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Synthesis, characterization and magnetic properties of cyanide bridged 1-D metal-coordination polymers based on $[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2]^-$

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Synthesis, characterization and magnetic properties of cyanide bridged 1-D metal-coordination polymers based on $[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2]^-$

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A new series of transition metal complexes $\text{K}[\text{M}^{\text{II}}(\text{s-bqdi})_2][\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 10\text{H}_2\text{O}$ (s-bqdi = semibenzoquinonediiminate, $\text{M}^{\text{II}} = \text{Co}$ (**2**), Ni (**3**), and Cu (**4**)) have been synthesized. These complexes have been characterized by elemental analyses, FT IR, Far IR, FAB mass, UV-Vis, TGA, CV measurements, and powder XRD. The powder XRD patterns of **2**, **3**, and **4** show that they are isostructural with hexagonal primitive lattice structures. The coordination polymers display 1-D chain networks. Magnetic properties of the $\text{Co}^{\text{II}}\text{Fe}^{\text{III}}$ complex studied by a SQUID magnetometer reveal low-temperature antiferromagnetic interaction.

Keywords: 1-D chain; Semibenzoquinonediiminate; Hexagonal primitive; Antiferromagnetic interaction

1. Introduction

The design of extended architectures with novel spin-carrier topologies starting from molecular precursors is an area of immense interest [1–5]. A successful strategy leading to heteropolymetallic systems consists of self-assembly involving anionic, cationic, or neutral building blocks. One of the building blocks contains a paramagnetic ion along with a potential bridging ligand and another contains a potential coordination site, which on association give rise to such molecular species. For instance, many cyanide-bridged paramagnetic metal complexes of different dimensionalities ranging from 0-D to 3-D networks [6–12] exhibit interesting spontaneous magnetization [11, 13–15] and photomagnetic properties [16, 17]. One dimensional assemblies were generally constructed using two of the six cyanide groups of hexacyanometallate, as bridging moiety, which possess different structural motifs like rope-ladder-like chain [7], zig-zag chain [8], etc. These systems may contain the same or different transition metal ions. Magnetic properties of polynuclear complexes and networks are highly sensitive to geometry. The magnetic properties of cyano-bridged compounds can easily be tuned

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by combining $[M(CN)_n]^{m-}$ mononuclear building blocks and in this regard, cyano-bridged compounds seem to be quite promising. Electronic interactions between adjacent metals mediated through linear $M(\mu-CN)M'$ linkages affect the physical properties of metal cyanide-derived materials *viz.* color, conductivity, and magnetism. Cyanide-bridged complexes were among the first examples studied for mixed valence and metal–metal charge transfer [18]. Cyanometallate complexes are efficient building blocks for rationally constructing well-defined materials because they stabilize a variety of transition metal centers, oxidation states, and also efficiently communicate spin information [17, 19–23].

A plethora of cyano-bridged bimetallic compounds have been prepared, with potential applications as high Tc magnetic materials [24, 25], and in SMM [26–28], SCM [29, 30], photo-induced magnetism [31, 32], magnetochirality [33, 34], etc. The negative charge, good donor properties, and capability to act as terminal and bridging ligands make the cyanide group the most appealing ligand in designing extended heterometallic topologies with fascinating magnetic properties [17, 35–43]. In a cyano-bridged complex, the cyanide ion can propagate ferro or antiferromagnetic interactions between the metal ions it links. This is largely due to their preferential linear and strongly covalent binding to transition metals, which leads to high values of antiferromagnetic exchange coupling constants [44].

Hetero-metallic complexes are of interest for the design of new magnetic materials, because magnetic interactions between two non-equivalent paramagnetic centers may lead to a situation that cannot be encountered with species containing only one center; hetero-spin complexes can provide unexpected structural topologies [45, 46]. Magnetic interactions between nearest non-equivalent neighbor spin carriers may be ferromagnetic or antiferromagnetic with non-compensation of the local spin. Molecular magnets synthesized by substitution of four out of six CN^- ligands of hexacyanoferrate by two bidentate ligands have been reported by Colacio *et al.* [47]. Magnetic studies of chain-like $[Mn(salpn)][Fe(bipy)(CN)_4]$ reveal the presence of weak antiferromagnetic interactions between adjacent Fe^{III} and Mn^{III} ions [48]. Study of magnetic properties based on complete electron transfer series $[M-N_4]^Z$ ($Z = -2, -1, 0, +1, +2$) using ortho phenylenediamine (opd) has been studied. The central $Z=0$ member of nickel $Ni[C_6H_4(NH_2)_2]^0$ was originally prepared by Feigl and Fürth from the reaction of Ni^{2+} and opd in aqueous ammonia in the presence of air; by a similar route, $M[C_6H_4(NH_2)_2]^0$ ($M = Co, Ni, Pd, \text{ and } Pt$) have also been synthesized by Balch and Holm. They found that while the Co complex is paramagnetic, complexes of other metals are diamagnetic [49]. One-dimensional heterobimetallic complexes in which one unit is an $[M-N_4]$ open system like $M(s-bqdi)_2$ [38–44, 47–51] ($s-bqdi = \text{semibenzoquinonediiiminate}$, $M = \text{transition metal}$) have not been investigated to the best of our knowledge. This article deals with the synthesis, structural, and magnetic studies of $K[M^{II}(s-bqdi)_2][Fe^{III}(s-bqdi)_2(CN)_2]$ ($M^{II} = Co, Ni, \text{ and } Cu$).

