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VIBRATIONAL SPECTROSCOPIC AND THERMAL INVESTIGATIONS OF THE CYANO-BRIDGED POLYMERIC COMPLEXES WITH 3-AMINOMETHYLPYRIDINE

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ABSTRACT

New cyano-bridged polymeric complexes formulated as $[Co(H_2O)(ampy)Ni(CN)_4]\cdot H_2O$ and $[Ni(ampy)_2Ni(CN)_4]\cdot H_2O$ (ampy = 3-aminomethylpyridine: abbreviated henceforth as Co-Ni-ampy and Ni-Ni-ampy) have been obtained in powder form and characterized by vibrational (infrared and Raman) spectroscopy, thermal and elemental analyses. In previous study, structure of complex $[Cd(NH_3)(ampy)Ni(CN)_4]_n$ (Cd-Ni-ampy) was determined by single crystal X-ray diffraction methods. In this complex, the coordination environment of the Cd(II) ions are distorted octahedral geometry, whereas around the Ni(II) center is pyramidal. The spectral features suggest that Cd-Ni-ampy with Co-Ni-ampy are similar to each other and the ampy ligand is coordinated to metal ions as bidentate ligand. In addition, complex Ni-Ni-ampy is similar in structure to the Hofmann type complexes and its structure consists of polymeric layers of $|Ni–Ni(CN)_4|_\infty$ with the ampy ligand bounded to the nickel(II) atom. Thermal stabilities and decomposition products of the complexes were investigated using TG, DTG and DTA curves in the temperature range of 30 – 700 °C in the static air atmosphere.

Keywords: Vibrational spectra, Tetracyanonickelate(II), 3-aminomethylpyridine, Cyano-bridged complexes, Pyramidal

1. INTRODUCTION

Cyano-bridged polymeric complexes containing cyanometallate building blocks such as $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$, $[Pt(CN)_4]^{2-}$ and $[Au(CN)_4]^-$ have been intensely explored owing to their potential application as hosts for smaller molecules, molecular sieves, chemical sensors and ion exchangers [1-4]. In general, cyanometallate building blocks, $[M(CN)_x]^{n-}$ have been used to create one- (1D), two-(2D) and three-(3D) dimensional structures [5-8] due to the cyanide ion can coordinate as monodentate or bidentate ligand to different metal cations. Therefore, cyanometallates can easily form coordination polymers with transition-metal cations and the presence of cyanide can be readily determined with the C≡N vibrational stretch in the infrared and Raman spectra [9, 10]. Many researchers have focused on octahedral $[M(CN)_6]^{n-}$ but less have focused on square-planar $[M(CN)_4]^{n-}$ building blocks [11-13]. The square-planar building blocks are used extensively in the synthesis of Hofmann-type complexes. Hofmann-type complexes are given with the general formula $[M(L)_xM'(CN)_4]$ (where x = 2 or 1; M(II) = Co, Ni, Cu, Zn or Cd; M′(II) = Ni, Pd or Pt) form 2- or 3-dimensional polymeric structures by metal–ligand–metal bridge connections [4]. In the literature, there are too many cyano-bridged polymeric complexes obtained using $[Ni(CN)_4]^{2-}$ building unit [14-17].

In our previous study, we reported the preparation, vibrational (FT-IR and Raman) spectroscopic, thermal, and single-crystal X-ray diffraction studies of the cyano-bridged 3D heteronuclear polymeric complex with the formula $[Cd(NH_3)(\mu\text{-ampy})Ni(CN)_4]_n$, (ampy = 3-aminomethylpyridine) [18]. The crystal structure of Cd-Ni-ampy is shown in Figure 1. In the crystal structure of Cd-Ni-ampy, Ni(II) ion is pyramidal by the four carbon atoms of cyano ligands and one nitrogen atom of the ampy ligand and this geometry is rare for tetracyanonickelate (II) ion in the literature. The Cd(II) ion is six coordinated by the six N atoms from one ammonia, one ampy and four cyano ligands. We have extended this study and prepared $[Co(H_2O)(3ampy)Ni(CN)_4]\cdot H_2O$ and $[Ni(3ampy)_2Ni(CN)_4]\cdot H_2O$ (ampy = 3-aminomethylpyridine) complexes for the first time. Therefore, in the present article we describe the

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synthesis, vibrational study and thermal behavior of tetracyanonickelate(II) with the 3-aminomethylpyridine.

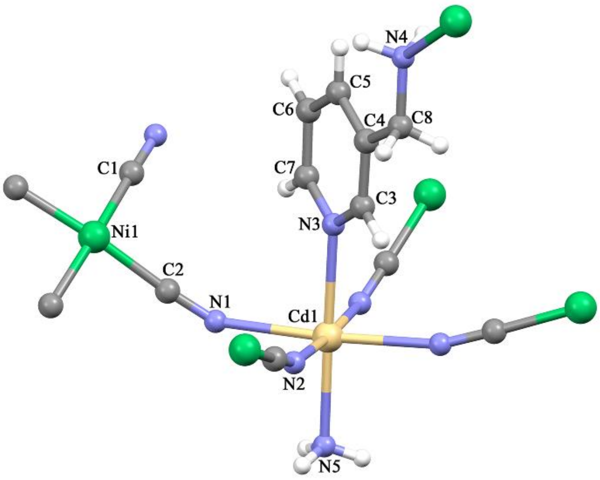


Figure 1. The asymmetric unit of Cd-Ni-ampy with the atom numbering scheme (The NH_3 in the crystal structure of complex Cd-Ni-ampy is replaced by H_2O ligand in complex Co-Ni-ampy) [18]

2. EXPERIMENTAL

2.1. Materials

Cobalt(II) chloride tetrahydrate ($CoCl_2·4H_2O$, 98%), nickel(II) chloride hexahydrate ($NiCl_2·6H_2O$, 97%), potassium cyanide (KCN, 96%) and 3-aminomethylpyridine ($C_6H_9N_2$, 97%) from commercial sources were used as received.

