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Two-Dimensional Heteronuclear Coordination Polymers Constructed by Cyanide and 3-(2-Aminoethyl)pyridine Ligands

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Abstract

Two new heteronuclear (Ni/Cd and Pd/Cd) 2D coordination polymers formulated as namely $\{[Cd(\mu\text{-}3aepy)_2Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O\}_n$ (**1**) and $[Cd(3aepy)Pd(\mu_4\text{-}CN)_4]_n$ (**2**) (3aepy = 3-(2-aminoethyl)pyridine) were obtained and determined using different techniques (FT-IR and Raman spectroscopies, single crystal X-ray diffraction, elemental, SEM–EDX and thermal analyses). Single crystal X-ray study of the complexes revealed that the Ni(II) and Pd(II) ions are coordinated with four cyanide-carbon atoms in square planar geometries. The Cd(II) ions are bridged by 3aepy ligands to generate $[Cd_2(3aepy)_2]^{2+}$ cation and adjacent cations are further linked to cyanide ligands from $[Ni(\mu\text{-}CN)_4]^{2-}$ anion, generating corrugated rectangular grid-like 2D sheets in **1**. Whereas, the Cd(II) and Pd(II) ions are bridged by cyanide ligands, generating corrugated rectangular grid-like 2D sheets in **2**. The Cd1 is possessed the distorted octahedral coordination geometry with six nitrogen atoms from two 3aepy and four cyanide ligands. The Cd2 is coordinated by four nitrogen atoms from cyanide ligands to form a square-planar geometry. Furthermore, the most remarkable properties of the complexes are the existence of the intermolecular C–H···M interactions between M(II) and hydrogen atoms of the 3aepy ligands (M(II) = Ni and Pd).

Keywords Tetracyanonickelate(II) complex · Tetracyanopalladate(II) complex · 3-(2-aminoethyl)pyridine complex · Cyanide complex · C–H···Ni interaction · C–H···Pd interaction

1 Introduction

Cyanide complexes have a number of well-studied structural and functional building blocks that they can use to create larger functional architectures. Brief bridging pseudohalide ligands such as cyanides, azides and nitrile donors are versatile ligands that can connect transition metal ions in diverse ways in the solid state [1]. Tetracyanometallate anions (a tetracyanometallate anion is centered by a divalent d^8 transition metal: Ni, Pd or Pt) are suitable building blocks as the tetracyanometallate anion with auxiliary ligands and thus to form molecular and various (1D, 2D and 3D) structures. Cyanometallate complexes are used in potential application such as information records, adsorbents for gases, sensing, as molecular sieves, batteries, biomedicine, imaging, and water purification biologically active agents as catalysis and as single molecule magnets [2–6]. The two-dimensional (2D) structures of cyanide complexes are very amazing because they indicate many matchless features that are not observable in bulk materials [3].

There was great interest in the activated by transition metal complexes of C–H bonds since many years. In this context, there are many transition metal complexes demonstrating agostic or anagostic C–H···M interactions in the literature [7–11]. These interactions are seen as Lewis acid-Lewis base interactions; wherein the former metal center acts as Lewis acid, while the latter adopts the role of Lewis base [10]. Recently, several instances of three-center four-electron agostic interaction have been presented [11–17].

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C–H···M interactions are related to d^8 systems and are thought to be important in comprehension catalytic reactions [18]. Also, the C–H···M interaction plays a role of great importance in the creation of the supramolecular network [19].

3-(2-aminoethyl)pyridine was selected as an auxiliary ligand because of the possible interesting complex structures arising from its two donor atoms. In the literature, the 2-(2-aminoethyl)pyridine ligand can coordinate as a chelate ligand through two donor atoms or it can use all of its donor atoms for coordination [20]. In the second condition, the 3aepy can coordinate to only one metal ion utilization all two of its donor atoms or it can create a bridge between two metal ions. Tetracyanopalladate(II) complexes synthesized by Kuchar et al. consists of Cu(II) linked through $[Pd(CN)_4]^{2-}$ and they investigated the effect of the situation on the pyridine ring of the 2-aminoethyl arm in the 2-(2-aminoethyl)pyridine, 3-(2-aminoethyl)pyridine and 4-(2-aminoethyl)pyridine [20].

