

SYNTHESES AND CHARACTERIZATIONS OF THE CYANIDE-BRIDGED HETERONUCLEAR POLYMERIC COMPLEXES WITH 2-ETHYLIMIDAZOLE

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ABSTRACT. Three new cyano-bridged heteronuclear polymeric complexes, $[\text{Cu}(\text{etim})_3\text{Ni}(\text{CN})_4]_n$, $\{[\text{Zn}(\text{etim})_3\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}\}_n$ and $[\text{Cd}(\text{etim})_2\text{Ni}(\text{CN})_4]_n$ (*etim* = 2-ethylimidazole, hereafter abbreviated as Cu–Ni–*etim*, Zn–Ni–*etim* and Cd–Ni–*etim*) have been prepared in powder form and characterized by FT-IR and Raman spectroscopies, thermal (TG, DTG and DTA) and elemental analyses. The spectral features of the complexes suggest that the Ni(II) ion is four coordinate with four cyanide-carbon atoms in a square planar geometry, whereas the Cu(II) and the Zn(II) ions of the Cu–Ni–*etim* and the Zn–Ni–*etim* complexes are completed by nitrogen atoms of two cyano groups of $[\text{Ni}(\text{CN})_4]^{2-}$ coordinated to the adjacent M(II) ions and three nitrogen atoms of the *etim* ligands. The Cd(II) ion of the Cd–Ni–*etim* complex is six-coordinate, completed with the two nitrogen atoms of the *etim* ligands and the four nitrogen atoms from bridging cyano groups. Polymeric structures of the Cu–Ni–*etim* and the Zn–Ni–*etim* complexes are 1D coordination polymer, while complex the Cd–Ni–*etim* presents a 2D network. The thermal decompositions in the temperature range 30–700 °C of the complexes were investigated in the static air atmosphere.

KEY WORDS: Tetracyanonickelate(II) complex, 2-Ethylimidazole complex, Cyanide-bridged complex, Vibration spectra, Thermal analysis

INTRODUCTION

Coordination polymers include metal ions linked by coordinated ligands into an endless array. This endless net must be defined by coordination bonds. Coordination polymers can form surprising supramolecular contractions which indicate regulation one, two, three dimensional due to coordination bonds. Cyanometallate complexes in coordination polymers have an important place and they are known to be among the first coordination compounds that has been prepared, studied, described and used up to now. Therefore, they have still continued actuality in the coordination chemistry [1-3]. Additionally, cyanometallate complexes exhibiting polymeric structures have found many application areas such as electrical conductivity [4], molecular sieves and ion exchange materials [5], molecular magnetic nanowires [6] and host-guest systems [7].

Cyanide anions having binding ability to various center atoms are used in the synthesis of one, two or three dimensional structures in organometallic and coordination chemistry. Cyanometallate building blocks containing cyanide groups, $[\text{M}(\text{CN})_x]^{n-}$ such as $[\text{Ni}(\text{CN})_6]^{4-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Pd}(\text{CN})_4]^{2-}$, $[\text{Pt}(\text{CN})_4]^{2-}$ and $[\text{Au}(\text{CN})_4]^-$ have been extensively utilized to form multidimensional networks [3, 8-10]. This is due to fact that both the carbon and the nitrogen ends of the cyanide ion act as Lewis bases that can coordinate two different metal cations acting as the corresponding Lewis acids. Accordingly, cyanometallate readily forms coordination polymers when reacted with transition-metal cations and can promote strong magnetic exchange. However, there have been many studies on octahedral $[\text{M}(\text{CN})_6]^{n-}$ but little interest has been drawn to square-planar $[\text{M}(\text{CN})_4]^{n-}$ [M(II) = Ni, Pd or Pt] bridging units [11-13]. The well-known Hofmann-type structures consist of building blocks $[\text{M}(\text{CN})_4]^{n-}$ and the general

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formula is shown as $[M(L)_xM'(CN)_4]_n$ [where $x = 2$ or 1 ; $M(II) = Mn, Fe, Co, Ni, Cu, Zn$ or Cd ; $M'(II) = Ni, Pd$ or Pt] [14].

In our previous studies, we reported the tetracyanonickelate(II) or tetracyanopalladate(II) complexes with imidazole [15], N-methylimidazole [16], 2-methylimidazole [15, 17], 4(5)-methylimidazole [18] and 1-ethylimidazole [19]. In this study, three new complexes using 2-ethylimidazole molecule, $[Cu(etim)_3Ni(CN)_4]_n$, $\{[Zn(etim)_3Ni(CN)_4] \cdot H_2O\}_n$ and $[Cd(etim)_2Ni(CN)_4]_n$, were synthesized and investigated by vibrational spectral (FT-IR and Raman), thermal and elemental analyses techniques.

