthetic Procedure: Bis(4-bromophenyl-cyanoformazanate) nickel(II)complex In a round-bottom flask, formazan ligand (L_1) (0.529 g, 1.30 mmol, MW = 407.06 g mol $^{-1}$) was dissolved in 95% ethanol (50 mL). Nickel chloride ($NiCl_2 \cdot 6H_2O$) (0.159 g, 0.67 mmol, MW = 237.69 g · mol -1) was added to this solution, keeping a metal-to-ligand molar ratio of about 1:2.The reaction mixture stirring for 16 hr and reflex open to air. Product kept for room temperature and filtered the solid ,clean with absolute ethanol (3 × 10 mL), affording A as a brown red microcrystalline solid, yield: 0.435 g (82.2%)

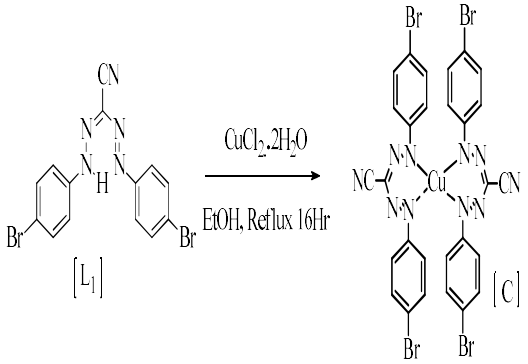
Scheme 2. Synthesis of 1,5-Bis(4-bromophenyl-cyanoformazanate) cobalt(II) complex.



3.1b)Synthetic Procedure:1,5-Bis(4-bromophenyl-cyanoformazanate)cobalt(II)

complex. In a round-bottom flask, formazan ligand (L_1) (0.529 g, 1.30 mmol, MW = 407.06 g mol $^{-1}$) was dissolved in 95% ethanol (50 mL). and cobalt(II) nitrate hexa hydrated $Co(NO_3)_2 \cdot 6H_2O$ (0.128 g, 0.67 mmol) was added to this solution, keeping a metal-to-ligand molar ratio of about 1:2. The reaction mixture was stirring for 16 hr. and reflux to open atmosphere. After completion the reaction mixture kept for room temperature .filter the product wash with absolute ethanol (3 × 10 mL), affording B as a brick red microcrystalline solid

Scheme 3. Synthesis of 1,5-Bis(4-bromophenyl-cyanoformazanato)copper(II)complex



3.1c)Synthetic Procedure: 1,5-Bis(4-bromophenyl-cyanoformazanato)copper(II)complex In a round-bottom flask, formazan ligand (L_1) (0.529 g, 1.30 mmol, MW = 407.06 g mol $^{-1}$) was dissolved in 95% ethanol (50 mL). and copper(II) chloride dihydrate ($CuCl_2 \cdot H_2O$, 0.114 g, 0.67 mmol) was added to this solution, keeping a metal-to-ligand molar ratio of about 1:2. The reaction mixture was stirring for 16 hr. and reflux, to open atmosphere. After completion the reaction mixture kept for room temperature .filter the product wash with absolute ethanol (3 × 10 mL) , affording C as a maroon microcrystalline solid, yield: 0.426 g (80.70%).

Bis(4-bromophenyl-cyanoformazanate)nickel(II)complex(3.1a):UV–vis 410 nm (LMCT).,296 nm (n→π*, N=N / C=N sites), 270 nm (, π→π*, aromatic phenyl rings)**FT-IR:** 3307 cm⁻¹ (Hydrogen Bonding, N–H stretch),2222 cm⁻¹ (C≡N stretch),1622 cm⁻¹ (C=N azomethine),1330 cm⁻¹ (N=N / C–N),1058 / 980 cm⁻¹ (C–H in-plane bending, phenyl),816 cm⁻¹ (C–H oop, p-Br-Ar),538 cm⁻¹ (Ni–N coordination). **TG-DTA** Initial loss at 30–180 °C (theo. –, obs. 15.00%); CN- removal at 180–350 °C (theo. 5.97%, obs. 6.20%); major Ar-Br decomposition at 350–600 °C (theo. 71.66%, obs. 62.50%); ligand-core breakdown at 600–1000 °C (theo. 15.63%, obs. 15.80%); final NiO residue above 1050 °C (theo. 8.57%, obs. 9.50%). **XRD: =** 29.99°

