



One-dimensional cyano-bridged heterometallic (Cu/Ni and Cu/Pd) complexes with 1-ethylimidazole

Fulya Çetinkaya^a, Güneş Süheyla Kürkçüoğlu^{a,*}, Okan Zafer Yeşil^b, Tuncer Hökelek^c, Hakan Dal^d

^a Eskişehir Osmangazi University, Faculty of Arts and Science, Department of Physics, 26480 Eskişehir, Turkey

^b Eskişehir Osmangazi University, Faculty of Arts and Science, Department of Chemistry, 26480 Eskişehir, Turkey

^c Hacettepe University, Faculty of Engineering, Department of Physics, 06800 Beytepe Ankara, Turkey

^d Anadolu University, Faculty of Science, Department of Chemistry, 26470 Eskişehir, Turkey

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ABSTRACT

Two new cyano-bridged heteronuclear polymeric complexes, $[\text{Cu}(\text{etim})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{etim})_4\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**2**) (etim = 1-ethylimidazole) were synthesized and characterized by FT-IR and Raman spectroscopies, thermal (TG, DTG and DTA) and elemental analyses and single crystal X-ray diffraction techniques. They crystallize in the triclinic system and $P\bar{1}$ space group. The two compounds are isostructural, and their crystal structures are formed by quasi-linear chains exhibiting $[-\text{Cu}(\text{etim})_4-\mu\text{-NC}-\text{M}(\text{CN})_2-\mu\text{-CN}-]_n$ composition. The Ni(II) or Pd(II) ions is four coordinate with four cyanide-carbon atoms in a square planar geometry and the Cu(II) ion exhibits a distorted octahedral coordination by four etim ligands and two bridging cyano groups.

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1. Introduction

Polymeric structure in the form of cyano-bridged complexes of the last few years has been investigated in the studies [1]. The cyano group as a ligand can be bound by various modes. There are two binding modes which are generally the most common and often occur in 1D cyano complexes; the cyano group can act as a terminal ligand with the carbon donor atom or the cyano group bonded through both carbon and nitrogen donor atoms acting as a μ_2 -bridging ligand [2]. The C-end of the cyano group as a ligand produces a strong field effect, while the N-end of the cyano group behaves as a medium ligand with ligand field strength lower than ammonia [2]. This property of the cyano group has been explored in the construction of many oligomeric and polymeric structures with different dimensionalities [3–10].

Cyano complexes possessing various degrees of dimensionality and containing paramagnetic central atoms have often been the subject of magnetic studies. In this case, the cyano group or cyano complex anion in addition to its structural function also exhibits an important electronic function: it forms an exchange path mediating the interaction among spins localized on paramagnetic centers. Moreover, if the cyano complex anion has a non-zero magnetic moment, it also contributes to the magnetic properties of the compound studied.

In previous studies, the complexes of imidazole and its methyl derivatives with the metal(II) ion were described in several [11–17]. We have recently reported the $\{[\text{Cu}4(5)\text{-Meim}]_4[\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}\}_n$ [3], $[\text{Cd}(\text{mim})_2\text{Ni}(\mu\text{-CN})_4]_n$, $[\text{Cd}(\text{im})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]_n$ [18], $\text{trans-}[\text{M}(\text{N-Meim})_2\text{Ni}(\mu\text{-CN})_4]_n$ (M=Cu(II), Zn(II) or Cd(II)) [4] and $[\text{Cu}(\text{N-Meim})_4\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$, $[\text{Zn}(\text{N-Meim})_3\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$, $[\text{Cd}(\text{N-Meim})_2\text{Pd}(\mu\text{-CN})_4]_n$ [19] tetracyanonickelate(II) or tetracyanopalladate(II) complexes with a 4(5)-methylimidazole, imidazole, 2-methylimidazole and N-methylimidazole, respectively. In this study, we have prepared the cyano-bridged heteronuclear polymeric complexes of the form $\{[\text{Cu}(\text{etim})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**) and $[\text{Cu}(\text{etim})_4\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**2**) and characterized by spectral (FT-IR and Raman), thermal and elemental analyses. The crystal structures of the complexes **1** and **2** have also been determined by X-ray single crystal diffraction.

2. Experimental

2.1. Material and Instrumentation

Copper(II) chloride dihydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, 98%), nickel(II) chloride hexahydrate ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, 98%), palladium(II) chloride (PdCl_2 , 99%), 1-ethylimidazole ($\text{C}_5\text{H}_8\text{N}_2$, 95%) and potassium cyanide (KCN, 96%) were purchased from commercial sources and used without further purification. The FT-IR spectra of the complexes were recorded as KBr pellets in the range of $4000\text{--}400\text{ cm}^{-1}$ (2 cm^{-1} resolution) on a Perkin Elmer 100 FT-IR spectrometer which

* Corresponding author. Tel.: +90 222 2393750; fax: +90 222 2393578.

E-mail address: gkurkcuo@ogu.edu.tr (G.S. Kürkçüoğlu).

