



RESEARCH ARTICLE

SYNTHESIS AND SPECTROSCOPIC STUDIES OF COPPER(II)/COBALT(III) CYANIDE COMPOUNDS WITH IMIDAZOLE, 1-METHYLIMIDAZOLE, AND 2-METHYLIMIDAZOLE

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Abstract

New Cu(II)/Co(III) cyanide compounds, $[\text{Cu}_3(\text{L})_4\text{Co}_2(\text{CN})_{12}] \cdot n\text{H}_2\text{O}$, with imidazole and methyl derivatives of imidazole have been synthesized in powder form and analyzed using elemental analyses, vibrational (FT-IR and Raman) spectroscopy, and powder X-ray diffraction (PXRD). The elemental analyses of all compounds for C, H, and N were performed and formulas of the compounds were calculated according to the results obtained. In addition, the phase purity of the compounds was confirmed through powder X-ray diffraction (PXRD) analysis. The results of PXRD patterns and vibrational spectroscopic show that the structural characteristics of Cu-Co-L [L = Imidazole(im), 1-methylimidazole(1-meim), and 2-methylimidazole(2-meim)] compounds are analogous to each other. The spectral properties of the Cu-Co-L compounds were obtained by considering the characteristic peak values of cyanide, imidazole, 1-methylimidazole, and 2-methylimidazole ligands.

Keywords

Hexacyanocobaltate(III) compound,
Imidazole and its methyl derivatives,
Vibrational spectra

Time Scale of Article

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1. INTRODUCTION

Imidazole and its derivatives are a group of organic molecules defined by a five-membered ring structure with two nitrogen atoms located at the 1st and 3rd positions. Imidazole has the formula $\text{C}_3\text{H}_4\text{N}_2$, and its structure is aromatic, similar to pyrrole and pyridine, making it a crucial component in many biological molecules, including histidine and biotin [1]. Derivatives of imidazole can have various substituents attached to the ring, which can significantly alter their chemical properties and biological activities [2]. Imidazole, 1-methylimidazole, and 2-methylimidazole ligands coordinate to the cobalt center via the nitrogen atom within the imidazole ring. The position and type of substitution (methyl group) on the imidazole ring affect the electronic properties and steric hindrance, which in turn influence the stability and structure of the resulting compound [3, 4]. The imidazole or its derivatives can coordinate directly to the $[\text{Co}(\text{CN})_5]^{2-}$ unit, forming compounds such as $[\text{Co}(\text{CN})_5]^{2-} \cdot (\text{L})_n$ where L represents imidazole, 1-methylimidazole, or 2-methylimidazole, and n indicates the number of coordinated ligand molecule [5, 6]. These compounds can exhibit varying magnetic and electronic properties depending on the type of imidazole derivative and its coordination mode [7].

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When imidazole or its derivatives form compounds with copper(II) (e.g., $[\text{Cu}(\text{im})_n]^{2+}$), these copper(II) compounds can further interact with the hexacyanocobaltate(III) ion, $[\text{Co}(\text{CN})_6]^{3-}$, to form mixed-metal compounds. These compounds often have the general formula $[\text{Cu}(\text{L})_n][\text{Co}(\text{CN})_6]$, where L can be imidazole, 1-methylimidazole, or 2-methylimidazole, and n represents the coordination number of the copper(II) ion [8-10]. The coordination of the copper(II) ion to imidazole derivatives can lead to either mononuclear or polynuclear compounds depending on the ligand's steric and electronic properties [11]. The $[\text{Co}(\text{CN})_6]^{3-}$ anion typically serves as a bridge between the copper(II) centers, which can result in the formation of extended polymeric structures or discrete binuclear species [12].

In imidazole compounds, the position and presence of methyl groups can have significant effects. Methyl groups, being electron-donating groups, can increase the electron density on the nitrogen atom of the imidazole. This can affect the strength of the bond with the coordinating metal ion. When 1-methylimidazole and 2-methylimidazole form compounds with metal ions such as copper(II), the distribution of electrons in the bond structure can change in different ways. Methyl groups can create steric hindrance in the imidazole ring, affecting the coordination geometry and stability of the compound. The difference between 1-methylimidazole and 2-methylimidazole arises from these steric effects appearing in different positions. The position (1 or 2) of the methyl group in the imidazole can change the coordination ability of the nitrogen atom. 1-methylimidazole generally shows stronger binding, while the binding ability of 2-methylimidazole may decrease due to steric hindrance. Methyl groups affect the stability of the compound by changing the steric and electronic properties of the ligand. More bulky and sterically hindered compounds may have lower stability. In the Cu-Co-1meim compound, 1-methylimidazole forms a strong bond and may increase the stability of the compound. However, in the Cu-Co-2meim compound, bonding may become more difficult due to steric hindrance, resulting in lower stability. Cyanide-bridged coordination polymers are being studied for innovative chemical designs because of their magnetic, optical, electrical, catalytic, and biological properties [13-17].