EXPERIMENTAL

Materials

Nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$ -97%, Riedel-de Haen), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$ -99%, Merck), zinc(II) chloride ($ZnCl_2$ -96%, Merck), cadmium(II) chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5H_2O$ -99%, Across Organics), potassium cyanide (KCN-96%, Sigma-Aldrich) and 2-ethylimidazole ($C_5H_8N_2$ -98%, Sigma-Aldrich) from commercial sources were used as received.

Syntheses of the complexes

To water solution of nickel(II) chloride hexahydrate (1 mmol, 0.238 g) was added a solution of potassium cyanide (4 mmol, 0.260 g) in water solution and $K_2[Ni(CN)_4] \cdot H_2O$ complex was obtained as crystallized. The $K_2[Ni(CN)_4] \cdot H_2O$ (1 mmol, 0.259 g) complex was dissolved in distilled water, then 1 mmol of the metal(II) chloride ($CuCl_2 \cdot 2H_2O = 0.170$ g, $ZnCl_2 = 0.136$ g and $CdCl_2 \cdot 2.5H_2O = 0.228$ g) dissolved in distilled water were added to this solution under stirring and the $M[Ni(CN)_4] \cdot H_2O$ [$M = Cu(II), Zn(II)$ or $Cd(II)$] complexes obtained were filtered and dried in air. To 1 mmol of $M[Ni(CN)_4] \cdot H_2O$ [$Cu[Ni(CN)_4] \cdot H_2O = 0.244$ g, $Zn[Ni(CN)_4] \cdot H_2O = 0.246$ g or $Cd[Ni(CN)_4] \cdot H_2O = 0.293$ g] aqueous solution, 2 mmol of the *etim* (0.192 g) dissolved in ethyl alcohol were slightly added to this solution under stirring. The final mixtures were stirred for 3 h at room temperature. The products obtained were filtered and washed with water, ethanol and ether, respectively, and dried in air. The freshly prepared complexes were analyzed for C, H and N with the following results: Anal. found (calcd.) (%) for $C_{19}H_{24}N_{10}NiCu$ ($M_w = 514.70$ g/mol) : C, 43.94 (44.34); H, 4.90 (4.70); N, 26.84 (27.21); for $C_{19}H_{26}N_{10}ONiZn$ ($M_w = 534.56$ g/mol) : C, 42.50 (42.69); H, 4.91 (4.90); N, 25.37 (26.20); for $C_{14}H_{16}N_8NiCd$ ($M_w = 467.43$ g/mol) : C, 35.18 (35.97); H, 3.44 (3.45); N, 23.91 (23.97).

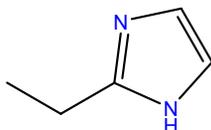
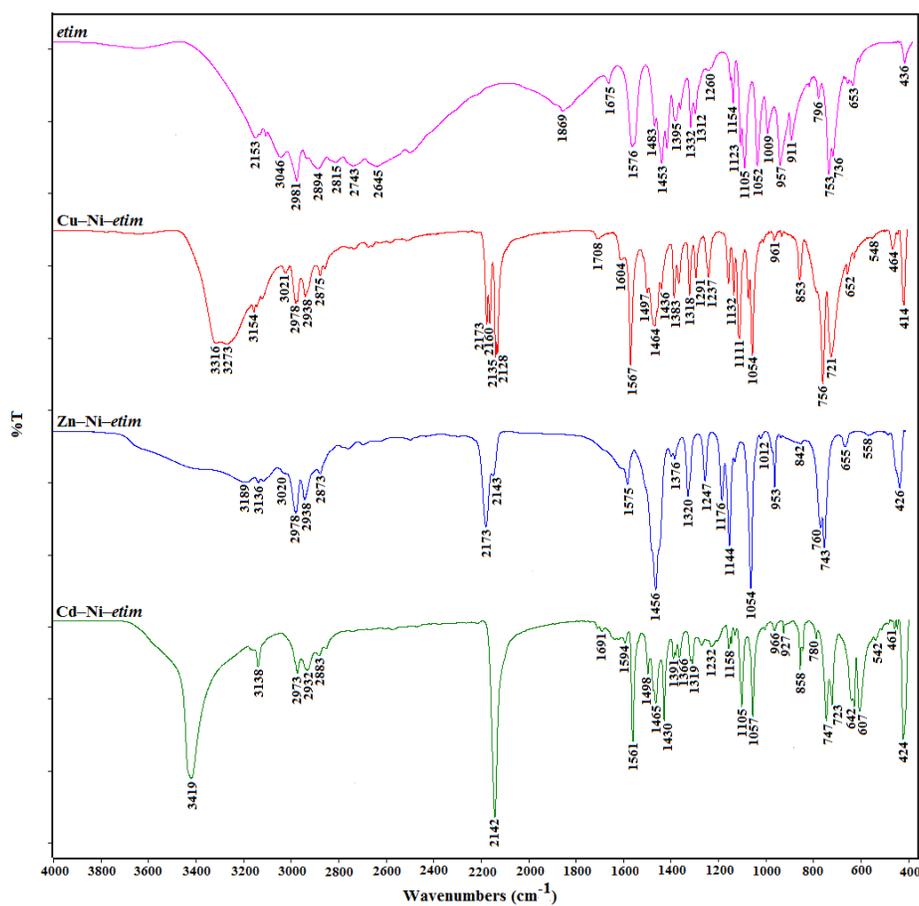
Measurements