2. Experimental

2.1. Physical measurements and materials

In this study, *o*-Phenylenediamine (CDH), $K_3[Fe(CN)_6]$ (Ranbaxy Laboratories) and hydrated M(II) salts such as $CoCl_2 \cdot 6H_2O$ (BDH, laboratory reagents), $NiCl_2 \cdot 6H_2O$

(SD Fine Chemical Pvt. Ltd.), and $\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$ (Aldrich) were used as supplied. Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyzer. Infrared spectra were recorded on a Varian 3100 FT-IR Excalibur spectrophotometer from 4000 to 400 cm^{-1} (KBr) and 400 to 100 cm^{-1} (nujol film). Solid-state electronic spectra were recorded on a UV-1700 Pharma spec. Shimadzu UV-Vis spectrophotometer in nujol mull. TGA data were recorded on a Diamond TG/DTA, Perkin Elmer, USA. X-ray powder diffraction pattern was obtained on ID 3000 Rich Scifert X-Ray Diffraction System using $\text{Cu-K}\alpha$ ($\lambda = 1.540598\text{ \AA}$) radiation. FAB mass spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer/Data System using Argon/Xenon (6 kV, 10 mA as the FAB gas). For cyclic voltammetry, a conventional three-electrode system in a single compartment cell was used. The working electrode was platinum and the counter electrode was a platinum wire. All potentials were measured with respect to a non-aqueous Ag/Ag^+ (ACN) reference electrode ($E^\circ = 0.25\text{ V vs. NHE}$). CV measurement was made using bi-potentiostat (model no. ARDE4E, Pine instruments company) with a software-supported e-corder 201, Australia. The magnetic susceptibility data of vacuum-dried, powdered polycrystalline sample were measured with a superconducting quantum interface device (SQUID; type MPMS XL Quantum Design) magnetometer. The molar magnetic susceptibility χ_M was studied in the range 300–2 K in a magnetic field strength of 1 T. Magnetization *versus* field measurement was performed with a PPMS-14T (Quantum Design) magnetometer. The data were corrected for contribution of the sample holder. Corrections for the diamagnetic response of the complexes, due to closed atomic shells as estimated from Pascal's constants [52], were applied. The program JulX written by E. Bill was used for simulation and analysis of magnetic susceptibility data (http://ewww.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php). JulX calculates the magnetic properties using the usual spin Hamiltonian approach $H = -2\text{JS}_i\text{S}_j$ (where i and j make reference to the different paramagnetic centers) to describe the interactions between the two paramagnetic transition metals present in the dinuclear complex.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $\text{K}[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (1). Triethylamine (0.5 mL) was added to a solution of *o*-phenylenediamine (5 mmol) in 150 mL of methanol. The resulting brown solution was filtered to remove insoluble material, if any. An aqueous solution (5 mL) of potassium ferricyanide (2 mmol) was added immediately to a clear solution of opd. The solution became turbid and dark green. After stirring the reaction mixture in an open beaker for 1 h, a dark brown solid was formed, which was filtered and washed with methanol (5 mL, two times) and hot ethanol (5 mL, two times), and then dried under reduced pressure (1, dark green, 45% based on opd, decomposes above 280°C). Anal. Calcd for $\text{KFeC}_{14}\text{H}_{16}\text{N}_6\text{O}_2$ (%): C, 42.54; H, 4.08; and N, 21.26. Found (%): C, 42.63; H, 4.17; and N, 21.34. UV-Vis (Nujol; λ_{max} , nm): 428, 265, and 206. FT-IR (KBr, cm^{-1}): $\nu(\text{N-H}) + \nu(\text{O-H})$ 3400vs, $\nu(\text{C}\equiv\text{N})$ 2031vs, $\nu(\text{C}\text{---}\text{Ns-bqdi})$ 1690sh, $\nu_s(\text{C-C}) + \delta(\text{N-H})$ 1623s, $\rho(\text{C-H}) + \nu(\text{C-N})$ 1540vs, $\nu(\text{C-N}) + \delta(\text{ring})$ 1479m, $\rho(\text{C-H}) + \nu(\text{C-C})$ 1369w, $\nu(\text{C-N})$ 1241sh, $\rho(\text{N-H}) + \rho(\text{C-H}) + \nu(\text{ring})$ 1084s, $\omega(\text{C-H}) + \omega(\text{N-H})$ 850w, $\pi(\text{ring})$ 755m, $\omega(\text{O-H})$ 675w, $\nu(\text{ring})$ 590w, $\pi(\text{ring}) + \nu(\text{Fe-N})$ 476m.