2.2. Syntheses of the Complexes

The $K_2[Ni(CN)_4]·H_2O$ complex was synthesized according to literature [19]. 1 mmol (0.259 g) of $K_2[Ni(CN)_4]·H_2O$ was dissolved in distilled water (10 mL) under stirring at room temperature, then 1 mmol of the metal(II) chloride ($CoCl_2·4H_2O$ = 0.202 g or $NiCl_2·6H_2O$ = 0.238 g) prepared with distilled water (10 mL) was added to the dissolved $K_2[Ni(CN)_4]·H_2O$ dropwise. The colors of $Co[Ni(CN)_4]·H_2O$ and $Ni[Ni(CN)_4]·H_2O$ are pink and pale blue, respectively. A mixture of {$Co[Ni(CN)_4]·H_2O$ = 0.240 g, 1 mmol or $Ni[Ni(CN)_4]·H_2O$ = 0.239 g, 1 mmol} in water (10 mL), ampy (2 mmol, 0.216 g) dissolved in ethanol (10 mL) was stirred at 40 °C for 4 h in a temperature-controlled bath. The obtained complexes were filtered and washed with pure water and ethanol, respectively and dried in air. The freshly prepared complexes were analyzed for C, H and N, and elemental analysis data of the complexes were given in Table 1.

Table1. Elemental analysis data of the complexes

Complex	Molecular formula	$M_{wt.}$ (g/mol)	Elemental analyses					
			C%		H%		N%	
			Calc.	Found	Calc.	Found	Calc.	Found
$[Co(H_2O)(3ampy)Ni(CN)_4]·H_2O$	$C_{10}H_{12}N_6O_2NiCo$	365.87	32.83	34.01	3.31	3.45	22.97	22.69
$[Ni(3ampy)_2Ni(CN)_4]·H_2O$	$C_{16}H_{18}N_8ONi_2$	437.74	42.17	42.69	3.98	4.05	24.59	25.26

2.3. Measurements

Elemental analyses were carried out on a LECO, CHNS-932 analyzer for C, H and N at the Middle East Technical University Central Laboratory in Ankara, Turkey. The infrared spectra of discs (KBr) of fresh samples were recorded in the range of 4000 – 400 cm^{-1} with a 2 cm^{-1} spectral resolution by using a Perkin Elmer 100 FT-IR spectrometer, which was calibrated by means of polystyrene and CO_2 bands. Raman spectrum of the synthesized complexes were recorded between 4000 and 250 cm^{-1} on a Bruker Senterra Dispersive Raman apparatus using 785 nm laser excitation. 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 ºC using platinum crucibles.

3. RESULTS AND DISCUSSION

3.1 Vibrational Spectra

3.1.1. 3-Aminomethylpyridine vibrations

The infrared spectra of the ampy, the infrared and Raman spectra of Co-Ni-ampy and Ni-Ni-ampy are illustrated in Figures 2-4, respectively. The vibrational assignments of the ampy ligand observed in the spectra of the complexes were made according to the 2-aminomethylpyridine ligand [20-22] and were given in Table 2, together with the wavenumbers of the free ampy molecule in the liquid phase. So far, there has been no comprehensive vibrational study of 3-aminomethylpyridine molecule. However, the infrared spectral data of 2-aminomethylpyridine [22] have been reported. The proposed assignment of the infrared bands of the ampy in the complexes were performed by considering the infrared spectral data of 2-aminomethylpyridine that have very similar chemical groups to those of 3-aminomethylpyridine. It has been noted that infrared data on the ampy complexes are not abundant in the literature. Only a few papers have been found in the literature concerning the geometric parameters of 2-aminomethylpyridine ligands and calculation of vibration frequencies [20, 21]. Depending on the ligand and the metal coordination environment, 3-aminomethylpyridine can act as a bridging ligand, monodentate ligand or a chelating ligand. The 3-aminomethylpyridine can coordinate to metal ions by nitrogen atom of the pyridine ring and amino nitrogen atom and show a bridged ligand feature. In the literature, there are a limited number of structurally characterized complexes of metal(II) tetracyanometallate with 3-aminomethylpyridine as a ligand, which encouraged us to study the complexation tendency of Cd(II) with 3-aminomethylpyridine in the presence of the ambidentate cyano ligand [18, 23, 24].