In the literature, the metal compounds utilizing the imidazole ligand and its derivatives have been studied [7, 18-28]. However, specific research on hexacyanometallate(III) compounds with imidazole and its derivatives is scarce [29, 30]. As a continuation of these studies, we present three new copper(II)/cobalt(III) cyanide compounds with im, 1-meim and 2-meim ligands $[\text{Cu}_3(\text{im})_4\text{Co}_2(\text{CN})_{12}] \cdot 3\text{H}_2\text{O}$ (Cu-Co-im), $[\text{Cu}_3(1\text{-meim})_4\text{Co}_2(\text{CN})_{12}] \cdot 6\text{H}_2\text{O}$ (Cu-Co-1meim) and $[\text{Cu}_3(2\text{-meim})_4\text{Co}_2(\text{CN})_{12}] \cdot 6\text{H}_2\text{O}$ (Cu-Co-2meim). In addition, in previous studies, cyanide-bridged compounds with imidazole, 1-methylimidazole and 2-methylimidazole ligands were synthesized and their structural and spectroscopic analyses were performed. However, no study was found on how the changes in methyl groups affect the vibrational wavenumbers in spectroscopic studies. Therefore, the change in vibrational wavenumbers of methyl groups in imidazole derivatives during compound formation was investigated and compared with the compounds found in the literature.

2. EXPERIMENTAL

Copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Acros, 98%), potassium hexacyanocobaltate(III) ($\text{K}_3[\text{Co}(\text{CN})_6]$, Acros, 95%), imidazole ($\text{C}_3\text{N}_2\text{H}_4$, Sigma Aldrich, 98%), 1-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, Merck, 99%), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, Himedia, 97%), ammonia solution (NH_4OH , Merck, 25%) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Merck) were obtained from commercial suppliers and used directly without additional purification. Elemental analyses were conducted at the TÜBİTAK Ankara Test and Analysis Laboratory using a LECO CHNS-932 analyzer. The vibrational spectra of the compounds were obtained using a Perkin Elmer 100 FT-IR and Bruker Senterra Dispersive Raman spectrometer, respectively. PXRD was conducted using a PANalytical Empyrean instrument with Cu-K α radiation.

The compounds were synthesized as follows;

Synthesis of $K_3[Co(CN)_6]$

Firstly, 2 mmol (4.80 g) of cobalt(II) chloride hexahydrate was dissolved in 50 ml of distilled water and stirred for 15 minutes. To the stirring solution, 4 mmol (3.00 g) of KCN dissolved in 20 ml of distilled water was added dropwise over 10 minutes. The reddish brown precipitate of cobalt(II) cyanide was filtered through filter paper and washed with 10 ml of cold water and then with acetone. Secondly, the resulting $Co(CN)_2$ was transferred to a 250 ml erlenmeyer flask and a solution of KCN dissolved in 25 ml of distilled water (6.00 g) was added to this solution. Finally, the obtaining dark red potassium hexacyanocobaltate(II) $\{[K_4Co(CN)_6]\}$ solution was heated to the boiling point and kept at the boiling point for 10 or 15 minutes. The solution acquired the yellow color of potassium hexacyanocobaltate(III) and was filtered while hot. After a few days at room temperature, yellow crystals of the salt $\{K_3[Co(CN)_6]\}$ were formed.

Synthesis of the Cu-Co-L compounds

1 mmol $K_3[Co(CN)_6]$ (0.332 g) was dissolved in 10 mL of water and 10 mL of ammonia. Then, 1 mmol Cu(II) acetate monohydrate $[Cu(CH_3COO)_2 \cdot H_2O]$ (0.199 g) dissolved in 20 mL of water was added to the solution and this solution was stirred for 15 minutes. Finally, 4 mmol ligand [imidazole (0.272 g), 1-methylimidazole (0.328 g) or 2-methylimidazole (0.328 g)] dissolved in 5 mL ethanol and 5 mL water was added dropwise to the mixture and stirred at 50 °C for 4 hours. The solution was filtered and then allowed to stand at room temperature. The synthesis of compounds is illustrated by Figure 1. The compounds were then analyzed for carbon, hydrogen, and nitrogen, yielding the following results: Anal. calc. (%) for $[Cu_3(im)_4Co_2(CN)_{12}] \cdot 3H_2O$, $C_{24}H_{22}Co_2Cu_3N_{20}O_3$ ($M_w = 947.07$ g/mol): C, 30.44; H, 2.34; N, 29.58; found C, 30.65; H, 2.69; N, 29.66; for $[Cu_3(1-meim)_4Co_2(CN)_{12}] \cdot 6H_2O$, $C_{28}H_{36}Co_2Cu_3N_{20}O_6$ ($M_w = 1057.22$ g/mol): C, 31.81; H, 3.43; N, 26.50; found C, 31.50; H, 3.69; N, 26.66; for $[Cu_3(2-meim)_4Co_2(CN)_{12}] \cdot 6H_2O$, $C_{28}H_{36}Co_2Cu_3N_{20}O_6$ ($M_w = 1057.22$ g/mol): C, 31.81; H, 3.43; N, 26.50; found C, 31.10; H, 3.30; N, 26.42.