Recently, tetracyanonickelate(II), tetracyanopalladate(II) and tetracyanoplatinate(II) complexes with 3-aminomethylpyridine [21], 4-aminomethylpyridine [22–25] and 4-(2-aminoethyl)pyridine [26] ligands were reported our research. As far as we know, no vibrational and structural studies have been published for transition metal(II)-cyanide complexes of 3-(2-aminoethyl)pyridine (3aepy). As a part of our continuing research, we report herein the preparation, structural and spectroscopic characterization of two new cyanide-bridged one-dimensional heterometallic complexes, $\{[Cd(\mu\text{-}3aepy)_2Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O\}_n$ (**1**) and $[Cd(3aepy)Pd(\mu_4\text{-}CN)_4]_n$(**2**), based on the modified square planar tetracyanometallate(II) building blocks, $[M(CN)_4]^{2-}$ (M(II) = Ni or Pd; 3aepy = 3-(2-aminoethyl)pyridine). Complexes were structurally characterized by using different techniques such as elemental analysis, SEM–EDX analysis, single crystal X-ray diffraction, vibrational (FT-IR and Raman) spectroscopies and thermal analysis.

2 Experimental Details

2.1 Materials and Apparatus

The potassium cyanide (KCN-96%, Sigma-Aldrich), nickel(II) chloride hexahydrate ($NiCl_2$•$6H_2O$-97%, Riedel–de Haen), palladium(II) chloride ($PdCl_2$-99%, Aldrich), cadmium(II) chloride hemi(pentahydrate) ($CdCl_2\cdot 2.5H_2O$-99%, Across Organics) and 3-(2-aminoethyl) pyridine (3aepy-98%, Alfa-Aesar) were commercially available and could be used without purification. A CHNS-932 (LECO) Elemental Analyzer was used to obtained results for elemental C, H and N content SEM–EDX analysis was carried out with a Hitachi Regulus 8230 FE-SEM.. FT-IR spectra of the complexes, $K_2[Ni(CN)_4]$ and $K_2[Pd(CN)_4]$ were collected with Attenuated Total Reflectance (ATR) via Perkin-Elmer FT-IR 100 spectrometer in the wavenumber range of 4000–225 cm^{-1} with an average of 16 scan and 4 cm^{-1} of spectral resolution at room temperature. Raman spectra of the complexes, $K_2[Ni(CN)_4]$ and $K_2[Pd(CN)_4]$ have been recorded in the 4000–225 cm^{-1} range via Bruker Senterra Dispersive Raman Microscope using the 785 nm line of a 3B diode laser. Thermogravimetric analyses (TGA) for the complexes were carried out with A Perkin Elmer Diamond TG/DTA thermal analyzer in a static air atmosphere with a heating rate of 10 K/min from 30 to 700 °C using platinum pans.

2.2 Syntheses of the Complexes

2.2.1 Preparation of $Cd[M(CN)_4]\cdot H_2O$ (M(II) = Ni or Pd)

Solid metal chloride ($NiCl_2\cdot 6H_2O = 0.238$ g or $PdCl_2 = 0.177$ g, 1 mmol) and KCN (0.260 g, 4 mmol) were dissolved in distilled water (10 mL).The obtained solution was stirred at 60 °C for 2 h and then allowed to cool slowly to room temperature. $K_2[Ni(CN)_4]$ and $K_2[Pd(CN)_4]$ crystals appeared within a couple of days. A mixture of 1 mmol $K_2[M(CN)_4]$ (M(II)=Ni, 0.241 g or M = Pd, 0.289 g) and 1 mmol $CdCl_2\cdot 2.5H_2O$ (0.228 g) was stirred at 50 °C for 30 min in the water to obtain yellow crystals of $Cd[M(CN)_4]\cdot H_2O$ (M(II)=Ni and Pd). The obtained crystals were taken from the beaker and dried in air.

2.2.2 Preparation of $\{[Cd(\mu\text{-}3aepy)_2Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O\}_n$ (1) and $[Cd(3aepy)Pd(\mu_4\text{-}CN)_4]_n$ (2)

A solution of 3aepy (0.244 g, 2 mmol) in water (10 mL) was added dropwise with stirring at 50 °C to a solution of $Cd[Ni(CN)_4]\cdot H_2O$ (0.293 g, 1 mmol) dissolved in water (10 mL). The solution was stirred for 5 h at 55 °C and then filtered. By evaporation in air at room temperature, the single crystals suitable for X-ray determination were obtained after a week. The scheme showing the formation of the complexes was given in Scheme S1.