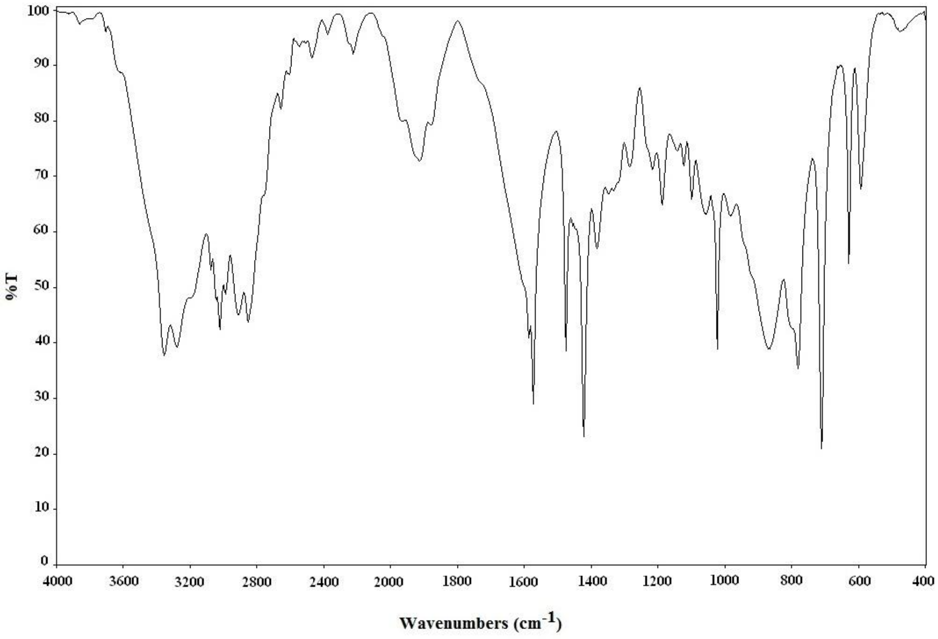


Figure 2. The infrared spectra of the ampy ligand

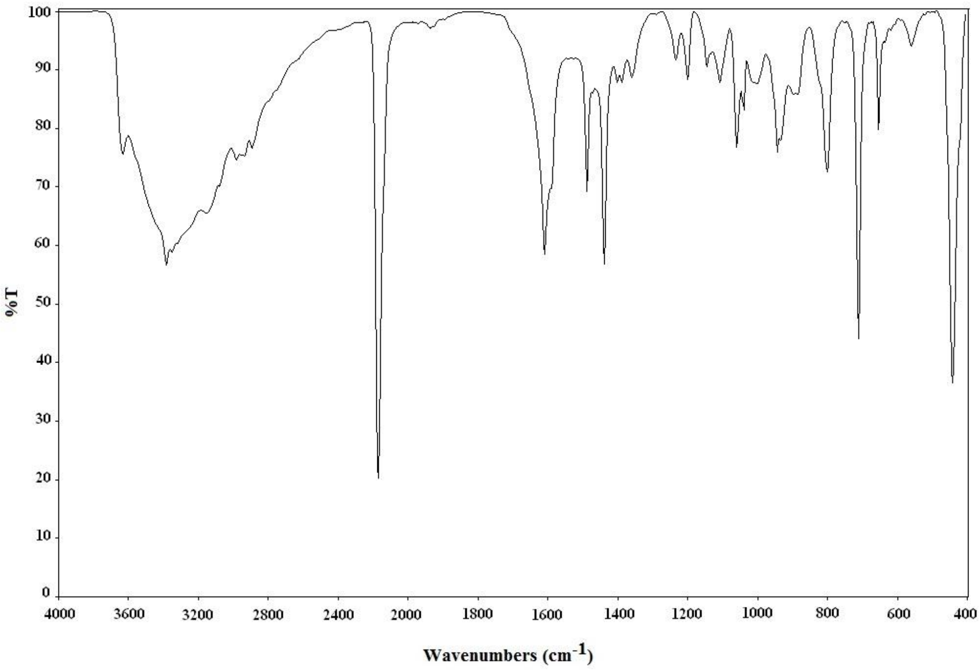
Table 2. The vibrational wavenumbers (cm^{-1}) of the ampy in the complexes