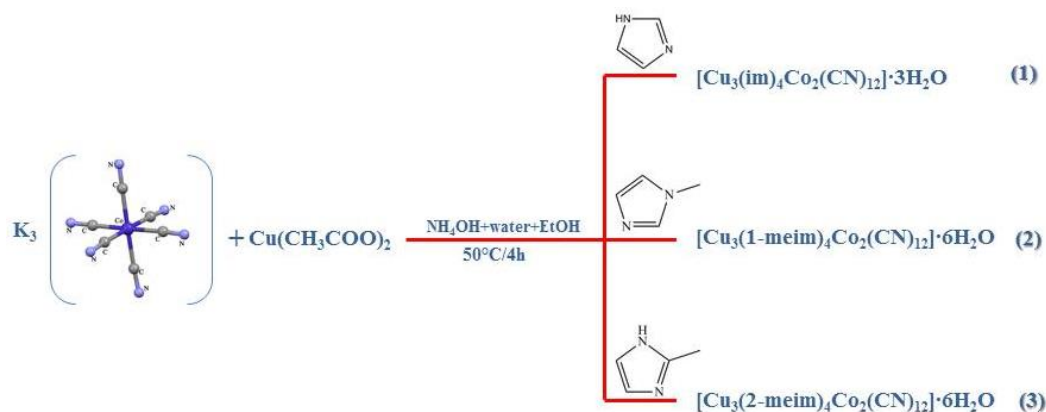


Figure 1. Synthesis scheme of the compounds

3. RESULTS AND DISCUSSION

3.1. Spectral (FT-IR and Raman) Analysis

The vibrational spectra of the compounds can be seen in Figures 2- 4 and are listed in Tables 1-3. As these figures demonstrate, the bands corresponding to the ligands in the vibrational spectra confirm the presence of ligands (im, 1-meim, and 2-meim) within the compounds. Vibrational wavenumbers and assignments for ligands are taken from studies in the literature and are given in Tables 1-3 [31-33]. The

proposed assignments for imidazole are derived from general literature data, and the corresponding values for coordinated ligands are consistent with data reported in the literature [24, 31]. The distinction between ligands is the presence of the CH₃ group in meim. Extra bands may appear due to the presence of the CH₃ group. In the vibration spectrum of Cu-Co-1meim and Cu-Co-2meim compounds, the absorption bands arising from ν and δ methyl vibrations contain more than the Cu-Co-im compound. In the FTIR and Raman spectra of the Cu-Co-1meim or Cu-Co-2meim compounds, it was observed that the stretching vibration wavenumbers of the methyl groups of the 1-methylimidazole or 2-methylimidazole ligands were shifted to lower or higher wavenumbers, respectively, compared to the methyl groups in the free ligand. These shifts were also observed in other cyanide-bridged compounds such as Cu-Pd-1meim or Cu-Pd-2meim [26, 34].