Elemental analyses were performed using a CHNS-932 (LECO) analyzer for C, H and N at the Middle East Technical University Central Laboratory in Ankara, Turkey. The FT-IR spectra of the *etim* and the complexes were recorded as KBr pellets in the range of $4000-400$ cm^{-1} (2 cm^{-1} resolution) on a Perkin Elmer 100 FT-IR spectrometer which was calibrated using polystyrene and CO_2 bands. The Raman spectra of the complexes were recorded in the range of $4000-250$ cm^{-1} on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves of the complexes in a static air atmosphere at a heating rate of 10 $K\ min^{-1}$ in the temperature range $30-700$ $^{\circ}C$ using platinum crucibles.

RESULTS AND DISCUSSION

2-Ethylimidazole vibrations

The *etim* molecule containing two nitrogen atoms can donate electrons. The nitrogen atom can coordinate with a transition-metal ion and form complexes with different properties. The molecular structure of the *etim* is shown in Scheme 1.

Scheme 1. The molecular structure of the *etim*.Figure 1. The FT-IR spectra of the *etim* and the complexes.

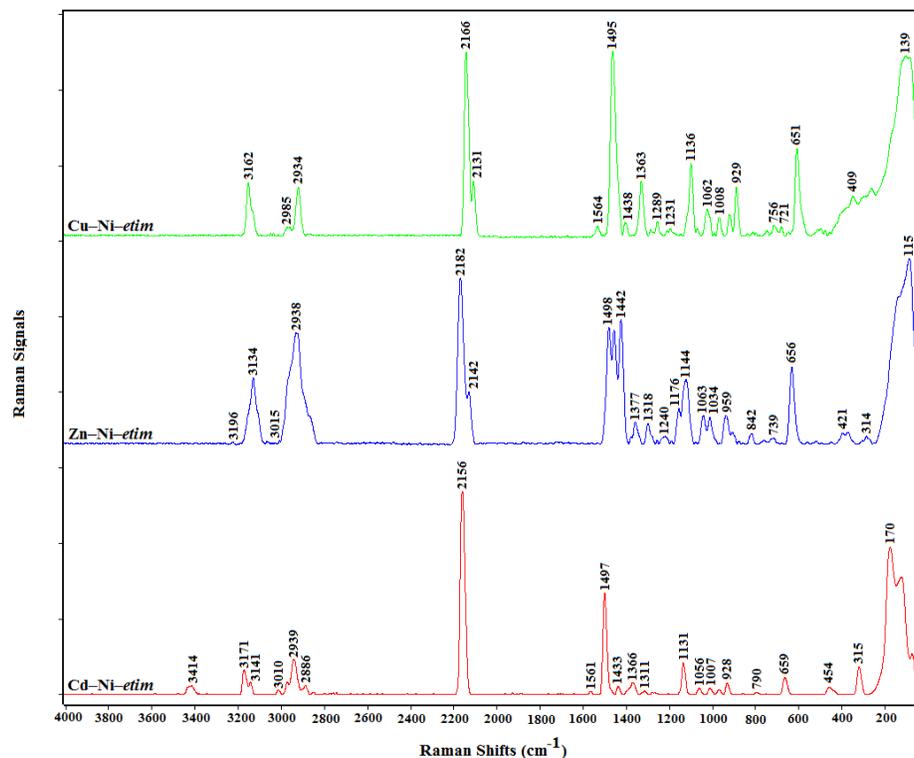


Figure 2. The Raman spectra of the complexes.

