Cyano Bridged Bimetallic Compounds of the Type $M^{2+}$-NC-Fe$^{3+}$ ($M = \text{Co, Ni, Cu, Zn, Cd}$) Using the $[\text{Fe(CN)}_6]^{3-}$ Building Block and their Antibacterial Evaluation

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Abstract: Reactions between $[\text{M(L)}]^2+$ [M = Cu(II), Co(II), Cd(II), Zn(II) and Ni(II)] and $[\text{Fe(CN)}_6]^{3-}$ give rise to cyano-bridged assembled bimetallic complexes. Their structures have been proposed by elemental analyses, IR, UV-VIS and $^1$H NMR spectra, conductance and magnetic measurements studies. The structure is supposed to consist of zigzag chains formed by an alternate array of the cations and $[\text{Fe(CN)}_6]^{3-}$ anion having neutral Ni$_2$Fe$_2$ units. Each hexacyanoferrate(III) ion connects three nickel(II) ions using three cis CN$^-$ groups and the remaining CN$^-$ groups are terminal. The bridging cyanide ligands co-ordinate to the metal ion in a $trans$ fashion forming $trans$-ML(CN)$_2$ moieties. Antibacterial activity of some of the prepared complexes has also been investigated against three human pathogen bacteria.

Keywords: cyano-bridged bimetallic complex; [M(L)]$^2+$ cations; [Fe(CN)$_6$]$^{3-}$ anion; antibacterial studies

1. INTRODUCTION

Multimetallic species are ubiquitous in nature as active sites in a variety of metalloenzymes and are playing a significant and expanding role in industrial chemical catalysts. Such complexes are useful in the storage and transport of active substances through membranes. Mixed ligand complexes have been used in the analysis of semiconductor materials. Mixed ligand complexes have been found to be of wide range of theoretical treatment including orbital modes for magnetic exchange coupling. Use of two dissimilar metals in the design of coordination compounds can potentially give rise to more complex physical properties and also to an even greater diversity of the polymeric structures [1-3].

It is well known that the cyanide ion can coordinate to one metal ion through the carbon atom acting as a monodentate ligand or connect two metal ions as a bridging ligand through both the carbon and nitrogen atoms. Magnetic interactions between paramagnetic metal ions through the cyanide bridge have been extensively investigated. Stair-shaped 2D honeycomb networks, $[\text{NiL}_4][\text{Fe(CN)}_6]$·9H$_2$O and $[\text{NiL}_4][\text{Cr(CN)}_6\text{(NO)}]$·10H$_2$O (L = 3,10-dimethyl-1,3,6,8,10,12-hexaaazacyclotetradecane, 3,10-dimethyl-1,3,6,8,10,12-hexaaazacyclotetradecane), have been reported [4]. Cyanide-bridged bimetallic assemblies based upon hexacyanometalate building blocks, $[\text{M(CN)}_6]^{3-}$ (M=Fe, Cr, Mn, Co), provide a rich variety of magnetic and magneto-optical properties [5, 6]. Mallah and co-workers have recently presented a cyano-bridged NiII-CrIII assembly, $[\text{Ni(cyclam)}][\text{Cr(CN)}_6]$·6H$_2$O [7]. Ohba et al. [8] synthesized the interesting polymeric complex, $[\text{Ni}(\text{pn})_2][\text{Fe(CN)}_6]\text{ClO}_4$·2H$_2$O (pn = 1,2-diaminopropane), bridged by cyanide ligands between Ni(II) and Fe(III). The addition of $[\text{Fe(CN)}_6]^{3-}$ to $[\text{Cu(L)}]^2+$ (L = (N-ethyl)ethylenediamine, (N-propyl)ethylenediamine, diethylenetriamine) gives a polynuclear complex with cyanide bridges between Cu(II) and Fe(III) of the formula $[\text{Cu(L)}]_n[\text{Fe(CN)}_6]_2\cdot x\text{H}_2\text{O}$ [9,10]. Suzuki et al. [11] and Zou et al. [12] prepared and characterized cyanide-bridged complexes of $[\text{Cu(L)}]_n[\text{Fe(CN)}_6]_2\cdot x\text{H}_2\text{O}$ (L = dipropyleneetriamine).