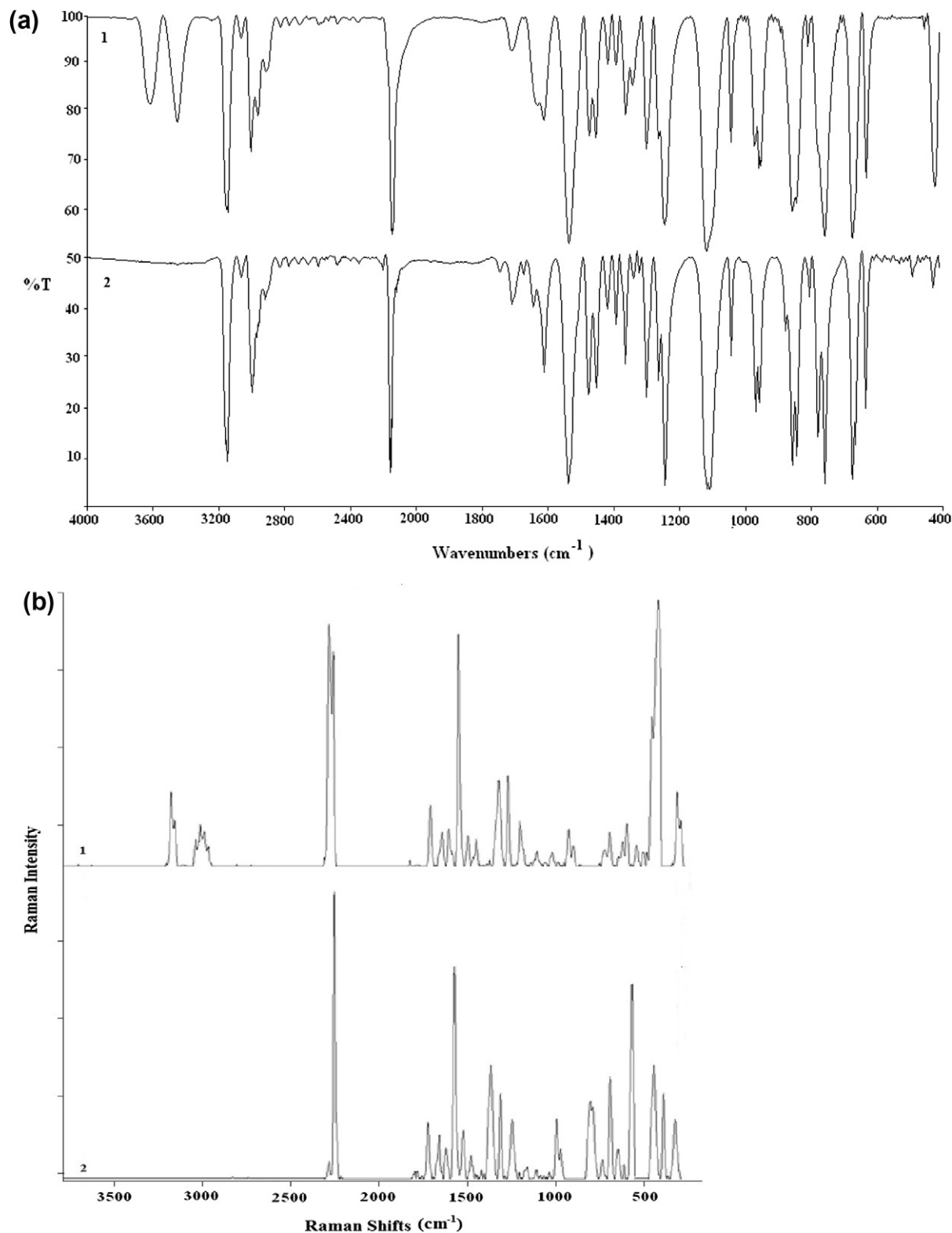


Fig. 1. (a) The FT-IR and (b) Raman spectra of complexes.

was calibrated using polystyrene and CO₂ bands. The Raman spectra of the complexes were recorded in the range of 4000–250 cm⁻¹ on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm. Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 K min⁻¹ in the temperature range of 30–1000 °C using platinum crucibles. Elemental analyses

were carried out on LECO, CHNS-932 analyzer for C, H and N at the Middle East Technical University Central Laboratory.

2.2. Crystallographic analyses

Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using MoK α radiation

Table 1
The vibration wavenumbers (cm⁻¹) of 1-ethylimidazole in the complexes.

Assignments [23]	Etim (liquid)	1		2	
		FT-IR	Raman	FT-IR	Raman
$\nu_s(\text{CH})$ of CH=CH	3134 sh	3148 m	3159 m	3147 m	3159 vw
$\nu_{as}(\text{CH})$ of CH=CH	3107 m	3121 m	–	3122 m	–
$\nu_{as}(\text{CH}_3)$, $\nu_{as}(\text{CH}_2)$	2981 s	2987 m	3000 w	2985 m	2999 vw
$\nu_s(\text{CH}_3)$, $\nu_s(\text{CH}_2)$	2940 m	2943 m	2954 m	2942 m	2955 vw
$\nu_s(\text{CH}_2)$	2889 w	2882 m	2890 w	2881 m	–
$\nu(\text{C}=\text{C})$ $\nu(\text{C}=\text{N})$	1676 w	1682 w	–	1684 w	–
$\nu(\text{R})$, combination	1596 w	1597 m	1535 w	1597 m	1536 m
	1510 vs	1514 s	–	1515 s	–
$\delta_{as}(\text{CH}_2)_{scis}$	1465 m	1469 m	1460 w	1468 m	1460 w
$\delta_{as}(\text{CH}_3)_{scis}$	1448 m	1446 m	1417 w	1445 m	1418 w
$\nu(\text{R})$, combination	1394 m	1396 m	–	1397 m	–
$\delta(\text{CH})$, $\nu(\text{R})$	1385 m	1379 m	–	1380 m	–
	1355 m	–	1357 m	1355 m	1356 s
$\nu(\text{R})$, $\delta(\text{CH}_2)_{twist}$	1287 m	1287 w	1299 w	1292 m	1299 w
Combination	1250 w	1259 m	–	1255	–
	1228 vs	1242 s	1246 w	1241 s	1243 w
$\rho(\text{CH}_3)$, $\rho(\text{CH}_2)$, $\nu(\text{R})$ combination	1194 sh	1191 w	–	1191	–
	1110 s	1122 s	1105 w	1120 s	1109 w
	1078 vs	1088 s	–	1090 s	–
$\delta(\text{R})$	1034 m	1037 m	1048 m	1036 m	1046 m
$\gamma(\text{CH})$	958 m	969 m	975 w	968 w	972 w
	908 s	908 w	–	908 vw	–
$\gamma(\text{CH})$, $\nu(\text{C}-\text{C})$	875 sh	851 sh	866 vw	856 sh	867 vw
	819 s	833 s	–	833 s	–
	742 s	748 s	–	749 s	–
$\nu(\text{CH}_2-\text{N})$, $\nu(\text{C}-\text{CH}_2)$	667 vs	657 s	671 w	657 s	667 w
$\delta(\text{C}-\text{H})$	624 m	617 s	637 w	618 m	640 w
$\delta(\text{CH}_2)$, $\nu(\text{C}-\text{C})$	515 vw	510 vw	–	510 vw	–

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

($\lambda = 0.71073 \text{ \AA}$) at $T = 100 \text{ K}$. Absorption correction by multi-scan [20] was applied. Structure was solved by direct methods [21] and refined by full-matrix least squares against F^2 using all data [21].