$\{[Cd(\mu\text{-}3aepy)_2Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O\}_n$(1) Yield: 0.365 g, 65.70% based on $Cd[Ni(CN)_4]\cdot H_2O$. Anal. Found (Calc.) (%) for $C_{18}H_{24}N_8NiO_2Cd$ (C, 38.54 (38.92); H, 4.54 (4.35); N, 20.20 (20.17%).

The synthesis of **2** was similar to that of **1** except $Cd[Pd(CN)_4]\cdot H_2O$ (0.340 g, 1 mmol) was substituted for $Cd[Ni(CN)_4]\cdot H_2O$.

$[Cd(3aepy)Pd(\mu_4\text{-}CN)_4]_n$ (**2**) Yield: 0.412 g, 95.81% based on $Cd[Pd(CN)_4]\cdot H_2O$. Anal. Found (Calc.) (%) for $C_{10}H_7N_6PdCd$ (**2**) (C, 28.20 (27.86); H, 2.91 (1.87); N, 18.20 (19.50%).

To ensure the presence of metal ions along with the other elements present within the complexes **1** and **2**, EDX analysis was carried out. As seen in Fig. S4, EDX analysis shows the presence of a Cd^{2+}, Ni^{2+} and Pd^{2+} in the structures.

2.3 Single-Crystal X-Ray Diffraction (SC-XRD) Analysis

Single-crystal diffraction analyses were performed for the complexes using a D8-QUEST diffractometer equipped with a graphite-monochromated Mo-Kα radiation 296 K. The crystal structures were solved by direct methods using SHELXS-2013 [27] and refined with SHELXL-2013 by full-matrix least-squares methods on reflection intensities (F^2) [28]. All non-hydrogen atoms were anisotropically refined with anisotropic displacement coefficients. The H atoms of carbon were located in a difference map refined freely. The following procedures were followed in our analysis: data collection and reduction: Bruker APEX2 [29]; absorption correction was applied using SADABS [30]; program used for molecular graphics were as follow: MERCURY programs [31]; software used to prepare material for publication: WinGX [32]. Crystallographic data and refinement parameters for the complexes are listed in Table 1. Selected bond lengths are given in Table 2.

Table 1 Crystal data and structure refinement parameters for complexes **1**–**2**

Crystal data	**1**	**2**
Empirical formula	$C_{18}H_{24}N_8O_2CdNi$	$C_{10}H_7N_6CdPd$
Formula weight	555.56	430.03
Crystal system	Triclinic	Monoclinic
Space group	P-1	C^2/m
a (Å)	7.8889 (10)	16.376 (2)
b (Å)	8.9276 (11)	7.6292 (9)
c (Å)	9.0188 (11)	15.0157 (17)
α (°)	97.348 (4)	90.00
β (°)	105.766 (5)	119.225 (4)
γ (°)	111.159 (4)	90.00
V (Å^3)	551.71 (12)	1637.2 (3)
Z	1	4
D_c (g cm^{-3})	1.672	1.745
μ (mm^{-1})	1.85	2.39
θ range (°)	3.0–28.4	3.0–28.3
Measured refls	27,572	18,186
Independent refls	2751	1921
R_{int}	0.037	0.065
S	1.08	1.14
R1/wR2	0.016/0.039	0.081/0.236
T_{max}/T_{min}	0.746/0.556	0.746/0.556

