



Synthesis, spectroscopic, thermal, and structural properties of cyano-bridged metal complexes containing tetracyanonickelate(II) building blocks with 4-aminomethylpyridine

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Abstract: New cyano-bridged metal complexes with chemical formulas $[\text{Fe}(\text{NH}_3)_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$, $[\text{Co}(\text{H}_2\text{O})_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$ and $[\text{Ni}(\text{NH}_3)_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$ (ampy = 4-aminomethylpyridine, hereafter abbreviated as Fe-Ni-ampy, Co-Ni-ampy and Ni-Ni-ampy) were obtained in the form of powders and examined by vibrational (infrared and Raman) spectroscopy, thermal (TG, DTG and DTA), and elemental analysis techniques. The infrared and Raman spectra of the complexes were performed in the range of $4000\text{--}400\text{ cm}^{-1}$ and $4000\text{--}250\text{ cm}^{-1}$, respectively. General information about the structural features of synthesized complexes was obtained by considering the changes in the cyano group and characteristic peaks of ampy. The cleavage of the $\nu(\text{CN})$ stretching bands in the infrared spectrum of the complexes shows that the terminal and bridge cyano groups are in the structure. Considering the variations in the vibrational frequencies of the cyano group and ampy ligand in the spectrum of the complexes, the Ni atom is in a square plane geometry with four cyano groups and two of these cyano groups are the bridge and the other two are terminal. In addition, the metal atoms [Fe(II), Co(II) or Ni(II)] are linked to the ring and amino nitrogen atoms of two symmetric ampy ligands, the two ammonia (two aqua ligands for Co-Ni-ampy) ligands and the two bridging cyano groups, and show a distorted octahedral geometry. The thermal degradation of the complexes was also studied between 30 and 950 °C using TG, DTG, and DTA techniques.

Keywords: Tetracyanonickelate(II), 4-aminomethylpyridine, Cyano-bridged complex, Vibration spectra, Thermal analysis.

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INTRODUCTION

Metal organic lattice framework structures (MOFs) are formed by binding by organic linkers of metal centers and these formed structures can be of one-, two-, and three-dimensional. MOFs have extraordinary high surface areas and most of them allow the permanent porous structures to be formed (1-3). Different sizes of porous structures

can be formed with changes of metal and organic linkers. Because of these porous structures, MOFs are the subject of many areas of work, including applications such as gas storage (4, 5), iodine adsorption (6), magnetic materials (7), ion exchange materials (8) and conductivity (9).

The cyano, azide and nitrile short bridge ligands are highly preferred ligands in the binding of transition

metals. By using cyano donor atoms, the cyano anion can either provide monodentate (C-) or bidentate (C-, N-) coordination. Cyano acts as a bridging ligand by binding to metal atoms through both carbon and nitrogen atoms or a terminal ligand by binding from carbon atoms to metal atoms. With this feature, the cyano ligand can produce different polymeric species (7, 10, 11).

The cyano anion is used as a bridging ligand between metal centers and additionally different neutral organic molecules such as 4-aminomethylpyridine, imidazole, and pyridine can be obtained metal organic lattice framework structures. In these structures, octahedral Fe, Co, or Ni, square pyramidal $[\text{Ni}(\text{CN})_5]^{3-}$, square-planar $[\text{Ni}(\text{CN})_4]^{2-}$, tetrahedral $[\text{Cd}(\text{CN})_4]^{2-}$, trigonal $[\text{Cu}(\text{CN})_3]^{2-}$ and linear $[\text{Ag}(\text{CN})_2]^-$ cyanometallics are used as main building blocking entities (12, 13). Between these building blocks, the square-planar $[\text{Ni}(\text{CN})_4]^{2-}$ cyanometallics were intensively studied (14-19). The cyano groups in the $[\text{Ni}(\text{CN})_4]^{2-}$ may exhibit two different arrangements in cyano-bridged metal complexes by acting as both a bridging and terminal ligands. In this case, 1D, 2D and 3D cyano-bridged complexes can be obtained.