1,5-Bis(4-bromophenyl-cyanoformazanate) cobalt(II) complex(3.1b): UV Data: 392 nm (LMCT, ligand → Co charge-transfer,**310 nm** (n → π*), azomethine C=N), .λmax **245 nm** (π → π*) aromatic / formazan skeleton). **FT-IR:** 3285 (weak O–H stretch, coordinated H_2O),2238 (medium, C≡N stretch, terminal nitrile),1634 (medium, C=N azomethine, formazan backbone), 1326 (strong, N=N / C–N, delocalized chelate ring),826 (mrdium, C–H oop, para-substituted bromophenyl rings), 486 (medium, Co–N coordination). **TG–DTA:** Dehydration occurs at 30–185 °C (calc. 3.79%, obs. 4.10%).185–350 °C CN fragmentation (calc. 40.98%, obs. 41.0%).Major ligand decomposition at 350–650 °C (calc. 68.91%, obs. 68.65%). Core Moiety decomposition at 650 - 1000 °C (calc. 13.40%, obs. 12.75%). Above 1000 °C, the residue corresponds to CoO formation (calc. 8.44%, obs. 8.70.0%). **X-RD:** at **25.21°** , **28.26°**and **40.89°**,

1,5-Bis(4-bromophenyl-cyanoformazanato)copper(II)complex (3.1b): UV Data: 392 nm (LMCT, ligand → Co charge-transfer), 310 **nm** (n → π*), azomethine C=N). λmax **245 nm** (π → π*) aromatic / formazan skeleton). **FT-IR:** 3258 cm⁻¹ (N–H/O–H stretch, H-bonded H_2O), 2234 cm⁻¹ (C≡N stretch, terminal nitrile), 1625 cm⁻¹ (C=N stretch, formazan backbone),1292 cm⁻¹ (N=N / C–N, delocalized chelate system),819 cm⁻¹ (Ar–C–H OOP, p-bromophenyl),512 cm⁻¹ (Cu–N, metal–nitrogen coordination). **TG-DTA:** Initial loss at(30–180 °C(theo. –, obs. 22.00%) . CN- removal at 180–350 °C (Theo: 5.65% obs.6%).59.00% (Theoretical: 67.80%) involves the breakdown of four phenyl rings and bromine atoms (Br_4 + C_{24}). (650–1000 °C):(N_8 + C_2) showing a loss of (Theo: 15.20%,obs: 15.50%). (above 1050 °C), leaving a stable residue of 10.30% (Theoretical: 8.65%) **X-RD: 12.98°**, **32.56°** and **39.88°**

Biological Activity :

The standardized Kirby-Bauer Disk Diffusion Method was used in determining the antibacterial potential [72] .In the preparation of the samples, 15mg of each complex was dissolved in 1 mL of DCM to form a concentration of 15 mg/mL. Filter paper disks then dipped into these solutions, then evaporated and placed on gram positive (S.

aureus ,Bacillus) and gram negative (E. coli, Salmonella) bacteria

Result and Discussion:

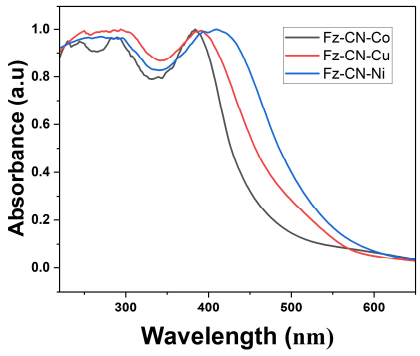


Figure No:1 UV- Visiable Specta of Fz-CN-Ni(A), Fz-CN-Co (B), Fz-CN-Cu (C)