Assignment [20]	ampy	Cu-amp-SCN [20]	Cd-Ni-ampy [18]		Co-Ni-ampy		Ni-Ni-ampy	
	Exp.		FT-IR	Raman	FT-IR	Raman	FT-IR	Raman
$\nu(NH_2)$ asym str of N-H in NH_2	3363 s	3567	3373 m	-	3373 m	-	3353 m	3352 vw
$\nu(NH_2)$ sym str of N-H in NH_2	3289 s	3502	3298 m	-	3342 w	-	3289 w	3299 w
$\nu(NH_2)^a$	3199 sh	-	3178 w	-	3141 w	-	3157 w	3177 vw
$\nu(CH)^a$	3052 s	-	-	3067 vw	3069 vw	3066 vw	3085 vw	3065 m
$\nu(CH)$ sym str of C-H in py ring	2996 s	3190	3023 vw	-	2998 vw	-	3043 vw	-
$\nu(CH_2)^a$	2918 s	-	2923 w	2931 vw	2926 vw	-	2948 w	2964 w
$\nu(CH_2)$ sym str of C-H in CH_2	2861 s	3025	2847 vw	-	2885 vw	-	2869 vw	-
νC=N) C=N str	1617 sh	1659	-	-	-	-	-	-
$\delta(NH_2)$ NH_2 scissoring	1590 s	1632	1594 m	1602 w	1605 s	1618 w	1590 s	1614 w
$\nu(CC)$ asym str of C=C in py ring	1576 s	1602	1580 w	1590 sh	1586 sh	1592 sh	1577 sh	1598 sh
$\delta(CH_2)^a$	1479 s	-	1480 m	1488 vw	1467 vw	1482 vw	1482 m	-
$\delta(CH_2)$ rocking in py, scissoring in CH_2	1426 vs	1464	1438 m	1446 vw	1434 s	1446 w	1441 sh	1448 w
$w(CH_2)$ wagging in CH_2 group	1388 m	1389	1426 m	1416 vw	1397 w	-	1432 m	1419 vw
$t(CH_2)^a$	1385 m	-	1354 w	1361 vw	1384 vw	1380 sh	1368 w	1372 vw
Ip bending of C–H, asym bend in py	1336 vw	1309	-	-	1356 vw	-	1334 w	-
$t(NH_2)^a$	1288 w	-	1316 w	1329 vw	-	-	-	1311 vw
scissoring in py ring	1191 m	1183	1222 m	-	1229 m	1243 w	1224 vw	1245 w
$\nu(skeletal)^a$	1146 m	-	1130 w	1189 vw	1195 m	1205 w	1194 m	1200 w
$\nu(skeletal)^a$	1102 m	-	1071w	1140 vw	1141 vw	1143 vw	1129 w	-
$\nu(skeletal)$ Ip bending in py ring	1060 m	1082	1050 m	1080 w	1103 w	1088 sh	1110 w	1086 sh
$\nu(skeletal)$ $\nu(C\text{-}N)^a$	1027 s	-	1030 m	1043 m	1055 m	1056 vs	1048 m	1048 s
$\nu(skeletal)$ scissoring in py ring	988 s	1036	937 m	993 vw	1034 m	-	1007 s	-
$t(CH_2)^a$	873 s	-	901 w	914 vw	940 m	920 vw	876 m	887 vw
$r(CH_2)$, $w(NH_2)^a$	802 sh	-	805 vw	804 vw	880 vw	-	-	-
rocking of C–H in py ring	785 m	768	785 m	-	796 s	814 m	790 s	820 w
rocking in NH_2	714 vs	706	705 s	-	706 vs	-	710 s	728 vw
sym str in py ring	632 m	660	645 w	657 vw	649 m	664 w	649 w	661 w
wagging in NH_2	596 m	614	604 w	618 vw	613 vw	622 w	634 vw	621 vw

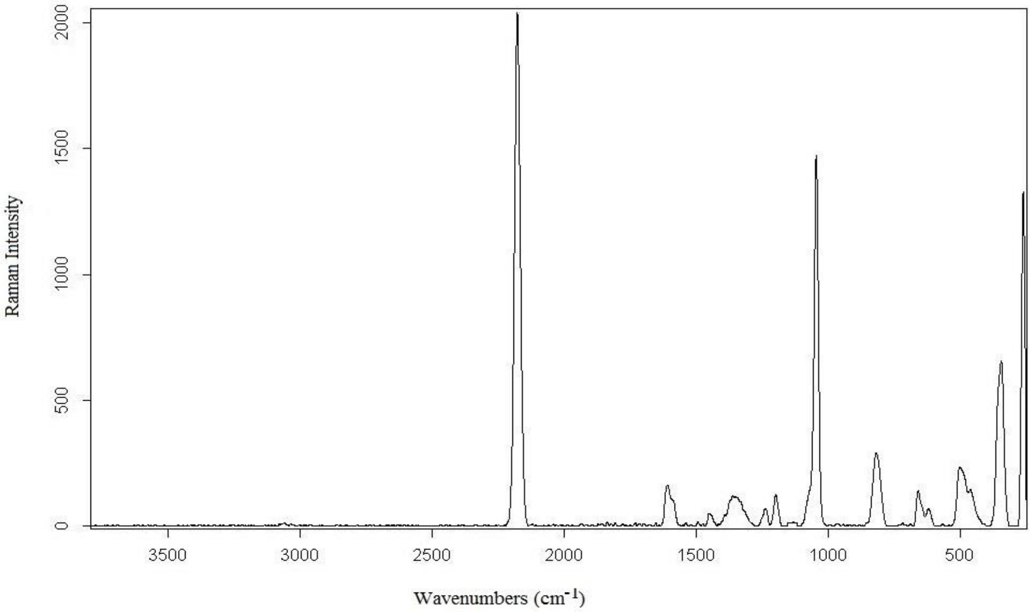
Abbreviations used: ν stretching, δ deformation, w wagging, t twisting, r rocking, py pyridine,str stretching, asym asymmetric, sym symmetric, ip in plane, s strong, m medium, w weak, sh shoulder, v very.
[a]Assignments are taken from ref. [22]