The literature survey reveals that such cyanide-bridged complexes show some exceptional structural behavior especially when one of the metals is iron. The mixed metal complexes have been found to be of the type $[\text{MLx}][\text{M’Ly}]$ where, $M = \text{Cu, Cd, Ni, Co, Zn}$ and $M’ = \text{Hg, Lx = ethylenediamine, aniline, NH}_3$.
and Ly = I; SCN⁻ [13]. In continuation, an attempt has been taken to prepare some of the bimetallic complexes using [Fe(CN)₆]³⁻ block. Spectral studies (UV, FTIR, NMR), magnetic susceptibility and conductance values of the prepared complexes help to characterize their structural features. Antibacterial activities of some of the prepared complexes have also been investigated.

2. MATERIAL AND METHODS

Chemicals

Ethylenediamine, aniline, methanol, chloroform and N, N-dimethylformamide (DMF) were obtained from Aldrich Chemical Company Ltd. Ammonium nitrate and potassium hexacyanoferrate were obtained from M/S Merak (Germany). Percarbonate acid, nitric acid, sulphuric acid and ammonia were obtained from BDH Chemicals Ltd. All chemicals except solvent were used as received. Solvents were dried by standard methods and distilled under an inert atmosphere.

Analytical Methods

The analyses of the metal contents of the prepared complexes were obtained by Atomic Absorption Spectrophotometer (model Thermo Scientific ICE-3000) from Biological Laboratory of Chittagong University, Chittagong. The Infrared spectra of the prepared complexes were obtained by FTIR spectrophotometer (Model- 8900, Shimadzu, Japan) using KBr as the matrix in the range 400-4000 cm⁻¹ from research laboratory of the Department of Chemistry, C.U. Chittagong. Polystyrene was used as the standard to calibrate the spectrophotometer. Electronic absorption spectra were run on Shimadzu UV-Visible Spectrophotometer (Model-1800) using 1 cm cells. An electro thermal melting point apparatus was used for the determination of the melting or decomposition points of the complexes. Using N, N-dimethylformamide (DMF) as the solvent, solutions of the complexes (of the order of 10⁻³ M) were used for conductivity measurements. Conductivity measurement was performed on a Philips Conductivity Meter (Model-HI 9255). Determination of conductivity of an electrolytic solution involves measuring of the electrical resistance of that solution at a particular temperature, usually 25°C. Magnetic susceptibility values of some of the prepared complexes were determined using the Magnetic Susceptibility Balance, (Sherwood Scientific) from in the laboratory of Chittagong University, Bangladesh.

Preparation of Bimetallic Complexes

Preparation of [M(L)]₂[Fe(CN)₆]₂

[Fe(CN)₆]³⁻ Solution: 2 mmol (0.65 g) potassium hexacyanoferrate was dissolved in about 40 mL of water. A clear solution of [Fe(CN)₆]³⁻ solution was formed.

[M(L)]²⁺ solution: In another beaker, 2 mmol (0.589 g) of water soluble metal salts, chloride, nitrate or sulphate was dissolved in about 50 mL of water. An excess amount of ethylenediamine, concentrated ammonia or aniline was added to it drop wise. The mixture solution was heated to boil for about 12-15 minutes.

[M(L)]₂[Fe(CN)₆]₂: Both the solutions were mixed together in their hot states (equation 1). The mixture was stirred for sometimes and allowed to cool with frequent stirring. The precipitate was formed almost immediately and the solid product formed was filtered off and washed with water and dried over calcium chloride.