3 Results and Discussion

3.1 Analysis of Crystal Structures

3.1.1 Complex 1

The X-ray single crystal study demonstrates that heterometallic complex **1** has 2D coordination polymer. The asymmetric unit of the complex **1** comprises of half a Cd(II) ion, half a Ni(II) ion, two cyanide, one 3aepy ligands and one non-coordinated water molecule. As shown in Fig. 1, the Cd(II) ion is located on inversion center and coordinated by two nitrogen atoms [Cd1–N3 = 2.3372(12) Å] from cyanide ligands and four nitrogen atoms [Cd1–N2 = 2.3511(11) Å and Cd1–N1^{i} = 2.4257(10) Å] from 3aepy ligands, thus giving a distorted octahedral coordination geometry [(i) x, y − 1, z]. The Ni(II) ion is coordinated by four carbon atoms [Ni1–C8 = 1.8619(12) Å and Ni1–C9 = 1.8641(16) Å] [24, 33–37] from cyanide ligands, thus showing a square planar coordination geometry. The Cd(II) ions are bridged by 3aepy ligands to generate $[Cd_2(C_7H_{10}N_2)_2]$ metalloligands, with the Cd···Cd separation is 8.928 Å. Adjacent these $[Cd_2(C_7H_{10}N_2)_2]$ metalloligands are further joined by Ni(II) ions and cyanide ligands, generating corrugated rectangular grid-like 2D sheets, with grid dimensions are 8.928 × 10.638 Å (Fig. 2) (defined by Cd···Cd distances). The intermolecular C–H···M interaction between Ni(II) ion and H atom of the 3aepy ligand [H3···Ni1^{ii} = 2.92(2) Å, C3···Ni1^{ii} = 3.3071(17) Å and C3–H3···Ni1^{ii} = 106.2(3)°] is the most outstanding property of the complex **1** [(ii) x − 1, y, z]. Complex **1** also contains one C≡N···π interaction between cyanide ligand and pyridine ring of the 3aepy ligand [N4···Cg(1) = 3.58 Å and C9≡N4···Cg(1) = 123°] (Fig. 3). In addition, the molecules are depended by C–H···N, O–H···N and N–H···O interactions (Table 3). The combination of these interactions produce 3D network.

3.1.2 Complex 2

The asymmetric unit of the heterometallic complex **2** composed of a half Cd(II), a half Pd(II) ion, one 3aepy ligand and two cyanide ligands (Fig. 4). The Cd(II) ions are of two coordination types. In the first of these coordination geometries, the Cd1 atom is located on inversion center and coordinated by two nitrogen atoms [Cd1–N1 = 2.317(19) Å] [21] from 3aepy ligands and four nitrogen atoms [Cd1–N3 = 2.348(9) Å] from cyanide ligands, resulting in a distorted octahedral coordination geometry. In the second coordination, the Cd2 atom exhibited square-planar geometry that formed via four nitrogen atoms [Cd2–N4 = 2.338(13) Å] from cyanide ligands. The Cd2–N2^{i} separation is 2.974(4) Å, this distance can be taken into account as bond; therefore the

Table 2 Selected bond distances for complexes **1**–**2** (Å, °)

Complex 1					
Cd1-N2	2.3511(11)	Cd1-N1^{i}	2.4257(10)	Cd1-N3	2.3372(12)
Ni1-C8^{ii}	1.8619(12)	Ni1-C9^{ii}	1.8641(16)		
Complex 2					
Cd1-N1	2.317(19)	Cd1-N3	2.348(9)	Pd1-C8	1.974(11)
Pd1-C7	1.978(10)	Cd2-N4	2.338(13)		

