

## SPECTROSCOPIC AND THERMAL STUDIES OF CYANO BRIDGED HETERO-METALLIC POLYMERIC COMPLEXES DERIVED FROM LIGANDS CONTAINING N AND S DONOR ATOMS

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**ABSTRACT.** The new cyano bridged hetero-metallic polymeric complexes  $[\text{Cu}(\text{dmu})_2\text{Pd}(\text{CN})_4]\cdot\text{H}_2\text{O}$  and  $[\text{Cu}(\text{H}_2\text{O})_2(\text{detu})_2\text{Pd}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$  (dmu = N,N'-dimethylthiourea, detu = N,N'-diethylthiourea; abbreviated henceforth as Cu-Pd-dmu and Cu-Pd-detu) have been synthesized for the first time in powder form and their structures have been determined by vibrational (FT-IR and Raman) spectroscopy, thermal and elemental analysis techniques. Using vibration spectra of the complexes, it has been discussed whether the ligands are bound to metal atoms or not. According to the results obtained from the spectra of the complexes, the palladium atom is four coordinated with four cyano groups in a square planar geometry whereas the copper(II) atom of Cu-Pd-detu is six coordinated with two bridging cyano groups, two aqua and two detu ligands (four bridging cyano groups and two dmu ligands for Cu-Pd-dmu) in a distorted octahedral geometry. In addition, complex Cu-Pd-dmu is similar to structure of the Hofmann type complexes and its structure consists of polymeric layers of  $[\text{Cu-Pd}(\text{CN})_4]_{\infty}$  with the dmu ligand bounded to the copper(II) atom. Thermal stabilities and decomposition products of the complexes were also investigated in the range of 30–1000 °C in the static air atmosphere using TG, DTG and DTA techniques.

**KEY WORDS:** Tetracyanopalladate(II), N,N'-dimethylthiourea, N,N'-diethylthiourea, Cyano-bridged complex, Vibration spectra

### INTRODUCTION

Cyano (CN<sup>-</sup>) is one of the ligands used extensively in the synthesis of coordination polymers [1-5]. This is because the cyano ligand is double-character and can bind to transition metal atoms in different ways. There are pairs of electrons on the carbon and nitrogen atoms of the cyano ligand. Thanks to these electron pairs, the ligand can coordinate to the metal as either a bidentate or two monodentate. The CN<sup>-</sup> ligand can be attached to the metal atom as a terminal ligand with the carbon atom, while also acting as  $\mu$ -bridge ligand using both carbon and nitrogen atoms [2, 6, 7]. Because of these properties of cyano ligand, one, two or three dimensional cyano bridged metal complexes were synthesized and their structures were illuminated [6, 8, 9]. Hofmann type complexes obtained using cyano ligand are among the cyano-bridged metal complexes. The general formula of these complexes produced using transition metals and various ligands is  $[\text{M}(\text{L})\text{M}'(\text{CN})_4]_n$ , where M is the transition metal atom (Mn, Fe, Co, Ni, Cu or Cd) having two values, M' is a square-planar coordinated transition metal atom having two values (Ni, Pd or Pt), and L is either a bidentate (such as pyrazine, pyridazine and 4-(2-aminoethyl)pyridine) or two monodentate (such as ammonia, pyridine and pyrrolidine) ligand [10-12]. The structures of these complexes have been elucidated in literature by using FT-IR and Raman spectroscopy [10-13]. According to this, the structures of the complexes are composed of  $[\text{M-M}'(\text{CN})_4]_{\infty}$  polymeric layers and in this structure  $[\text{M}'(\text{CN})_4]^{2-}$  anions are surrounded by  $[\text{ML}]^{2+}$  cations. M' atoms are coordinated to four carbon atoms of CN groups in a square plane structure. The M atoms are octahedrally surrounded by six donor (such as nitrogen, oxygen and sulfur) atoms, two of which are from ligands and the others are from cyanide groups. The ligand molecules are located to

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above and below of the layers. This structure provides a space similar to the rectangular box for guest molecules [10, 14].

The cyano-bridged complexes have been extensively obtained using various donor atoms such as nitrogen and oxygen [1-5, 15], but the cyano-bridged complexes obtained using the sulfur donor atom are particularly rare in the literature [14], which is  $[M(L)M'(CN)_4]_n$  type. In this study, we have obtained two new cyano bridged hetero-metallic polymeric complexes  $[Cu(dmtu)_2Pd(CN)_4] \cdot H_2O$  and  $[Cu(H_2O)_2(detu)_2Pd(CN)_4] \cdot 2H_2O$  with N,N'-dimethylthiourea or N,N'-diethylthiourea as ligands for the first time. The FT-IR and Raman spectra of these complexes were recorded in the range of  $4000-400\text{ cm}^{-1}$  and  $4000-250\text{ cm}^{-1}$ , respectively, and interpreted to determine the structures of the complexes. From the vibrational spectra of the resulting complexes, it was determined that both ligands were coordinated to metal atoms through which donor atoms. In addition, the changes in the characteristic vibration bands of both ligands involved in the complex formation were examined and the differences were determined. We have also reported up to  $1000\text{ }^\circ\text{C}$  in static air atmosphere the thermal decomposition behaviors of the complexes with TG, DTG and DTA techniques.