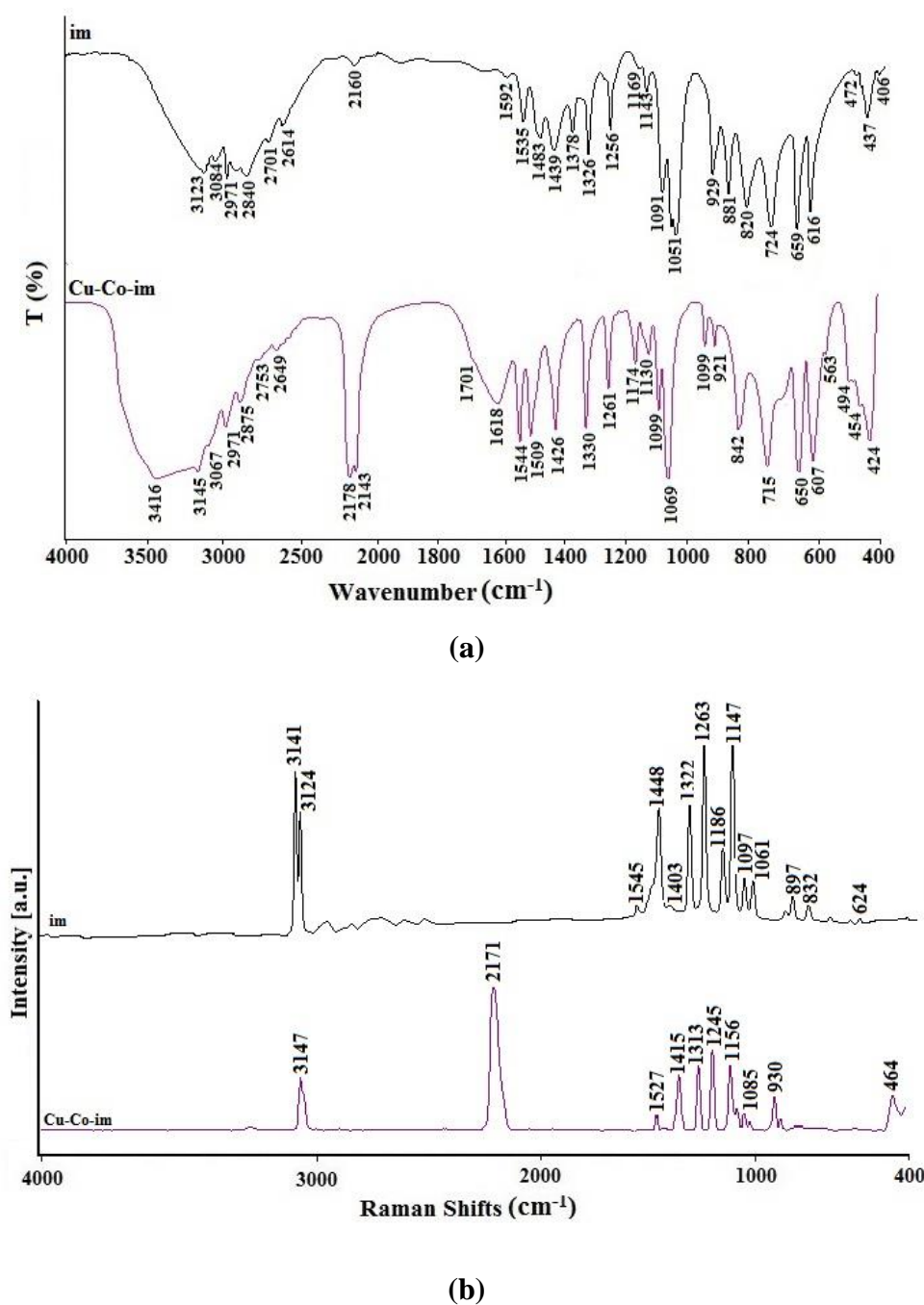
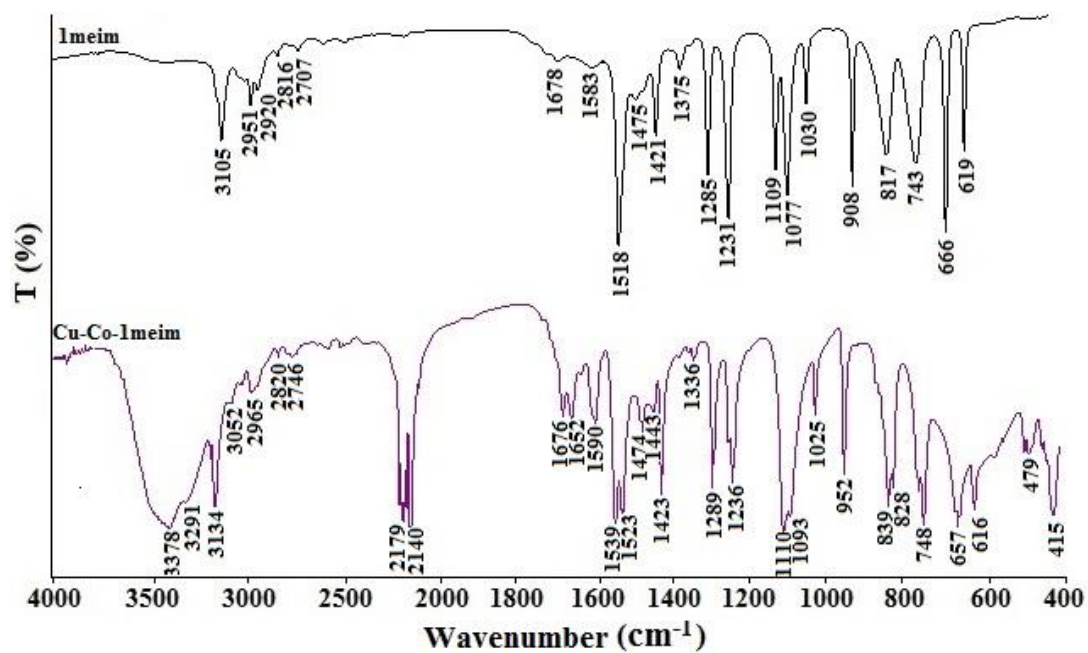
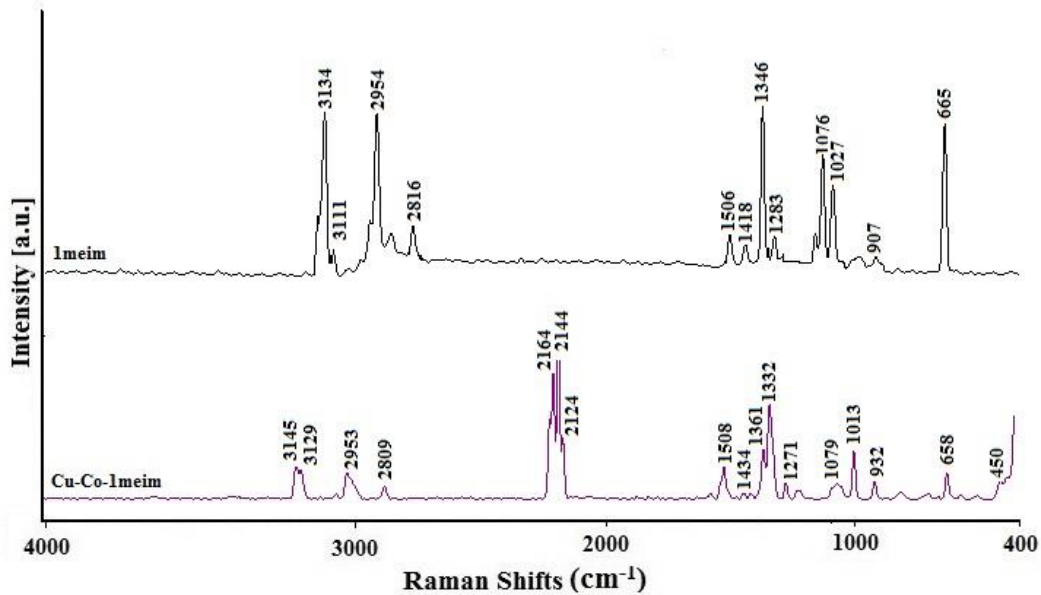