2.3. Syntheses of the complexes

$\text{K}_2[\text{M}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ni}(\text{II})$ or $\text{Pd}(\text{II})$) was prepared by mixing stoichiometric amounts of palladium(II) chloride (1 mmol, $\text{PdCl}_2 = 0.177 \text{ g}$) or nickel(II) chloride hexahydrate (1 mmol, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} = 0.237 \text{ g}$) in water (10 mL) with potassium cyanide (4 mmol, $\text{KCN} = 0.260 \text{ g}$) in water (10 mL) solution.

$\{[\text{Cu}(\text{etim})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**) and $[\text{Cu}(\text{etim})_4\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**2**) complexes were prepared by mixing together the water solution of 1 mmol (0.259 g) $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ or 1 mmol (0.306 g) $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot \text{H}_2\text{O}$. To this $\text{K}_2[\text{M}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ni}(\text{II})$ or $\text{Pd}(\text{II})$) solution, 1 mmol copper chloride dihydrate

Table 2
The wavenumbers (cm⁻¹) of the $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}(\text{II})$ or $\text{Pd}(\text{II})$) vibrations in the complexes.

Assignments [24,25]	$\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$	$\text{K}_2[\text{Pd}(\text{CN})_4] \cdot \text{H}_2\text{O}$	1	2
A_{1g} , $\nu(\text{C} \equiv \text{N})$	(2160) vs	(2169) vs	(2158) vs	(2189) s
B_{1g} , $\nu(\text{C} \equiv \text{N})$	(2137) m	(2159) s	(2130) vs	(2167) vs
E_{2g} , $\nu(\text{C} \equiv \text{N})$	2122 vs	2135 vs	2128 vs, 2118 vs	2140 vs, 2130 vs
Hot band	–	2096 w	–	2100 w
E_{2g} , $\nu(\text{M}-\text{C})$	540 w	486 w	546 vw	497 w
A_{2u} , $\pi(\text{M}-\text{CN})$	443 w	–	447 vw	–
A_{1g} , $\nu(\text{M}-\text{C})$	–	(436) m	–	(440) m
E_{2g} , $\delta(\text{M}-\text{CN})$	417 s	393 m	415 s	419 w

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

Table 3
Crystal data and structure refinement parameters for complexes.

Complexes	1	2
Empirical formula	$\text{C}_{24}\text{H}_{34}\text{N}_{12}\text{OCuNi}$	$\text{C}_{24}\text{H}_{32}\text{N}_{12}\text{CuPd}$
Formula weight (gmol ⁻¹)	628.87	658.57
T (K)	100(2)	–
λ (Å)	0.71073 MoK α	–
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.6717(2)	8.5606(2)
b (Å)	10.3082(2)	8.9656(2)
c (Å)	17.7374(4)	10.5456(3)
α (°)	79.638(2)	112.878(3)
β (°)	79.641(2)	101.431(3)
γ (°)	68.700(3)	96.338(2)
V (Å ³)	1441.76(5)	715.00(4)
Z	2	1
Absorption coefficient (mm ⁻¹)	1.431	1.409
D_{calc} (Mg m ⁻³)	1.449	1.529
θ range for data collection (°)	2.31–28.42	2.17–28.43
Measured reflections	26221	12737
Independent reflections	7226	3578
Reflections with $ I > 2\sigma(I)$	4270	3338
Absorption correction	multi-scan [20]	–
Refinement method	full-matrix least-squares on F^2 [21]	–
R_{int}	0.0409	0.0193
Final R indices $ I > 2\sigma(I)$	0.0415	0.0227
Final wR indices (all data)	0.1065	0.0661
Goodness-of-fit (GOF) on F^2	1.031	1.127
$\Delta\rho_{max}$ (e Å ⁻³)	0.732	1.034
$\Delta\rho_{min}$ (e Å ⁻³)	–0.484	–0.840

($\text{CuCl}_2 \cdot 2\text{H}_2\text{O} = 0.170 \text{ g}$) dissolved in water (10 mL) were added with continuous stirring approximately for 4 h at 50 °C in a temperature-controlled bath. The compounds obtained were filtered and washed with water and dried in air. To this 1 mmol of $\text{Cu}[\text{M}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (0.244 g for Ni(II) or 0.292 g for Pd(II)) aqua solution, 4 mmol of etim (0.385 g) dissolved in ethyl alcohol (10 mL) was added with continuous stirring approximately for 3 h at 50 °C in a temperature-controlled bath. The blue crystals were filtered and then cooled to room temperature. The complexes obtained were performed elemental analyses. Elemental analyses are in good agreement with the calculated values. *Anal. Calc.* for $\text{C}_{24}\text{H}_{34}\text{N}_{12}\text{CuNiO}$ (**1**) (628.87 gmol⁻¹): C, 45.83; H, 5.46; N, 26.73. *Found:* C, 45.94; H, 4.97; N, 27.05%. *Anal. Calc.* for $\text{C}_{24}\text{H}_{32}\text{N}_{12}\text{CuPd}$ (**2**) (658.57 gmol⁻¹): C, 43.77; H, 4.90; N, 25.53. *Found:* C, 43.62; H, 4.53; N, 25.65%.

3. Results and discussion

3.1. Vibrational spectra

The FT-IR and Raman spectra of complexes **1** and **2** are illustrated in Fig. 1. The spectra of complexes are found to be very similar. The FT-IR spectrum of complex **1** contains more absorption bands originating from $\nu(\text{OH})$ and $\delta(\text{OH})$ vibrations than those of

Table 4
Selected geometric parameters (Å, °) for **1** and **2**.