4) UV-Visible spectroscopic Analysis

π→π* Transitions: The bands of this high energy are seen at the (230-270 nm). They are accredited to electronic changes in aromatic rings of phenyl and the long π-conjugated system of formazan. This band is observed at 270 nm in the Ni(II) complex, 250 nm in the Co(II) complex, and 230 nm and 244 nm in the characteristic splitting of the Cu(II) complex[68]. n→π*: Bands in the 290-296 nm range associate with the n→π* transitions of the free electrons in the non-bonding states of the nitrogen atoms. The shift in the position of these bands towards the red direction in all three complexes, at 296 nm (Ni), 294 nm (Co), and 290 nm (Cu), shows the success in the interaction of the nitrogen lone pairs in the azo (N=N) and azomethine (C=N) groups with the metal centers [68]. Ligand-to-Metal Charge Transfer (LMCT): In the spectra of the complexes, a strong appearance of strong absorption bands was determined at 384-410 nm (Ni: 410 nm, Co: 392 nm, Cu: 384 nm). These are Ligand-to-Metal Charge transfer (LMCT).These bands indicate the electronic donation from the nitrogen donor orbitals of the formazan ligand to the vacant d-orbitals of the Ni(II), Co(II), and Cu(II) ions. This transition provides strong evidence for the formation of coordinate covalent bonds in the metal complexes.

The bands represent the electronic donation from the nitrogen donor orbitals of the formazan ligand to the vacant d-orbitals of the Ni(II), Co(II), and Cu(II) ions. This transition show strong evidence for the formation of coordinate covalent bonds in the metal complexes. The bands are attributed to the empty d-orbitals of the Ni(II), Co(II) and Cu(II) e^- accepting the donation from the nitrogen donor orbital of the formazan ligand. This transition has been good evidence for the formation of coordinate covalent bonds in the complex of the metal.

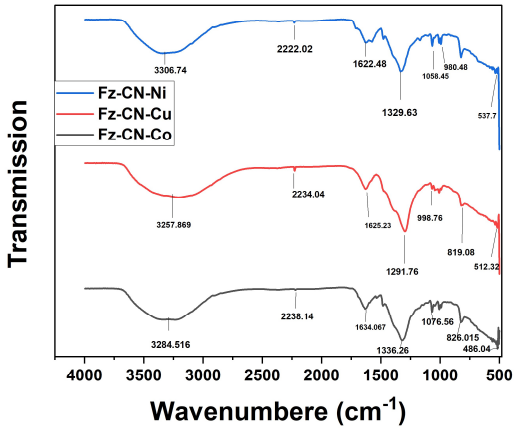


Figure No: 2 FTIR: FZ-CN-Ni(Blue color), FZ-CN-Co (black color), FZ-CN-Cu (Red color)

5] FT-IR Study of metal complexes.

The structural integrity of the formazanate structure and the coordination environment of the synthesized Fz-CN-Co(B), Fz-CN-Cu(C), and Fz-CN-Ni(A) complexes are definitively determined by the FT-IR spectra of these complexes exhibit in figure 2. Infra-red spectrum of the Fz-CN-Ni complex has a medium intensity band with 3306.74 cm^{-1}, which is assigned to (NH) vibration and is affected by a hydrogen-bonded system, but Fz-CN-Co and Fz-CN-Cu complexes have 3284.51 $cm^{-1}$and 3257.90 cm^{-1}, respectively. These latter peaks can be ascribed to the (O-H) stretching of the coordinated or lattice water molecules, which are again verified by the requirements of the coordination sphere. The typical cyanide (CN) residual nitrile (CN) vibrations are detected as 2238 cm^{-1} Co, 2234 cm^{-1} Cu, and 2222 cm^{-1}Ni, which proves that the cyano group has not been part of the primary coordination.

The formazan ligand coordination to the transition metal centers is shown in the changes in the backbone vibrations as the main ones. The conjugated imine (C=N) stretch is determined to be at 1634 cm^{-1} (Co), 1625 cm^{-1} (Cu), and 1622 cm^{-1} (Ni). These values are an indication of a shift in complexation, indicating that the nitrogen lone pairs are involved in the formation of the chelate ring. This can be supported by having bands in the range of 1291 -1329 cm^{-1} and 1384 -1409 cm^{-1} of the delocalized (N=N/C-N) stretching modes, which are

associated with the shared electronic nature of the stabilized formazanate chelate ring.