The ampy ligand has two nitrogen atoms, each of which is an unpaired electron pair. For this reason, the ampy ligand can be found in the complex formation through the ring nitrogen and amino nitrogen atoms. The ampy ligand is represented by a large number of absorption bands including $\nu(NH_2)$, $\nu(CH)$, $\delta(NH_2)$, $\nu(CC)$, $\delta(CH_2)$, ν(skeletal), rocking of C–H in py ring, rocking in NH_2 and other vibrational bands. Table 1 shows that the ampy ligand has infrared bands arising from the $\nu(NH_2)$ asymmetric and symmetric stretching frequencies in the 3363 – 3289 cm^{-1} range. These vibration bands, complex Co-Ni-ampy are assigned at 3373 cm^{-1} and 3342 cm^{-1} (at 3373 cm^{-1} and 3298 cm^{-1} for Cd-Ni-ampy), while complex Ni-Ni-ampy are assigned at 3353 cm^{-1} and 3289 cm^{-1} (at 3352 cm^{-1} and 3299 cm^{-1} for Raman), respectively. The $\nu(NH_2)$ asymmetric and symmetric stretching frequencies of the ampy ligand in Co-Ni-ampy were significantly shifted to higher frequency according to the free ligand in a similar manner to the complex Cd-Ni-ampy. On the other hand, the band about 1590 cm^{-1} assigned to the $\delta(NH_2)$ bending vibrations and this band in the infrared and Raman spectra of the complexes shifted to higher frequency in the range of 0-28 cm^{-1} comparing to the free ligand. In addition, no change was observed with respect to the free ligand in the $\delta(NH_2)$ bending vibrations of the ampy ligand in infrared spectra of complex Ni-Ni-ampy. In this case, we can say that the ampy ligand in complex Ni-Ni-ampy is not coordinated to the metal atom through the amine nitrogen, while the ampy coordinates to the metal atom through the amine nitrogen atom in complex Co-Ni-ampy.

When the nitrogen of the pyridine ring was found in complex formation, certain vibrational modes increase in value owing to the coupling the internal vibration modes of the ampy with M-N(pyridine) bond vibrations [14, 25]. The most important vibrational bands for the coordination to the metal atom via the nitrogen of the pyridine ring in the ampy ligand are $\nu(CH)$ in pyridine ring, rocking of C–H in pyridine ring, symmetric stretching in pyridine ring, scissoring in pyridine ring and ν(skeletal) vibrations. Especially, these bands in the infrared and Raman spectra of the complexes are showed a significant upward shift according to the free ligand. The ring ν(CH) modes of the ampy were found at 3052 cm^{-1}, and 2996 cm^{-1} and the ν(CH) stretching bands in the infrared spectra of the complexes have been assigned at 3069 cm^{-1} (at 3066 cm^{-1} for Raman) and 2998 cm^{-1} (for Co-Ni-ampy) and at 3085 cm^{-1} (at 3065 cm^{-1} for Raman) and 3043 cm^{-1} (for Ni-Ni-ampy). The pyridine ring bands in the infrared spectra of the ampy appear in 1200 – 980 cm^{-1} region and at 632 cm^{-1}. These bands of pyridine are shifted by 17 – 59 cm^{-1} to a higher frequency on complexation. Therefore, these results suggest that the ring nitrogen of the ampy for the both complexes is involved in complex formation.