Bond lengths			
1		2	
Cu1–N1	2.033(2)	Cu1–N1	2.4345(16)
Cu1–N3	2.038(2)	Cu1–N3	2.0235(15)
Cu1–N5	2.370(3)	Cu1–N5	2.0280(15)
Cu2–N7	2.043(2)	Pd1–C1	1.990(18)
Cu2–N9	2.016(2)	Pd1–C2	2.0004(19)
Cu2–N11	2.500(3)		
Ni1–C11	1.858(3)		
Ni1–C12	1.858(4)		
Ni2–C23	1.867(3)		
Ni2–C24	1.861(3)		
Bond angles			
1		2	
N1–Cu1–N3 ⁱ	88.51(9)	N3–Cu1–N1	90.03(6)
N1–Cu1–N3	91.49(9)	N3–Cu1–N1 ⁱⁱ	89.97(6)
N1–Cu1–N5	91.32(9)	N3–Cu1–N5	92.78(6)
N1–Cu1–N5 ⁱ	88.68(9)	N3–Cu1–N5 ⁱⁱ	87.22(6)
N3–Cu1–N5 ⁱ	89.98(9)	N5–Cu1–N1	90.00(6)
N3–Cu1–N5	90.02(9)	C1–Pd1–C2 ⁱ	87.77(7)
N9–Cu2–N7	89.98(9)	C1–Pd1–C2	92.23(7)
N9–Cu2–N7 ⁱⁱⁱ	90.02(9)		
C12–Ni1–C11	91.57(13)		
C12–Ni1–C11 ⁱⁱ	88.43(13)		
C24–Ni2–C23	89.33(12)		
C24–Ni2–C23 ^{iv}	90.67(12)		

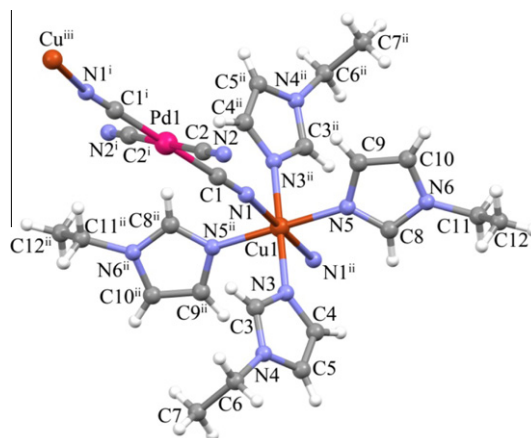
Symmetry codes: (i) 1 – x, –y, –z, (ii) 1 – x, –1 – y, –z, (iii) –x, –y, 1 – z, (iv) –x, 1 – y, 1 – z (for **1**), (i) –x, –y, –z, (ii) –x, 1 – y, 1 – z (for **2**).

Table 5
Hydrogen-bond geometry for complex **1** (Å, °)

D–H...A	D–H	H...A	D...A	D–H...A
O1–H11...N12 ⁱ	0.91(5)	2.41(5)	3.294(6)	164(5)
O1–H12...N6	0.93(6)	1.87(6)	2.782(6)	169(5)
C13–H13...O1 ⁱⁱ	0.93	2.41	3.242(5)	150

Symmetry codes: (i) x, y – 1, z, (ii) x, y + 1, z.

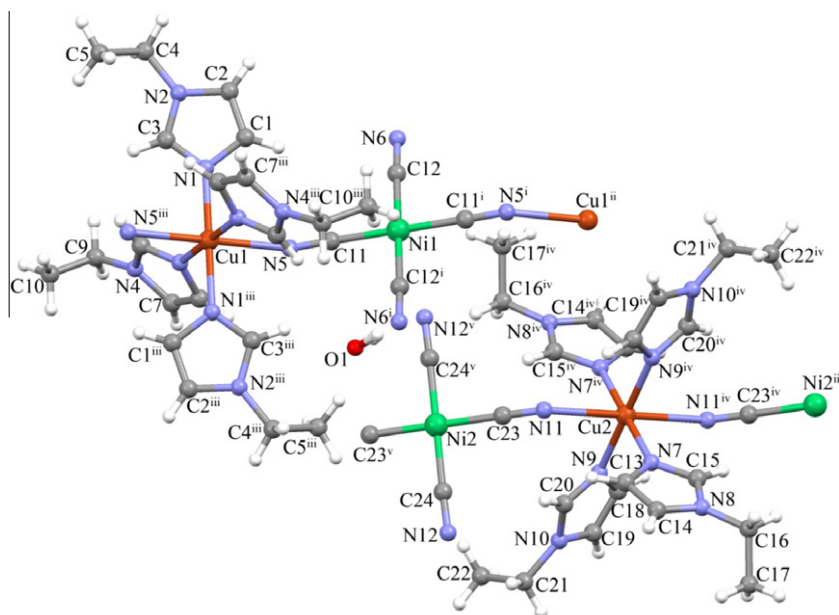
complex **2**. In complex **1**, the absorption band at about 3580 cm⁻¹ may be attributed to the symmetric (O–H) stretching mode of crystal water molecules. Single crystal X-ray data support the

**Fig. 3.** The molecular structure of complex **2**. Symmetry codes: (i) –x, –y, –z, (ii) –x, 1 – y, 1 – z, (iii) x, y – 1, z – 1.

presence of water in the complex. The absorption bands are observed in the region from 3432 to 3590 cm⁻¹ due to the asymmetric and symmetric ν(OH) stretching vibrations of the aqua molecules in the complex **1**. The shift to lower frequencies of these stretching modes and the shift to higher frequencies of the accompanying OH bending modes (1620–1650 cm⁻¹) may be attributed to hydrogen bonding in the compounds [22].

3.1.1. Ligand vibrations

The tentative assignments of the wavenumbers of the etim molecule observed in the FT-IR and Raman spectra of the complexes are given in Table 1, together with the wavenumbers for free etim [23]. The vibrational spectra of the complexes **1** and **2** are observed in the frequency range of 3100–3000 cm⁻¹ of the imidazole ring C–H stretching frequencies. As can be seen in Table 1, the etim ligand shows infrared bands in the 3000–2700 cm⁻¹ region are assigned to the ν(CH₃) and ν(CH₂) asymmetric and symmetric stretching frequencies. The absorption bands of the ν(CH₃) and ν(CH₂) groups in both complexes are observed in the frequency range of 2987–2760 cm⁻¹, and significantly shifted to lower or higher frequency compared to the

**Fig. 2.** The molecular structure of complex **1**. Symmetry codes: (i) 1 – x, 1 – y, –z, (ii) x, 1 + y, z, (iii) 1 – x, –y, –z, (iv) –x, 1 – y, 1 – z, (v) –x, 1 – y, 1 – z.

free ligand. The next region, 1700–1200 cm^{-1} , is mainly characteristic for asymmetric (1700–1600 cm^{-1}) and symmetric (1400–1300 cm^{-1}) [23] stretching vibrations C=C; C=N of imidazole ring as well as various C–H bond deformations (1460–1400 cm^{-1}); the region 1200–900 cm^{-1} is dominated by stretches of C–C, deformation vibrations of C–H as well as by ring vibrations. It is clear from Table 1 that most of the vibrational modes of ligand in the complexes have been increased in wavenumbers when compared with free ligand. These shifts can be explained as the coupling of the internal modes of the etim molecule with M–N_(etim) vibrations. Analogous shifts on coordination have been observed in the vibrational spectra of the other metal-coordinated imidazole complexes [3,4,18].