The 826 cm^{-1} (Co), 819. cm^{-1} (Cu), and 815.cm^{-1} (Ni) 826 $cm^{-1}$and 819. cm^{-1}respectively confirm an aromatic structure through the826 cm^{-1} (Co), 819 cm^{-1}(Cu), and 815 cm^{-1} (Ni) out-of-lane bending vibrations of the p-substituted bromophenyl ring Further in-plane bending 2(C-H) modes are also determined in the case of the Nickel complex as 1058 cm^{-1} and 980 cm^{-1}. The fact that new, non-ligand bands occur in the far-IR region, attributed to (M-N) vibrations, is the ultimate confirmation of the coordination of the metal-ligand. These are found at 486 cm^{-1}in the case of the Cobalt complex, 512 cm^{-1} in the case of the Copper complex, and 537 cm^{-1} in the case of the Nickel complex. All of these spectral characteristics are attributable to bidentate coordination behavior of the formazan ligand through its nitrogen donor atoms, which resulting the generation of stable transition metal complexes.

A

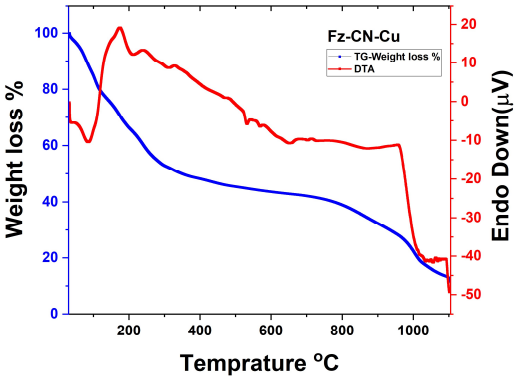
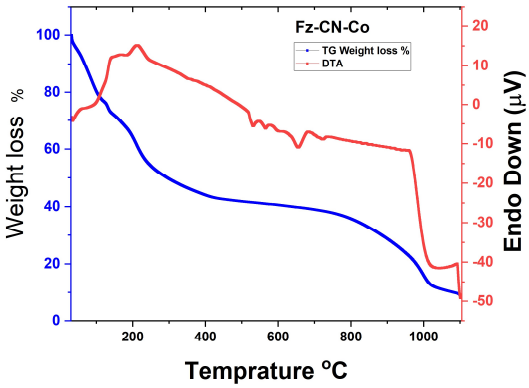
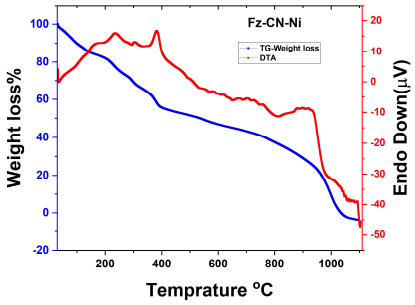


Figure No: 3
Fz-CN- Ni(A)





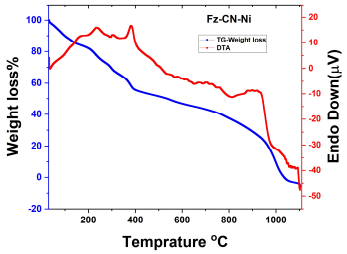


Figure No:5 Fz-CN- Cu(C)

Figure No:4 Fz-CN-Co(B).

6] TG-DTA:

6.1) Results and Discussion: Thermal Analysis (TG-DTA)

Thermal stability and coordination environment of the synthesized formazan-based complexes Fz-CN-Cu (C), Fz-CN-Ni (A), and Fz-CN-Co (B) were systematically studied by TGA and DTA techniques over the temperatures (30°C-1100^{0}C) Fig.3,4,5 thermograms are show multi-stage weight loss pattern that is systematic, which makes it easy to determine the presence of coordinated and lattice-trapped molecules.

6.2) Solvation Behavior and Dehydration:

The first thermal events vary considerably among the series on the basis of the coordination needs of the metal center. The Fz-CN-Co complex has a unique mass loss of 4.10% observed at 30-185°C, and that is very consistent with 3.79% that is needed to remove two coordinated aqua ligands. The comparatively high temperature of such dehydration, and a very sharp endothermic peak in the DTA curve at 120 °C, are diagnostic indicators that such water molecules are located in the primary coordination sphere. On the other hand, initial weight losses are much higher in Fz-CN-Cu and Fz-CN-Ni complexes of 22.00% and 15.00% , respectively. These are the losses at lower temperatures (under 100 °C), and they are equal to the theoretical values (21.50% and 14.72%) of the lattice-entrapped moisture and solvent molecules that are located in the macrocyclic lattice.