The FT-IR and Raman spectra of all of the complexes are given in Figures 1 and 2, respectively. The tentative assignments of the modes of vibration of the free *etim* and that of the *etim* molecules in the complexes are listed in Table 1. The FT-IR spectrum of the Zn-Ni-*etim* complex contains absorption bands originating from $\nu_{(\text{OH})}$ and $\delta_{(\text{OH})}$ vibrations. In the Zn-Ni-*etim* complex, the absorption bands observed from 3700 to 3328 cm^{-1} may be attributed to the $\nu_{(\text{OH})}$ stretching mode of the water molecule. The $\delta_{(\text{OH})}$ bending mode is also observed at about 1600 cm^{-1} in the Zn-Ni-*etim* complex. In all the heterocyclic compounds, the $\nu_{(\text{NH})}$ stretching vibrations are typically located in the region 3500–3300 cm^{-1} [20]. However, we have observed the $\nu_{(\text{NH})}$ stretching vibrations of the free *etim* at ca. 3153 cm^{-1} in FT-IR spectrum. The $\nu_{(\text{NH})}$ stretching vibrations of the *etim* ligand in the FT-IR and Raman spectra of the complexes were found to be between 3414 cm^{-1} and 3162 cm^{-1} and shifted to a higher frequency than the corresponding value of the *etim* molecule. This shift shows that the *etim* acts as monodentate ligand through the nitrogen atom of the imidazole ring. The in-plane (1375 cm^{-1}) and out-of-plane (753 cm^{-1}) bending vibrations of *etim* ligand are also supported to these shifts. The $\nu_{(\text{CH})}$ stretching vibrations arising from imidazole ring of the free *etim* are assigned at about 3136 cm^{-1} in the FT-IR spectrum and these vibrations are observed in the frequency range of 3171–3134 cm^{-1} in the vibration spectra of the complexes. As seen in Table 1, the *etim* ligand shows infrared bands in the 3110–2894 cm^{-1} region which are assigned to the $\nu_{(\text{CH}_3)}$ and $\nu_{(\text{CH}_2)}$ asymmetric and symmetric stretching frequencies, respectively. The absorption bands of the $\nu_{(\text{CH}_3)}$ and $\nu_{(\text{CH}_2)}$ groups in the complexes are observed in the region 3141–2932 cm^{-1} , and

significantly shifted to lower or higher frequencies compared to that of the free ligand. The $\rho_{(\text{CH}_2)}$ in-plane rocking vibration frequency is identified at 1105 cm^{-1} in the FT-IR spectrum of the *etim* and shifted to higher frequency compared to the free ligand in the complexes. The $\delta_{(\text{CH}_3)}$ in-plane and $\omega_{(\text{CH}_3)}$ out of plane bending modes are found at 1165 and 1123 cm^{-1} in the FT-IR spectrum, respectively. The bands obtained at 1009 and 957 cm^{-1} in FT-IR spectrum of the *etim* are assigned to CH_3 in-plane and out-of plane rocking modes, respectively. The $\nu_{(\text{C}=\text{N})}$ stretching vibration in the imidazole is assigned to the wavenumber 1675 cm^{-1} in FT-IR spectrum. The observed bands at 1576 , 1483 and 1453 cm^{-1} in FT-IR spectrum of the *etim* ligand are assigned to $\nu_{(\text{C}-\text{N})}$ stretching vibration. The $\nu_{(\text{C}-\text{C})}$ stretching vibrations are observed at 1431 and 1395 cm^{-1} in FT-IR spectrum and these vibrations in the complexes shifted to higher frequency region around $1-11\text{ cm}^{-1}$ at 1431 cm^{-1} and lower frequency region around $1-12\text{ cm}^{-1}$ at 1395 cm^{-1} , compared with the free *etim* molecule. These shifts can be explained as the coupling of the internal modes of the *etim* molecule with $\text{M}-\text{N}(\text{etim})$ vibrations. Similar shifts on coordination have been observed in the vibration spectra of the other metal-coordinated imidazole complexes [15-21].