3.1.2. $[M(\text{CN})_4]^{2-}$ (M=Ni(II) or Pd(II)) vibrations

The $\nu(\text{CN})$ vibrations are the most important absorption bands for cyano complexes. The cyano groups exhibit strong sharp absorption bands in vibrational spectra between 2200 and 2100 cm^{-1} , due to the stretching vibrations of the cyano group. The assigned wave numbers and modes for $[M(\text{CN})_4]^{2-}$ (M=Ni(II) or Pd(II)) group in complexes are given in Table 2, together with the vibrational wavenumbers of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [24] and $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [25]. The $[M(\text{CN})_4]^{2-}$ (M=Ni(II) or Pd(II)) anion possesses ideally D_{4h} symmetry and, thus, will have 16 fundamental vibrations ($2A_{1g}$, $1A_{2g}$, $2B_{1g}$, $2B_{2g}$, $1E_g$, $2A_{2u}$, $2B_{2u}$, and $4E_u$) [26,27]. Of these, A_{2u} and E_u are infrared active, while A_{1g} , B_{1g} , B_{2g} , and E_g are Raman active. The A_{2g} and B_{2u} vibrations are inactive. No B_{2g} modes were observed. The strong absorptions in the FT-IR spectra of the complexes between 2120 and 2140 cm^{-1} are associated with the cyano stretching vibrations. The A_{1g} and B_{1g} cyano stretching modes in the Raman spectra of the complexes are observed spectra between 2145 and 2180 cm^{-1} . The $\nu(\text{CN})$ vibration bands are observed as strong and sharp bands in the FT-IR and Raman spectra of the complexes. A splitting of the E_u mode is observed for complexes **1** and **2**. In these complexes, two strong bands are observed in the $\nu(\text{CN})$ and $\delta(\text{M}-\text{C}\equiv\text{N})$ regions of the FT-IR spectra due to Jahn–Teller effect [28,29]. These spectroscopic results are also supported by the crystal structure analyses of complexes **1** and **2**. Two strong bands are clearly seen in the FT-IR spectra at 2128 and 2118 cm^{-1} (for **1**) and at 2140 and 2130 cm^{-1} (for **2**). The two Raman fundamentals are assigned to

2130 and 2158 cm^{-1} (for **1**) or 2167 and 2189 cm^{-1} (for **2**) bands. From the FT-IR spectra of the complexes, it is determined that the stretching vibration of cyano has shifted to approximately 2–40 cm^{-1} higher frequency (see Table 2). In-plane bending vibration band, $\delta(\text{M}-\text{CN})$ (M=Ni(II) or Pd(II)) shifts to a higher frequency support the $\nu(\text{CN})$ stretching vibration band. Such frequency shifts have been observed for the other ion pair charge transfer complexes [30,31].

3.2. Structural analyses

Crystal data and structure refinement parameters for the complexes are presented in Table 3. Selected bond lengths and angles for **1** and **2** are collected in Table 4, and the hydrogen bonding geometry for complex **1** is given in Table 5. The molecular structures of **1** and **2** with the atom-numbering schemes are shown in Figs. 2 and 3, respectively. The crystallographic analyses revealed that the complexes, $\{[\text{Cu}(\text{etim})_4\text{Ni}(\mu-\text{CN})_2(\text{CN})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**) and $[\text{Cu}(\text{etim})_4\text{Pd}(\mu-\text{CN})_2(\text{CN})_2]_n$ (**2**), have cyanide-bridged polymeric chain (2,2-TT chain) structures, in which the nickel(II) or the palladium(II) ions are coordinated by the four cyanide ligands [two cyano groups are terminal and two cyano groups (in *cis* fashion) are bridged], and the Cu(II) ions are coordinated by the four symmetry related etim ligands and the two symmetry related bridging trans cyanide ligands. The coordination environments of the Cu(II) ions can be described as distorted octahedral geometry, whereas the Ni(II) or Pd(II) centre has square planar geometry.

The M–C (M=Ni(II) or Pd(II)) coordination bond lengths (Table 4) are in accordance with the corresponding values in $\{[\text{Cu}(4(5)\text{-Meim})_4][\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}\}_n$ [3] $[\text{Cd}(\text{im})_4\text{Ni}(\mu-\text{CN})_2(\text{CN})_2]_n$, $[\text{Cd}(\text{mim})_2\text{Ni}(\mu-\text{CN})_4]_n$ [18] and $[\text{M}(\text{N-Meim})_4\text{Pd}(\mu-\text{CN})_2(\text{CN})_2]_n$ (M=Cu(II), Zn(II) or Cd(II)) [19]. In the complex **1**, probably due to disorder, the C9–C10 bond length [1.397(7) Å] is very short for a C–C single bond. A disordering model was applied, but it was not successful. The N5 atom of cyano group is weakly coordinated to the Cu(II) ion [Cu1–N5 = 2.370 (3) Å] and longer than those of the equatorial Cu–N1/N3 [2.033 (2) and 2.038 (2) Å] bonds. In the complex **2**, the N1 atom of cyano group is weakly coordinated to the Cu(II) ion [Cu1–N1 = 2.434 (16) Å] and longer than those of the equatorial

