



RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION OF CYANIDE COMPLEXES WITH 2-(HYDROXYMETHYL)PYRIDINE BY VIBRATIONAL SPECTROSCOPIC, THERMAL STUDIES AND ELECTRICAL PROPERTIES

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ABSTRACT

In this investigation, we present synthesis and characterized of three new heteropolynuclear cyanide complexes with 2-(Hydroxymethyl)pyridine (hmpH) of $[M(H_2O)(hmpH)Ni(CN)_4]_2 \cdot nH_2O$, (M(II) = Fe, Co and Ni); n = 12 for Fe, 2 for Co and Ni). The obtained complexes have been studied by elemental, thermal analysis, FT-IR, and Raman spectroscopic measurement techniques. Considering the alterations in characteristic peaks of cyanide, aqua, and hmpH ligands, general knowledge about the structural features of the complexes was detected from the vibrational spectra. The Ni(II) ion is coordinated by four cyanide-carbon atoms forming a square planar geometry. In addition, thermal analyses and electrical features of the complexes were investigated.

Keywords: Cyanide complex; Tetracyanonickelate(II) complex; 2-(Hydroxymethyl)pyridine complex; FT-IR and Raman spectra; Thermal analyses

1. INTRODUCTION

Since Diesbach discovered Prussian blue in the 18th century, metal cyanide complexes containing cyanometallate building blocks have attracted significant interest in recent years. Due to the role of cyanide ion as a bridging ligand to connect transition metal ions, cyanometallate building blocks, $[M(CN)_x]_n$, were employed to create different dimensional molecular structures in these complexes [1-3]. Short bridging ligands like cyanides, azides and nitrile donors ensure a suitable way of linking transition metals in the solid state [1]. The cyanide ligand is rigid and adopts a linear coordination mode, supplying a presumable structure owing to rational design [1]. Therefore, cyanide ligands use as a ligand in the synthesis of coordination complexes has led to a wide area of research such as conductivity [2, 3], catalysts [4], ion conductors [5], spin crossover [6], porosity [7], sensors [8] and magnetic materials [9, 10].

Cyanide ligand can function as either a monodentate ligand or a bridging ligand resulting from the reactivity of a mononuclear complex with another metal ion via the nitrogen atom, thanks to its ambidentate nature [11]. Through the utilization of this particular attribute, the cyanide ligand has the capacity to generate different polymeric species [12-19]. Building blocks such as $[M(CN)_6]^{3-}$ (M(III) = Fe, Co, Cr or Mn) [20, 21], $[M(CN)_4]^{2-}$ (M(II) = Ni, Pd or Pt) [20-23], $[M(CN)_4]^{2-}$ (M = Zn, Cd or Hg) [24, 25], $[M(CN)_2]^-$ (M = Au or Ag) [26, 27] and auxiliary ligands such as pyridine, imidazole, and their derivatives with coordination bonds comprise the multi-dimensional cyanide complexes. In the design of metal complexes, ligands with cyanide groups and neutral molecules can be chosen as useful building blocks. In literature, ligands containing nitrogen, oxygen and sulfur atoms have been widely used to form cyanide complexes [28-30]. The architectures and topologies of metal-cyanide systems are

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strongly affected by the nature of the auxiliary ligand (density, volume, rigidity, etc.). As an auxiliary ligand, 2-(hydroxymethyl)pyridine in this work functions as a bidentate or chelate ligand via its -N and -O donor sites which is rare in the literature. Particularly important, because of their spectroscopic and electrochemical properties, are the discrete heteropolynuclear cyanide-bridged complexes. The heteropolynuclear cyanide complexes with 2-(hydroxymethyl)pyridine as chelate ligand have been limited [31, 32]. Therefore, we preferred the 2-(hydroxymethyl)pyridine as chelate ligand in this study.

In our previous studies, we have used hmpH for preparation of $[\text{Cu}(\text{hmp})_2][\text{Cu}(\text{hmpH})_2\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]_2 \cdot 4\text{H}_2\text{O}$, $[\text{Zn}_3(\text{hmp})_2(\text{hmpH})_4\text{Ni}_2(\mu\text{-N})_6(\text{CN})_2] \cdot 2\text{H}_2\text{O}$, $[\text{Cd}_2(\text{H}_2\text{O})_2(\text{hmpH})_2\text{Ni}(\mu\text{-CN})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]$, $[\text{Cu}(\text{hmpH})_2\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ and $[\text{Cu}(\text{hmpH})_2\text{Pt}(\mu\text{-CN})_2(\text{CN})_2]_n$ and the structural studies have been shown to act as a chelate ligand of hmpH [31, 32]. As part of our ongoing research, we report the syntheses, structural and physical characterizations of three cyanide-bridged heteronuclear complexes, $[\text{Fe}(\text{H}_2\text{O})(\text{hmpH})\text{Ni}(\text{CN})_4]_2 \cdot 12\text{H}_2\text{O}$, $[\text{Co}(\text{H}_2\text{O})(\text{hmpH})\text{Ni}(\text{CN})_4]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{H}_2\text{O})(\text{hmpH})\text{Ni}(\text{CN})_4]_2 \cdot 2\text{H}_2\text{O}$ (where hmpH = 2-(Hydroxymethyl)pyridine, abbreviated hereafter as **M-Ni-hmpH**).