## EXPERIMENTAL

### Materials

Copper(II) chloride dihydrate ( $CuCl_2 \cdot 2H_2O$ , 99%), palladium(II) chloride ( $PdCl_2$ , 99%), potassium cyanide (KCN, 96%) N,N'-dimethylthiourea ( $C_3H_8N_2S$ , 98%) and N,N'-diethylthiourea ( $C_5H_{12}N_2S$ , 98%) were purchased and used without further purification.

### Synthesis of $K_2[Pd(CN)_4] \cdot H_2O$

1 mmol of  $PdCl_2$  (0.177 g) was dissolved in 100 mL of distilled water. 4 mmol of KCN (0.260 g) dissolved in 100 mL of distilled water was added dropwise to this solution. The prepared solution was stirred with magnetic stirrer for 3 hours and then allowed to stand by filtration. Within two weeks, white  $K_2[Pd(CN)_4] \cdot H_2O$  compound was obtained as crystallized.

### Synthesis of $Cu[Pd(CN)_4] \cdot H_2O$

1 mmol of  $K_2[Pd(CN)_4] \cdot H_2O$  (0.306 g) complex was mixed with magnetic stirrer with distilled water for 5 minutes and dissolved. The aqueous solution of 1 mmol  $CuCl_2 \cdot 2H_2O$  (0.170 g) salt prepared in separate beaker was added dropwise to the  $K_2[Pd(CN)_4] \cdot H_2O$  solution in separate beaker. The solution was stirred in the magnetic stirrer at room temperature for 3 hours and then, blue  $Cu[Pd(CN)_4] \cdot H_2O$  compound was obtained as crystallized.

### Syntheses of $[Cu(dmtu)_2Pd(CN)_4] \cdot H_2O$ and $[Cu(H_2O)_2(detu)_2Pd(CN)_4] \cdot 2H_2O$

1 mmol of  $Cu[Pd(CN)_4] \cdot H_2O$  (0.292 g) was completely dissolved in 25 mL of distilled water. Into this solution, 2 mmol of the ligand dissolved in methanol (50%), ethanol (25%) and distilled water (25%) (dmtu = 0.208 g or detu = 0.264 g) was added dropwise. The resulting solution was stirred in the magnetic stirrer at  $40\text{ }^\circ\text{C}$  for 3 hours and then, the complexes obtained were filtered and washed with distilled water and ethanol, respectively and dried in air. The light brown complexes obtained in powder form were analyzed for C, H and N, and the results obtained: Anal. Found (Calcd.) (%) for  $C_{10}H_{18}N_8O_1S_2CuPd$  ( $M_w = 500.4\text{ g/mol}$ ): C, 23.40 (24.00); H, 3.61 (3.63); N, 21.10 (22.39); for  $C_{14}H_{32}N_8O_4S_2CuPd$  ( $M_w = 610.55\text{ g/mol}$ ): C, 27.39 (27.54); H, 4.58 (5.28); N, 18.03 (18.35).

*Measurements*

The complexes obtained 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 on a Perkin Elmer 100 FT-IR spectrometer using KBr pellets between 4000 and 400  $\text{cm}^{-1}$  (2  $\text{cm}^{-1}$  resolution), which was calibrated using polystyrene and  $\text{CO}_2$  bands. Raman spectra of the complexes obtained were recorded on a Bruker Senterra Dispersive Raman apparatus between 4000 and 250  $\text{cm}^{-1}$  using 785 nm laser excitation. Thermal analysis was carried out on Perkin Elmer Diamond thermal analyzer instrument in a static air atmosphere with a heating rate of 10  $\text{K min}^{-1}$  in the temperature region 30-1000  $^\circ\text{C}$ .