3M[L],Cl₂ + 2K₃[Fe(CN)₆] → [M(L)]₂[Fe(CN)₆] + 6KCl

(equation 1)

The following bimetallic complexes were prepared by procedure as stated above:

{[Zn(en)]₂[Fe(CN)₆]₂}{Color : Yellow; Yield : 95%; m. p. : >200°C}; {[Cd(en)]₂[Fe(CN)₆]₂}{Color: Yellow; Yield : 95%; m. p. : >200°C}; {[Ni(en)]₂[Fe(CN)₆]₂}{Color: Black; Yield : 95%; m. p. : >200°C}; {[Co(en)]₂[Fe(CN)₆]₂}{Color: Brown; Yield : 95%; m. p.:>200°C}; {[Cu(en)]₂[Fe(CN)₆]₂}{Color: Deep green; Yield : 95%; m. p.:>200 ° C}; {[Zn(NH₃)₆][Fe(CN)₆]₂}{Color: Yellow; Yield : 90%; m. p.: >200°C}; {[Ni(NH₃)₆][Fe(CN)₆]₂}{Color: Green; Yield : 95%; m. p.:>210°C}; {[Cu(NH₃)₆][Fe(CN)₆]₂}{Color: Brown; Yield : 95%; m. p.:>200°C}; {[Co(NH₃)₆][Fe(CN)₆]₂}{Color: Reddish brown; Yield : 95%; m. p.:>200°C}; {[Cd(NH₃)₆][Fe(CN)₆]₂}{Color: Orange; Yield : 95%; m. p.:>200°C}; {[Cd(Aniline)₆][Fe(CN)₆]₂}{Color : Whitish Brown; Yield : 90%; m. p.:>210°C}; {[Cu(Aniline)₆][Fe(CN)₆]₂}{Color: Deep green; Yield : 95%; m. p.:>200°C}; {[Ni(Aniline)₆][Fe(CN)₆]₂}{Color : Drak green; Yield : 95%; m. p.:>200°C}.
Test For of Antimicrobial Evaluation

Some of the new synthesized complexes were screened for their antibacterial activity against 6 different types of bacteria, gram positive- Bacillus cereus, gram negative- Salmonella typhi, Escherichia coli regarded as pathogen to man by the agar well diffusion method. All media and bacteria suspension were prepared using a suitable method. The in-vitro evaluation of antimicrobial activities was performed according to the diffusion technique. The bacteria were grown in nutrient broth at 37°C for 24 hours. The complexes were tested using diffusion on solid media. Sterile (5 mm) diameter sensitivity paper disc were impregnated with concentration of dimethyl formamide (DMF) and their bimetallic complexes at concentration of 50 μg cm⁻² and placed in the nutrient agar. The plates were then incubated for 24 hours. Additionally antibiotics disc for cephalosporin were tested as positive control. The results were recorded by measuring the growth inhibition (% zones of inhibition) surrounding the disc [13,14].

3. RESULTS AND DISCUSSION

Bimetallic mixed-ligand complexes were prepared by the reaction of [Fe(CN)₆]³⁻ with a different metal complexes using water as the solvent. All the complexes were obtained almost immediately after mixing of the component metal complex solutions. The reaction mixture was heated for about one hour at low temperature. The precipitate formed was separated out by filtration and preserved in a desiccator. During preparation of [{Cd(aniline)₃}[FeCN₆]₂⁻), the [Cd(aniline)₃]²⁺ complex solution was heated to dissolve the oily layer formed due to the presence of aniline. No sharp melting point was obtained. All complexes were decomposed at respective point. All complexes are insoluble in chloroform. Some of them are moderately soluble in methanol. All complexes are highly soluble in DMF.

Qualitative Characterization

Primarily, the complexes of mixed metals were characterized qualitatively by the following procedure:

A little amount of the prepared complex was taken in a test tube. Then concentrated nitric acid (HNO₃) was added to the sample and gently warmed on a water bath for the decomposition.

(a) Identification test of Cd²⁺ ions: The sample which is acidic, add a few drops of potassium ferrocyanide K₄Fe(CN)₆. Greenish white precipitate or coloration confirms Cd²⁺ ion.

(b) Identification test of Cu²⁺ ions: The sample which is acidic, add a few drops of potassium ferrocyanide K₄Fe(CN)₆. If copper is present, a maroon precipitate of Cu₄[Fe(CN)₆] will appear and the coloration confirms Cu²⁺ ion.

(c) Identification test of Fe³⁺ ions: Add 1 mL of HCl(conc.), 2 mL of H₂O and a few drops of KSCN to a test tube. The appearance of a dark red color due to the production of Fe(SCN)₃ complex ion confirms the presence of iron.