2.2.2. Synthesis of $\text{K}[\text{Co}^{\text{II}}(\text{s-bqdi})_2][\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 10\text{H}_2\text{O}$ (2). $\text{Co}^{\text{II}}(\text{s-bqdi})_2$ has been synthesized by the method reported in literature [49]. A light brown solution obtained by dissolving $\text{Co}^{\text{II}}(\text{s-bqdi})_2$ (5 mmol) in methanol (80 mL) was filtered to remove insoluble material and added to a freshly prepared solution of $\text{K}[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (3 mmol) dissolved in 4 mL of water. A microcrystalline precipitate appeared after a few minutes. The resulting mixture was stirred for 12 h at room temperature. Black microcrystalline precipitate was filtered and washed successively with water, water:ethanol (1:1, v/v), and ether and then dried under reduced pressure (2, black, 52%, decomposes above 280°C). Anal. Calcd for $\text{KCoFeC}_{26}\text{H}_{44}\text{N}_{10}\text{O}_{10}$ (%): C, 38.52; H, 5.47; and N, 17.28. Found (%): C, 38.61; H, 5.38; and N, 17.36. UV-Vis (Nujol; λ_{max} , nm): 464, 419, 390, 276, 245, and 204. FAB mass (m/z): 811 (M^+). FT-IR (KBr, cm^{-1}): $\nu(\text{N-H}) + \nu(\text{O-H})$ 3374s, $\nu(\text{C}\equiv\text{N})$ 2082vs, $\nu(\text{C}\equiv\text{N}-\text{s-bqdi})$ 1690sh, $\nu_{\text{s}}(\text{C-C}) + \delta(\text{N-H})$ 1616m, $\rho(\text{C-H}) + \nu(\text{C-N})$ 1515s, $\rho(\text{C-H}) + \nu(\text{C-C})$ 1413w, $\nu(\text{C-N})$ 1232w, $\delta(\text{ring})$ 1148w, $\pi(\text{ring})$ 756w, $\omega(\text{O-H})$ 676w, $\nu(\text{ring})$ 590m, $\pi(\text{ring}) + \nu(\text{Fe-N})$ 462s, $\nu(\text{Fe-CN})$ 379m, $\nu(\text{Co-N})$ 287sh, $\nu(\text{Co-NC})$ 168vs, $\delta(\text{C-Fe-C})$ 97vs.