[Ni(CN)₄]²⁻ group vibrations

The modes of vibration of the $[\text{Ni}(\text{CN})_4]^{2-}$ group of the complexes are given in Table 2. In order to assign the bands attributable to the $[\text{Ni}(\text{CN})_4]^{2-}$ ion in the spectra, we refer to the work of McCullough et al. who presented vibrational data for the salt $\text{Na}_2\text{Ni}(\text{CN})_4$ in the solid state [22]. Symmetrical vibration band $[\nu(\text{CN}), E_g]$ of complex $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ is observed at 2120 cm^{-1} , A_{1g} and B_{1g} symmetry stretching vibrations arising from Raman active $\nu_{(\text{C}=\text{N})}$ vibration are observed at 2160 and 2137 cm^{-1} . In FT-IR and Raman spectra of the complexes the dominant feature is represented by strong and sharp well identifiable absorption bands due to the $\nu_{(\text{C}=\text{N})}$ stretching vibrations [1, 23]. The cyanide groups exhibit strong and sharp absorption bands in vibrational spectra between 2200 and 2100 cm^{-1} , due to the stretching vibrations of the cyanide group. The $\nu_{(\text{C}=\text{N})}$ stretching vibrations are an important tool to distinguish between terminal and bridging character in the cyanide complexes. The bridging cyanide frequencies in cyano-bridged complexes are usually observed at higher wavenumbers than those of the terminal cyanide. Shifting to higher wavenumbers of the cyanide stretching frequency upon the formation of cyanide bridges occur due to both the kinematic coupling and increasing the CN force constant when a second metal center is attached to the CN unit. In the FT-IR spectra of the complexes, the $\nu_{(\text{C}=\text{N})}$ absorption bands are observed at 2173 , 2160 , 2135 and 2128 cm^{-1} (for the $\text{Cu}-\text{Ni}-\text{etim}$), 2173 and 2143 cm^{-1} (for the $\text{Zn}-\text{Ni}-\text{etim}$) and 2142 cm^{-1} (for the $\text{Cd}-\text{Ni}-\text{etim}$). Thus, in the $\text{Cu}-\text{Ni}-\text{etim}$ complex, the two high wavenumbers, 2173 cm^{-1} and 2160 cm^{-1} , correspond to the bridging cyanide and the two low wavenumbers, 2135 cm^{-1} and 2128 cm^{-1} , correspond to the terminal cyanide. Additionally, in the $\text{Zn}-\text{Ni}-\text{etim}$ complex, the two $\nu_{(\text{CN})}$ bands, which appeared at 2173 and 2143 cm^{-1} , can be assigned to the bridging and terminal cyanide groups, respectively. However, the $\text{Cd}-\text{Ni}-\text{etim}$ complex contains only one $\nu_{(\text{C}=\text{N})}$ absorption band at 2142 cm^{-1} belonging to the bridging cyano groups. From the FT-IR spectra of the complexes, it is determined that the $\nu_{(\text{C}=\text{N})}$ stretching vibrational mode of the cyanide has shifted to approximately $22-53\text{ cm}^{-1}$ higher frequency (see Table 2). The cyanide stretching bands in the Raman spectra of the complexes were observed at 2166 and 2131 cm^{-1} in the $\text{Cu}-\text{Ni}-\text{etim}$, at 2182 and 2142 cm^{-1} in the $\text{Zn}-\text{Ni}-\text{etim}$, at 2156 cm^{-1} in the $\text{Cd}-\text{Ni}-\text{etim}$, respectively. On the other hand, the in-plane bending vibrational mode, $\delta_{(\text{NiCN})}$ was observed at 414 cm^{-1} in the FT-IR spectrum of the $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ which was shifted to the higher frequency range around $1-12\text{ cm}^{-1}$ for the complexes. This result supports the shift of $\nu_{(\text{C}=\text{N})}$ stretching vibrational band. Such frequency shifts have been observed for the other cyanide complexes [15, 16, 19, 24]. The representative illustrations of the complexes are shown in Scheme 2.

Table 1. The modes of vibration of the *etim* in the complexes (cm⁻¹).