Figure 2. The FT-IR (a) and Raman (b) spectra of the Cu-Co-im compound

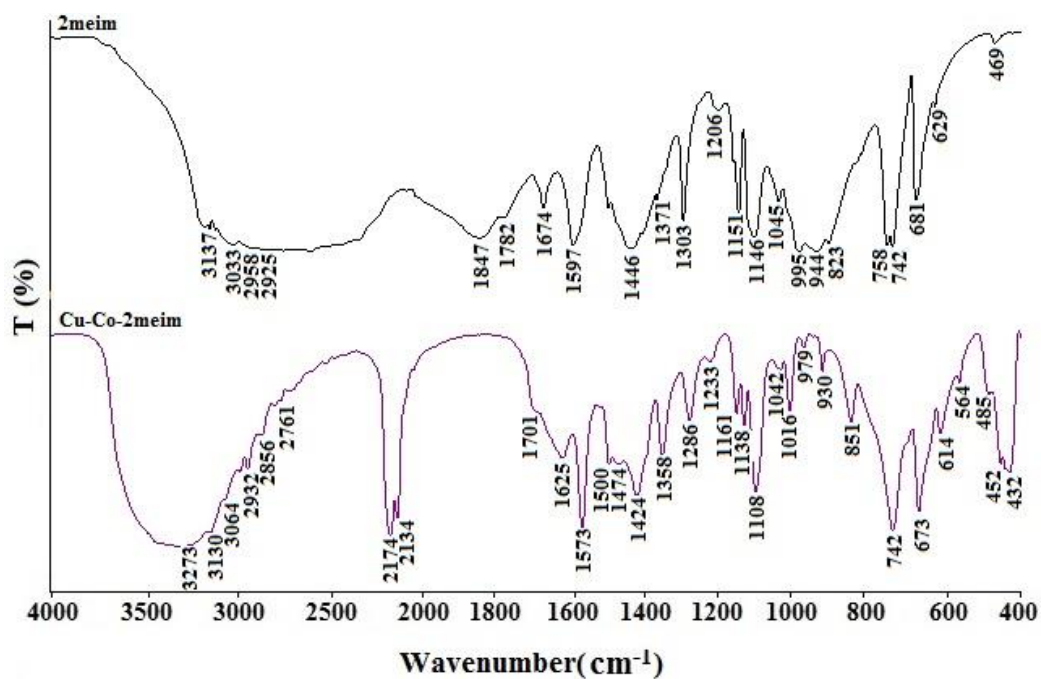


(a)