**RESULTS AND DISCUSSION***Vibrations of ligands*

After dissolving the solid dmtu or detu molecule in chloroform, the spectrum of dmtu or detu was taken in the FT-IR region (4000-400)  $\text{cm}^{-1}$ . The FT-IR spectrum and characteristic peaks of the dmtu, detu and chloroform molecule are given in Figure 1. The FT-IR and Raman spectra of the synthesized complexes are given in Figures 2 and 3. Experimentally obtained vibration frequencies of dmtu or detu and the previously determined vibration assignments of the dmtu molecule were given in Table 1, together with the wavenumbers in the complexes [16, 17]. The vibration assignments of the detu ligand were not available in the literature according to our research, but dmtu and detu had very similar spectral properties. Therefore, dmtu vibration bands were used for detu vibration bands. In addition, the vibration assignments and wavenumbers of the ethyl group were taken from N-ethylthiourea [18]. The dmtu or detu has nitrogen and sulfur atoms, and can coordinate to metal atoms through these atoms. Significant changes in vibrational frequencies of ligands coordinated to metal are observed. The most important vibration bands of ligands are  $\nu(\text{NH})$ ,  $\nu(\text{CN})$  and  $\nu(\text{CS})$  vibration bands. If coordination to metal occurs via nitrogen atom of ligands,  $\nu(\text{CS})$  stretching vibration frequencies are expected to shift upwards while  $\nu(\text{NH})$  stretching vibration frequencies are expected to shift downward, but if coordination occurs via sulfur atom,  $\nu(\text{CS})$  stretching vibration frequencies are shifted downwards while  $\nu(\text{CN})$  stretching vibration frequencies are shifted upwards [18-20]. Symmetric and asymmetric  $\nu(\text{NH})$  stretching vibration bands which are seen in strong or medium density in the range of 3500-3000  $\text{cm}^{-1}$  expand due to the presence of intermolecular hydrogen bonds and produce spectral complexity that is not completely resolved in this region. In addition, these  $\nu(\text{NH})$  stretching vibration bands are generally overlapped with  $\nu(\text{OH})$  stretching vibration bands of water. The  $\nu(\text{NH})$  stretching vibration band of the free ligand at 3270  $\text{cm}^{-1}$  occurs as a broad and strong band due to hydrogen bonds. In the spectrum of complexes, this band was observed to shift upwards. After complex formation, the effect of metal ions on the ligand is more pronounced on the CN and CS bond. This effect increases the partial double bond character in the CN bond while decreasing the double bond character of the CS bond. The  $\nu(\text{CN})$  stretching vibration band at 1564  $\text{cm}^{-1}$  in the FT-IR spectrum of the ligand was observed as a sharp and strong band. These stretching vibration bands observed in spectrum of the complexes are shifted to higher values; this shows that the sulfur atom of ligands is involved in the complex formation. The  $\nu(\text{CS})$  stretching vibration wavenumber occurs as a sharp and strong band at 756  $\text{cm}^{-1}$  in the FT-IR spectrum of the ligands and was observed to shift to lower wavenumbers at 722 and 736  $\text{cm}^{-1}$  in the FT-IR and Raman spectra of Cu-Pd-dmtu, respectively but was observed to shift to higher wavenumbers in the spectrum of Cu-Pd-detu [21]. The most important spectral changes due to complex formation occur in the decrease of the  $\nu(\text{CS})$  stretching vibration wavenumber. In contrast, in some complex formations these vibrations are strongly coupled with other modes and the  $\nu(\text{CS})$  stretching vibration

wavenumbers shift upward. These changes in the vibration frequencies confirm that the ligands are bound to the metal atoms via the sulfur atom. Other significant bands of the free ligands are the  $\nu(\text{CH}_3)$  between 3076 and 2966  $\text{cm}^{-1}$ , the  $\nu(\text{CH}_2)$  at 2937 and 2876  $\text{cm}^{-1}$ , the  $\delta(\text{NH})$  at 1504  $\text{cm}^{-1}$ , the  $\nu(\text{C}'\text{N})$  at 1038 and 1050  $\text{cm}^{-1}$ , and  $\delta(\text{CNC}'')$  at 666  $\text{cm}^{-1}$ . In the complexes, these vibration bands show upward or downward shifts in frequency according to those of the free ligands.

#### *Water vibrations*

Water molecules have three fundamental vibrations; asymmetric and symmetric  $\nu(\text{OH})$  stretching, and  $\delta(\text{HOH})$  bending. In general, asymmetric and symmetric  $\nu(\text{OH})$  stretching, and  $\delta(\text{HOH})$  bending vibrations are observed in the 3700-3200  $\text{cm}^{-1}$  region and in the 1700-1600  $\text{cm}^{-1}$  region, respectively. In addition, lattice or coordinated water absorbs between 3550 and 3200  $\text{cm}^{-1}$  [7, 22]. In the spectrum of the complexes, stretching bands of coordinated water molecules with stretching bands of NH vibrations in ligands overlap in the range of 3450-3200  $\text{cm}^{-1}$ . The stretching vibration wavenumbers of uncoordinated water molecules for Cu-Pd-dmtu were found at 3628 and 3553  $\text{cm}^{-1}$  but were not observed for Cu-Pd-detu. In the infrared spectrum of Cu-Pd-dmtu and Cu-Pd-detu, the  $\delta(\text{HOH})$  bending vibration of water molecules was also found at 1663 and 1654  $\text{cm}^{-1}$ , respectively.