2. EXPERIMENTAL

2.1. Materials and Instrumentation

The study utilized essential chemical substances including iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), cobalt(II) chloride (CoCl_2 , 99%), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 97%), potassium cyanide (KCN, 96%) and 2-(Hydroxymethyl)pyridine ($\text{C}_6\text{H}_7\text{NO}$, 98%). These chemicals were of reagent grade and were employed without undergoing additional purification.

Elemental analysis of the percentage of hydrogen, carbon and nitrogen atoms was performed on a LECO, CHNS-932 analyzer. The FT-IR and Raman spectra of the complexes were recorded at room temperature as pure solids by using a Perkin Elmer 100 FT-IR spectrometer with ATR (Attenuated Total Reflection) and Bruker Senterra Dispersive Raman instrument using 785 nm laser excitation in the range of $4000\text{-}250\text{ cm}^{-1}$, respectively. Thermal analyzes of the complexes were recorded simultaneously in a static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range of $30\text{-}1000\text{ }^\circ\text{C}$ using platinum crucibles on a Perkin Elmer Diamond TG/DTA thermal analyzer. The electrical conductivity values were determined using the four-probe technique at room temperature. This was done by applying a programmable direct current (dc) using the Keithley 2601 A System Sourcemeter to the sample pellets. The pellets were specifically designed to be 1 mm thick and 1.0 cm in diameter, and were subjected to a hydraulic pressure of 10 tons.

2.2 Preparation of the Complexes

The synthesis of the complexes was prepared in a mention similar to that described method in cited literature [33], but hepH ligand was replaced by hmpH ligand (0.218 g; 2 mmol). As a mention [33] reference, the synthesis of the complexes in three stages; in the first stage $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, in the second stage $\text{M}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [$\text{M}(\text{II}) = \text{Fe, Co or Ni}$] and in the final stage $[\text{M}(\text{H}_2\text{O})(\text{hmpH})\text{Ni}(\text{CN})_4]_2 \cdot n\text{H}_2\text{O}$ [$\text{M}(\text{II}) = \text{Fe, Co and Ni; hmpH} = 2\text{-}(\text{Hydroxymethyl})\text{pyridine}$]. The powder forms of the complexes were all produced.

3. RESULTS AND DISCUSSION

3.1. Elemental Analyses

In Table 1, the analytical data, elemental analyses (C, H and N), molar ratio and color of the **M-Ni-hmpH** ($\text{M}(\text{II}) = \text{Fe, Co or Ni}$) complexes are detailed. There is agreement between the calculated and

measured elemental analysis values. Based on the obtained data, the prepared complexes are formulated and composition has been determined by elemental analyses.

Table 1. Results of elemental analysis of the complexes.

Complex	Molecular formula	M _{wt.} (g/mol)	Elemental analyses						Color
			C%		H%		N%		
			Calc.	Found	Calc.	Found	Calc.	Found	
[Fe(H ₂ O)(hmpH)Ni(CN) ₄] ₂ ·12H ₂ O	C ₂₀ H ₄₂ N ₁₀ O ₁₆ Ni ₂ Fe ₂	907.68	26.46	25.65	4.66	4.26	15.43	15.08	Brown
[Co(H ₂ O)(hmpH)Ni(CN) ₄] ₂ ·2H ₂ O	C ₂₀ H ₂₂ N ₁₀ O ₆ Ni ₂ Co ₂	733.71	32.74	34.87	3.02	3.63	19.09	18.35	Pink
[Ni(H ₂ O)(hmpH)Ni(CN) ₄] ₂ ·2H ₂ O	C ₂₀ H ₂₂ N ₁₀ O ₆ Ni ₄	733.23	32.76	34.57	3.02	3.31	19.10	18.77	Pale Blue

3.2 Vibrational Spectra of the Complexes

The FT-IR and Raman spectra of the ligands (aqua and hmpH) and obtained complexes are presented in Figures 1 and 2. The characteristic peaks hmpH observed with shifts their positions in the spectra of the complexes studied are listed in Table 2, together with free hmpH wavenumbers for comparison [34]. The fact that the vibrational spectral properties of the complexes are very close to each other indicates that they have similar structures [31, 32].