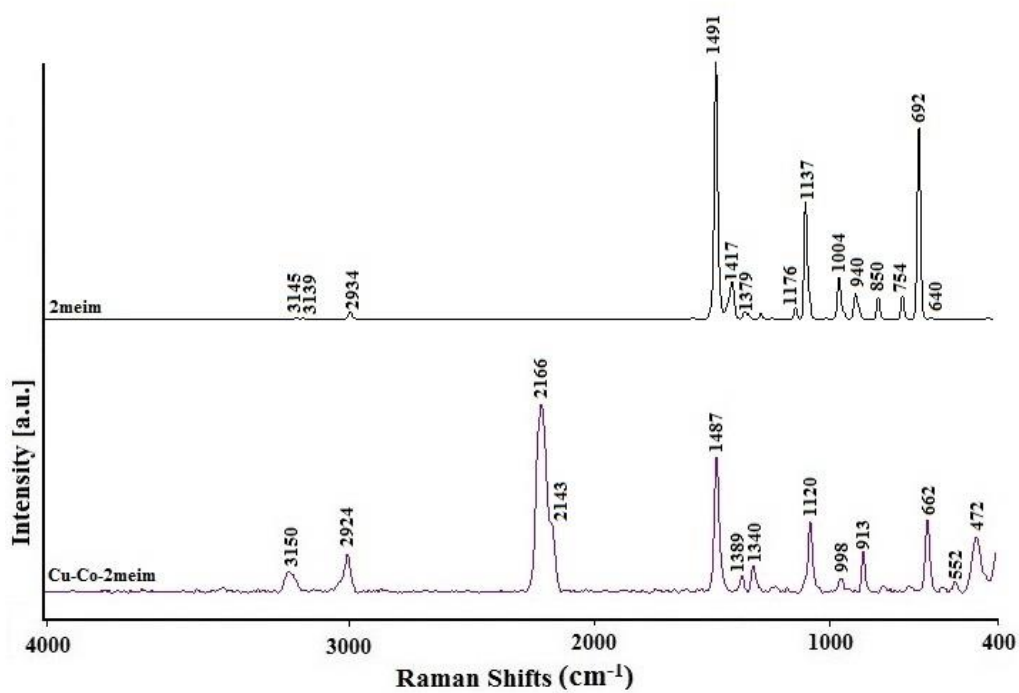


(b)

Figure 3. The FT-IR (a) and Raman (b) spectra of the Cu-Co-lmeim compound



(a)



(b)

Figure 4. The FT-IR (a) and Raman (b) spectra of the Cu-Co-2meim compound

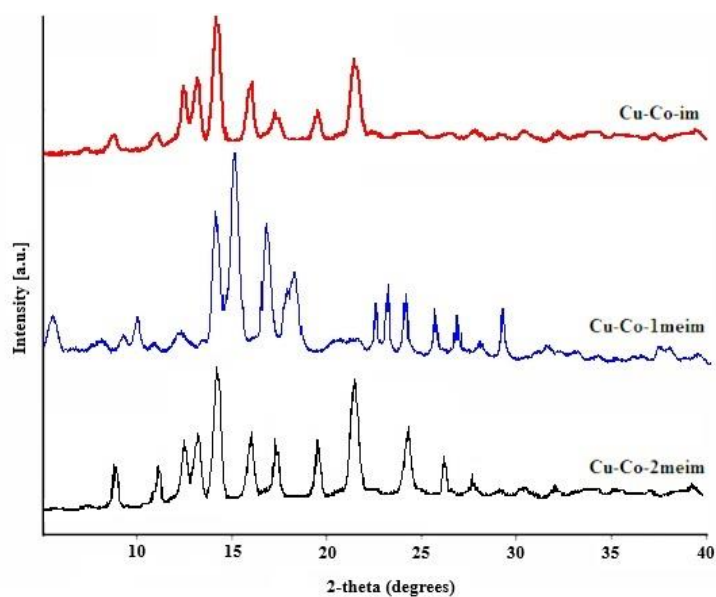


Figure 5. The powder XRD patterns of the compounds

Table 1. The FT-IR and Raman wavenumbers of the imidazole in the compound (cm^{-1})

Assignments [31]	im		Cu-Co-im	
	FT-IR	Raman	FT-IR	Raman
v(NH)	3123 w	3141 m	3145 w	3147 w
v(CH)	3048 w	3124 m	3067 sh	3070 vw
v(CH)	2971 w	-	2971 w	-
v(CH)	2919 w	-	2875 w	-
δ (NH)	1545 m	1545 w	1544 s	1527 w
δ (CH)	1483 m	-	1426 s	1482 vw
δ (NH)	1439 m	1403 vw	-	1415 m
δ (CH)	1326 m	1322 s	1330 s	1313 m
δ (CH)	1256 m	1263 m	1261 m	1245 m
v(CN)	1143 m	1147 vs	1174 m	1156 m
v(CN)	1091 s	1097 m	1099 m	1085 vw
v(CN)	1051 vs	1061 m	1069 vs	1057 vw
δ_{ring}	929 m	924 vw	951 w	930 w
δ_{ring}	881 m	900 w	842 m	900 vw
γ (CH)	820 m	832 w	-	829 vw
γ (CH)	724 s	746 vw	715 s	738 vw
τ_{ring}	659 s	660 vw	650 vs	675 vw
τ_{ring}	616 s	624 vw	607 s	627 vw
γ (NH)	437 m	-	454 m	464 m

Assignments: v, stretching; π , out of plane vibration; δ , in- plane vibration; s, strong; m, medium; w, weak; v, very; sh; shoulder.