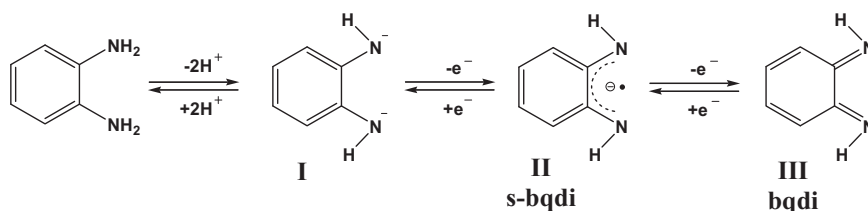
2.2.3. Synthesis of $\text{K}[\text{Ni}^{\text{II}}(\text{s-bqdi})_2][\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 10\text{H}_2\text{O}$ (3). $\text{Ni}^{\text{II}}(\text{s-bqdi})_2$ was synthesized using the reported method [49]. $\text{Ni}^{\text{II}}(\text{s-bqdi})_2$ (5 mmol) was dissolved in methanol (65 mL). The resulting bluish-green solution was filtered to remove insoluble material and treated with a freshly prepared solution of $\text{K}[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (3 mmol) dissolved in water (4 mL). After 1 h the color of the solution turned from green to dark brown and a dark precipitate formed; stirring was continued for 12 h at room temperature. Brown black microcrystalline precipitate was filtered and washed successively with water, water:ethanol (1:1, v/v) and ether and then dried under reduced pressure (3, brown black, 32%, decomposes above 280°C). Anal. Calcd for $\text{KNiFeC}_{26}\text{H}_{44}\text{N}_{10}\text{O}_{10}$ (%): C, 38.53; H, 5.47; and N, 17.28. Found (%): C, 38.61; H, 5.35; and N, 17.34. UV-Vis (Nujol; λ_{max} , nm): 889, 522, 426, 324, 264, and 224. FAB mass (m/z): 810 (M^+). FT-IR (KBr, cm^{-1}): $\nu(\text{N-H}) + \nu(\text{O-H})$ 3374s, $\nu(\text{C}\equiv\text{N})$ 2092vs, $\nu(\text{C}\equiv\text{N}-\text{s-bqdi})$ 1690sh, $\nu_{\text{s}}(\text{C-C}) + \delta(\text{N-H})$ 1619m, $\rho(\text{C-H}) + \nu(\text{C-N})$ 1529s, $\rho(\text{C-H}) + \nu(\text{C-C})$ 1367w, $\nu(\text{C-N})$ 1237w, $\delta(\text{ring})$ 1151w, $\omega(\text{C-H}) + \omega(\text{N-H})$ 850w, $\pi(\text{ring})$ 754w, $\omega(\text{O-H})$ 671w, $\nu(\text{ring})$ 589m, $\pi(\text{ring}) + \nu(\text{Fe-N})$ 466m, $\nu(\text{Fe-CN})$ 390w, $\nu(\text{Ni-N})$ 283vs, $\nu(\text{Ni-NC})$ 168vs, $\delta(\text{C-Fe-C})$ 82s.

2.2.4. Synthesis of $\text{K}[\text{Cu}^{\text{II}}(\text{s-bqdi})_2][\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 10\text{H}_2\text{O}$ (4). $\text{Cu}^{\text{II}}(\text{s-bqdi})_2$ was synthesized by the method reported [50]. $\text{Cu}^{\text{II}}(\text{s-bqdi})_2$ (5 mmol) was dissolved in 200 mL of hot methanol. The resulting deep brown solution was filtered to remove insoluble material and added to freshly prepared $\text{K}[\text{Fe}^{\text{III}}(\text{s-bqdi})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$ (2 mmol) dissolved in 4 mL of water. The mixture was kept on a stirrer for 12 h at room temperature. Black microcrystalline precipitate appeared, was filtered, washed repeatedly with water, water:ethanol (1:1, v/v) and ether and then dried under reduced pressure (4, black, 35%, decomposes above 280°C). Anal. Calcd for $\text{KCuFeC}_{26}\text{H}_{44}\text{N}_{10}\text{O}_{10}$ (%): C, 38.30; H, 5.44; and N, 17.18. Found (%): C, 38.22; H, 5.39; and N, 17.23. UV-Vis (Nujol; λ_{max} , nm): 973, 482, 395, 253, and 224. FT-IR (KBr, cm^{-1}): $\nu(\text{N-H}) + \nu(\text{O-H})$ 3370s, $\nu(\text{C}\equiv\text{N})$ 2091vs, $\nu(\text{C}\equiv\text{N}-\text{s-bqdi})$ 1685sh, $\nu_{\text{s}}(\text{C-C}) + \delta(\text{N-H})$ 1620m, $\rho(\text{C-H}) + \nu(\text{C-N})$ 1529s, $\rho(\text{C-H}) + \nu(\text{C-C})$ 1365w, $\nu(\text{C-N})$ 1236w, $\delta(\text{ring})$ 1148w, $\omega(\text{C-H}) + \omega(\text{N-H})$ 842w, $\pi(\text{ring})$ 754w, $\omega(\text{O-H})$ 672w, $\nu(\text{ring}) + \nu(\text{Cu-N})$

589m, $\pi(\text{ring}) + \nu(\text{Fe-N})$ 478w, $\nu(\text{Fe-CN})$ 385w, $\nu(\text{Cu-N})$ 282vs, $\nu(\text{Cu-NC})$ 163vs, $\delta(\text{C-Fe-C})$ 91s.

3. Results and discussion

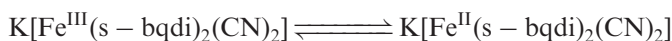
We see that *o*-Phenylenediamine [50] exists in the following three forms: *o*-phenylenediamine dianion (I), the anionic radical, *s*-bqdi (II), or the neutral diimine molecule, *o*-benzoquinonediimine (bqdi), (III), according to the following scheme.