We reported tetracyanometallate(II) complexes with 4-aminomethylpyridine (20-24). As a part of our continuing work on cyano-bridged metal complexes, cyano-bridged metal complexes of the type $[\text{M}(\text{NH}_3)_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$, and $[\text{Co}(\text{H}_2\text{O})_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$ [ampy = 4-aminomethylpyridine; M = Fe(II) or Ni(II)] were synthesized using cyano, 4-aminomethylpyridine, two ammonia (two aqua ligands for Co-Ni-ampy) ligands. Structural properties of the resulting complexes were illuminated by vibrational (infrared and Raman) spectroscopy, elemental and thermal analysis methods.

EXPERIMENTAL

Materials

Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), cobalt(II) chloride tetrahydrate ($\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 97%), potassium cyanide (KCN, 96%) and 4-aminomethylpyridine ($\text{C}_6\text{H}_9\text{N}_2$, 97%) were purchased from commercial sources.

Syntheses of the complexes

The cyano-bridged metal complexes were synthesized in three stages; in the 1st stage $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, in the 2nd stage $\text{M}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [M = Fe(II), Co(II) or Ni(II)] and in the final stage $[\text{M}(\text{NH}_3)_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$, and $[\text{Co}(\text{H}_2\text{O})_2(\text{ampy})\text{Ni}(\text{CN})_4]_n$ [ampy = 4-aminomethylpyridine; M = Fe(II) or Ni(II)]. The $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ complexes were prepared

according to literature (25). 1 mmol (0.259 g) of tetracyanonickelate(II) was dissolved in distilled water, and 1 mmol of the metal(II) chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O} = 0.199$ g, $\text{CoCl}_2 \cdot 4\text{H}_2\text{O} = 0.202$ g and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} = 0.238$ g) was dissolved in distilled water and added to the stirring tetracyanonickelate(II) solution and then, the $\text{M}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [M = Fe(II), Co(II) or Ni(II)] has been obtained. The colors of $\text{Fe}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, $\text{Co}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ and $\text{Ni}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ are brown, pink and pale blue, respectively. A mixture of $\{\text{Fe}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O} = 0.237$ g, 1 mmol, $\text{Co}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O} = 0.240$ g, 1 mmol or $\text{Ni}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O} = 0.239$ g, 1 mmol} in water (10 mL), ampy (2 mmol, 0.216 g) dissolved in ethanol (10 mL) and ammonia for Fe-Ni-ampy and Ni-Ni-ampy (2 mmol, 0.034 g) was stirred at 40 °C for 4 h in a temperature-controlled bath. The resulting complexes were filtered and washed with distilled water and ethanol respectively, and dried in air. These complexes were analyzed for C, H, and N, and the results obtained: Anal. Found (Calcd.) (%) for brown $\text{C}_{10}\text{H}_{14}\text{N}_8\text{FeNi}$ ($M_w = 360.81$ g/mol) : C, 33.45 (33.29); H, 3.68 (3.91); N, 30.76 (31.06); for pink $\text{C}_{10}\text{H}_{12}\text{N}_6\text{O}_2\text{CoNi}$ ($M_w = 365.87$ g/mol) : C, 33.54 (32.83); H, 3.79 (3.31); N, 21.89 (22.97); for pale blue $\text{C}_{10}\text{H}_{14}\text{N}_8\text{Ni}_2$ ($M_w = 363.66$ g/mol) : C, 32.13 (33.03); H, 4.39 (3.88); N, 30.41 (30.81).

Measurements

The synthesized complexes were analyzed for C, H, and N with a LECO CHN-932 analyzer at the Middle East Technical University Central Laboratory in Ankara, Turkey. The infrared spectra were recorded as KBr pellets between 4000 and 400 cm^{-1} (2 cm^{-1} resolution) on a Perkin Elmer 100 FT-IR spectrometer, which was calibrated using 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. Thermal analysis curves of the obtained complexes were performed in a static air atmosphere at a heating rate of 10 K min^{-1} in the temperature region 30-950 °C using Perkin Elmer Diamond TG/DTA thermal analyzer instrument.