#### *Vibrations of the $[\text{Pd}(\text{CN})_4]^{2-}$ group*

According to the data obtained from the FT-IR and Raman spectra, vibration frequencies resulting from Pd-C≡N-Cu and Pd-C≡N type structures in the complexes were given in Table 2. In addition, vibration assignments of  $[\text{Pd}(\text{CN})_4]^{2-}$  ion were performed according to vibration assignments in Jones's study [23]. Since  $[\text{Pd}(\text{CN})_4]^{2-}$  ion has nine atoms, it has twenty one fundamental vibrations. Fifteen of these fundamental vibrations are in-plane vibrations and six are out of plane vibrations. The distribution of out-of-plane vibrations is  $2A_{2u}$ ,  $2B_{2u}$  and  $E_g$  while the distribution of in-plane vibrations according to symmetry type is  $2A_{1g}$ ,  $A_{2g}$ ,  $2B_{1g}$ ,  $2B_{2g}$  and  $4E_u$ , eighty of these vibrations are the FT-IR ( $2A_{2u}$ ,  $2B_{2u}$ ,  $4E_u$ ) active and seven are Raman ( $2A_{1g}$ ,  $2B_{1g}$ ,  $2B_{2g}$ ,  $E_g$ ) active. In aqueous solutions and complexes of cyanide, the  $\nu(\text{CN})$  stretching frequency can be identified easily by FT-IR and Raman spectroscopy since it gives a strong and sharp peak in the region of (2200-2000  $\text{cm}^{-1}$ ). The  $\nu(\text{CN})$  stretching frequency of free cyanide  $\text{CN}^-$  is found at 2080  $\text{cm}^{-1}$  in the FT-IR spectrum but if the cyanide is coordinated with a metal,  $\nu(\text{CN})$  stretching frequency of cyanide shifts to higher values (2135  $\text{cm}^{-1}$  for  $\text{K}_2[\text{Pd}(\text{CN})_4]\cdot\text{H}_2\text{O}$ ). If there are both Pd-C≡N-Cu type bridge and Pd-C≡N type terminal structures in the structures of complexes, the splitting of the  $\nu(\text{CN})$  stretching bands in the FT-IR spectrum of the complexes can be observed [7, 22]. In the literature, the  $\nu(\text{CN})$  stretching frequency of terminal cyano groups in the complexes is more close to that of  $\text{K}_2[\text{Pd}(\text{CN})_4]\cdot\text{H}_2\text{O}$  but the  $\nu(\text{CN})$  stretching frequencies of bridging cyano groups are higher according to the related terminal groups of the cyano groups [3, 5, 24]. In the FT-IR spectrum of the cyano complexes, the  $\nu(\text{CN})$  stretching vibration frequency was observed at 2153  $\text{cm}^{-1}$  (for Cu-Pd-dmtu), and 2153, 2109 and 2071  $\text{cm}^{-1}$  (for Cu-Pd-detu). According to this, the  $\nu(\text{CN})$  stretching band in the complex Cu-Pd-detu was split and was appeared as three separate peaks. The high frequency peak belongs to the bridge cyano ligands (Pd-C≡N-Cu type) and the low frequency peaks belong to the terminal cyano ligands (Pd-C≡N type). In the FT-IR spectrum of the complex Cu-Pd-dmtu, it was observed that the  $\nu(\text{CN})$  stretching band was not split and that only bridge cyano ligands (Pd-C≡N-Cu type) were present in the structure of the complex. The  $\nu(\text{CN})$  stretching frequencies of bridge cyano ligands in FT-IR spectrum of the complexes are higher 18  $\text{cm}^{-1}$  than in  $\text{K}_2[\text{Pd}(\text{CN})_4]\cdot\text{H}_2\text{O}$  salt. This shift is thought to be caused by the mechanical coupling between the internal vibration modes of  $[\text{Pd}(\text{CN})_4]$  group with M-NC

vibrations [4, 25].  $[\text{Pd}(\text{CN})_4]^{2-}$  ion is bound to the metal atoms (Cu(II)) from the nitrogen ends and forms  $[\text{Cu-Pd}(\text{CN})_4]_{\infty}$  type polymeric layers. Here, the dependence to the metal of the  $\nu(\text{CN})$  stretching vibration frequencies can also reveal the intensity of the metal with N bond. Therefore, the stronger bond creates the higher vibration frequency and the  $\nu(\text{CN})$  stretching vibration frequency increases depending on the bond strength. The  $A_{1g}$  and  $B_{1g}$  symmetry modes at  $2169$  and  $2159\text{ cm}^{-1}$  in the Raman spectrum of  $\text{K}_2[\text{Pd}(\text{CN})_4]\cdot\text{H}_2\text{O}$  were seen, respectively and these modes in the complexes were observed at  $2191$  and  $2172\text{ cm}^{-1}$  (for Cu-Pd-dmtu), and  $2153\text{ cm}^{-1}$  (for Cu-Pd-detu). In addition to  $\nu(\text{CN})$  band,  $\nu(\text{PdC})$ , and  $\delta(\text{PdCN})$  bands appear in the low frequency region in FT-IR and Raman spectra of the complexes. These bands appear in the regions  $550\text{--}420\text{ cm}^{-1}$  in spectra of the complexes. In particular, in-plane bending vibration frequencies  $[\delta(\text{PdCN})]$  shift to a higher frequency by supporting the  $\nu(\text{CN})$  stretching vibration frequencies. The structures of the complexes according to the spectroscopic results are shown in Figures 4 and 5.