Symmetry codes: (i) -x + 1, -y + 1, -z; (ii) -x + 2, -y + 1, -z + 1 for **1**

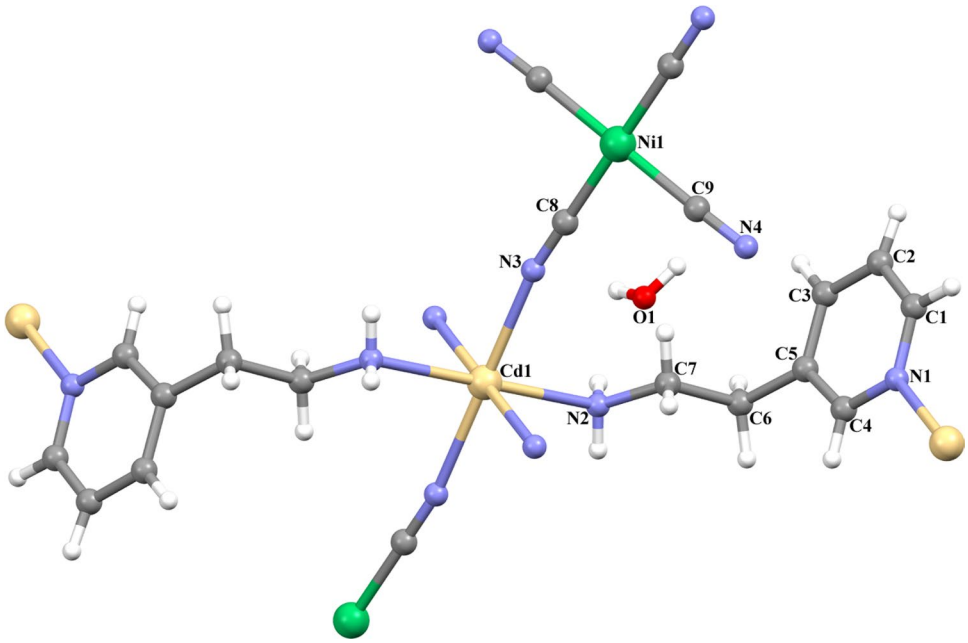
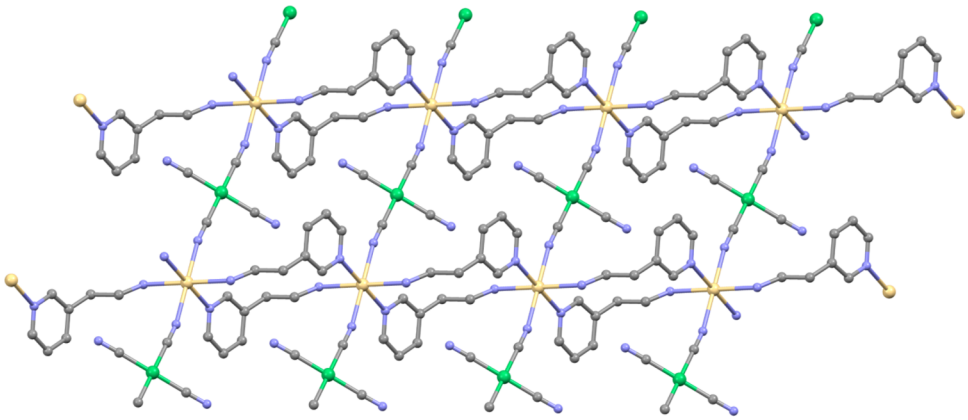


Fig. 1 The molecular structure of **1** showing the atom numbering scheme

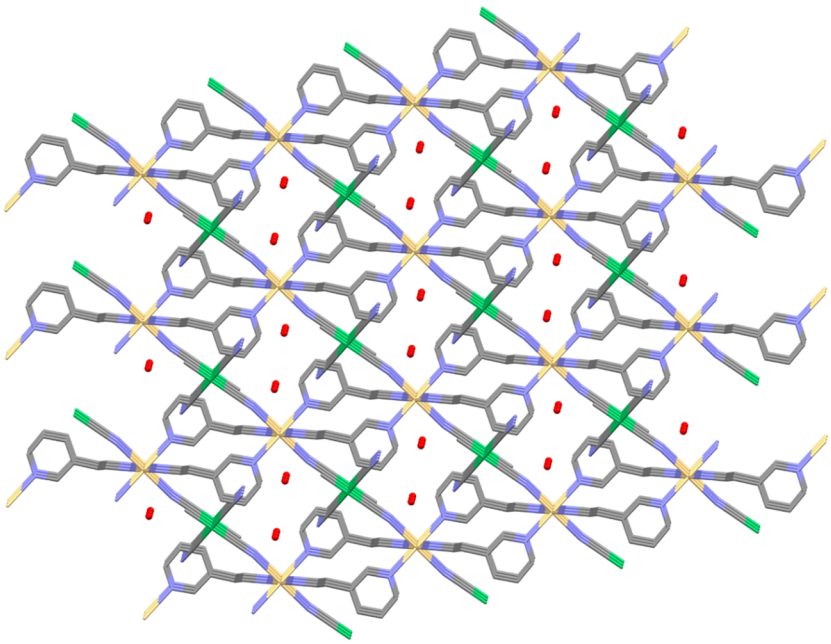
coordination around of Cd2 atom is pseudo-octahedral coordination geometry [(i) x, y − 1, z − 1]. The Pd(II) ion is also located on inversion center and surrounded by four cyanide ligands, the Pd–C bond distances are 1.974 (11) and 1.978 (10) Å, respectively. The coordination around Pd(II) ion is square-planar. The Cd(II) and Pd(II) ions are bridged by cyanide ligands, generating corrugated rectangular grid-like 2D sheets, with grid dimensions are 5.433 × 5.433 Å (Fig. 5) (defined by Cd···Pd distances). The most striking features of the complex **2** are the presence of the intermolecular N–H···Cd and C–H···Pd interactions between metal atoms and H atoms of the 3aepy ligands: Cd2···H2A [2.73(2) Å] and Cd2···N2 [2.974(4) Å] distances and N2–H2A···Cd2 [98.10(2)°] angle (for N–H···Cd) (Fig. 5) and Pd1···H2 [2.87(2) Å] and Pd1···C2 [3.661(2) Å] distances and C2–H2···Pd1 [140.01(1)°] angle (for C–H···Pd) (Fig. 6). As can be seen in the literature [38–40], these interactions distances are not long; therefore these interactions may be taken into account as bonds. Complex **2** also contains one π···π interaction which is occurs between the two symmetry-related pyridine rings. The distance between the ring centroids is 3.909(4) Å. The intermolecular π-π interactions connection the polymeric chains into a two-dimensional network, in which they appear to be efficient in the stabilization of the crystal structure (Fig. 6).