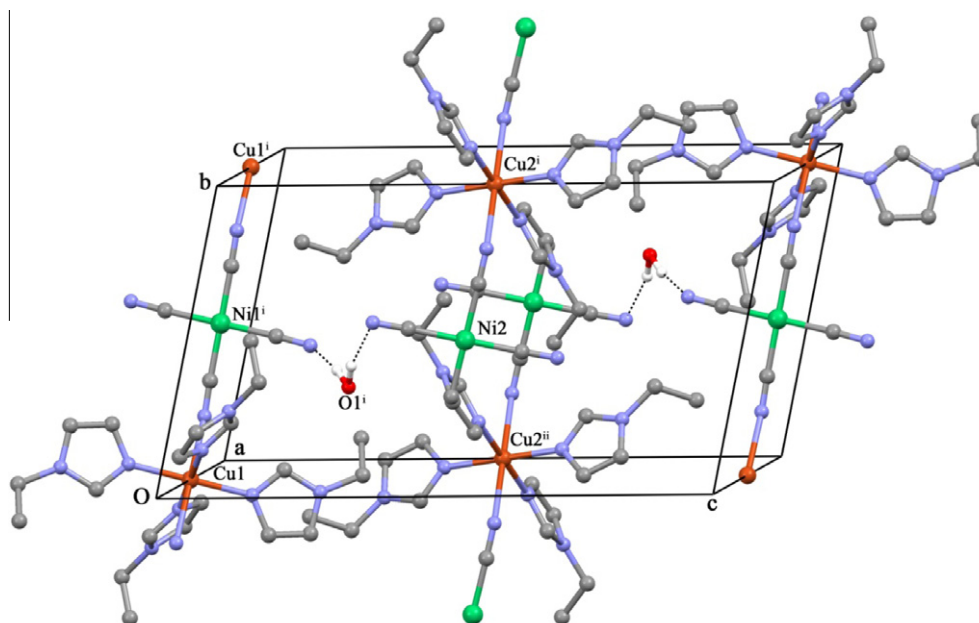


Fig. 4. A view of the crystal packing of complex **1**. Hydrogen bonds are shown as dashed lines. H-atoms not involved in hydrogen bonding have been omitted for clarity ((i) $x, 1+y, z$; (ii) $1+x, y, z$).

Cu–N3/N5 [2.023 (15) and 2.028 (15) Å] bonds due to the Jahn–Teller effect. Such bond lengths have been observed for the other copper(II) complexes [3–10].

The crystal packing of **1** is composed of hydrogen bonding and C–H... π interactions. The adjacent 1D chains are connected to each other by O–H...N hydrogen bonds [O1...N6 = 2.782 (6) and O1...N12ⁱ = 3.294 (6) Å, (i) x, y – 1, z] to form two-dimensional network (Fig. 4). These 2D networks are extended into a 3D supramolecular framework by C–H... π interactions (Table 5 and Fig. 5). These C–H... π interactions were observed between C5–H5A, C14–H14 and imidazole rings (Cg1 and Cg2) (Cg1=N1, C1, C2, N2, C3; Cg2=N9, C18, C19, N10, C20; C5...Cg1 = 3.430 and C14...Cg2 = 3.356 Å) (Fig. 5).

The adjacent 1D chains in **2** are linked to each other by the C–H... π interactions to form 2D network. These C–H... π interactions were observed between C7 and H7A and imidazole rings (Cg1=N5, C8, N6, C10, C9) (Fig. 6). The distance between the C7 atom and centroid of the imidazole ring is 3.657 Å.

3.3. Thermal analyses

Thermal behavior of the complexes was studied by TG, DTG and DTA in the temperature range of 30–1000 °C in the static air atmosphere. Thermal decomposition curves of **1** and **2** are presented in Figs. 7 and 8, respectively. Thermal decomposition of the complexes **1** and **2** proceeds in three and four degradation steps, respectively (Figs. 7 and 8). The thermal decomposition in the temperature range of 35–118 °C is related to one water molecule of the complex **1**. The weight loss associated with this stage, 1.98% which is very close to the calculated value of 2.86%, corresponds to the loss of one water molecule as will be described. The stages of the temperature range of 118–414 °C (for **1**) and 105–210 °C (for **2**) are related to the successive decompositions of the four (for **1**) and two (for **2**) etim ligand, respectively [found (Calc.)% = 59.98 (61.14) (for **1**) and found (Calc.)% = 30.52 (29.19) (for **2**)]. In the following stages, the remaining four cyano groups and one etim ligand decompose between 414 and 504 °C (for **1**) and 210 and