6.3) Fragments of Ligands and Structural Collapse:

The major ligand-mediated degradation occurs at temperatures above 180 °C in all complexes, beginning with the breaking of electron-withdrawing cyano groups. In the case of the Fz-CN-Ni, the loss of nitrile is observed to be 6.20% this stage, and an exothermic peak of 230 °C occurs. The steepest thermal event of the whole series is the structural collapse that happens under 350 °C to 650 °C. This step is the oxidative cleavage of the four moieties of bromophenyl. In this region, the Fz-CN-Co complex exhibits a significant weight loss of 68.65% and matches the weight loss of 68.91 % perfectly. It is an exothermic phase in which exothermic DTA signals are observed, indicating the presence of high-energy halogenated aromatic substituents combustion.

6.4) Residue Analysis and Stoichiometry:

The ultimate degradation of the nitrogen-based formazanate core causes a stable level plateau at above 1050 °C. The remaining amounts of Cu (10.30% .), Ni (9.50% Obs.), and Co (8.70% Obs.) are in line with the synthesis of the corresponding metal oxides (CuO, NiO, and Co_3O_4)[74]. In particular, the Fz-CN-Co residue of 8.70 % compares to the theoretical value of 8.44 % Co_3O_4, which is a good confirmation of the metal to ligand stoichiometry of 1:2 .

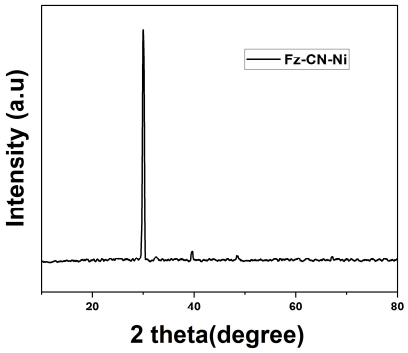


Figure no:6 Fz-CN-Ni of **XRD**

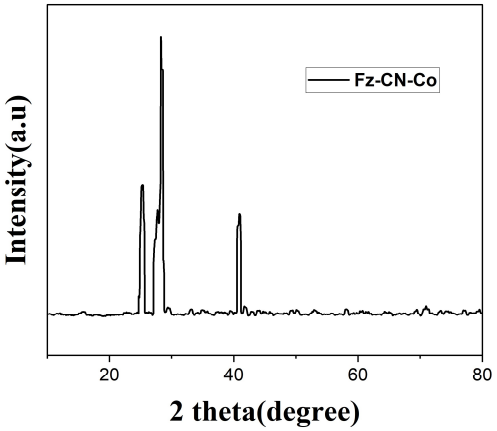


Figure no:7 Fz-CN-Co **XRD**

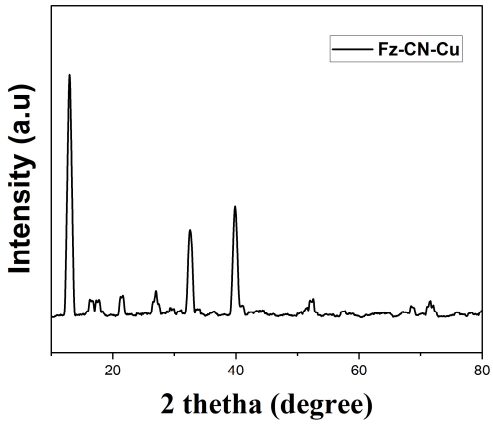


Figure no:8 Fz-CN-Cu of **XRD**

7] X-RD:
Powder X-RD Analysis:

The crystallinity, phase purity, and structural integrity of the synthesized Ni(II), Cu(II), and Co(II) formazanate complexes were investigated using X-ray Diffraction (XRD) patterns at 10 to 80° as shown in the (Fig.6-8). The diffraction peaks of all three complexes exhibit clear and well-defined reflections with a good signal-to-noise ratio, indicating the formation of highly crystalline coordination compounds rather than amorphous polymeric phases[62,63]. For the Ni(II) complex, the major diffraction peak appears at 29.99° (Fig.6), confirming the crystalline nature of the complex[65,66]. Moreover, in the case of the Cu (II) complex, the prominent diffraction reflection occurs at 2Θ =12.98°,32.56°,39.88° (Fig. 8). This diffraction behavior is consistent with π–π stacking interactions between aryl-substituted formazan rings within a 1:2 (ML_2) coordination environment[64,65]. Furthermore, the Co(II) complex shows a distinct diffraction pattern with its strongest peak located at 2Θ = 25.21°,28.26°,40.89°(Fig.7), suggesting the formation of a stable transition metal–nitrogen coordinated framework [64 ,67]. These peaks confirms the complete coordination of the metal ions within the bidentate ligand environment, demonstrating the high phase purity of the synthesized chelate complexes [66, 67].

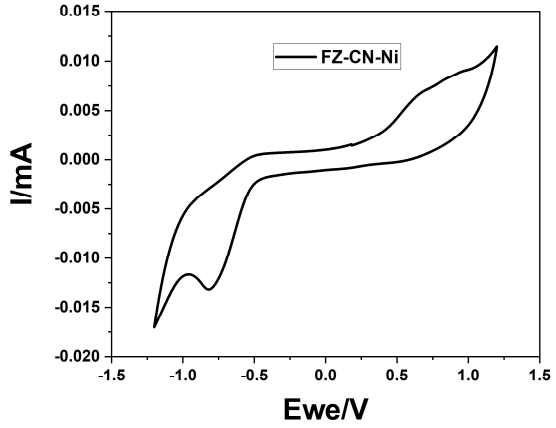


figure No:9 Fz-CN-Ni CV Monogram

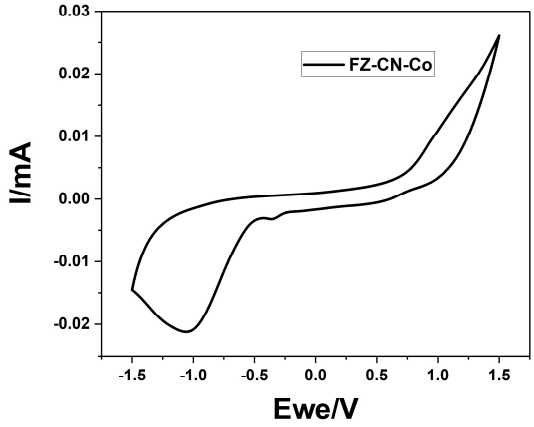


figure No:10 Fz-CN-Co CV Monogram

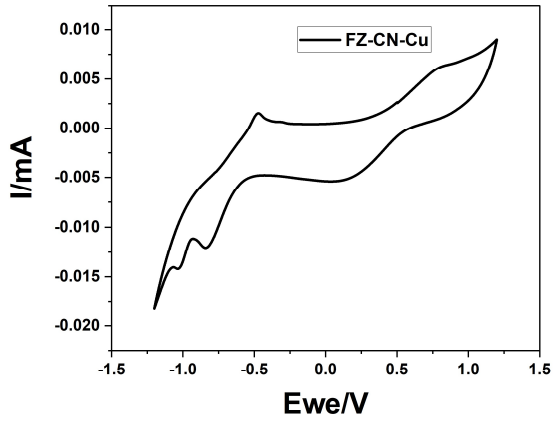


figure No:11 Fz-CN-Cu CV Monogram

8] Cyclic voltammetry :

Electrochemical behavior of formazonate complex:

The electrochemical properties are study with help of cyclic voltammetry .Voltagram of the formazonate complex 0.1mmol in ACN acetonitrile solution (Fig. 9 to 11) shows the redox processes event range of 1.5 to -1.5.