3.2 Spectral (FT-IR and Raman) Analysis

The FT-IR and Raman spectra of the complexes are displayed on Figure S1 and Figure S2, respectively. The vibrational wavenumbers of the $[M(CN)_4]^{2-}$ [M(II) = Ni(II) and Pd(II)] groups for the complexes in FT-IR and Raman spectra are given in Table 4, together with the vibration wavenumbers of $K_2[Ni(CN)_4]$ [41] and $K_2[Pd(CN)_4]\cdot H_2O$ [42] for comparison. The existence of $[M(CN)_4]^{2-}$ (M(II) = Ni and Pd) anions in the obtained complexes is demonstrated by cyanide stretching vibrations at 2000 and 2200 cm^{-1} whose positions are a significant tool to distinguish between terminal and bridging character of cyanide group. The description of FT-IR spectrum becomes much clearer and more useful when the crystal structure of the complex is known [43].



(a)



(b)

Fig. 2 An infinite 2D (**a**) and 3D (**b**) layer in **1**

The FT-IR spectra of the mononuclear compounds, $K_2[Ni(CN)_4]$ and $K_2[Pd(CN)_4]\cdot H_2O$, showed a band at 2120 and 2135 cm^{-1}, respectively. In the FT-IR spectra, ν(CN) stretching bands show at 2150 cm^{-1} for **1**, 2163 cm^{-1} and 2152 cm^{-1} for **2**. The ν(CN) stretching bands belonging to the cyanide groups are clearly seen at 2163 and 2137 cm^{-1} for **1** and at 2188 and 2173 cm^{-1} for **2** in Raman spectra. When the spectral and crystallographic data of the complexes were compared, the results were found to be compatible with each other. According to this, C8≡N3 and C9≡N4 bond lengths in **1** are observed as 1.142(1) and 1.143(3) Å, respectively. The bridged Cd–$N_{cyanide}$ bond length, [Cd1–N3 = 2.337(1) Å], affecting the position of the ν(C≡N) absorption band, is essentially different which result in one absorption band in the FT-IR spectrum. No splitting of ν(CN) stretching mode of **1** occurs at 2150 cm^{-1} in the FT-IR spectrum, because of the bridging and terminal ν(CN) absorption bands cause overlapping. The C7≡N3 and C8≡N4 bond lengths in **2** are observed as 1.144(2) and 1.136(2) Å, respectively. The bridged Cd–$N_{cyanide}$ bond length, [Cd1–N3 = 2.350(1) Å], effecting the position of the ν(C≡N) absorption band, is essentially different which result in one absorption band in the FT-IR spectrum. According to the literature, the terminal cyanides $\nu(CN)_t$ in