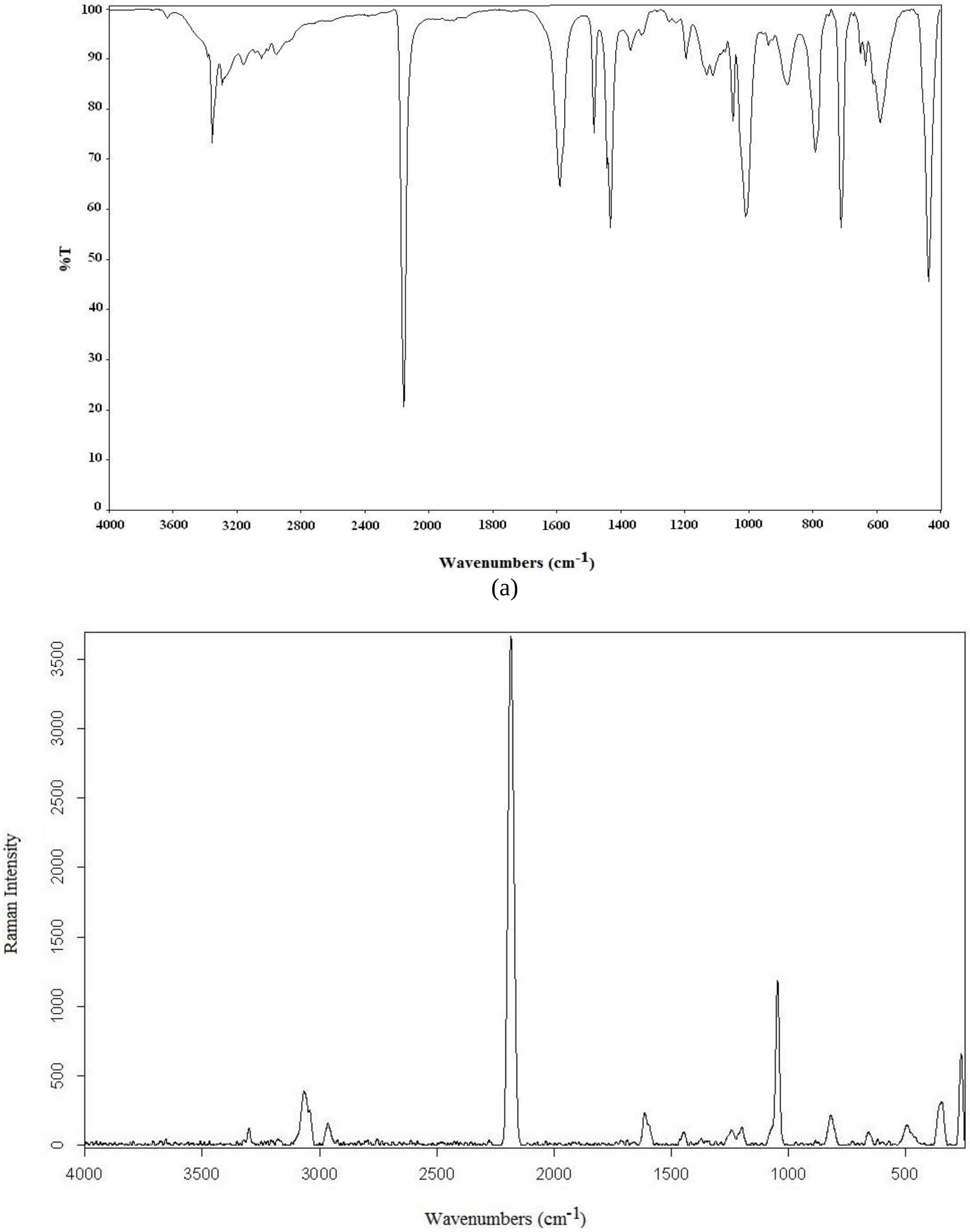


(a)



(b)

Figure 3. The infrared (a) and Raman (b) spectrum of Co-Ni-ampy



(a)

(b)

Figure 4. The infrared (a) and Raman (b) spectrum of Ni-Ni-ampy

3.1.2. Water vibrations

There are three vibration bands that originate from ν(OH) (the asymmetric and symmetric stretching) and δ(HOH) (bending) vibrations of water molecules. Coordinated and uncoordinated water molecules are found in Co-Ni-ampy, while one stretching band corresponding to uncoordinated water molecules is observed in the infrared spectrum of Ni-Ni-ampy. The water molecules found in infrared spectra of the complexes show infrared absorptions at 3623 cm^{-1} [ν(OH) for Co-Ni-ampy)] and 3630 cm^{-1} [ν(OH) for Ni-Ni-ampy)]. In addition, δ(HOH) bending bands with the δ(HOH) bending bands of the water molecules in Co-Ni-ampy and Ni-Ni-ampy overlap around 1605 cm^{-1} and 1588 cm^{-1}, respectively.

3.1.3. $[Ni(CN)_4]^{2-}$ Group vibrations

The vibration assignments and wavenumbers of the $[Ni(CN)_4]^{2-}$ group in the complexes are given in Table 3, together with the vibration wavenumbers of $K_2[Ni(CN)_4]\cdot H_2O$ in the solid phase. The assignments of vibration bands of the $[Ni(CN)_4]^{2-}$ group in the complexes are assigned on the basis of the ion $[Ni(CN)_4]^{2-}$ in $Na_2[Ni(CN)_4]$ reported by McCullough et al [26]. The most important vibration bands of the $[Ni(CN)_4]^{2-}$ group are strong and sharp the ν(CN) stretching vibration band and the δ(Ni–CN) in-plane bending vibration band [27, 28]. These stretching and in-plane bending vibrations exhibit strong and sharp absorption bands in the range of (2200 – 2100) cm^{-1} and (450 – 400) cm^{-1} for cyanometallate complexes, respectively. In the synthesized tetracyanonickellate anion, the ν(CN) stretching vibration band is shown at 2122 cm^{-1}. The coordination to second metal of the cyano group through the N atom in the tetracyanonickellate anion shifts the position of the ν(CN) absorption band to higher wavenumbers due to the kinematic coupling [29-31]. The ν(CN) stretching vibration frequencies in the infrared spectra of both Co-Ni-ampy and Ni-Ni-ampy are observed as a single peak at 2162 cm^{-1} (2135 cm^{-1} for Cd-Ni-ampy) and 2152 cm^{-1}, respectively. From the infrared spectra of the complexes, it is determined that the stretching vibration of cyano has shifted to 30 cm^{-1} and 40 cm^{-1} higher frequency, respectively. The appearance of a single cyano stretching peak in the synthesized complexes indicates that the four cyano groups act as bridge ligands. In the resulting complexes, the A_{1g} cyano stretching mode is observed at 2182 cm^{-1} (for Co–Ni–ampy) and 2184 cm^{-1} (for Ni–Ni–ampy) but B_{1g} cyano stretching mode is not observed. In the Raman spectra of the complexes, the A_{1g} mode shifted to higher wavenumbers around 23 cm^{-1} compared to those of the free $[Ni(CN)_4]^{2-}$ groups. On the other hand, the δ(Ni–CN) in-plane bending vibration band of $K_2[Ni(CN)_4]\cdot H_2O$ is found as one strong and sharp band at 414 cm^{-1}. In infrared spectra of Co-Ni-ampy and Ni-Ni-ampy, the δ(Ni–CN) bands appear as strong bands at 438 cm^{-1} and 436 cm^{-1}, respectively. In-plane bending vibration band, δ(Ni–CN) shifts to a higher frequency and support the ν(CN) stretching vibration band. The ν(CN) and δ(Ni–CN) vibrational wavenumbers of the $[Ni(CN)_4]^{2-}$ group in the complexes are found to be similar to those of cyano-bridged complexes [32, 33].