The electrochemical architectures of the transition metal complexes specifically the 3-cyanoformazanate derivatives [NiL_2], [CoL_2], and [CuL_2] (Fig. 9 to 11) are systematically evaluated using cyclic voltammetry to elucidate the nature of metal–ligand electronic communication within these coordinated frameworks [59,68]. The structural integration of the strongly electron-withdrawing cyano substituent -CN at the 3-position of the formazanate core exerts a powerful inductive effect across the coordination sphere, significantly lowering the energy of the ligand-localized π-molecular orbitals (LUMO) and stabilizing the reduced states across the entire series . While the ligand framework provides a uniform electronic template, the resulting kinetic pathways and charge-transfer mechanisms are strictly dictated by the specific d-orbital configuration and geometric preferences of the central transition metal ion.

For the nickel(II) complex (**Fz-CN-Ni**) (Fig. 9), the coordination environment enforces a highly rigid, symmetrical pseudo-square planar framework. This configuration yields an electrochemically efficient, quasi-reversible single-electron reduction wave characterized by a cathodic peak potential E_{pc} of -0.82 V and a corresponding anodic return peak Epa of -0.50 V. This pristine feature represents a stable, ligand-centered electron uptake process $[Ni^{II}L_2]^0 + e^- \leftrightarrow [Ni^{II}L(L^{\cdot-})]^-$), where the structural invariance of the nickel matrix prevents major spatial displacements during electron injection, thereby minimizing the inner-sphere reorganization energy barrier and ensuring excellent cycling reversibility(65).

In contrast, the cobalt (II) analogue (**Fz-CN-Co**) (Fig.10) utilizes its coordination manifold to access a highly dense electronic profile. The complex demonstrates a chemically irreversible cathodic reduction wave localized at -1.05 V, pointing to a rapid, post-electron-transfer intramolecular spin-state relaxation or coordinate-sphere restructuring that prevents a directly coupled return wave. Upon reversing the scan direction toward positive potentials, an expansive, continuously climbing multi-electron anodic wave emerges from +0.60 V and extends past +1.5 V. This high-magnitude current response confirms that the cobalt network successfully facilitates multi-electron transport by mixing metal-centered Co(II) valence shifts seamlessly with sequential, overlapping ligand-localized oxidations.[59,71]

The copper(II) derivative (**Fz-CN-Cu**) (Fig.11)exhibits a unique configurationally trapped pathway dominated by severe structural hysteresis within its coordination matrix. The cathodic sweep features a convoluted, split reduction cascade with peak maxima at -0.85 V and -1.05 V, which resolves into a single, intensely sharp anodic return peak at -0.48 V upon reversal. This distinctive signature provides direct evidence of a classic electrochemical-chemical (EC) mechanism governed by Jahn-Teller distortions; the native square-planar Cu(II) framework dynamically collapses into a preferred tetrahedral Cu(I) geometry during the reduction phase, imposing a formidable geometric activation barrier that drives the highly asymmetrical charge-transfer kinetics observed for the copper complex.[59,63]

9] Antimicrobial activity:

Organic ligands coordinated with transition metals usually increase their biological potency dramatically over that of the parent ligand. The polarity of the metal ion is the main reason for this phenomenon, which is explained by Tweedy Chelation Theory [72](Tweedy, 1964) that concludes that the polarity of the metal ion decreases during the chelation process because the positive charge of the metal ion is partially replaced by the donor groups of the formazan ligand. The decrease of the polarity enhances the lipophilicity of the complex, enabling it to bypass the lipid bilayer of the bacterial cell membrane.

9.1) Results and Comparative Analysis

The forzonate complexes showed different degrees of activity against tested pathogens. The experimental data were recorded as zone of inhibition (ZOI) diameter (mm) and are presented as: **Figure No: 9. Antimicrobial study of A = [Fz-CN-Ni], B = [Fz-CN-Co], C = [Fz-CN-Cu]**

Complex Code	Metal Ion	Bacillus (G+)	S. aureus (G+)	E. coli (G-)	Salmonella (G-)
Fz-CN-Ni	Nickel (II)	21.00 mm	25.00 mm	0.00 mm	0.00 mm

Fz-CN-Co	Cobalt (II)	14.00 mm	17.00 mm	7.00 mm	11.00 mm
Fz-CN-Cu	Copper(II)	14.00 mm	15.00 mm	0.0 mm	12.00 mm