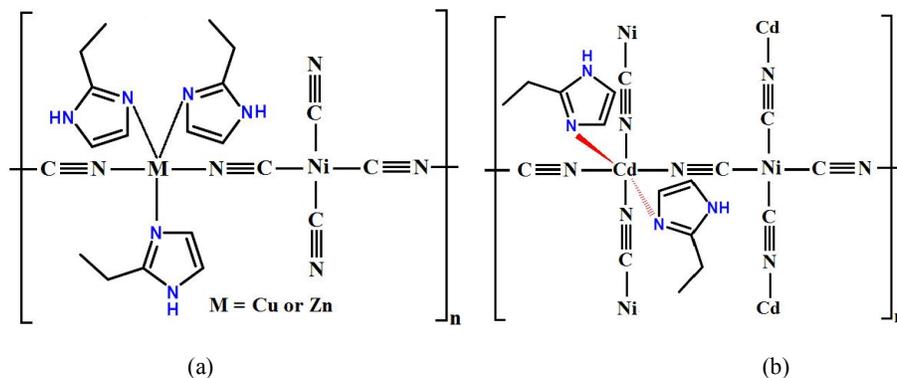
Assignments [20]	<i>Etim</i> (liquid)	Cu–Ni– <i>etim</i>		Zn–Ni– <i>etim</i>		Cd–Ni– <i>etim</i>	
		FT-IR	Raman	FT-IR	Raman	FT-IR	Raman
$\nu_{(\text{NH})}$ (99)	3153 w	3316 vs	3162 m	3189 w	3196 vw	3419 vs	3414 w
$\nu_{(\text{CH})}$ (97)	3136 vw	3154 w	-	3136 w	3134 s	3138 w	3171 w
$\nu_{\text{as}(\text{CH}_3)}$ (98)	3110 w	3120 vw	-	3112 vw	-	-	3141 w
$\nu_{\text{s}(\text{CH}_3)}$ (99)	3046 w	3021 w	-	3020 sh	3015 sh	-	3010 w
$\nu_{\text{as}(\text{CH}_2)}$ (96)	2981 m	2978 m	2985 w	2978 m	-	2973 w	2970 w
$\nu_{\text{s}(\text{CH}_2)}$ (98)	2894 w	2938 w	2934 m	2938 w	2938 vs	2932 w	2939 m
$\nu_{(\text{C}=\text{N})}$ (90)	1675 w	1708 w	-	-	1718 vw	1691 vw	-
$\nu_{(\text{C}=\text{N})}$ (86)	1576 vs	1567 vs	1564 w	1575 m	-	1561 vs	1561 vw
$\nu_{(\text{C}=\text{N})}$ (87)	1483 w	1497 vw	1495 vs	1499 sh	1498 vs	1498 w	1497 s
$\nu_{(\text{C}=\text{N})}$ (86)	1453 vs	1464 vs	-	1456 vs	1474 vs	1465 m	-
$\nu_{(\text{C}-\text{C})}$ (96)	1431 w	1436 vw	1438 w	-	1442 vs	1430 s	1433 w
$\nu_{(\text{C}-\text{C})}$ (96)	1395 m	1383 m	-	1390 vw	1395 vw	1391 vw	-
$\delta_{(\text{NH})}$ (78), $\delta_{(\text{CN})}$ (19)	1375 vw	-	-	1376 w	1377 w	1382 vw	-
R bend1 (75), $\delta_{(\text{CC})}$ (18)	1332 m	1364 w	1363 m	-	-	1366 w	1366 w
R bend2 (72), $\delta_{(\text{CC})}$ (20)	1312 w	1318 m	1320 w	1320 s	1318 w	1319 w	1311 vw
$\delta_{(\text{CH})}$ (78), $\delta_{(\text{CN})}$ (20)	1260 vw	1291 w	1289 w	-	1276 vw	1273 w	1276 vw
$\delta_{(\text{CH})}$ (88), $\delta_{(\text{CN})}$ (18)	1245 vw	1237 w	1231 vw	1247 m	1240 w	1232 w	1226 vw
$\delta_{(\text{CH}_3)}$ (98)	1165 vw	1200 vw	-	1176 m	1176 m	1207 vw	1200 vw
$\delta_{(\text{CH}_3)}$ (97)	1154 w	1154 w	-	1144 s	1144 s	1158 w	-
$\delta_{(\text{CH}_3)}$ (99)	1123 w	1132 w	1136 m	-	-	1132 w	1131 m
$\tau_{(\text{CH}_2)}$ (71), $\delta_{(\text{CN})}$ (18)	1105 vs	1111 vs	1108 vw	1122 vw	-	1105 vs	-
$\omega_{(\text{NH})}$ (62), $\omega_{(\text{CH})}$ (22)	1052 vs	1054 vs	1062 w	1054 vs	1063 m	1057 vs	1056 w
$\tau_{(\text{CH}_3)}$ (74)	1009 m	1007 vw	1008 w	1012 vw	1034 m	1007 vw	1007 w
$\tau_{(\text{CH}_3)}$ (76)	957 vs	961 w	959 w	953 m	959 m	966 w	965 w
$\omega_{(\text{CH})}$ (65), $\omega_{(\text{CC})}$ (23)	911 m	930 vw	929 m	929 vw	930 w	927 w	928 w
$\delta_{(\text{CC})}$ (75), $\omega_{(\text{CN})}$ (23)	796 w	853 w	852 vw	842 vw	842 w	858 m	854 vw
$\omega_{(\text{CH})}$ (63), $\omega_{(\text{CN})}$ (24)	753 vs	756 vs	756 vw	760 s	784 vw	780 w	790 vw
$\delta_{(\text{CC})}$ (72), $\delta_{(\text{CN})}$ (20)	736 s	721 s	721 vw	743 vs	739 w	747 vs	748 vw
$\tau\text{R bend1}$ (60)	653 vw	652 w	651 s	655 w	656 s	642 m	659 w
$\tau\text{R bend2}$ (61)	626 vw	625 vw	-	-	-	607 m	-

Abbreviations: ν – stretching; ν_{as} – asymmetric stretching; ν_{s} – symmetric stretching; δ – bending; ω – out-of-plane bending; R – ring; τ – rocking.

Table 2. The modes of vibration of the $[\text{Ni}(\text{CN})_4]^{2-}$ group in the complexes (cm⁻¹).

Assignments [22]	$\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$	Cu–Ni– <i>etim</i>	Zn–Ni– <i>etim</i>	Cd–Ni– <i>etim</i>
$A_{1g}, \nu_{(\text{CN})}$	(2160) vs	(2166) vs	(2182) vs	(2156) vs
$B_{1g}, \nu_{(\text{CN})}$	(2137) m	(2131) m	(2142) m	-
$E_{1g}, \nu_{(\text{CN})}$	2120 vs	2173 s, 2160 s, 2135 vs, 2128 vs	2173 vs, 2143 sh	2142 vs
$\nu_{(\text{CN})}^{13}$	2084 vw	2090 vw	-	-
$E_{1g}, \nu_{(\text{NiC})}$	542 w	548 vw	558 vw	542 vw
$A_{21g}, \pi_{(\text{NiCN})}$	443 w	441 vw	477 vw	461 w
$E_{1g}, \delta_{(\text{NiCN})}$	414 vs	414 vs	426 vs	424 vs

The symbols ν , δ and π refer to valence, in-plane and out-of-plane vibrations, respectively. s strong, m medium, w weak, sh shoulder, v very. The bands observed in the Raman spectra are given in parentheses.