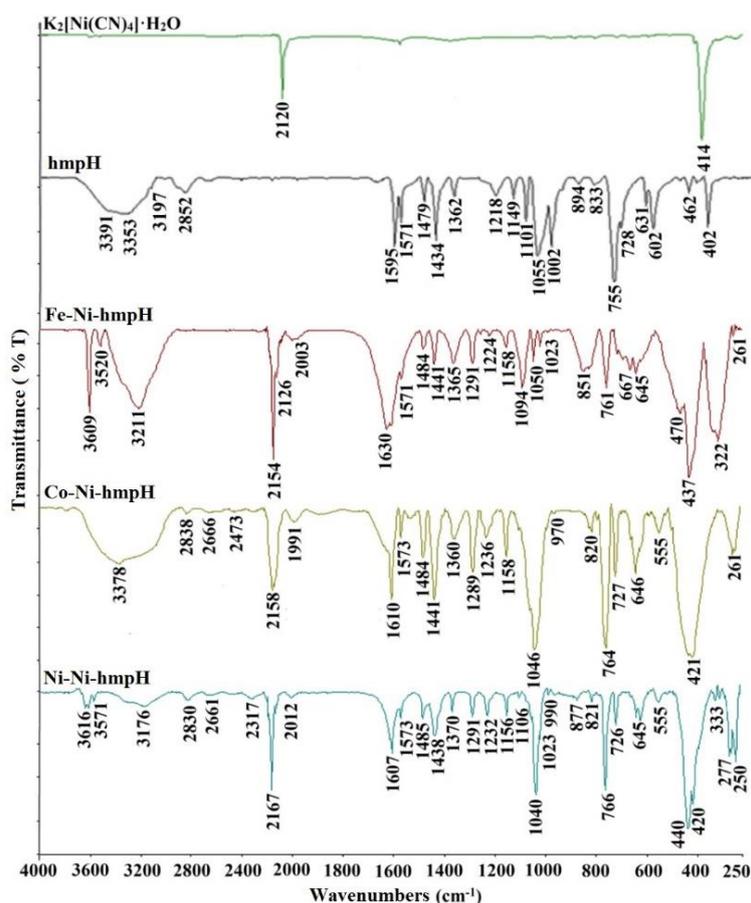


Figure 1. The FT-IR spectra of $K_2[Ni(CN)_4] \cdot H_2O$, hmpH and the complexes

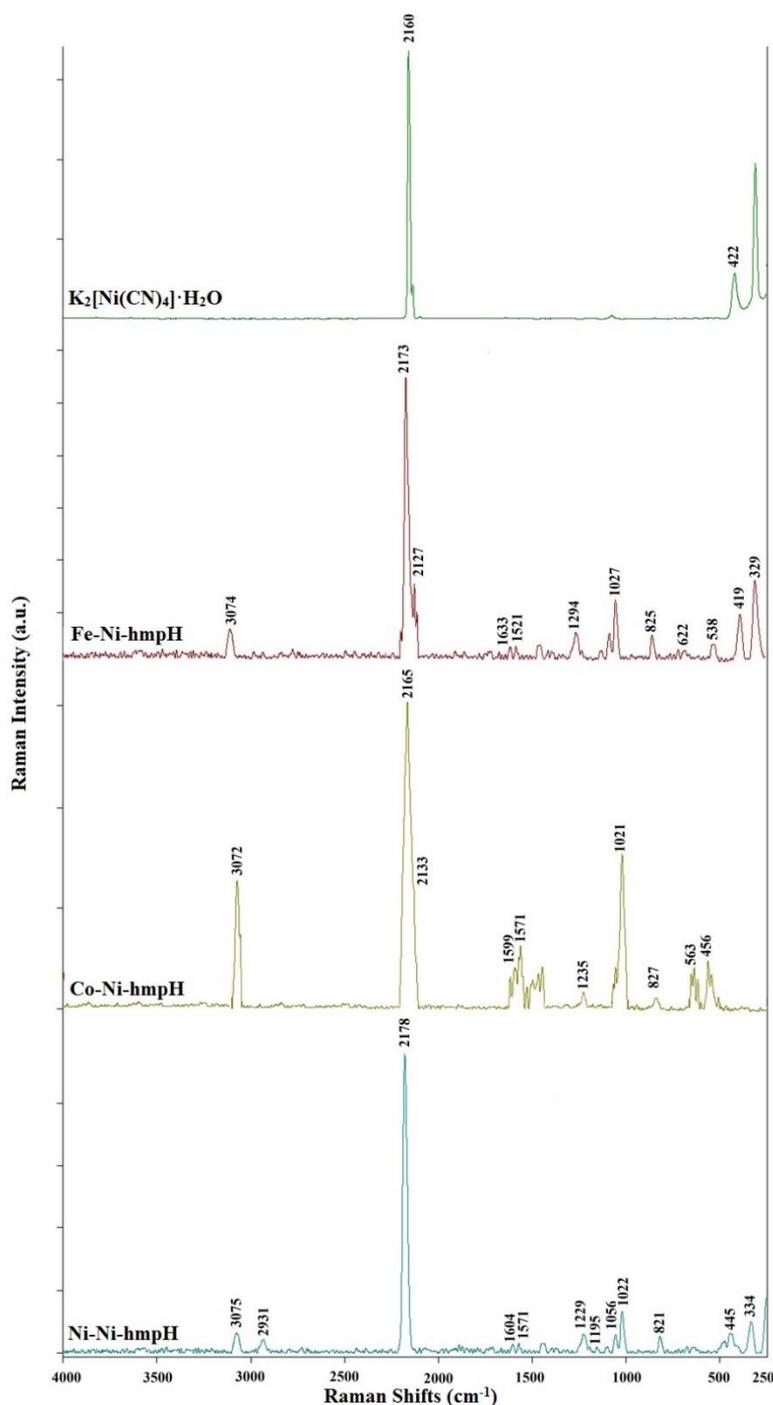


Figure 2. Raman spectra of K₂[Ni(CN)₄]·H₂O and the complexes.