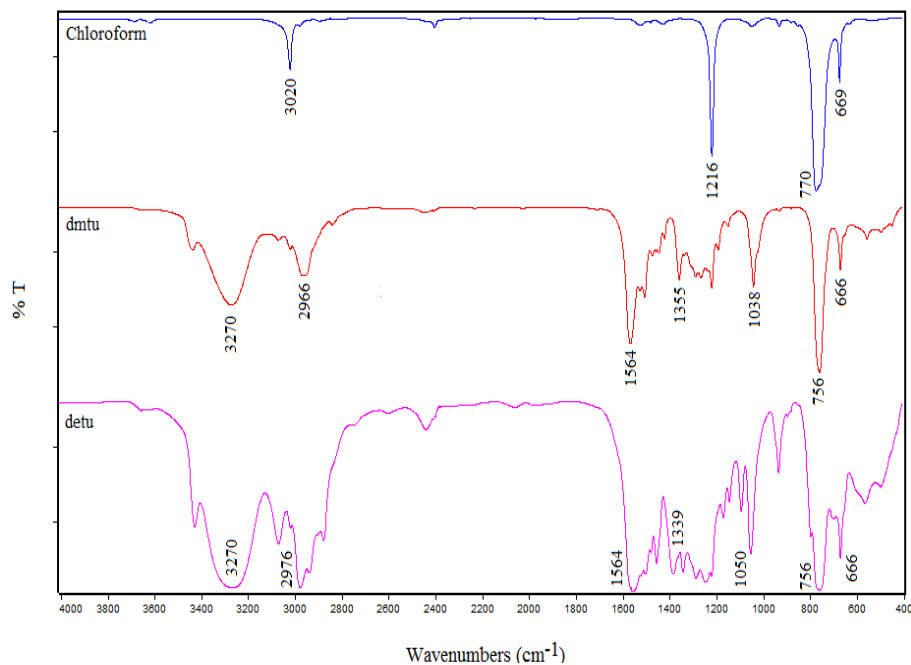


Figure 1. The infrared spectrum and characteristic peaks of the dmtu, detu and chloroform molecule.

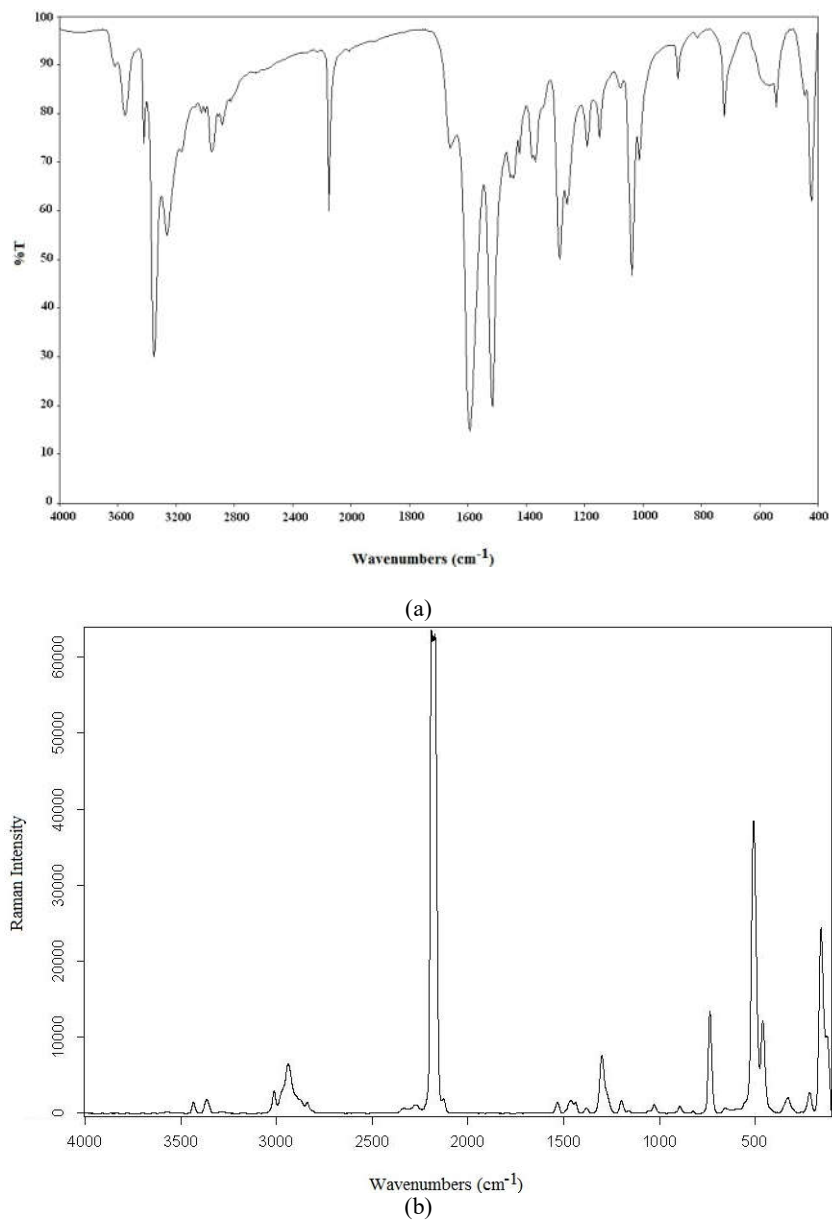
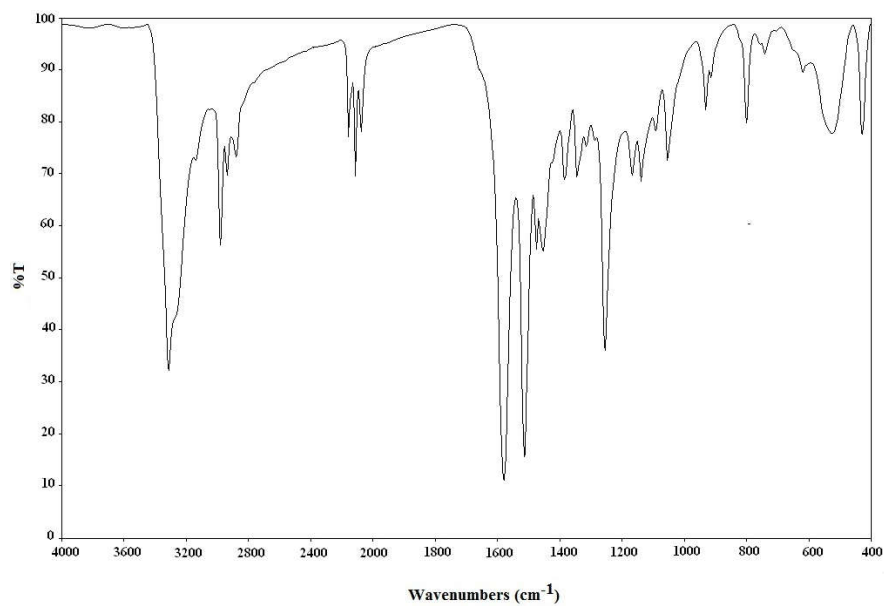
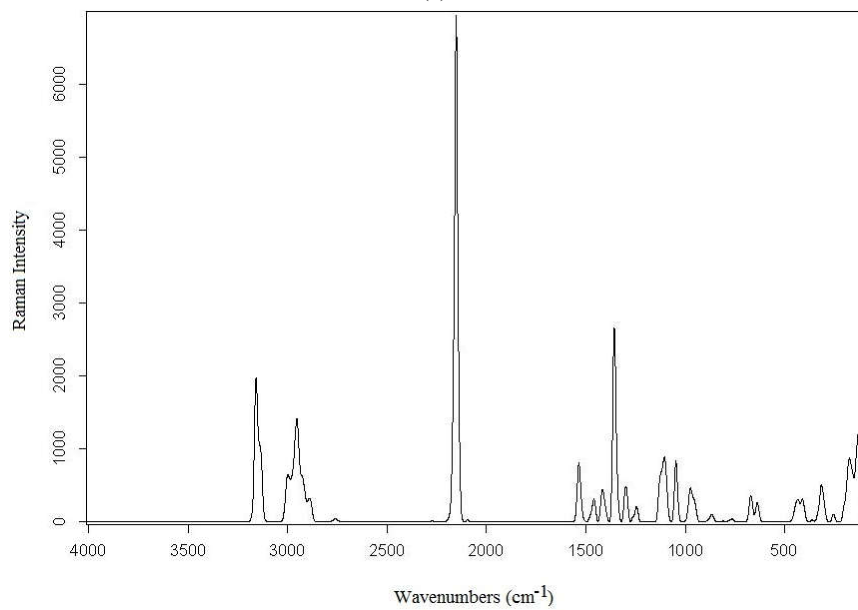