Table 3. The vibrational wavenumbers of the $[Ni(CN)_4]^{2-}$ group in the complexes (cm^{-1})

Assignment [26]	$K_2[Ni(CN)_4]\cdot H_2O$	Cd-Ni-ampy [18]	Co-Ni-ampy	Ni-Ni-ampy
A_{1g}, ν(CN)	(2160) vs	(2168) vs	(2182) vs	(2184) vs
B_{1g}, ν(CN)	(2137) m	-	-	-
E_u, ν(CN)	2122 vs	2159 sh, 2146 sh, 2135 vs	2162 vs	2152 vs
E_u, ν(^{13}CN)	2084 w	2102 sh	-	-
E_u, ν(NiC)	542 w	531 m	556 w	586 w
A_{2u}, π(NiCN)	443 w	463 w	-	-
E_u, δ(NiCN)	414 s	420 s	438 vs	436 vs

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. The vibrational frequencies in the Raman spectrum are enclosed in parentheses.

According to the obtained spectroscopic results, it was found that the ampy ligand in complex Co-Ni-ampy coordinate to the metal atoms (Co and Ni) via the pyridine ring nitrogen and amino nitrogen atoms, whereas the ampy ligand in complex Ni-Ni-ampy coordinates to the metal (Ni) via the pyridine ring nitrogen atom. The cyano ligand also acts as a bridge ligand in the complexes. In this case, it is considered that the structures of the complexes according to the obtained spectral data are as shown in Figures 1 and 5. As seen in Figure 1, the NH_3 in the crystal structure of complex Cd-Ni-ampy is replaced by H_2O ligand in complex Co-Ni-ampy.

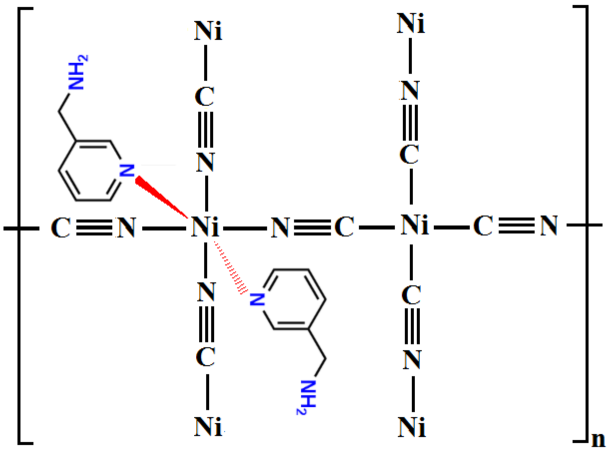


Figure 5. The representative molecular structures of complex Ni-Ni-ampy

3.2. Thermal Analyses

Thermal decomposition behaviors of the complexes were performed by TG, DTG and DTA methods in the temperature range of 30 – 700 °C in static atmosphere of air. The thermal decomposition curves for Co-Ni-ampy and Ni-Ni-ampy are shown in Figures 6 and 7. Thermal decomposition of Co-Ni-ampy takes place in the two stages. In the first stage, complex Co-Ni-ampy loses both coordinated and uncoordinated water molecules in a single step in the temperature range of 30 – 162 °C [Found (Calcd.) (%) = 7.22 (9.85)]. In following stage, one ampy ligand and four cyanide ligands are separated from the structure in the temperature range of 162 – 374 °C [Found (Calcd.) (%) = 55.65 (58.00)] and exothermic peak appears at ca. 329 °C in the DTA curve. The final decomposition products were identified as CoO and NiO [Found (Calcd.) (%) = 37.13 (40.68)]. Complex Ni-Ni-ampy is stable up to 40 °C and after that the complex is degraded in two stages. In the first stage, one uncoordinated water and one ampy ligand between 40 °C and 363 °C are released [Found (Calcd.) (%) = 24.13 (27.68)]. In the second stage, within 363 – 694 °C the decomposition continues with liberating of one ampy ligand and four cyanide ligands [Found (Calcd.) (%) = 43.01 (46.56)] exothermic peak appears at ca. 378 °C in the DTA curve. The final residue product was found to be 2(NiO) [Found (Calcd.) (%) = 32.86 (32.77)] and they are identified by FT-IR spectroscopy. The recorded TG, DTG and DTA curves promoted the formula unit found from elemental analyses and the vibrational spectroscopic studies of the complexes.