Coordination of *s*-bqdi with transition metal ions gives square planar geometry with molecular orbitals delocalized over the entire system. During complex formation by two *s*-bqdi, the free radical present on each ligand undergoes spin coupling [53]. The FAB mass spectra (Supplementary material, figure S1 (a) and (b)) of **2** and **3** exhibit molecular ion peak at 811 and 810, respectively, revealing formation of the compounds. The appearance of single band due to $\nu(\text{CN})$ in the IR spectra of the heterobimetallic complexes shows the presence of only one type of CN^- . The position of $\nu(\text{CN})$ is characteristic of bridging cyanide. The absorption in the UV-Vis spectra is characteristic of $\text{Fe}_{\text{L,S}}^{\text{III}}$. Excellent fitting of magnetic data over the entire temperature range is also indicative of $\text{Fe}_{\text{L,S}}^{\text{III}}$ in these coordination polymers.

3.1. Electrochemistry

The cyclic voltammetric measurement of **1** at Pt electrode in propylene carbonate using 0.1 mol L^{-1} TBAP supporting electrolyte at a potential scan rate of 100 mV s^{-1} reveals the presence of Fe^{+3} in the complex. In the cyclic voltammogram (figure 1), two peaks A and B in the forward scan are observed at -0.68 and $+1.65 \text{ V}$, respectively. In the reverse scan, peak C was obtained at $+0.118 \text{ V}$, while a sharp peak D was observed at -0.65 V . The reduction (cathodic) peak at -0.65 V and the reoxidation (anodic) peak at -0.68 V are due to the following reversible reaction.



This gives the formal redox potential (reduction) as $E^\circ = -0.66 \text{ V}$ versus Ag/Ag^+ , very much close to that observed by Chaudhuri *et al.* [54] for Fe^{III} -to- Fe^{II} reduction. Peaks at $+1.65$ and $+0.118 \text{ V}$ are due to the presence of free radical in the complex.

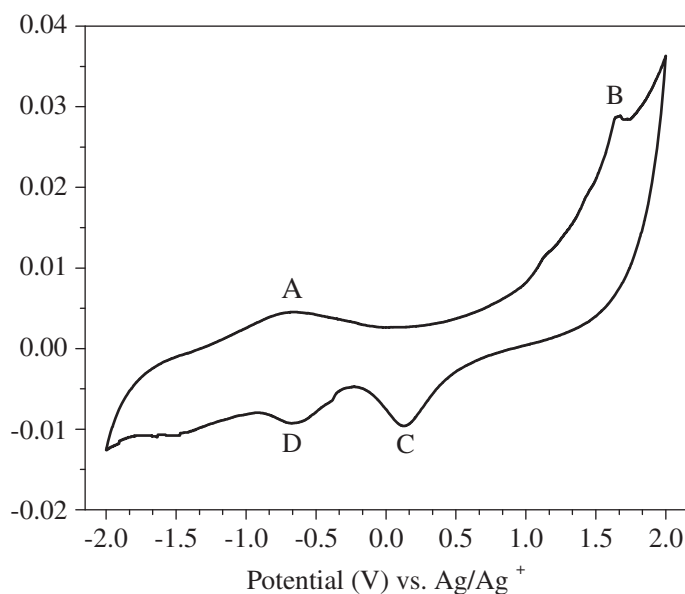


Figure 1. Cyclic voltammogram of **1** at a scan rate of 100 mV s^{-1} .

3.2. Infrared spectral study

The $\nu(\text{CN})$ of KCN observed at 2080 cm^{-1} shifts to higher frequency [55] upon coordination to metal ions. In $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ $\nu(\text{CN})$ appears at 2118 cm^{-1} ; upon substitution of four CN^- ions with two s-bqdi in **1**, $\nu(\text{CN})$ shifted to 2031 cm^{-1} (Supplementary material, figure S2 (a)) rather than shifting to higher frequency due to bridging nature of CN^- because of the kinematic effect. The lowering in $\nu(\text{CN})$ is attributed to π -back bonding as reported for metal carbonyls.

Heterobimetallic complexes **2**, **3**, and **4** contain cyanide in the bridged fashion only, supported by a single $\nu(\text{CN})$ band (Supplementary material, figure S2(b)). This absorption lies in the order $\text{Co} < \text{Ni} \approx \text{Cu}$, as expected from the electronegativity [56] of the metal ions. Thus, 1-D chain structure has been proposed for **2**, **3**, and **4**.