Figure 2. The infrared (a) and Raman (b) spectrum of Cu-Pd-dmtu



(a)



(b)

Figure 3. The infrared (a) and Raman (b) spectrum of Cu-Pd-detu.

Table 1. The vibrational wavenumbers of ligands in the complexes (cm<sup>-1</sup>).

Assignments <sup>a</sup>	Dmtu (CHCl <sub>3</sub> )	Detu (CHCl <sub>3</sub> )	Cu-Pd-dmtu		Cu-Pd-detu	
	FT-IR	FT-IR	FT-IR	R	FT-IR	R
v(NH) free, trans	3435 w	3427 w	3425 w	3433 w	3311 vs	-
v(NH) bonded, trans	3270 vs	3270 vs	3356 vs, 3262 m	3364 w	3135 w	3159 m
v(CH <sub>3</sub> ) <sup>b</sup>	3070 w	3069 m	3076 m	-	-	-
v(CH <sub>3</sub> ) <sup>b</sup>	3019 w	3018 w	3028 m	3012 vw	-	3000 sh
v(CH <sub>3</sub> ) <sup>b</sup>	2966 s	2976 s	2955 m	2938 w	2978 m	2954 w
v <sub>as</sub> (CH <sub>2</sub> ) <sup>c</sup>	-	2937 w	-	-	2933 m	2926 sh
v <sub>s</sub> (CH <sub>2</sub> ) <sup>c</sup>	-	2876 w	-	-	2875 w	2891 vw
(NCH <sub>3</sub> )	2840 w	-	2886 m	2839 vw	-	-
70%v <sub>a</sub> (CN)+30% δ <sub>a</sub> (NH)	1564 s	1564 vs	1593 vs	-	1578 vs	-
79%δ <sub>s</sub> (NH)+10%v(CS)+10%δ(NCN)	1504 m	1504 vs	1516 vs	1533 vw	1511 vs	1535 w
δ <sub>a</sub> (CH <sub>3</sub> )	1471 w	1476 w	1455 m	1464 vw	1473 w	1459 w
δ(CH <sub>2</sub> ) <sup>c</sup>	-	1442 w	-	-	1451 w	-
76%δ <sub>a</sub> (NH)+24%v <sub>a</sub> (CN) or 62%v <sub>s</sub> (CN)+20%δ <sub>s</sub> (NH)+ 18% v(CS)	1419 w	1454 m	1443 m	1439 vw	1423 sh	1417 w
δ <sub>s</sub> (CH <sub>3</sub> )	1355 m	1339 s	1379 m	1382 vw	1382 m	1357 m
2x667 or v(CS) + δ(NCS)	1286 m	1284 m	1286 m	1301 w	1313 vw	1300 w
δ(NH)(47) <sup>b</sup> , v(CN)(21) <sup>b</sup> , δ(NCN)(11) <sup>b</sup>	1263 w	1242 w	1261 w	-	1253 s	1246 vw
v(NC)(58) <sup>b</sup> , δ(NH)(13) <sup>b</sup>	1189 w	1168 w	1191 w	1199 w	1165 w	-
v(NC)(44) <sup>b</sup> , r(CH <sub>3</sub> )(16) <sup>b</sup>	1148 w	1140 w	1149 w	1162 vw	1137 w	1124 sh
(CH <sub>3</sub> ) rock or 2x δ(NCS)	-	1090 m	-	-	1090 w	1105 w
79%v <sub>s</sub> (C'N)+21% δ(NCN)	1038 m	1050 vs	1039 s	1027 vw	1052 w	1048 w
91%v <sub>a</sub> (C'N)+9% δ <sub>a</sub> (CNC')	878 vw	878 w	881 w	894 vw	929 w	866 vw
83%v(CS)+10%v <sub>s</sub> (CN)+ 7%v <sub>s</sub> (C'N)	756 vs	756 vs	722 w	736 w	798 m	764 vw
(NH) out-of-plane bending	-	696 vw	-	-	739 w	-
53%δ <sub>a</sub> (CNC')+35%δ(NCS)+ 11%v <sub>a</sub> (C'N)	666 m	666 vs	-	657 w	618 w	671 w
δ(NCS)	649 sh	594 sh	544 w	508 s	592 sh	638 w
v(OH) <sub>as</sub>	3700-3200	-	3628 w	-	3400 sh	-
v(OH) <sub>s</sub>	3700-3200	-	3553 w	-	-	-
δ(HOH)	1700-1600	-	1663 w	-	1654 sh	-