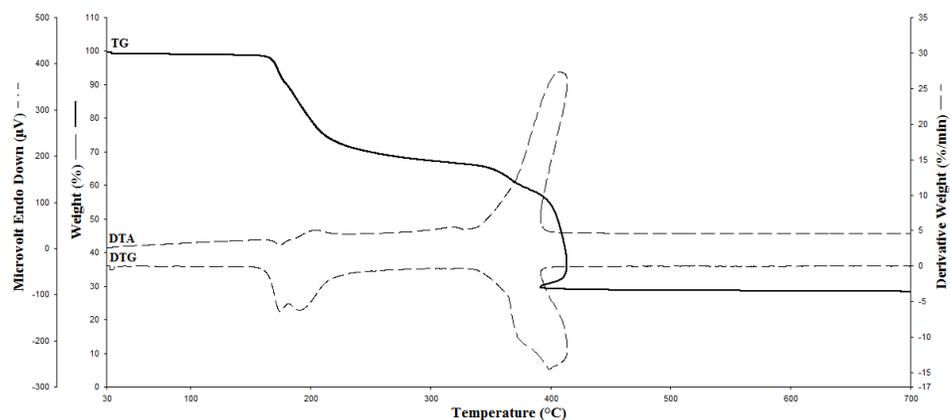
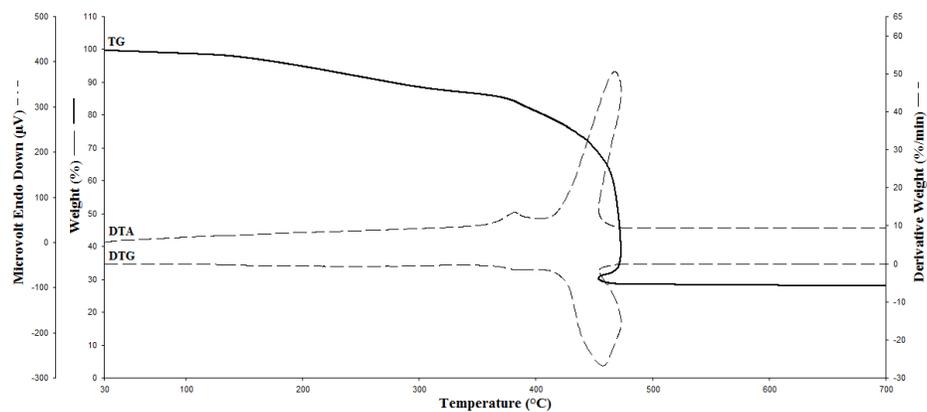
Scheme 2. The representative illustration of the Cu–Ni–*etim* and the Zn–Ni–*etim* (a) and the Cd–Ni–*etim* (b). The water molecule is not shown in the Zn–Ni–*etim*.

Thermal analysis

Thermal decomposition behaviors of the complexes were performed in temperature range 30–700 °C in static air atmosphere. Thermoanalytical data and thermal decomposition curves of the complexes are given in Table 3 and Figures 3–5, respectively. Thermal decomposition of the complexes proceeds in the three stages. In the first stage, the Cu–Ni–*etim* and the Cd–Ni–*etim* complexes lose the one *etim* ligand in a single step in the temperature range of 161–192 °C for the Cu–Ni–*etim* and 98–291 °C for the Cd–Ni–*etim*, but the Zn–Ni–*etim* complex loses one water molecule between 30 and 160 °C. In the second stage, the endothermic peaks in the temperature range 192–407 °C for the Cu–Ni–*etim* and 160–463 °C for the Zn–Ni–*etim* correspond to the loss of the two *etim* ligands but in the temperature range 291–407 °C for the Cd–Ni–*etim* are released the one *etim* ligand. These values were found as following; the two *etim* ligands for the Cu–Ni–*etim* and the Zn–Ni–*etim*, the one *etim* ligand for the Cd–Ni–*etim* [found (calcd.) (%) = 35.17 (37.35) for the Cu–Ni–*etim*, 33.05 (35.96) for the Zn–Ni–*etim* and 19.64 (20.56) for the Cd–Ni–*etim*]. In the following stages of the Cu–Ni–*etim* and the Cd–Ni–*etim* complexes, the remaining four cyanide groups decompose as exothermic in the 407–476 °C temperature range for the Cu–Ni–*etim* and in the 407–435 °C temperature range for the Cd–Ni–*etim*. In the next step in the Zn–Ni–*etim* complex, the remaining four cyanide groups and the one *etim* ligand decompose between 463 and 504 °C. The final decomposition products were identified as CuO and NiO for the Cu–Ni–*etim*, ZnO and NiO for the Zn–Ni–*etim* and CdO and NiO for the Cd–Ni–*etim* [found (calcd.) (%) = 28.78 (29.96) for the Cu–Ni–*etim*, 28.42 (29.19) for the Zn–Ni–*etim* and 42.08 (43.45) for the Cd–Ni–*etim*]. The thermal decomposition products were identified by FT-IR spectroscopy.