3.3. UV-Vis studies

The UV-Vis spectrum of opd shows bands at 241 and 292 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In **1**, these transitions are observed at 210 and 264 nm along with a new band at 428 nm due to Fe(III) (Supplementary material, figure S3). Nayak *et al.* [57] reported reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ by *trans*-1,2-diaminocyclohexane (L) to $[\text{Fe}(\text{CN})_6]^{4-}$ in $[\text{Ni}^{\text{II}}\text{L}_2]_2[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$; the absorption maximum at 420 nm for Fe(III) completely vanished on reduction to Fe(II). In **1**, a band at 428 nm supports the fact that iron is present as Fe(III). The spectrum of $\text{K}_3[\text{Fe}(\text{CN})_6]$ shows a band at 415 nm, identified as $\text{L}(\text{CN}^-)_g \rightarrow \text{T}_{2g}$ symmetry-forbidden charge transfer allowed by mixing CN^- orbitals with higher orbitals of opposite parity to those of iron, by vibrations [58]. The solid-state spectra of **2–4** show bands at 419, 426, and 482 nm, respectively,

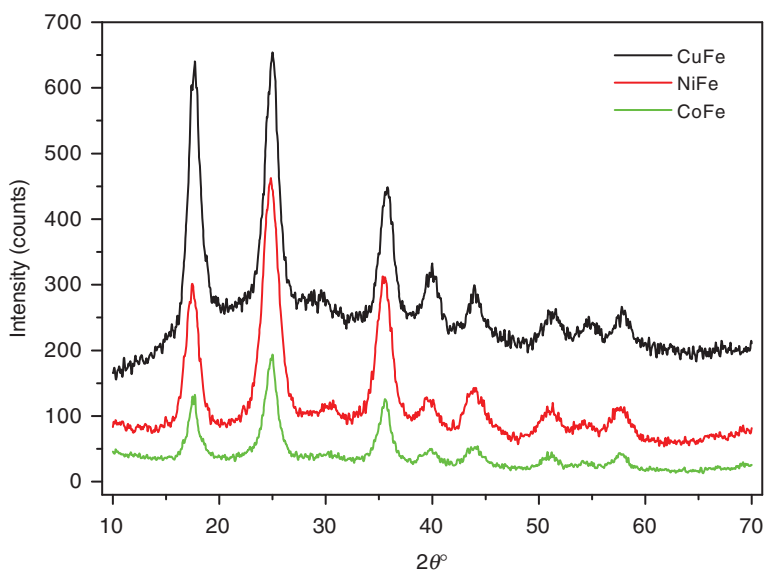


Figure 2. X-ray powder diffractograms of **2**, **3**, and **4**.

which can be ascribed to a $L(\text{CN}^-)_g \rightarrow T_{2g}$ symmetry-forbidden charge transfer, as found in the spectrum of ferricyanide. Complexes **2–4** also absorb at 464, 889 and 973 nm, assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$, ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$, and ${}^2E_g \rightarrow {}^2T_{2g}(\text{D})$ transitions of Co(II), Ni(II), and Cu(II), respectively. These spectral features are characteristic of octahedral stereochemistry around metal(II).

3.4. Thermal stability

In order to confirm the stability of complex, thermogravimetric analysis of **2** was carried out in air with a heating rate of $10^\circ\text{C min}^{-1}$ from 50°C to 700°C . TGA curve (Supplementary material, figure S4) shows distinct weight loss in two stages. The first (31.2%) takes place from 50°C to 100°C , attributed to loss of all lattice water and a semi-benzoquinonediimine (Calcd 35.3%). Weight loss in the second step (33.5%) at $100\text{--}242^\circ\text{C}$ is in good agreement with loss of three semi-benzoquinonediimine molecules. Since the TG analysis was carried out in air, the iron and cobalt must be oxidized to Fe_2O_3 and CoO , respectively. Assuming the residue corresponds to Fe_2O_3 and CoO , the observed residue (26.1%) is in good agreement with the calculated value (28.94%).

3.5. X-ray powder diffraction studies

X-ray powder diffractograms of **2**, **3**, and **4** are given in figure 2 and the observed diffraction data i.e. d values, relative intensities, and 2θ are given in supporting tables S1, S2, and S3, respectively. Using Ito's method [59] of indexing, we found that all three samples are hexagonal primitive with cell parameters for **2**: $a = b = 17.8291 \pm 0.0075 \text{ \AA}$,

$c = 24.9558 \pm 0.0331 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$; for **3**: $a = b = 17.4614 \pm 0.0118 \text{ \AA}$, $c = 24.9236 \pm 0.0153 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$; and for **4**: $a = b = 17.4838 \pm 0.0073 \text{ \AA}$, $c = 24.9498 \pm 0.0132 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. Using these unit cell parameters, calculated diffraction data and indices of **2–4** are included in supporting tables S1, S2, and S3, respectively.