3.2.1. Aqua vibrations

The aqua molecule has vibrations as asymmetrical OH stretching bands, symmetrical OH stretching bands, and OH bending bands. The $\nu(\text{OH})$ stretching vibration bands of the coordinated aqua molecules, both symmetric and asymmetric, are detected in the region 3700 cm^{-1} - 3300 cm^{-1} [35]. Furthermore, the entity of aqua molecules shows up as two shoulders at 1690 cm^{-1} and 1620 cm^{-1} owing to $\delta(\text{OH})$ deformation vibrations. In our former study, the presence of water molecules in the structures of the complexes was determined by vibration analysis and supported by X-ray diffraction of the complexes

such as $[\text{Cd}(\text{H}_2\text{O})(2\text{mpz})\text{Ni}(\mu\text{-CN})_4]_n$ [36]. The $\nu(\text{OH})$ stretching vibrations of the aqua molecules have been experimentally detected at 3609 and 3520 cm^{-1} in **Fe-Ni-hmpH**, 3784 cm^{-1} and 3690 cm^{-1} in **Co-Ni-hmpH** and 3616 and 3571 cm^{-1} in **Ni-Ni-hmpH** (see Figure 3). The $\nu(\text{OH})$ deformation vibration in complexes is found to be 1630 cm^{-1} in **Fe-Ni-hmpH**, 1641 cm^{-1} in **Co-Ni-hmpH** and 1651 cm^{-1} in **Ni-Ni-hmpH**.

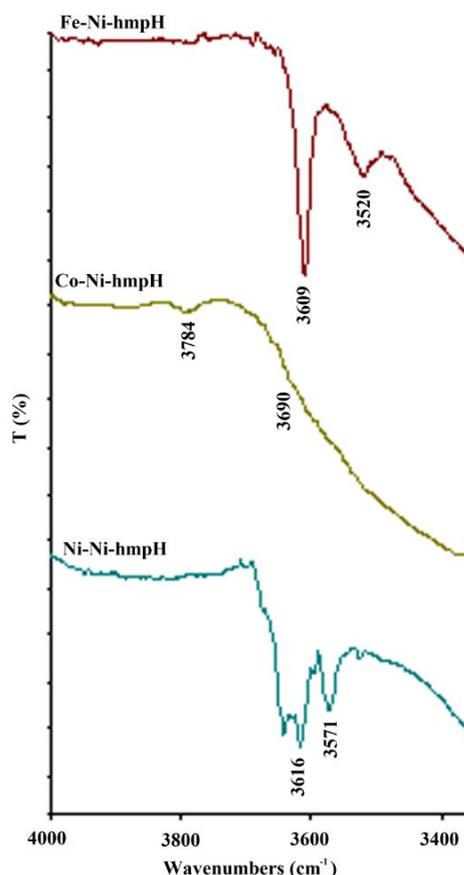


Figure 3. FT-IR spectra of water molecules in obtained complexes.

3.2.2. 2-(Hydroxymethyl)pyridine vibrations

In the literature, there are various studies conducted with hmpH by many researchers. The $\nu(\text{OH})$ vibrations of hmpH are shown the strong and broad absorption bands in the range $3500 - 3200$ cm^{-1} [37]. The $\nu(\text{OH})$ stretching band is detected at frequency of 3211 cm^{-1} for **Fe-Ni-hmpH**, 3378 cm^{-1} for **Co-Ni-hmpH**, 3374 cm^{-1} for **Ni-Ni-hmpH** in the FT-IR spectra but this band is absent from the Raman spectrum.

As stated in the literature, most aromatic complexes in the region $3100 - 3000$ cm^{-1} in FT-IR spectra have their own bands [38-42]. $\nu(\text{CH})$ stretching vibrations in the complexes are detected in the region of $3136 - 3010$ cm^{-1} in FT-IR spectra and $3075 - 3031$ cm^{-1} in Raman spectra. The asymmetric $\nu(\text{CH}_2)$ stretching vibration are detected at 2913 cm^{-1} in **Fe-Ni-hmpH**, 2915 cm^{-1} in **Co-Ni-hmpH** and 2917 cm^{-1} in **Ni-Ni-hmpH**. In the complexes; the symmetric $\nu(\text{CH}_2)$ stretching vibrations are detected at 2838 cm^{-1} in **Fe-Ni-hmpH** and in **Co-Ni-hmpH**, 2830 cm^{-1} in **Ni-Ni-hmpH** in the FT-IR spectra and are determined at 2848 cm^{-1} in **Fe-Ni-hmpH** and at 2825 cm^{-1} in **Co-Ni-hmpH**, 2839 cm^{-1} in **Ni-Ni-hmpH** in the Raman spectra. The $\gamma(\text{CH})$ out of plane deformation is detected in the region of $1000 - 700$ cm^{-1} [43]. In the complexes; these vibrations are found at 992 and 822 cm^{-1} in **Fe-Ni-hmpH**, at 970 and 820 cm^{-1} in **Co-Ni-hmpH** and 990 , 908 and 818 cm^{-1} in **Ni-Ni-hmpH** in the FT-IR spectra.