RESULTS AND DISCUSSION

Ligand vibrations

The infrared spectrum of the ampy ligand is shown in Figure S1. The infrared and Raman spectra of the obtained cyano-bridged metal complexes are given in Figures S2-S7. The infrared vibration frequencies of the ampy (liquid) and the vibration (Infrared and Raman) frequencies of the obtained cyano-bridged metal complexes together with the vibrational assignments of the ampy ligand according to (26) are presented in Table 1. Asymmetric and symmetric stretching vibrations and deformation vibrations of the free ammonia ligand are found in

the 3400-3000 cm^{-1} and 1650-550 cm^{-1} regions, respectively (27). In the infrared spectrum of Fe-Ni-ampy and Ni-Ni-ampy, the $\nu(\text{NH}_3)$ and $\delta(\text{NH}_3)$ vibration frequencies are identified at 3381 cm^{-1} and 1661 cm^{-1} for Fe-Ni-ampy, at 3381 and 1672 cm^{-1} for Ni-Ni-ampy, respectively. In general, the $\nu(\text{OH})$ and $\delta(\text{HOH})$ vibration frequencies appear in the 3560-3200 and 1700-1600 cm^{-1} regions, respectively (27, 28). The aqua ligand of Co-Ni-ampy displays a sharp peak of $\nu(\text{OH})$ at 3544 cm^{-1} . In the infrared spectrum of Co-Ni-ampy, the $\delta(\text{HOH})$ bending vibration of the aqua ligand was also found at 1695 cm^{-1} .

The ampy ligand has unpaired electrons on the nitrogen atom. The ampy ligand which has these electron pairs can coordinate as monodentate or bidentate ligand to metal atoms. When the coordination takes place via the amino nitrogen atom of the ampy ligand, the N-H bond is weakened and the NH_2 stretching frequencies are lowered. In this case, the M-N bond is stronger, whereas the N-H bond is weaker. Furthermore, if the NH_2 group of the ampy ligand makes a hydrogen bond, the N-H stretching frequencies are further reduced. In addition, the out of plane bending frequencies of NH_2 shift to higher frequency region (27, 29, 30). As presented in Table 2, symmetric and asymmetric wavenumbers of the $\nu(\text{N-H})$ belonging to the NH_2 group in the ampy ligand are found at 3367 and 3292 cm^{-1} . In the infrared spectrum of the complexes, the strong vibration bands at 3346 and 3274 cm^{-1} for Fe-Ni-ampy, at 3346 and 3292 cm^{-1} for Co-Ni-ampy and at 3346 and 3274 cm^{-1} for Ni-Ni-ampy are identified as the stretching vibrations belonging to the NH_2 group. The $\nu(\text{N-H})$ belonging to the NH_2 group of the ampy in the obtained complexes are lower than those of the free ampy ligand. The band identified at 1602 cm^{-1} in the infrared spectrum of the free ampy determined as the out-of-plane bending vibration of NH_2 and observed at a higher frequency according to the free ampy ligand in the spectrum of the complexes. Shifts in the NH_2 stretching and bending vibration frequencies are sensitive to metal. On the other hand, when the ampy ligand is linked to metal atoms from the ring nitrogen atom, there are significant shifts in the ring stretching and the deformation vibration frequencies. Especially, the increase in ring stretching frequencies is observed (17, 23, 31). The ring stretching modes of the free ampy ligand, $\nu(\text{skeletal})$ assigned as the strong and sharp bands at 1220, 1088, 1065 and 994 cm^{-1} in the infrared spectrum of the free ampy. In the complexes, the metals are N-bonded (ring) since the $\nu(\text{skeletal})$ of the free ligand is shifted to higher frequencies around 3-40 cm^{-1} . Other significant bands of the free ampy ligand are the $\nu(\text{CH})$ at 3070 and 2991 cm^{-1} , the $\nu(\text{CH})$ at 2991 cm^{-1} and 2898 cm^{-1} , the $\nu(\text{CC})$ at 1560 cm^{-1} , the $\delta(\text{CH}_2)$ at 1496 and 1446 cm^{-1} , the $\text{t}(\text{CH}_2)$ at 877