All three complexes show similar diffraction patterns and relative intensities which demonstrate that these are isostructural. The cell parameters ' a ', ' b ' and ' c ' show an increasing trend: NiFe ($a = b = 17.4614 \text{ \AA}$, $c = 24.9236$) < CuFe ($a = b = 17.4838 \text{ \AA}$, $c = 24.9498$) < CoFe ($a = b = 17.8291 \text{ \AA}$, $c = 24.9558$), in agreement with the trend in ionic radii: Ni < Cu < Co.

3.6. Direct current magnetic susceptibilities and magnetization

Solid-state variable-temperature magnetic susceptibility measurements were performed on vacuum-dried, microcrystalline samples of **2**, restrained in eicosane to prevent torquing. The dc magnetic susceptibility (χ_M) data were collected from 2.00–300 K in a 10 kG (1 T) field. They are plotted as $\chi_M T$ versus T and χ_M^{-1} versus T in figure 3(a) and (b), respectively. The $\chi_M T$ value at room temperature is $4.43 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($\mu_{\text{eff}} = 5.95 \mu_B$), a value that is greater than expected for magnetically non-interacting low-spin Fe^{III} and high-spin Co^{II} [60] ions through the spin-only formula, *ca.* $2.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with an average $g = 2$; $\mu_{\text{eff}} = 4.24 \mu_B$. This indicates that there exists significant spin–orbit coupling of the $^2T_{2g}$ ground term for low-spin octahedral Fe^{III} ions [61] and an unquenched orbital contribution typical of the $^4T_{1g}$ ground state in octahedral Co^{II} complexes [62, 63]. It is likely that at room temperature there is ferromagnetic coupling between the two metal ions. The experimental data are fitted to a Curie–Weiss law in the temperature range 34–300 K, with a Curie constant of $4.82 \text{ cm}^3 \text{ K mol}^{-1}$, in good agreement with the expected spin-only value of $4.43 \text{ cm}^3 \text{ K mol}^{-1}$ ($g = 2$) corresponding to the sum of the contributions of a Fe^{III} ($S = 1/2$) and a Co^{II} ($S = 3/2$) ions. The steady decrease in $\chi_M T$ from room temperature to 2 K can be attributed to the combined effect of the spin–orbit coupling effects of the low-spin octahedral Fe^{III} ion with a $^2T_{2g}$ ground term, spin–orbit coupling of the octahedral Co^{II} ion with a $^4T_{1g}$ ground term, antiferromagnetic exchange through bridging cyanide and/or zero-field splitting due to anisotropy. To investigate the magnitude of the magnetic interaction between Fe^{III} and Co^{II} , a fit of the data was made using a model for a 1-D polymeric chain. A best fit was obtained with $J_{12} = -25.82 \text{ cm}^{-1}$, $g_{\text{Fe}} = 1.920$, $g_{\text{Co}} = 2.126$, $\text{TIP} = 10 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $\Theta = -0.78 \text{ K}$. The shape of the plot of $\chi_M T$ and the overall negative Weiss constant suggests antiferromagnetic coupling dominates the overall intramolecular exchange interactions within the 1-D complex. Saturation of the magnetization is not reached to the maximum experimental field applied, $H = 10 \text{ T}$; instead, a maximum value of $2.62 N\beta$ is measured at 2 K, figure 3(c). The M values are still increasing and saturation is not achieved. This is most likely due to thermal population of the ground-state and of other low-lying spin-states occurring even at 2 K. The zero-field splitting [1, 64] and Zeeman effects will also influence the shape and size of M versus H plots. The value of magnetization at maximum experimental field and the lack of saturation are in agreement with antiferromagnetic interactions.