Table 2. The FT-IR and Raman wavenumbers of the hmpH in complexes (cm⁻¹).

Assignments [34]	hmpH	hmpH [33]		Fe-Ni-hmpH		Co-Ni-hmpH		Ni-Ni-hmpH	
		Experimental	Calculated	FT-IR	Raman	FT-IR	Raman	FT-IR	Raman
v(OH)	3391 s	3400 s	3398	3211 m	3286 m	3378 m	-	3374 m	-
v(CH)	3101 vw	3103 s	3102	3132 sh	-	3100 w	-	3136 vw	-
v(CH)	3066 w	3075 s	3079	3067 sh	3075 m	3070 m	3072 vw	3072 sh	3075 m
v(CH)	3050 sh	-	3059	-	3031 w	-	3042 vw	-	-
v(CH)	3014 vw	3022 m	3037	3012 sh	-	3015 w	-	3010 sh	-
v _a (CH ₂)	2903 vw	2914 m	2919	2913 w	2900 w	2915 w	2933 vw	2917 w	2935 w
v _s (CH ₂)	2853 m	2856 s	2890	2838 w	2848 m	2838 w	2825 m	2830 w	2839 vw
v(C=C)	1595 s	1595 vs	1599	1610 s	1631 m	1610 s	1621 w	1607 s	1628 vw
v(C=C)	1570 m	1575 vs	1582	1571 m	1570 w	1573 m	1571 m	1573 s	1572 m
v(C=N)	1477 m	1482 s	1478	1484 m	-	1488 m	-	1485 m	-
v(CC)	1454 sh	-	1467	1441 m	1435 w	1441 m	1457 m	1439 m	1450 s
δ(CH ₂)	1434 s	1437 vs	1436	-	-	-	1445 s	1438 m	1439 m
v(CC)	1360 m	1386 m	1407	1365 m	1395 vw	1360 m	1403 vw	1370 m	1397 vw
v(CC)	1320 vw	1329 m	1300	-	1335 w	-	1316 vw	-	1320 w
v(CN)	1280 vw	1268 w	1277	1291 m	1294 vw	1289 m	1286 w	1291 m	1291 m
β(OH)	1217 m	1228 m	1229	1224 m	1261 vw	1236 m	1235 m	1232 w	1228 w
β(CH)	-	-	1224	-	-	-	-	-	-
β(CH)	1148 m	1160 m	1164	1158 m	1189 vw	1158 m	1163 vw	1156 m	1157 m
β(CH)	1100 m	-	1147	-	1126 w	1107 w	1123 vw	1106 vw	1128 vw
v(CO)	1057 s	1110 s	1096	1094 m	1096 m	1066 s	1061 w	1058 m	1056 m
β(CH)	1052 sh	1068 vs	1048	1050 vs	1027 m	1046 vs	1023 m	1040 s	1022 m
γ(CH)	-	-	1042	-	-	-	-	-	-
ω(CH ₂)	1002 m	1019 vs	1011	1023 w	-	1023 m	-	1023 m	-
γ(CH)	993 m	1007 s	992	992 w	-	970 m	981 vw	990 w	987 w
ρ(CH ₂)	960 v	974 w	991	933 vw	966 vw	935 vw	977 vw	947 vw	968 vw
τ(CH ₂)	957 v	-	955	921 vw	919 vw	927 vw	939 w	932 vw	940 w
γ(CH)	909 vw	910 w	891	-	889 vw	-	-	908 vw	905 vw
γ(CH)	893 w	818 w	797	822 m	846 vw	820 w	827 m	818 m	820 m
γ(OH)	755 vs	777 vw	753	761 s	773 vw	764 vs	768 m	766 s	760 w
β(CCC)	727 m	746 m	729	720 m	737 vw	727 s	739 w	726 m	736 w
β(CCC)	632 m	622 m	627	645 m	653 vw	646 m	659 m	645 m	646 w
β(CC)	570 sh	-	582	-	560 vw	-	563 m	555 w	567 m
β(CNC)	464 m	469 w	461	470 w	476 vw	458 sh	475 w	461 w	480 w
β(CO)	422 w	426 m	431	437 w	429 vw	439 s	445 w	440 s	442 m
γ(CCC)	402 s	389 w	406	338 m	340 vw	-	334 m	333 k	336 m
γ(CCC)	281 vw	228 m	222	261 vw	-	261 w	287 vw	250 m	252 m

Abbreviations used: v-stretching; β - in-plane bending; δ - deformation; ρ - rocking; γ - out of plane bending; ω - wagging and τ - twisting/torsion; s, strong; m, medium; w, weak; sh, shoulder; v, very.