(d) Identification test of Ni²⁺ ions: Make the solution slightly alkaline with NH₄OH. Add a few drops of alcoholic dimethyglyoxime, (C₄H₆O₂N₂). If nickel is present, a red solution of nickel(II) dimethyglyoxime, Ni(C₄H₆O₂N₂)₂ should appear.

(e) Identification test of Zn²⁺ ions: In the solution, NaOH is carefully added in a drop wise manner, white Zn(OH)₂ will precipitate and if excess NaOH is added, then it dissolve in excess NaOH.

The Ni²⁺ and Fe³⁺ ions can be separated by adding ammonia. The Ni²⁺ ion is converted to the deep-blue hydrazo-complex ion, Ni(NH₃)₆²⁺, which stays in solution. While the Fe³⁺ ion, which does not readily form a hydroxo-complex with ammonia, re-precipitate as iron(III) hydroxide.

IR Spectra

The infrared spectra for the present complexes were taken in the range 400-4000 cm⁻¹ that help to indicate the main νC-H, νC=C, νC≡N, νC=N, νN-H, νM-N etc. stretching modes. With few exceptions, it is a general observation that the spectrum behavior of the free ligands changes by the interpretation of the band shifts which depends on the attribution of the observed frequencies. For the present systems the infrared spectra of the metal complexes (Table 1) provide information about their formation.

The bands 3320–3295, 2990–2965, 1600–1585 and 1580-1520 assigned to vN(H), νC-H, νC=C, νC≡C (aromatic) for the bimetallic complexes have been stated by Pryma and Hamza et al. [15-16]. Otherwise, broad absorption bands due to the N–H (~3234 cm⁻¹) or C–H (~3095 cm⁻¹) stretching as well as deformation vibrations (NH₂, 1630–1578 cm⁻¹) are
present together with the pattern of fingerprint region corresponding to the three coordinated molecules of en [17]. The bands appearing at 1315-1400 cm\(^{-1}\) have been assigned to \(v_{\text{C=N}}\) mode [13].

A number of authors have assigned a band near 2060 - 2136 cm\(^{-1}\) to \(v_{\text{C=N}}\) for bimetallic complexes [18-21]. The frequencies near 2115 cm\(^{-1}\) are assigned as the nonbridging CN stretching vibrations. The vibration frequency of free CN\(^{-}\) anion of terminal coordinated cyanide groups at 2080 cm\(^{-1}\) is blue shifted due to a coordination, removing electrons from weakly antibonding 5\(\sigma\) orbital during metal-carbon \(\sigma\) bond formation, like in K\(_3\)[Fe(CN)\(_6\)] which displays one sharp absorption band at 2118 cm\(^{-1}\) [17]. The shift of \(v(\text{C=}\text{N})\) to higher wave number (2140 cm\(^{-1}\)) compared with that of K\(_3\)[Fe(CN)\(_6\)] or K\(_3\)[Cr(CN)\(_6\)] (2119 cm\(^{-1}\)) suggests a lowered symmetry about the [Fe(CN)\(_6\)]\(^{3-}\) entity and the formation of CN- bridges [5,6,22]. The higher frequencies of \(v_{\text{C=N}}\) that appear at 2153- 2146 cm\(^{-1}\) than the peak observed in K\(_3\)[Fe(CN)\(_6\)], are assigned to the stretching vibration of the equatorial CN- ligands in agreement with the M-CN-M’ bridging nature of these cyano groups. The \(v_{\text{C=N}}\) stretching frequencies of these CN groups depend on the electronegativity, crystal field stability, oxidation number, and coordination number of the metal ion [23].

On the basis of these studies, the band observed for the present complexes in the regions of 970-1260, 1520-1600, 1332-1468, 2040-2361 cm\(^{-1}\) have been assigned as due to \(v_{\text{C-C}}, v_{\text{C=C}}, v_{\text{C=N}}, \) and \(v_{\text{C=N}},\) respectively. Appearance of strong \(v_{\text{CN=CN}}\) modes of the prepared bimetallic complexes in the regions 2040-2100 and 2100-2361 cm\(^{-1}\) is a good indication of M-CN-Fe coordination of the cyanato group. For all the complexes, the presence of \(v_{\text{MN}}\) vibration at 420-690 cm\(^{-1}\) confirms coordination and N- donor character of the ligands to the metal ion [24, 25].