Abbreviations used; s strong, m medium, w weak, sh shoulder, v very, v stretching, δ bending and r rocking.

<sup>a</sup>Taken from Ref. [16]. <sup>b</sup>Taken from Ref. [17]. <sup>c</sup>Taken from Ref. [18].

Table 2. The wavenumbers of the [Pd(CN)<sub>4</sub>]<sup>2-</sup> vibrations in the complexes (cm<sup>-1</sup>).

Assignments [23]	K <sub>2</sub> [Pd(CN) <sub>4</sub> ]·H <sub>2</sub> O	Cu-Pd-dmtu	Cu-Pd-detu
A <sub>1g</sub> , v(C≡N)	(2169) vs	(2191) vs	-
B <sub>1g</sub> , v(C≡N)	(2159) s	(2172) vs	(2153) vs
E <sub>u</sub> , v(C≡N)	2135 vs	2153 s	2153 m, 2109 s, 2071 m
v( <sup>13</sup> CN)	2097 w	-	-
E <sub>u</sub> , v(Pd-C)	486 w	544 w	524 m
A <sub>1g</sub> , v(Pd-C)	(436) w	-	(434) w
E <sub>u</sub> , δ(Pd-CN)	400 m	422 m	428 m

Abbreviations used; s strong, m medium, w weak, sh shoulder, v very, v stretching, δ bending. \*Raman spectra are given in parenthesis.



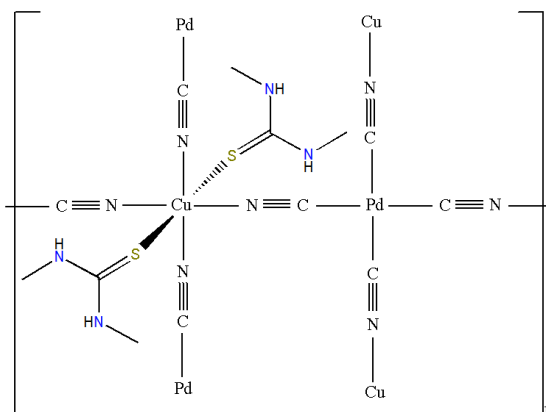


Figure 4. Representation of molecular structures of Cu-Pd-dmtu (Uncoordinated water molecules are not shown in the figure).

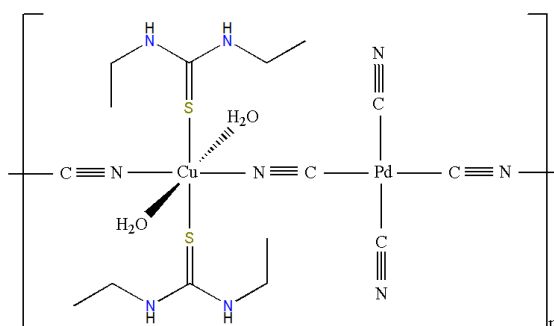


Figure 5. Representation of molecular structures of Cu-Pd-detu (Uncoordinated water molecules are not shown in the figure).