It is very difficult to define C=N, C-N vibrations as it is possible to mix more than one band in this region [34]. The v(CC) stretching bands of the pyridine ring in the free hmpH yields a vibration peak at 1595, 1570, 1360 and 1320 cm⁻¹ wavenumbers in its FT-IR and Raman spectra, respectively, while this vibration peak occurs at 1630, 1571 and 1365 cm⁻¹ in **Fe-Ni-hmpH**, at 1610, 1573 and 1360 cm⁻¹ in **Co-Ni-hmpH** and 1607, 1573 and 1370 cm⁻¹ in **Ni-Ni-hmpH** in the FT-IR spectra and at 1631, 1570 and 1395 cm⁻¹ in **Fe-Ni-hmpH**, at 1621, 1571 and 1403 cm⁻¹ in **Co-Ni-hmpH** and are shown 1628, 1572 and 1397 cm⁻¹ in **Ni-Ni-hmpH** in the Raman spectra. The v(C=N) stretching skeletal bands are observed in the range 1627 - 1566 cm⁻¹ [44-47]. These bands shown at 1484 cm⁻¹ in **Fe-Ni-hmpH**, 1484 cm⁻¹ in **Co-Ni-hmpH** and 1485 cm⁻¹ in **Ni-Ni-hmpH** are assigned to the v(C=N) stretching vibration in the FT-IR spectra of the complexes. When the nitrogen atom of the pyridine aromatic ring participates in complex formation, specific vibration bands shows higher values due to the coupling with M-N_{hmpH} bond vibrations [48-50]. v(CO) stretching vibration bands are observed at 1057 cm⁻¹ for free hmpH in the FT-IR spectrum. This band is observed at 1094 cm⁻¹ in **Fe-Ni-hmpH**, 1066 cm⁻¹ in **Co-Ni-hmpH** and 1058 cm⁻¹ in **Ni-Ni-hmpH** in the FT-IR spectra of the complexes. Additionally, v(CO) stretching vibration band are observed at 1096 cm⁻¹ in **Fe-Ni-hmpH**, 1061 cm⁻¹ in **Co-Ni-hmpH** and 1056 cm⁻¹ in **Ni-Ni-hmpH** in the Raman spectra. This vibration bands in the vibrational spectra of the complexes support each other. The other vibration wavenumbers of hmpH and the complexes are observed in Table 2.

3.2.3 [Ni(CN)₄]²⁻ anion vibrations

Because of its negative charge, the CN⁻ ion may function as both an electron donor (by giving up an electron to the metal) and an electron acceptor (by taking one from the metal). The σ -donation ability also increases when electrons are removed from the weakly antibonding molecular orbital, which results in an increase in the value of $\nu(\text{CN})$. On the other hand, its π -accepting properties decrease when electrons are added to the π bonding orbital, which results in a decrease in the value of $\nu(\text{CN})$. The $\nu(\text{CN})$ stretching vibration bands are considered to be one of the principal vibrational characteristics exhibited by cyanide complexes. $\nu(\text{CN})$ stretching vibrations are dependent to the surroundings of the cyanide ligands. Strong and distinct absorption bands that can be clearly identified in the region of 2200 - 2000 cm^{-1} are defined by the $\nu(\text{CN})$ stretching vibrations originating from the cyanide groups [11]. Due to a reduction in the π -acceptance of the CN⁻ ligand, these bands shift to higher frequencies between 2100 and 2200 cm^{-1} during oxidation of the metal center. Since the electronegativity of Ni(II) is less than that of Pd(II) and Pt(II), the σ -donation will be the least, and it is anticipated that the $\nu(\text{CN})$ will be the lowest [11].

Table 3. Vibrational wavenumbers of the polymeric sheet and metal-ligand vibrations in the complexes (cm^{-1}).

Assignments	K ₂ [Ni(CN) ₄]·H ₂ O [50]	Fe-Ni-hmpH	Co-Ni-hmpH	Ni-Ni-hmpH
A _{1g} , $\nu(\text{C}\equiv\text{N})$	(2160) vs	(2173) vs	(2165) vs	(2178) vs
B _{1g} , $\nu(\text{C}\equiv\text{N})$	(2137) m	(2127) m	(2133) m	-
E _u , $\nu(\text{C}\equiv\text{N})$	2122 vs	2154 vs, 2126 m	2158 vs, 2139 s	2167 vs, 2136 m
$\nu(^{13}\text{CN})$	2084 w	2003 w	2091 w	2012 vw
E _u , $\nu(\text{Ni}-\text{C})$	540 w	558 vw	555 w	555 w
A _{2u} , $\pi(\text{Ni}-\text{CN})$	443 w	458 w	437 m	440 m
E _u , $\delta(\text{Ni}-\text{CN})$	417 s	437 vs	421vw	420 s

Abbreviations used; s strong, m medium, w weak, sh shoulder, v very. The symbols ν , δ and π refer to valence, in-plane and out-of-plane vibrations, respectively.

Raman bands are given in parentheses.