The Electronic Spectra

The visible ultraviolet spectroscopy is a simple but powerful tool for the interpretation of chemical bonds and structure of most chelates. Because of the insolubility of the presently prepared complexes in common organic solvents, the spectra of the prepared complexes were run in dimethylformamide. The peaks observed below 350 nm are assumed as due to \(\pi\rightarrow\pi^*\), \(n\rightarrow\pi^*\) and \(n\rightarrow\sigma^*\) transitions. And the peaks observed near 420 nm may be assigned as LMCT due to the presence of ferrichexacyanate which is assumed by comparison with the solution spectrum of the complex. Some intense bands below 500 nm can be assigned to the absorptions of [Fe(CN)\(_6\)]\(^{3-}\) [26]. All show an absorption band at longer wavelengths compared to that of the [Fe(CN)\(_6\)]. The bands at around 530 nm in the visible region for the prepared complexes can be assigned to \(d-d\) transition. The shift to longer wavelengths is attributed to stabilization of the Fe(III) \(d\) orbitals due to the weakening of the \(\sigma\)-donor properties of the CN- ligands. The observation of a near-IR absorption band for the Zn(II) complex as well as the Cd(II) complex suggests that this band is not an inter valence charge transfer band [5].

\(^{13}\text{C}\) NMR Spectra

Splitting of the \(^{13}\text{C}\) NMR signal approximately at 132.5 (\(\delta\)) for the complex, [Zn(Ani)\(_6\)][Fe(CN)\(_6\)], indicates the presence of both nonbridged and bridging cyanate [27]. In addition multiplet at 135(\(\delta\)) complies with phenyl group of aniline.

Magnetic Measurements

From the experimental values of magnetic measurements of some of the prepared complexes, it is revealed that \{[Zn(en)\(_3\)]_2[Fe(CN)\(_6\)]\} and \{[Cd(en)\(_3\)]_2[Fe(CN)\(_6\)]\} complexes are diamagnetic thus indicating the \(d^{10}\) electronic configuration in such complexes. The effective magnetic moment for remaining complexes at room temperature was above 2.0 B.M. and it is higher than expected the spin-only value but similar to the value of 2.25 B.M. obtained for K\(_3\)[Fe(CN)\(_6\)]. From the experimental values of magnetic measurements of some of the prepared complexes, it is found that magnetic moments of some of the complexes are lower than the expected theoretical spin only values. The possible reason of such lower magnetic moment may be due to some antiferromagnetic interactions in the mixed metal complex. The exchange interactions seem to be super exchange type and most likely through the cyanato groups. However, weak bonds and longer bond lengths may hide or prevent possibility of exchange interactions.

Molar Conductance

The molar conductance values of the presently prepared complexes are shown in Table 1 (Solution of complexes is ca. 10\(^{-3}\) M). The low conductance values
03-106 ohm$^{-1}$cm$^{-2}$mol$^{-1}$ of the prepared complexes in DMF solutions strongly support proposed formulation of the prepared complexes. This suggests $+2$ oxidation states of the metal ions present in such complexes.