cm^{-1} and $\text{r}(\text{NH}_2)$ at 591 cm^{-1} . In the complexes, these vibration bands show upward or downward shifts in frequency according to those of the free ampy ligand. Therefore, infrared and Raman spectra show that the ampy ligand in the obtained complexes is N-bonded from both ring nitrogen atom of pyridine and NH_2 group.

Vibrations (infrared and Raman) of the $[\text{Ni}(\text{CN})_4]^{2-}$ group

The vibrational assignments and frequencies of the tetracyanonickelate(II) in the complexes are included in Table 1. The assignments of vibrational bands belonging to vibrations (infrared and Raman) of the tetracyanonickelate(II) in the obtained complexes are performed using that of the solid $\text{Na}_2[\text{Ni}(\text{CN})_4]$ salt presented by McCullough *et al.*, (32). The distinctive band in the cyano-bridged metal complexes is the vibration band of the cyano group. The $\nu(\text{CN})$ stretching vibration band of the cyano group gives a strong and sharp peak in the range of 2200-2000 cm^{-1} and can be easily determined in the spectrum of the complexes. The $\nu(\text{CN})$ stretching vibration frequency of free cyano ligand in ionic KCN is determined at 2080 cm^{-1} (27). When the cyano ligand is coordinated to a metal atom from the carbon atom, the $\nu(\text{CN})$ stretching vibration frequency is undergoes a blue-shift. In this case, the M-CN type terminal property is seen in the complexes (23, 33-35). If the cyano ligand is bound to two separate metal atoms from both the carbon and the nitrogen atom, $\nu(\text{CN})$ stretching vibration occurs more blue shift and the M-CN-M' type bridge forms in the complexes. Both terminal and bridge property of cyano ligand in the cyano-bridged metal complexes is intensively observed (23, 33-35). The terminal Ni-CN of obtained complex $\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ exhibits a distinctive peak at 2120 cm^{-1} in the infrared spectra. In the infrared spectrum of the cyano-bridged metal complexes, the $\nu(\text{CN})$ stretching vibration frequency is observed at 2124 cm^{-1} (for Fe-Ni-ampy), 2123 cm^{-1} (for Co-Ni-ampy) and 2125 cm^{-1} (for Ni-Ni-ampy). The $\nu(\text{CN})$ stretching vibration frequencies in the complexes M-Ni-ampy ([Fe(II), Co(II) or Ni(II)]) are closer that of the terminal Ni-CN. M-CN-M' type bridge in the cyano complexes can easily be determined with infrared spectroscopy. According to this, the $\nu(\text{CN})$ stretching vibration in obtained cyano-bridged metal complexes were determined at 2162 and 2143 cm^{-1} (for Fe-Ni-ampy), 2160 cm^{-1} (for Co-Ni-ampy), 2162 and 2143 cm^{-1} (for Ni-Ni-ampy). Bridge $\nu(\text{CN})$ stretching vibration wavenumbers in obtained cyano-bridged metal complexes are usually identified at higher frequencies due to kinematic binding, which is a mechanical limitation upon the bridging cyano ligand bound to the second metal (13, 17, 27). The cleavage of the $\nu(\text{CN})$ supports the presence of bridges and terminal cyano groups in the cyano-bridged metal complexes. In the resulting

complexes, the A_{1g} and B_{1g} cyano stretching modes are observed at 2186 and 2169 cm^{-1} (for Fe-Ni-ampy), 2187 cm^{-1} (for Co-Ni-ampy), 2187, 2170 and 2150 cm^{-1} (for Ni-Ni-ampy). This data show that the A_{1g} and B_{1g} modes are observed to have higher wavenumbers in the region of 9–27 cm^{-1} in obtained cyano-bridged metal complexes. In addition, the modes originating from $\nu(\text{NiCN})$ and