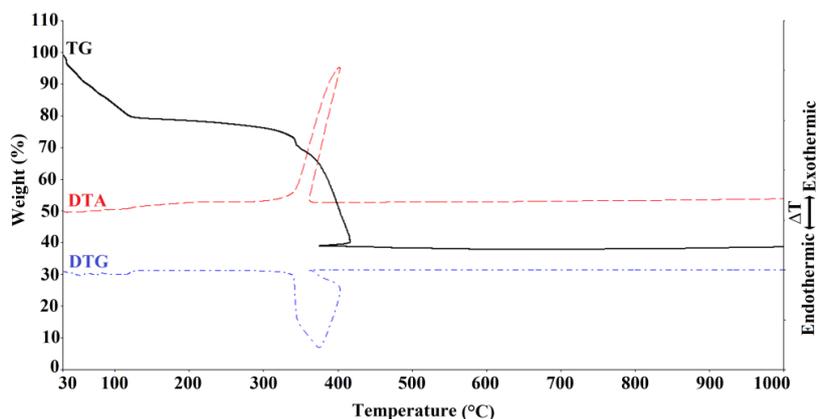
The vibrational wavenumbers for [Ni(CN)₄]²⁻ group in K₂[Ni(CN)₄]·H₂O and in complexes **Fe-Ni-hmpH**, **Co-Ni-hmpH** and **Ni-Ni-hmpH** are presented in Table 3. Based on the work of Mc Cullough et al., who provided vibrational data for the [Ni(CN)₄]²⁻ in Na₂[Ni(CN)₄], the bands of the [Ni(CN)₄]²⁻ in the complexes were assigned [51]. Because the tetracyanometallate(II) anion in this salt was not coordinated to the Na cation, it is possible to regard it as an isolated unit with D_{4h} symmetry. Because of this, it may be used as a reference to remark on vibrational shifts that occur when M-NC bonding occurs [52, 53].

The constitution of a cyanide bridge in the complex can be determined by the $\nu(\text{C}\equiv\text{N})$ band shift in the FT-IR spectrum [19, 54-57]. The $\nu(\text{C}\equiv\text{N})$ absorption band recorded at the highest wavenumber in the complexes can be assigned to the vibration of the structurally identical bridged cyanide group. Mononuclear compound K₂[Ni(CN)₄]·H₂O exhibited a band at 2122 cm^{-1} which can be assigned to the $\nu(\text{CN})$ stretching band, while complexes **Fe-Ni-hmpH**, **Co-Ni-hmpH** and **Ni-Ni-hmpH** exhibited strong absorptions at 2154 and 2126 cm^{-1} ; 2158 and 2139 cm^{-1} and 2167 and 2136 cm^{-1} in the FT-IR spectra, respectively. This stretching band of K₂[Ni(CN)₄]·H₂O complex shows spectra between 2160 cm^{-1} and 2137 cm^{-1} in the Raman spectra. The A_{1g} and B_{1g} cyanide stretching modes in the Raman spectra of the complexes are shown in spectra 2173 and 2127 cm^{-1} for **Fe-Ni-hmpH**, 2165 and 2133 cm^{-1} for **Co-Ni-hmpH** and 2178 cm^{-1} for **Ni-Ni-hmpH**.

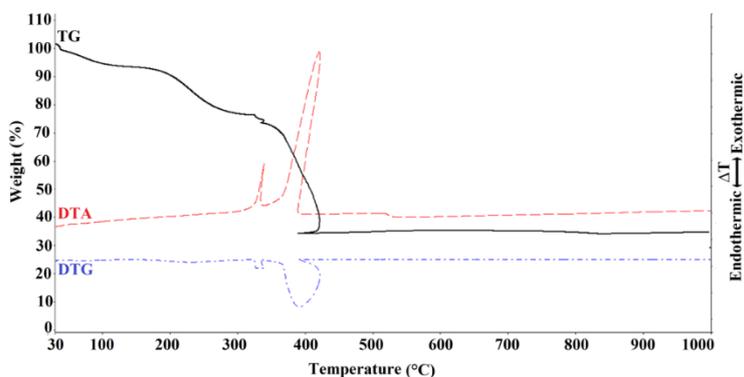
On the other hand, the $\nu(\text{Ni}-\text{CN})$ stretching and $\delta(\text{Ni}-\text{CN})$ in-plane bending vibration bands of K₂[Ni(CN)₄]·H₂O in the low frequency region of the FT-IR spectra is found as 556 cm^{-1} and 441 cm^{-1} , respectively [58]. These bands observed at 558 cm^{-1} and 417 cm^{-1} in **Fe-Ni-hmpH**, 555 cm^{-1} and 437 cm^{-1} in **Co-Ni-hmpH**, 555 cm^{-1} and 440 cm^{-1} in **Ni-Ni-hmpH** in the FT-IR spectra of the complexes, respectively.