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

Assignments [32]	1-meim		Cu-Co-1meim	
	FT-IR	Raman	FT-IR	Raman
v(CH)	3132 sh	3134 m	3165 w	3145 m
v(CH)	3106 m	3111 m	3134 s	3129 m
v(CH)	3025 w	-	3009 w	2994 w
v(CH ₃)	2987 w	-	2965 w	-
v(CH ₃)	2952 m	2954 m	2950 w	2953 m
v(NH)	2765 w	-	2746 m	-
v _{ring} , δ(CH ₃)	1558 w	-	1590 m	1561 w
v _{ring} , δ(CH ₃)	1515 vs	-	1539 vs	-
v _{ring} , δ(CH ₃), v(N-CH ₃),	1506 w	1506 w	1523 vs	1508 m
δ(CH ₃), v _{ring}	1471 w	-	1474 m	1434 w
δ(CH ₃), v _{ring}	1420 s	1418 w	1423 s	1406 w
v _{ring} , δ(CH ₃)	1383 w	-	-	-
v _{ring} , δ(CH ₃)	1358 m	1346 vs	-	1361 m
v _{ring} , δ(CH ₃)	1330 w	-	1336 w	1332 s
δ(CH), v _{ring}	1284 s	1283 w	1289 s	1271 w
v _{ring} , δ(CH ₃), v(N-CH ₃)	1229 vs	1230 w	1236 s	1226 w
v(CN)	1107 s	-	1110 vs	1128 vw
v(CN)	1076 vs	1076 m	1093 vs	1079 w
δ(CH ₃), v _{ring}	1028 s	1027 m	1025 m	1013 m
δ _{ring} , v _{ring}	907 s	907 w	952 s	932 w
γ(CH)	815 s	817 vw	828 s	834 w
γ(CH)	737 s	740 vw	748 s	728 w
v(N-CH ₃), v _{ring}	662 vs	665 m	657 s	658 m
δ _{ring}	615 s	616 w	616 m	601 w

Assignments: v, stretching; π, out of plane vibration; δ, in- plane vibration; s, strong; m, medium; w, weak; v, very, sh; shoulder.

Table 3. The FT-IR and Raman wavenumbers of the 2-methylimidazole in the compound (cm⁻¹)

Assignments [33]	2-meim		Cu-Co-2meim	
	FT-IR	Raman	FT-IR	Raman
v(CH)	3137 m	3139 vw	3130 s	3137 m
v(CH)	3110 m	-	-	-
v(CH)	3033 m	-	3064 sh	3056 vw
v(CH ₃)	2958 s	-	2978 s	2989 vw
v(CH ₃)	2925 s	2934 w	2932 s	2925 m
v(NH)	2765 w	-	2761 m	-
v _{ring}	1597 s	-	1573 s	-
δ(CH ₃)/v _{ring}	1446 s	1491 vs	1424 s	1484 s
δ(CH ₃)	1371 s	1379 w	1358 m	1384 m
v _{ring}	1303 s	-	1286 m	1343 m
δ(NH)	1154 s	1176 w	1161 m	-
δ(CH)	1114 s	1137 s	1138 m	1122 m
v(CN)	1091 s	-	1108 s	-
v(CN)	1051 vs	-	-	-
δ(CH ₃)	1046 w	-	1042 w	-
v _{ring} or γ(CH)	995 vs	1004 m	979 w	997 w
γ(NH)	944 s	940 m	930 w	913 m
γ(CH)/δ _{ring}	823 sh	850 m	851 m	836 vw
δ(CH)	758 vs	754 m	742 vs	735 vw
v(C=C)	681 vs	690 vs	673 vs	665 s
γ _{ring}	629 w	640 vw	-	-
τ _{ring}	616 s	-	614 m	608 w
γ(NH)	469 m	-	452 s	473 m

Assignments: v, stretching; π, out of plane vibration; δ, in-plane vibration; s, strong; m, medium; w, weak; v, very, sh; shoulder.

From the Tables, it is observed that the vibrational modes of most of the ligands in the compounds have an overall increase in wavenumber compared to the free ligands. These shifts can be attributed to the coupling of Cu-N (im or meim) vibrations. Similar shifts have been noted in imidazole compounds coordinated with metals [24, 35, 36]. In particular, the distinct vibrations mainly related to $\nu(\text{NH})$ (3123 cm^{-1} for im), $\nu(\text{CH})$ (3048, 2971 and 2919 cm^{-1} for im, 3106 cm^{-1} for 1meim and 3137 cm^{-1} for 2meim), $\nu(\text{CH}_3)$ (2952 cm^{-1} for 1meim and 2958 and 2925 cm^{-1} for 2meim), ν_{ring} (1515 cm^{-1} for 1meim and 1597 cm^{-1} for 2meim), $\delta(\text{NH})$ (1545 cm^{-1} for im), $\delta(\text{CH}_3)$ (1358 and 1107 cm^{-1} for 1meim and 1371 and 1046 cm^{-1} for 2meim), $\nu(\text{CN})$ (1143, 1091 and 1051 cm^{-1} for im, 1107 and 1076 cm^{-1} for 1meim and 823 cm^{-1} for 2meim), δ_{ring} and ν_{ring} (929 and 881 cm^{-1} for im, 907 cm^{-1} for 1meim, and 1091 and 1051 cm^{-1} for 2meim), $\nu(\text{C}=\text{C})$ (681 cm^{-1} for 2meim), τ_{ring} (659 and 616 cm^{-1} for im and 616 cm^{-1} for 2meim), and $\nu(\text{N}-\text{CH}_3)$ and ν_{ring} (662 cm^{-1} for 1meim) indicate the bonding of the ligand via its nitrogen atom, with significant delocalization of the negative charge across the nitrogen atoms in the ring. In the spectrum of the compounds, these distinct vibrations showed significant upward and downward shifts. These shifts indicate that the ligands coordinate with the copper ion via nitrogen. Similarly, in the cyanide-bridged compounds we previously made with imidazole and its derivatives, coordination to transition metals via the nitrogen in the imidazole ring was observed [23-26].