$\delta(\text{NiCN})$ vibrations for the obtained cyano-bridged metal complexes are determined between 600 and 400 cm^{-1} . In the infrared spectrum of M-Ni-ampy [M(II) = Fe(II), Co(II) or Ni(II)], the modes found at 557 and 429 cm^{-1} in Fe-Ni-ampy, 557 and 438 cm^{-1} in Co-Ni-ampy, 555 and 429 cm^{-1} in Ni-Ni-ampy are expressed as the $\nu(\text{NiCN})$ and $\delta(\text{NiCN})$ vibrations, respectively.

Table 1 The vibrational wavenumbers of the tetracyanonickelate(II) group in M-Ni-ampy (cm^{-1}).

Assignments (32)	$\text{K}_2[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$	Fe-Ni-ampy	Co-Ni-ampy	Ni-Ni-ampy
A_{1g} , $\nu(\text{CN})$	(2160) vs	(2186) s, (2169) vs	(2187) vs	(2187) s, (2170) vs
B_{1g} , $\nu(\text{CN})$	(2137) m	(2150) vs	-	(2150) vs
E_{u_g} , $\nu(\text{CN})$	2120 vs	2162 s, 2143 s, 2124 vs	2160 vs, 2126 m	2163 s, 2143 s, 2125 s
$\nu(^{13}\text{CN})$	2084 vw	2087 vw	2097 vw	2084 vw
E_u , $\nu(\text{NiC})$	542 w	557 w	557 w	555 m
A_{2u_g} , $\pi(\text{NiCN})$	443 w	468 vw	486 w	472 vw
E_u , $\delta(\text{NiCN})$	414 vs	429 s	438 s	429 s

ν ; valence, δ ; in-plane, π ; out-of-plane, s; strong, m; medium, w; weak, sh; shoulder, v; very. The vibrational frequencies in the Raman spectrum are enclosed in parentheses.

As a result, the ampy ligand acts as a bridge ligand between metals, while the cyano ligand acts as a terminal and bridging ligand. In this case, it is

considered that the structures of the complexes according to the obtained spectral data are as shown in Figs. 1 and 2.

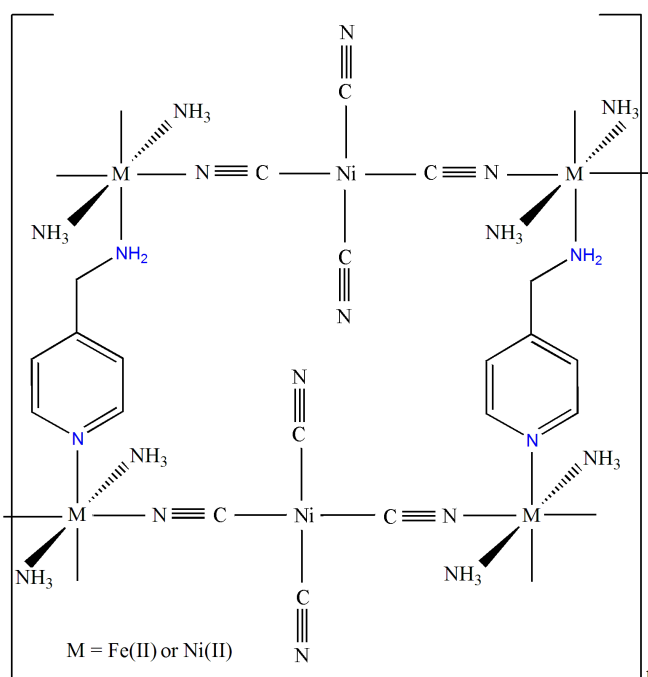


Figure 1. Representation of molecular structures of Fe-Ni-ampy and Ni-Ni-ampy.