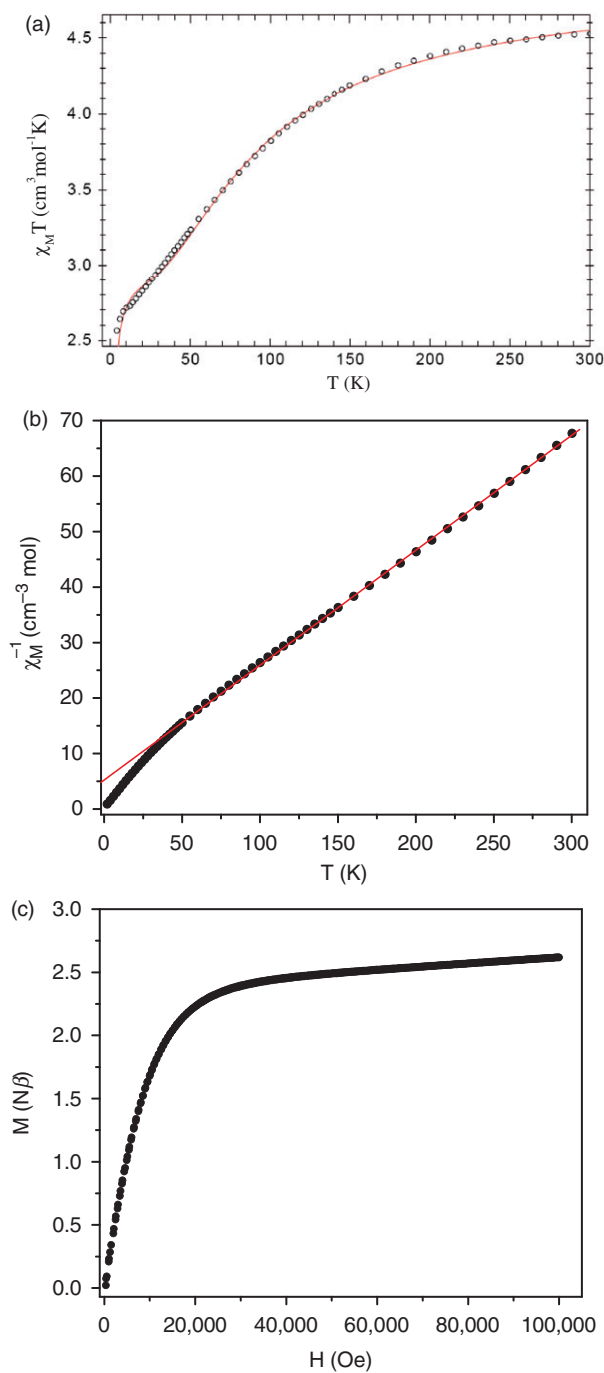


Figure 3. (a) $\chi_M T$ vs. T plot for **2** at 1 T. The solid red line was calculated with the parameters reported in the text. (b) χ_M^{-1} vs. T plot for **2**. The solid red line shows a Curie-Weiss fit over 34–300 K. (c) Magnetization vs. field (Oe) measurements for **2** (2 K).

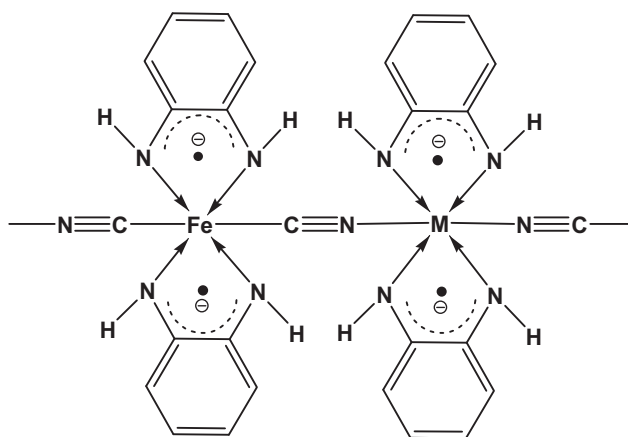


Figure 4. Schematic representation of $K[M^{II}(s\text{-bqdi})_2][Fe^{III}(s\text{-bqdi})_2(CN)_2] \cdot 10H_2O$ ($M^{II} = Co, Ni$ and Cu).

4. Conclusion

The 1-D cyano-bridged heterobimetallic assemblies $K[M^{II}(s\text{-bqdi})_2][Fe^{III}(s\text{-bqdi})_2(CN)_2] \cdot 10H_2O$ ($M^{II} = Co, Ni$ and Cu) have been synthesized and characterized. IR spectrum of $[Fe^{III}(s\text{-bqdi})_2(CN)_2]$ shows that $N_{s\text{-bqdi}} \rightarrow Fe$ σ -bond causes lowering of $\nu(CN)$. The single band observed for $\nu(CN)$ in the spectra of **2–4** indicates the presence of only one type of cyanide (bridged). The UV-Vis spectra show the presence of Fe^{III} in low-spin state. The spectra of **2–4** suggest octahedral coordination. The CV measurement confirms +3 iron in the complex. The X-ray powder diffraction studies reveal that all the heterobimetallic complexes are isostructural having primitive hexagonal unit lattice structure. The magnetic studies indicate antiferromagnetic interaction between the $Co_{H.S.}^{II}$ and $Fe_{L.S.}^{III}$. The complexes are shown in figure 4.

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