For these compounds, the $\nu(\text{C}\equiv\text{N})$ vibrations contain the most pronounced absorption band. Therefore, the $\nu(\text{C}\equiv\text{N})$ vibration peak reveals whether the structure has formed or not. In the FT-IR spectrum for $\text{K}_3[\text{Co}(\text{CN})_6]$, $\nu(\text{C}\equiv\text{N})$ vibration bands are seen at 2118 cm^{-1} [37]. In the FT-IR spectrum of the $\text{K}_3[\text{Co}(\text{CN})_6]$ compound used, the $\nu(\text{CN})$ vibration band was observed at 2126 cm^{-1} . The FT-IR spectrum of the compounds contains two distinct cyanide stretching vibrations at 2178 and 2143 cm^{-1} for Cu-Co-im, 2179 and 2140 cm^{-1} for Cu-Co-1meim, and 2174 and 2134 cm^{-1} for Cu-Co-2meim. In addition, one Raman fundamental is assigned to 2171 cm^{-1} for Cu-Co-im, two Raman fundamentals are 2164 and 2144 cm^{-1} for Cu-Co-1meim and 2166 and 2143 cm^{-1} for Cu-Co-2meim. Accordingly, cyanide groups are subject to cleavage in the compounds. In the spectrum of the compounds, the vibration band close to 2126 cm^{-1} indicates the free $\nu(\text{CN})$ vibration band, while the higher $\nu(\text{CN})$ vibration band indicates the bridge cyanide groups. Therefore, it shows that the cyanide groups are cleaved into two as free and bridge in the compounds. In cyanide-bridged compounds, the frequencies of the bridging cyanide are typically observed at a higher range. This phenomenon is attributed to kinematic coupling, which acts as a mechanical constraint on the bridging cyanide, limiting its movement due to its connection to a second metal center. Considering the shifts observed in the vibrational spectra of the compounds, it is concluded that the imidazole binds to the metal via the nitrogen in its ring, and the cyanides bind to the metals both freely and in a bridging manner.

3.2. Powder X-ray Diffraction (PXRD) Analyses

The PXRD patterns of im, 1-meim or 2-meim hexacyanocobaltate(III) copper(II) compounds are recorded and are given in Figure 5. The PXRD patterns show that the crystal structure is formed and that Cu-Co-im, Cu-Co-1meim, and Cu-Co-2meim structures are obtained in a very pure form. The maximum peaks corresponding to 2θ angles of 13.16°, 13.45°, 14.95°, 16.30°, and 21.56° for Cu-Co-im, 14.03°, 15.78°, 17.24°, and 18.04° for Cu-Co-1meim, and 13.23°, 14.18°, 16.20°, 17.53°, and 21.96° for Cu-Co-2meim indicate the crystal formation and purity. In addition, the element and spectroscopic analysis results prove the accuracy of these expected structures in PXRD patterns.

4. CONCLUSION

In this study, Cu(II) metal compounds containing hexacyanocobaltate(III) with the chemical formulas $[\text{Cu}_3(\text{L})_4\text{Co}_2(\text{CN})_{12}] \cdot n\text{H}_2\text{O}$ were obtained in powder form. Vibrational spectroscopy, powder-XRD and element analysis techniques were used to explain the structures of the compounds. Spectroscopic results showed that the im, 1meim, or 2meim ligands coordinate directly to copper(II) atoms and the cyanide

ligand to cobalt atoms. In addition, cyanide groups were observed to act both freely and as bridges. PXRD determined that the compounds were pure and crystalline. In addition, elemental, spectroscopic, and PXRD data support the similarity in the structural properties of the compounds.

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CONFLICT OF INTEREST

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

CRedit AUTHOR STATEMENT

Güneş Süheyla Kürkçüoğlu: Writing, Investigation, Supervision, Conceptualization, Original draft. **Dursun Karaağaç:** Investigation, Writing, Draw graph, Drawing a table. **Seray Kekeç:** Writing, Visualization, Draw graph, Drawing a table.

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