Table 2. The vibrational wavenumbers of the liquid ampy and the ampy in the complexes (cm⁻¹).

Assignment (26)	ampy (liquid)	Fe-Ni-ampy		Co-Ni-ampy		Ni-Ni-ampy	
		Infrared	Raman	Infrared	Raman	Infrared	Raman
v(NH ₂)	3367 vs	3346 s	3354 w	3346 s	3346 vw	3346 s	3353 vw
v(NH ₂)	3292 s	3274 s	3291 w	3292 s	3271 vw	3274 s	3292 w
v(NH ₂)	3197 sh	3188 m	3200 vw	3197 sh	3190 vw	3188 m	3200 vw
v(CH)	3070 s	3090 w	3088 w	3073 m	3078 vw	3091 w	3088 w
v(CH)	2991 s	2972 w	2983 vw	2972 w	2964 vw	2971 w	2982 vw
v(CH ₂)	2898 s	2936 w	2946 w	-	-	2935 w	2946 vw
v(CH ₂)	2849 s	2829 vw	2847 vw	2855 sh	-	2851 vw	2842 vw
v(C=N)	1652 sh	1661 vw	1666 vw	1695 w	1681 vw	1671 vw	1668 vw
δ(NH ₂)	1602 vs	1612 s	1625 w	1618 s	1627 w	1612 s	1625 w
v(CC)	1560 vs	1582 m	1592 vw	1563 m	1586 vw	1582 m	1595 vw
δ(CH ₂)	1496 s	1505 w	1516 vw	1506 w	1509 vw	1505 w	1516 vw
δ(CH ₂)	1446 s	1457 vw	1468 vw	-	1451 vw	1457 m	1452 vw
ω(CH)	1416 vs	1423 s	1434 vw	1428 s	1437 vw	1424 s	1434 w
t(CH)	1387 s	1376 w	1373 vw	1369 w	1363 vw	1375 w	1371 vw
t(NH ₂)	1287 m	1324 w	1335 vw	1322 vw	1332 vw	1324 w	1333 vw
v(skeletal)	1220 s	1249 s	1254 w	1227 m	1223 w	1249 s	1255 w
v(skeletal)	1088 m	1094 w	1104 vw	1093 w	1091 w	1094 m	1092 w
v(skeletal)	1065 s	1072 w	1084 w	1072 w	-	1072 w	-
v(skeletal)	994 vs	1014 s	1026 m	1017 s	1034 w	1015 s	1027 m
t(CH ₂)	877 vs	874 vw	885 vw	876 vw	898 vw	874 vw	886 vw
r(CH ₂), ω(NH ₂)	822 sh	819 w	831 w	852 vw	862 vw	819 w	832 w
r(NH ₂)	667 w	646 m	680 w	689 vw	679 w	646 m	680 w
r(NH ₂)	591 s	615 w	621 vw	563 w	535 w	615 m	612 vw

v; stretching, δ; deformation, ω; wagging, t; twisting, r; rocking, s; strong, m; medium, w; weak, sh; shoulder, v; very.