Table 3. Thermoanalytical data of the complexes.

Complexes	Stage	Temperature range (°C)	DTG _{max} (°C)	Removed group	Mass loss %		Mass loss %		Residue
					Calculated	Found	Calculated	Found	
[Cu(<i>etim</i>) ₃ Ni(CN) ₄]	1	161 - 192	174 (+)	<i>etim</i>	18.67	16.29			
[Cu(<i>etim</i>) ₂ Ni(CN) ₄]	2	192 - 407	195 (+)	2(<i>etim</i>)	37.35	35.17			
[CuNi(CN) ₄]	3	407 - 476	411 (-)	4(CN)	20.21	19.76	29.96	28.78	CuO+NiO
[Zn(<i>etim</i>) ₃ Ni(CN) ₄]-H ₂ O	1	30 - 160	-	H ₂ O	3.37	2.95			
[Zn(<i>etim</i>) ₃ Ni(CN) ₄]	2	160 - 463	-	2(<i>etim</i>)	35.96	33.05			
[Zn(<i>etim</i>)Ni(CN) ₄]	3	463 - 504	467 (-)	<i>etim</i> +4(CN)	37.42	35.13	29.19	28.42	ZnO+NiO
[Cd(<i>etim</i>) ₂ Ni(CN) ₄]	1	98 - 291	287 (+)	<i>etim</i>	20.56	19.92			
[Cd(<i>etim</i>)Ni(CN) ₄]	2	291 - 407	320 (+)	<i>etim</i>	20.56	19.64			
[CdNi(CN) ₄]	3	407 - 435	419 (-)	4(CN)	22.26	20.81	43.45	42.08	CdO+NiO

Figure 3. The TG, DTG and DTA curves of the Cu-Ni-*etim*.Figure 4. The TG, DTG and DTA curves of the Zn-Ni-*etim*.

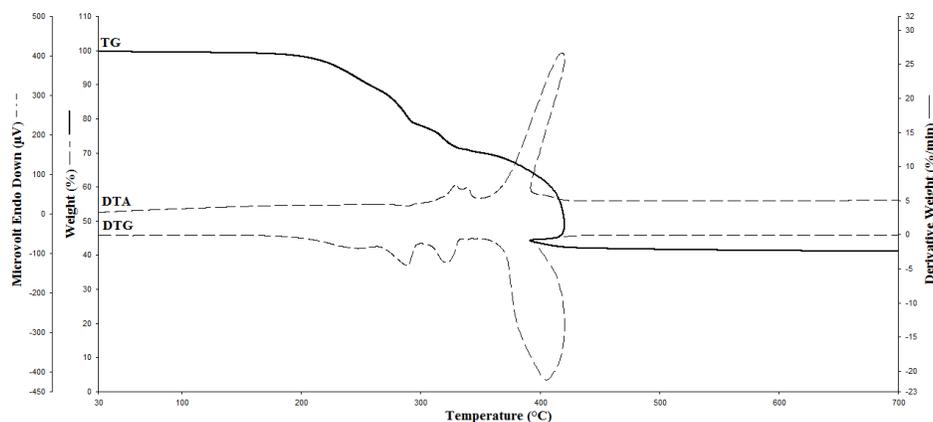


Figure 5. The TG, DTG and DTA curves of the Cd–Ni–*etim*.

CONCLUSION

In this study, we synthesized the three new heteronuclear polymeric complexes, $[\text{Cu}(\text{etim})_3\text{Ni}(\text{CN})_4]_n$, $\{[\text{Zn}(\text{etim})_3\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}\}_n$ and $[\text{Cd}(\text{etim})_2\text{Ni}(\text{CN})_4]_n$. We investigated these complexes using vibration (FT-IR and Raman) spectroscopy, thermal and elemental analyses techniques. On the basis of the spectroscopic results, we suggest that the polymeric structures of the Cu–Ni–*etim* and the Zn–Ni–*etim* complexes consist of 1D coordination polymer, while the Cd–Ni–*etim* complex presents a 2D network. The Ni(II) ion is four coordinate with four cyanide-carbon atoms in a square-planar geometry. Furthermore, the Cu(II) and Zn(II) ions are five coordinate with the three *etim* ligands and the two bridging cyanide groups, whereas the Cd(II) ion is six coordinate with the two *etim* ligands and the four bridging cyanide groups. We also showed that thermal analyses of the complexes support the spectroscopic results.

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