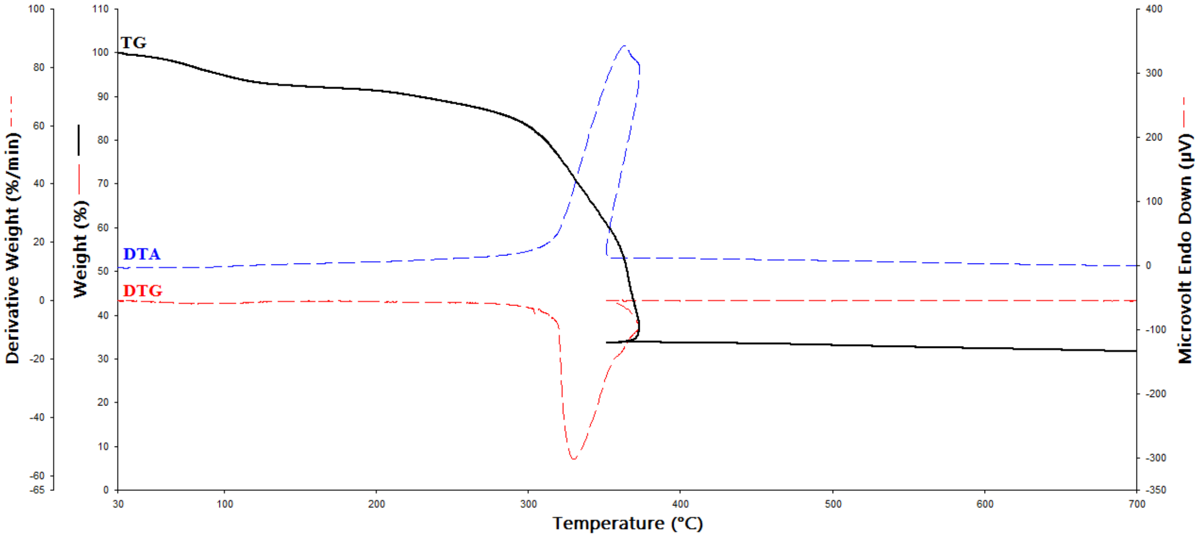


Figure 6. The TG, DTG and DTA curves of Co-Ni-ampy

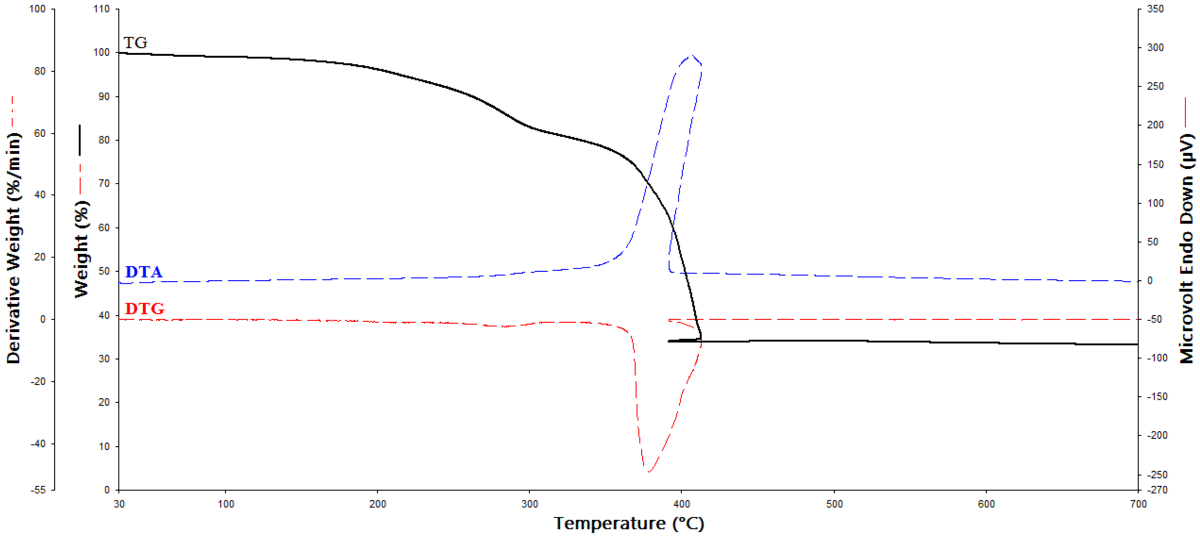


Figure 7. The TG, DTG and DTA curves of Ni-Ni-ampy

4. CONCLUSION

Here we report the results of our study on synthesis and thermal, elemental and spectral characterization of $[Co(H_2O)(ampy)Ni(CN)_4]\cdot H_2O$ and $[Ni(ampy)_2Ni(CN)_4]\cdot H_2O$ (ampy = 3-aminomethylpyridine). In previous study, structure of complex $[Cd(NH_3)(ampy)Ni(CN)_4]_n$ was determined by single crystal X-ray diffraction methods. The Ni(II) ions are five coordinate with four cyanide–carbon atoms and one ampy ligand in pyramidal and the Cd(II) ion exhibits a distorted octahedral coordination by one ampy and one ammonia ligand and four bridging cyano groups. Vibration assignments are given for all the observed bands and the spectral feature also supported to the structure of cyano-bridged polymeric complexes. Spectroscopic results show that Cd-Ni-ampy with Co-Ni-ampy are similar to each other and the ampy ligand is coordinated to metal ions as bidentate ligand. The spectral data obtained indicate that complex Ni-Ni-ampy is similar in structure to the Hofmann type complexes and its structure consists of polymeric layers of $|Ni–Ni(CN)_4|_\infty$ with the ampy ligand bounded to the nickel(II) atom. The ampy ligands in complex Ni-Ni-ampy have been coordinated as a monodentate ligand bonding only through pyridine ring nitrogen of the ampy ligand. These polymeric layers are held in parallel by Van der Walls interactions between the ampy ligands. Thermal analyses of the complexes are also supported the spectroscopic conclusion.

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