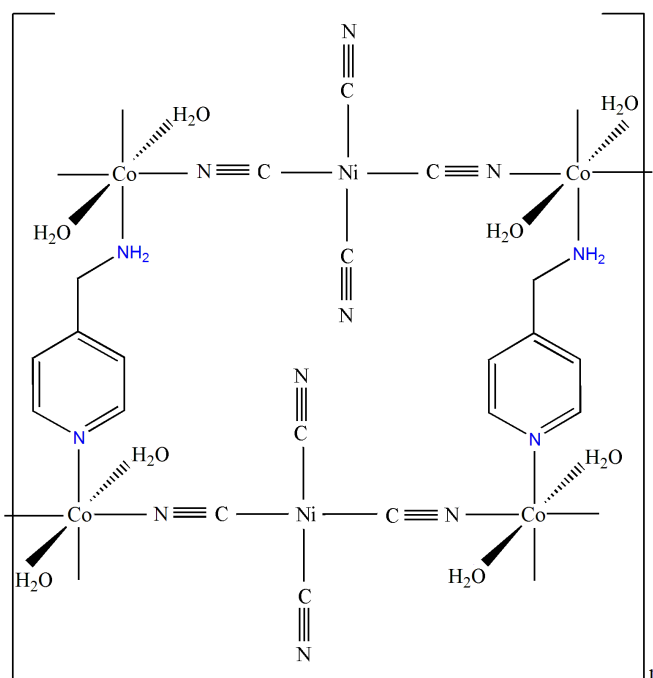


Figure 2. Representation of molecular structures of Co-Ni-ampy.

Thermal Analysis

Thermal decompositions of the synthesized complexes were investigated by TG, DTA, and DTG methods in a static aereal atmosphere at 30-950 °C temperature range. Thermal analyses of the synthesized complexes are given in Figures S8-S10. Thermal degradation of the complexes began at approximately 150, 30 and 180 °C for Fe-Ni-ampy, Co-Ni-ampy, and Ni-Ni-ampy, respectively. As seen in Figures S8-S10, TG, DTA, and DTG curves of Fe-Ni-ampy, Co-Ni-ampy, and Ni-Ni-ampy are similar to each other and thermal decomposition of the complexes occurs in two stages. In the first stage, two ammonia ligands between 65 and 174 °C [Found (Calcd.) (%) = 9.46 (9.43)] for Fe-Ni-ampy, between 65 and 213 °C [Found (Calcd.) (%) = 9.83 (9.36)] for Ni-Ni-ampy and two aqua ligands between 30 and 101 °C [Found (Calcd.) (%) = 9.88 (9.85)] for Co-Ni-ampy are released from the structure of the complexes. In the second stages, the loss of the one ampy ligand and the four cyano ligands take place between 174 °C and 628 °C for Fe-Ni-ampy ($DTA_{max} = 413$ °C), 101 and 910 °C for Co-Ni-ampy ($DTA_{max} = 353$ °C) and 213 °C and 685 °C for Ni-Ni-ampy ($DTA_{max} = 346$ °C). The remaining products after the loss of the ligands were found to be *FeO* and *NiO* for Fe-Ni-ampy, *CoO* and *NiO* for Co-Ni-ampy and $2(NiO)$ for Ni-Ni-ampy [Found (Calcd.) (%) = 40.20 (40.61) for Fe-Ni-ampy, 37.14 (40.89) for Co-Ni-ampy and 39.13 (41.07) for Ni-Ni-ampy].

CONCLUSIONS

In this article, we have prepared and reported new cyano-bridged metal complexes with chemical formulas $[M(NH_3)_2(ampy)Ni(CN)_4]_n$, and $[Co(H_2O)_2(ampy)Ni(CN)_4]_n$ [ampy = 4-aminomethylpyridine; M = Fe(II) or Ni(II)]. According to the spectral data obtained from the complexes, the coordination environment of the M(II) atoms is coordinated to the octahedral geometry by the ring and amino nitrogen atoms of two symmetric ampy ligands, two nitrogen atoms of two ammonia ligands (two oxygen atoms of two aqua ligands for Co-Ni-ampy) and two symmetric nitrogen atoms of the cyano groups, while the Ni(II) atom is coordinated to the square-plane geometry by the four carbon atoms of the cyano groups. In addition, it has been concluded that cyano ligand along with ring nitrogen and NH_2 group of the ampy is involved in the formation of complexes. The spectral properties reveal that the complexes are composed of two dimensional networks. When the thermal properties of the complexes are examined, the two ammonia ligands (two aqua ligands for Co-Ni-ampy) are first released from the unit formula of the complexes, then an ampy and four cyano groups are released. In addition, the thermal degradation of the complexes between 30 and 950 °C are in good agreement with elemental analysis results.

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