#### Thermal study

Thermal degradation behaviors of the complexes were determined in static air atmosphere between 30 and 1000 °C. The TG, DTG and DTA graphics of the complexes are given in Figures 6 and 7. As seen from the thermal analysis curves of the complexes, the thermal degradation of the complexes takes place in two stages and these degradation curves support the unit formulas of the complexes. Complex Cu-Pd-dmtu and complex Cu-Pd-detu are stable up to 195 and 179 °C, respectively. In the first step, the dmtu and water molecules between 195 and 363 °C for Cu-Pd-dmtu [found (calcd.) (%) = 41.12 (45.23)] and, the detu and water molecules between 179 and 348 °C for Cu-Pd-detu [found (calcd.) (%) = 53.49 (55.11)] were released from the structure of the complexes. A mass increase was observed around 365 °C in the TG curve of Cu-Pd-dmtu and around 330 °C in the TG curve of Cu-Pd-detu. The reason for this mass increase is that the complex in the static air atmosphere performs surface oxidation reactions. Therefore, cyano groups in these reactions undergo oxidation. The mass increase observed in the TG curve of both complexes was followed by the decomposition of the reaction products resulting from the oxidation of the complexes. This process is accompanied by an

exothermic effect as a result of the separation of cyano groups from the structure of the complexes (DTA<sub>max</sub> at 369 and 429 °C for Cu–Pd–dmu and at 316, 345 and 407 °C for Cu–Pd–detu). In the second step, three of four cyano groups in the temperature region of 363–1000 °C for Cu–Pd–dmu [found (calcd.) (%) = 14.45 (15.59)] and four cyano groups in the temperature region of 348–749 °C for Cu–Pd–detu [found (calcd.) (%) = 19.59 (17.04)] were degraded. The final thermal decomposition products were found to be a mixture of CuCN and PdO for Cu–Pd–dmu [found (calcd.) (%) = 44.43 (42.36)] and metal oxides (CuO and PdO) for Cu–Pd–detu [found (calcd.) (%) = 33.90 (33.07)].

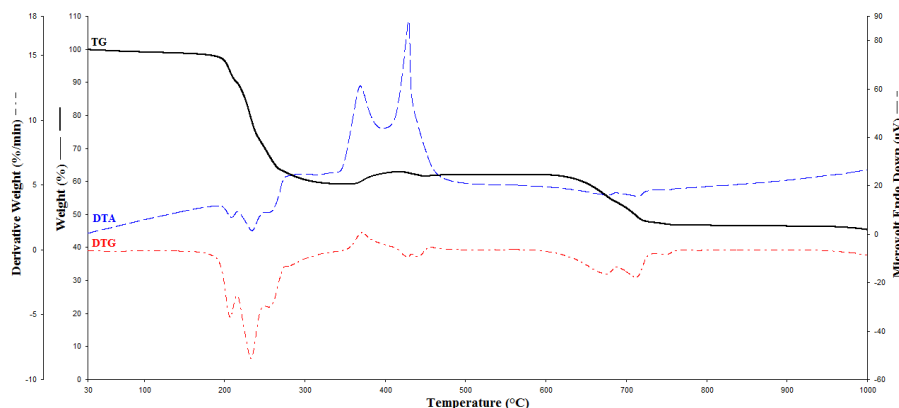


Figure 6. The TG, DTG and DTA curves of Cu–Pd–dmu.

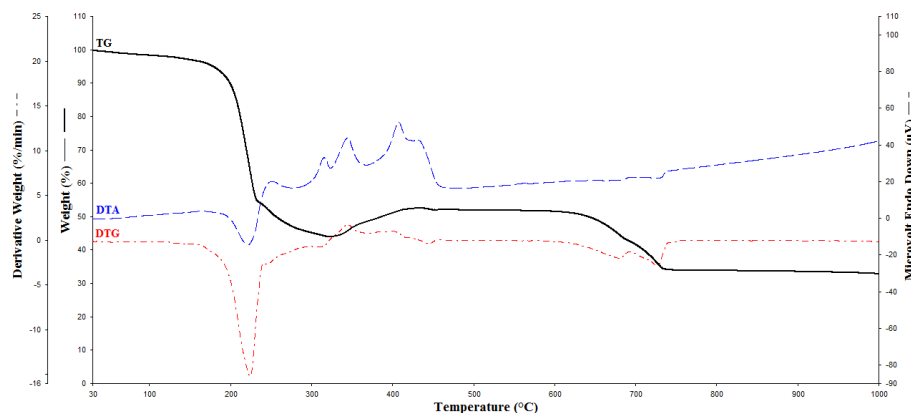


Figure 7. The TG, DTG and DTA curves of Cu–Pd–detu.

## CONCLUSIONS

The complexes obtained in this study are examples of cyano-bridged metal complexes. The structure and properties of these complexes have been elucidated using spectroscopic, thermal and elemental analysis techniques. As a result of the spectroscopic examination of the complexes, the cyano ligand have acted as bridge in complex Cu–Pd–dmu while acts as

terminal and bridge in complex Cu–Pd–detu. In complex Cu–Pd–dmu, the dmu ligand is coordinated to the copper(II) ions of the adjacent layers of  $[\text{Cu–Pd}(\text{CN})_4]_{\infty}$  and became an example of Hofmann type complexes. In complex Cu–Pd–detu,  $[\text{Pd}(\text{CN})_4]^{2-}$  anions and  $[\text{Cu}(\text{H}_2\text{O})_2(\text{detu})_2]^{2+}$  cations bind via bridging cyano ligands and form the one dimensional structure of the complex. Furthermore, the dmu or detu ligands are bonded to the copper metal atoms via a sulfur atom as monodentate. In the complexes, the palladium atom has square plane geometry while the copper(II) atom has octahedral geometry. In addition, thermal and elemental analysis results supported the correct structure of the complexes.

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