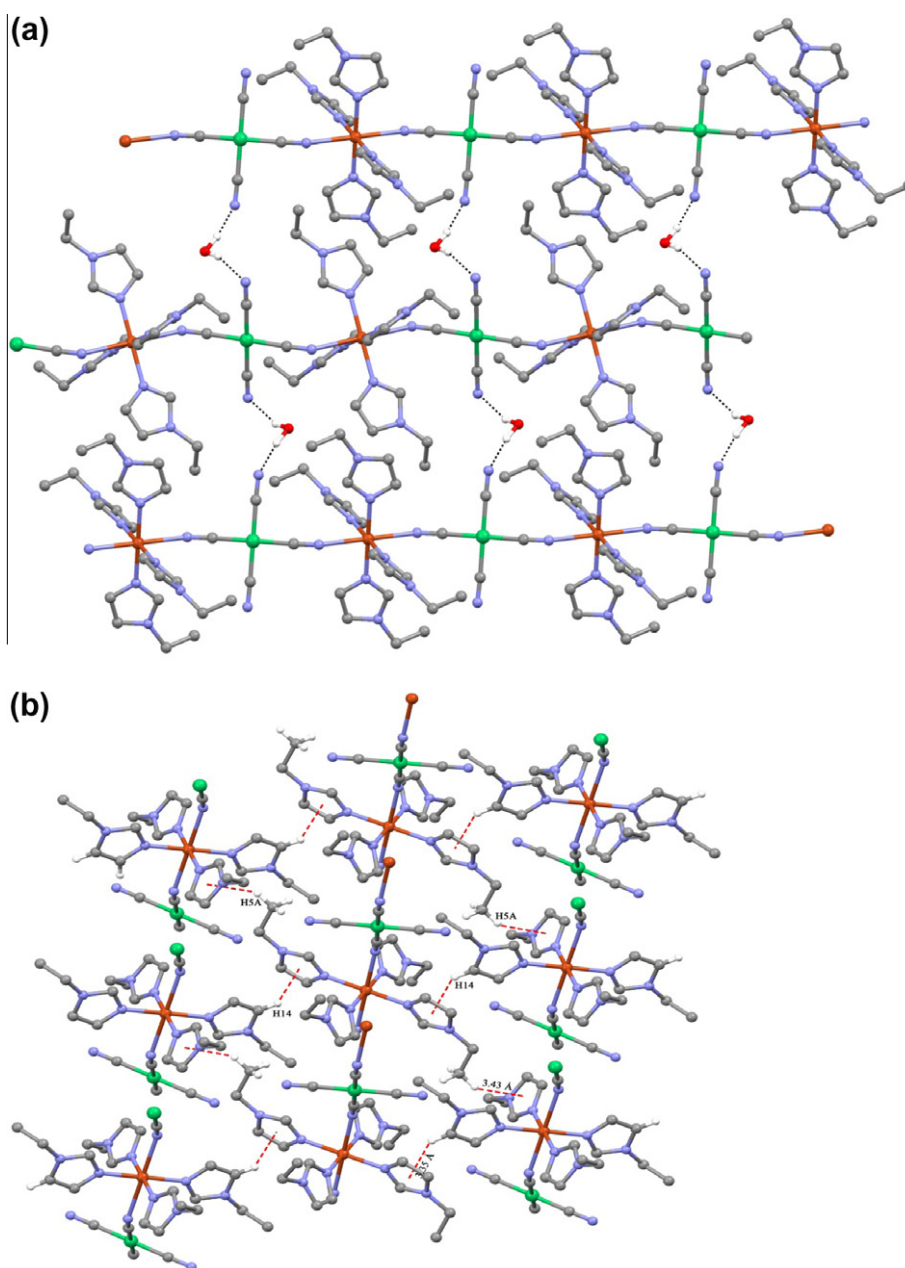


Fig. 5. (a) A view of the hydrogen-bonding interactions and (b) C–H... π interactions in **1**

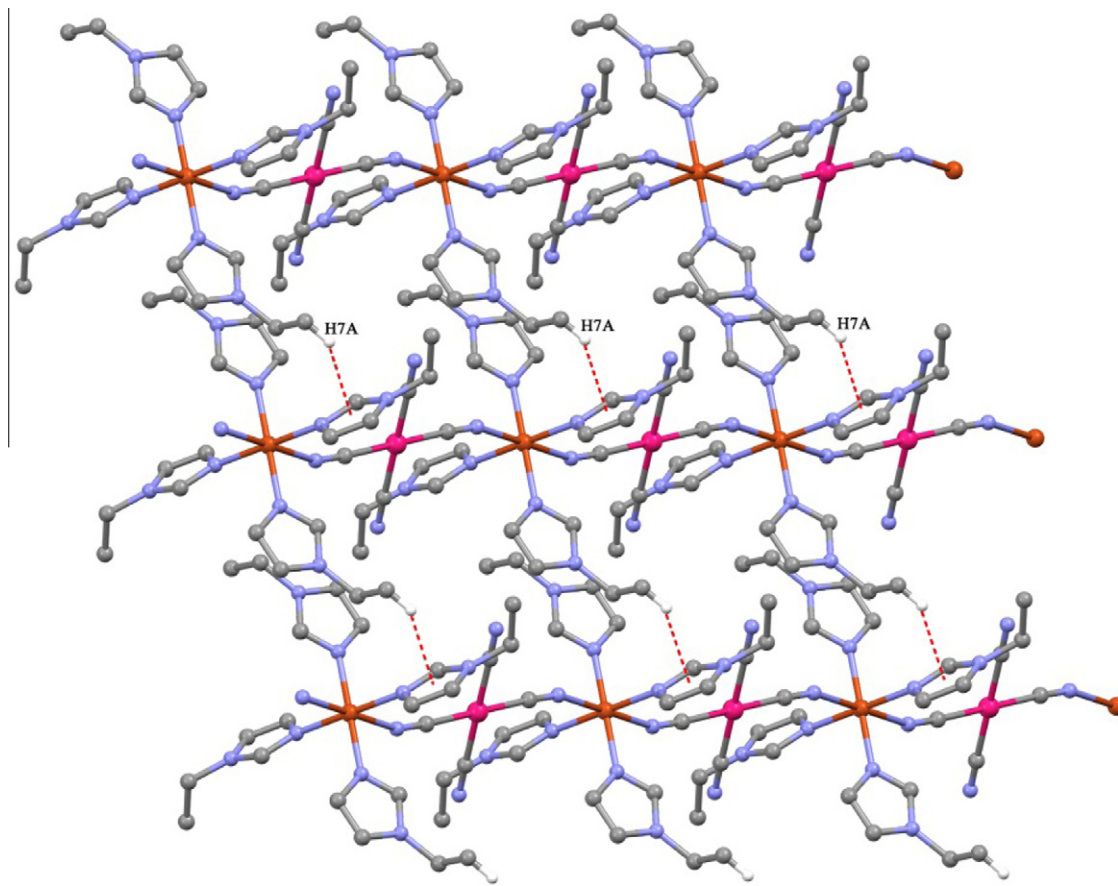


Fig. 6. A view of the C–H... π interactions in **2**.