3.3 Thermal Behaviors of the Complexes

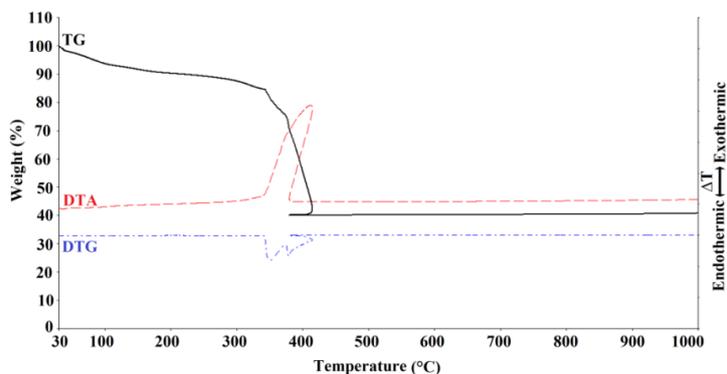
The thermal behaviors of complexes are performed by TG, DTA and TGA methods in the temperature range of 30 - 1000 °C. The TG, DTA and TGA curves are present in Figure 4. The thermal behaviors of the **M-Ni-hmpH** (M(II) = Fe, Co or Ni) complexes are similar and decomposition takes place in three stages.



(a)



(b)



(c)

Figure 4. The TG, DTG and DTA curves of **Fe-Ni-hmpH** (a), **Co-Ni-hmpH** (b) and **Ni-Ni-hmpH** (c)

Firstly, aqua ligands are cleaved from the structure in the temperature range of 31-37 °C for **Fe-Ni-hmpH**, 31-140 °C for **Co-Ni-hmpH** and 34-128°C for **Ni-Ni-hmpH** [found (calcd.): 2.91% (2.77%) in **Fe-Ni-hmpH**, 8.53% (9.82%) in **Co-Ni-hmpH** and 7.24% (9.82%) in **Ni-Ni-hmpH**]. The second stages of the complexes lose hmpH ligands in the temperature range of 36-340 °C for **Fe-Ni-hmpH**, 140-384 °C for **Co-Ni-hmpH** and 128-356°C for **Ni-Ni-hmpH** [found (calcd.): 26.83% (24.08%) in **Fe-Ni-hmpH**, 30.26% (29.74%) in **Co-Ni-hmpH** and 12.47% (14.88%) in **Ni-Ni-hmpH**]. The following stage for the complexes is related with the exothermic removal of -CN groups in the temperature range of 340-410 °C [DTA_{max} = 402 °C; found: 22.97%, calcd.: 24.76% for **Fe-Ni-hmpH**], 384-846 °C [DTA_{max} = 421 °C; found: 27.91%, calcd.: 228.36% for **Co-Ni-hmpH**] and -CN groups and one hmpH at 356-418 °C [DTA_{max} = 413°C; found: 40.95%, calcd.: 43.27% for **Ni-Ni-hmpH**]. The final degradation products are identified as MO and NiO (M = Fe, Co and Ni, found: 34.60%, calcd.: 32.34% in **Fe-Ni-hmpH**, found: 40.78 %, calcd.: 38.96% in **Co-Ni-hmpH** and found: 40.02%, calcd.: 40.74% in **Ni-Ni-hmpH**).

3.4 Electrical Conductivity

The electrical conductivity values of the polymeric complexes were measured with four probe techniques. Sample pellets obtained from the complexes were designed with a thickness of 1 mm and a diameter of 1.0 cm under 10 tons of hydraulic pressure. The electrical conductivity is achieved owing to intra-molecular and inter-molecular interactions. The similar electrical conductivity measurements were observed for cyanide complexes [33, 59]. Experimental electrical conductivities values of the complexes are $2.94 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ for **Fe-Ni-hmpH**, $8 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ for **Co-Ni-hmpH** and at $7.0 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ for **Ni-Ni-hmpH**. As can be seen from here, the complexes at room temperature show a weak semiconductive behavior.

4. CONCLUSIONS

In our study, a new series of three tetracyanonickelate(II) complexes have been synthesized by using hmpH ligand and characterized by vibration spectroscopic techniques (FT-IR and Raman), elemental analysis, thermal characterization and electrical conductivity. The Ni(II) ion exhibit a square planar coordination geometry by four carbon atoms from the cyanide ligands. Infrared and Raman spectra show the presence of vibrational bands of functional groups of hmpH ligand and $[\text{Ni}(\text{CN})_4]^{-2}$ anion. In addition, the FT-IR spectra of the complexes indicated the entity of terminal and bridged cyanide ligands in the complexes. Thermal analysis demonstrates that all the complexes have similar nature and decomposed in three steps resulting in MO and NiO as the eventual product of the thermal decomposition process. Also, elemental, spectroscopic, and thermal data support the identity in structural features of the complexes. Solid-state electrical conductivity of the complexes shows their semiconducting behavior.

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Elvan Sayın: Writing – review & editing, Investigation. **Güneş Süheyla Kürkçüoğlu:** Supervision, Data curation, Methodology.

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- $[\{\text{Fe}^{\text{III}}(\text{bipy})(\text{CN})_4\}_2\text{Zn}^{\text{II}}]\cdot 2\text{H}_2\text{O}$ [bipy= 2, 2'-Bipyridine; M= Mn and Zn]. Inorg chem 2002; 41: 818-826.
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