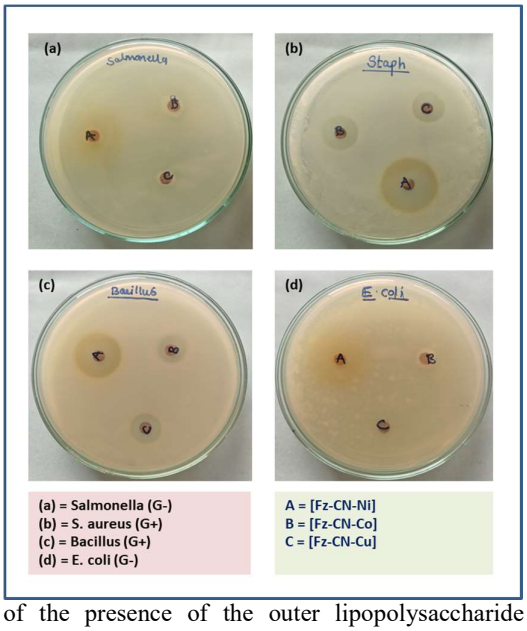
Table 1: Measured Zones of Inhibition (Diameter in mm) of Fz-CN-Ni(A), Fz-CN-Co(B), Fz-CN-Cu(C)

Gram-Positive Response

The complexes were selective to Gram-positive strains, with Nickel(II) formazan (FZ-CN-Ni) having the most activity against Staphylococcus aureus (25.00mm),Table 1. This extreme sensitivity is explained by the fact that Gram-positive bacteria have a simpler cell wall structure and, therefore, the metal complex penetrates the cytoplasm more easily [67].

Gram-Negative Response

Gram-negative bacteria such as Escherichia coli and Salmonella typhi are more resistant because



of the presence of the outer lipopolysaccharide membrane, which in turn acts as a barrier to permeability[73] .Intriguingly, Copper(II) complex [Fz-CN-Cu(II)] & exhibited a selective and potent activity on Salmonella (12.00 mm),Table 1, the Cobalt(II) complex [Fz-CN-Co(II)] was the one with the broad-spectrum activity as it managed to inhibit the action of E. coli(7.00mm) as well as in Salmonella (11.0 mm).

10] Conclusion

This paper presents a set of transition metal complexes [Ni(II), Co(II), and Cu(II) using a 3-cyano formazan (Fz-CN) structure, which could be successfully synthesized and characterized. The mode of bidentate coordination of the ligand was verified by spectroscopic studies (UV and IR). The UV-Visible showed characteristic LMCT bands and significant changes in $\pi \rightarrow \pi^*$, and the FT-IR analysis revealed a significant reduction in the frequencies of (C=N) and (N=N) bands, which indicated that nitrogen atoms represented the main sites of donation. The structural geometry of the complexes was supported by thermal studies (TG-DTA). The Co(II) complex showed the loss of coordinated water, which was in favor of an octahedral structure, and either Ni(II) or Cu(II) complexes had different thermal decomposition profiles, which indicated other possible geometries, including a square planar complex and a tetrahedral complex. The electrochemical properties are consistent with a strong non-innocent character of the 3-cyanoformazanate backbone that enables tuning the electronic profile from chemically reversible, ligand centered radical transitions to complex, structurally distorted coordination manifolds. These redox-dependent pathways show the redox sensitivity of the cyano stabilized framework to fine-tune the advanced multi-electron transport and charge-storage properties. The antimicrobial analysis showed that the metal complexes have an increased bio-potency of the free formazan ligand. This is consistent with the chelation theory of Tweedy, which states that complexation reduces the polarity of the metal ion and the more lipophilic the complex becomes, the easier it can cross the cell membrane of the microbe. The Ni(II) complex had the greatest inhibitory activity against S. aureus, whereas the Co(II) complex had a broad-spectrum activity that was effective against both Gram-positive and Gram-negative bacteria. All the data mentioned above show that the 3-cyano group is a key factor in stabilizing the metal-formazan framework and improving its biological functionality, making such complexes potential precursors to future generations of metallo pharmaceutical applications.

Conflict of interest:

The authors declare no financial conflict of interest.

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DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language. The authors reviewed and edited the content and take full responsibility for the published work.

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