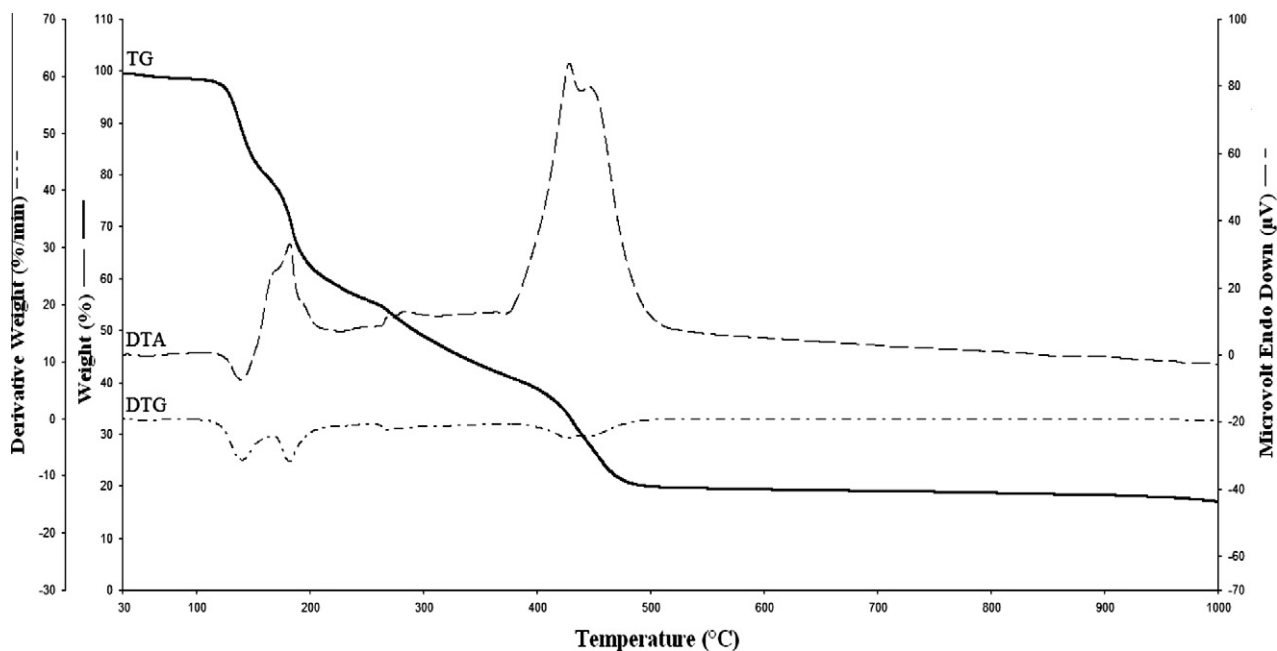


Fig. 7. TG, DTG and DTA curves of **1**.

267 °C (for **2**), respectively [found (Calc.)% = 14.80 (16.54) (for **1**) and found (Calc.)% = 15.65 (14.49) (for **2**)]. In the next step in complex **2**, the remaining one etim ligand is decomposed between 267 and 327 °C [found (Calc.)% = 11.60 (14.49)]. In the following stage of complex **2**, the remaining four cyano groups decom-

pose between 327 and 394 °C [found (Calc.)% = 14.43 (15.80)]. The final thermal products obtained are CuO+MO (M=Ni(II) or Pd(II)) [found (Calc.)% = 19.79 (19.44) (for **1**) and found (Calc.)% = 27.79 (30.66) (for **2**)] and they are identified by FT-IR spectroscopy.

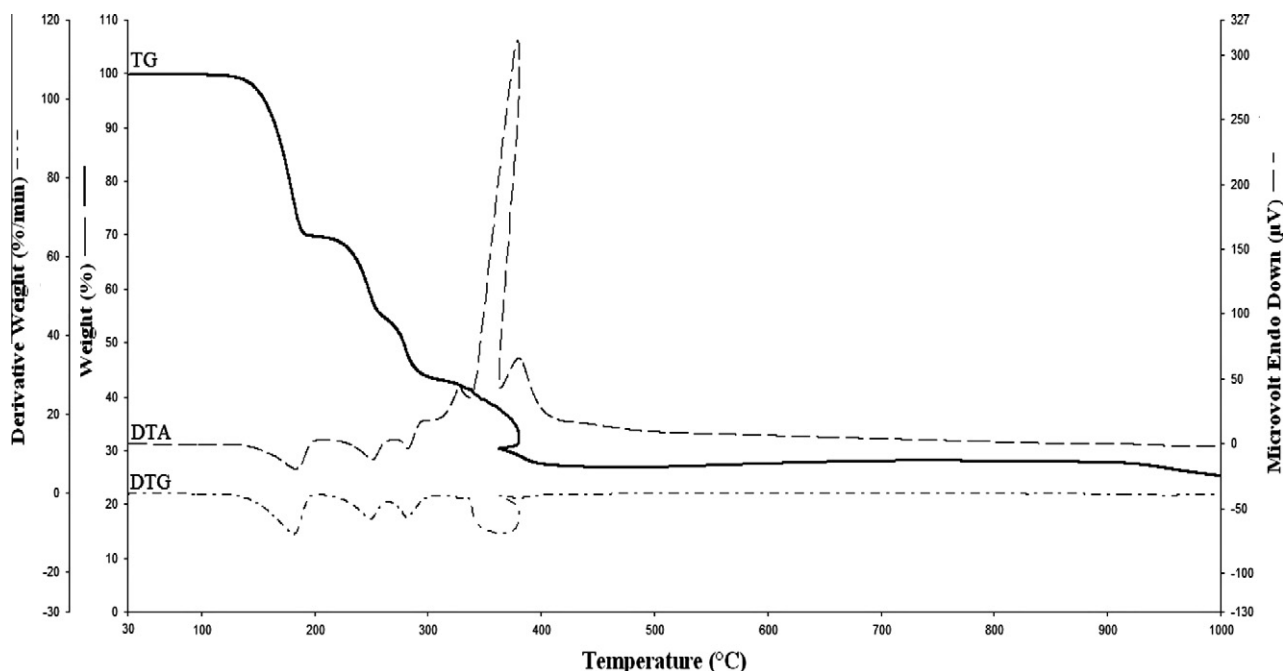


Fig. 8. TG, DTG and DTA curves of **2**.

4. Conclusion

We have synthesized and characterized the two new heteronuclear polymeric complexes, $\{[\text{Cu}(\text{etim})_4\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**) and $[\text{Cu}(\text{etim})_4\text{Pd}(\mu\text{-CN})_2(\text{CN})_2]_n$ (**2**). They crystallize in the triclinic system and space groups $P\bar{1}$. The Ni(II) or Pd(II) ion is four coordinate with four cyanide-carbon atoms in a square-planar geometry and the Cu(II) ion exhibits a distorted octahedral coordination by four etim ligands and two bridging cyano groups. The two complexes are isostructural and they are built up of 2,2-TT chains exhibiting $[-\text{Cu}(\text{etim})_4-\mu\text{-NC}-\text{M}(\text{CN})_2-\mu\text{-CN-}]_n$ composition. The cyano-bridged Cu–Ni and Cu–Pd heterometallic complexes with etim were investigated using different analyses methods. The Jahn–Teller effect seen in the copper complexes has been observed in both of the complexes **1** and **2**. The data obtained from studies are supported by each other. Vibration assignments were given for all the observed bands and the spectral feature also promoted to the structures of the polymeric complexes.

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Appendix A. Supplementary data

CCDC 883770 and 883771 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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