Structure of Compounds

Discussion on structures of bimetallic assemblies available in the literature helps to exploit the probable geometry of the presently prepared complexes. The structure of compound [Ni(en)$_2$][Fe(CN)$_5$NO] shows polymeric zigzag chains which is formed by an alternated array of cis-[Ni(en)$_2$]$^{2+}$ cations and [Fe(CN)$_5$NO]$^{2-}$ anions. Nitroprusside anions are bridged to two cis-[Ni(en)$_2$]$^{2+}$ units through two CN-equatorial ligands in cis. The NO ligand and the other three CN-ligands are monodentate [23]. The unique structure of [Zn(cyclam)]$_3$[Fe(CN)$_6$]$_2$ consists of polymeric anionic chains of alternating [Zn(cyclam)]$^{2+}$ and [Fe(CN)$_6$]$^{3-}$ units and cationic trinuclear entities, [Zn(cyclam)-Fe(CN)$_6$-Zn(cyclam)] [28]. In Bimetallic assemblies, [Ni(en)$_2$][M(CN)$_6$]$_2$·3H$_2$O both cis and trans [Ni(en)$_2$] and [M(CN)$_6$] moieties are linked to give S-shaped Ni-NC-M-CN-Ni-NC-M-CN-Ni units which are cross linked to give ribbons. The asymmetric unit consists of two Fe(CN)$_6$$^{3-}$ anions, two cis-[Ni(en)$_3$]$^{2+}$ cations, one trans-[Ni(en)$_3$]$^{2+}$. A polymeric zigzag chain is formed by the alternate array of Fe(CN)$_6$$^{3-}$ and cis-[Ni(en)$_3$]$^{2+}$ ions, and two zigzag chains are combined by trans-[Ni(en)$_3$]$^{2+}$, providing a novel rope-ladder chain [29]. Present prepared bimetallic complexes, [M(L)$_3$] [Fe(CN)$_5$] are supposed to possess the zigzag chains formed by an alternate array of the cis-[M(L)$_3$]$^{2+}$ cations and [Fe(CN)$_5$]$^{3-}$ anion having neutral Ni$_2$Fe$_2$ units as shown in Figure 1. However, actual geometry is difficult to elucidate without crystallographic studies.

![Figure 1. Proposed structure of the [M(L)$_3$]Fe(CN)$_5$ complexes.](image)

Effect of Chemicals on Bacterial Growth

In the present work, the some of the prepared complexes, S$_1$, S$_3$, S$_4$, S$_6$, S$_8$, S$_{11}$, S$_{12}$, were selected for antibacterial activity against three human pathogenic bacteria. The results of the inhibition zone of the selected bacteria due to the effect of compounds are graphically presented in figure 2. The enhanced activity of the complexes is shown in figure 3.

It is found that, compounds S$_6$, S$_8$, S$_{11}$, S$_{12}$ are comparatively more effective against all testes organisms. They are quite effective against Salmonella typhi. S$_4$, S$_3$ are less effective against the tested organisms. S$_1$, S$_4$ and S$_7$ are found to be almost inactive against Bacillus cereus. Antibacterial activity of the complexes can be explained by the some important factors such as nature of the metal ion, metal ion coordinating site, hydrophilicity, hypophilicity and presence of co-ligands may have considerable influence on the antibacterial activity. The chelate complexes may deactivate various cellular enzymes which play vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment affected by the presence of metal ions, may be the reasons for the increased biological activities of the metal complexes. Therefore the antibacterial activity of the metal complexes cannot be ascribed to...
chelation alone but it’s an intricate blend of all of the above contributions.

![Figure 2.](image1.png)

**Figure 2.** The antibacterial activity of the tested metal complexes.

![Figure 3.](image2.png)

**Figure 3.** Zone of inhibition against *Bacillus cereus* by complexes S₁, S₄, and S₅.

4. CONCLUSION

A series of new bimetallic materials based on the [Fe(CN)₆]³⁻ building block has been described. The coordination chemistry of the [Fe(CN)₆]³⁻ anion has been extended to its association with the [M(L)₆]²⁺ complexes. The complexes have been found to be of the type [ML]₁[Fe(CN)₆]₂ where, M = Cu, Cd, Ni, Co, Zn and L = ethylenediamine, aniline, NH₃. The infrared spectra and metal analysis data indicate the formation of such complexes. Conductivity measurements indicate their electrolytic nature and +2 oxidation state of the metal ions present in such complexes. The magnetic measurements indicate some of the complexes to show antiferromagnetic interactions. The high yield of the
complexes indicates good possibilities of their analytical uses to determine metal contents of some related compounds. Further works are required to exploit and ascertain such possibilities. Biological screening of these compounds demonstrated their promising activity against different microbes.

5. REFERENCES AND NOTES