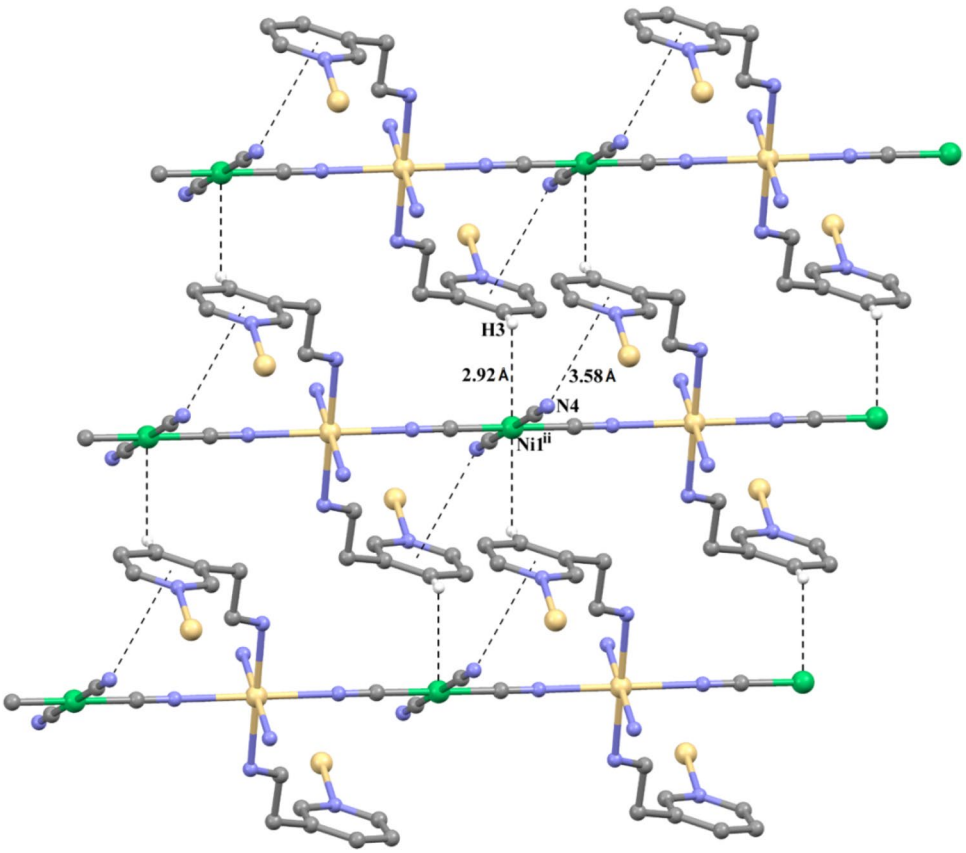


Fig. 3 C-H···Ni and C≡N•••π interactions in **1**

Table 3 Hydrogen-bond parameters for **1** (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
C1-H1···N3^{i}	0.96 (2)	2.635 (19)	3.3417 (19)	131
O1-H1B···N4^{vi}	0.79 (2)	2.11 (2)	2.873 (2)	161
N2-H2A···O1^{vii}	0.83 (2)	2.45 (2)	3.275 (2)	174
N2-H2B···O1	0.86 (2)	2.42 (2)	3.221 (2)	156

Symmetry codes: (i) x, y + 1, z; (vi) x-1, y-1, z; (vii) -x, -y, -z for **1**

cyanide-bridged complexes are generally appeared at lower frequencies than those of the bridging cyanide frequencies $\nu(CN)_b$ [44].

The cyanide complexes exhibit ν(MC) and δ(MCN) vibration bands in the low-frequency region. The ν(M–CN) stretching and δ(M–CN) bending bands in the 600–350 cm^{-1} are observed for $K_2[M(CN)_4]\cdot H_2O$ (M = Ni(II) and Pd(II)) in the low frequency region of the FT-IR spectrum [44]. The observed bands at 544 and 422 cm^{-1} for **1** and 491 cm^{-1} and 397 cm^{-1} for **2** in the FT-IR spectrum of might be attributed to the ν(M–C) stretching and δ(M–CN) bending vibrations, respectively. The FT-IR and Raman spectra of the complexes are very much consistent with the structural data presented.

3.3 Thermal Analysis

In order to study the thermal stabilities of the complexes, thermogravimetric analyses were undertaken on **1** and **2** under an air atmosphere in the temperature range of 30–700 °C as shown in Figure S3.

TG curve of complex **1** exhibits three decomposition stages. The first stages of **1** lose the endothermic remove of the crystal water molecules in the temperature range of 79–131 °C [found (calcd.): 6.91% (6.48%); DTA_{max} = 120 °C]. In the following stages, 3aepy ligands decompose between 131 and 334 °C [found (calcd.): 40.45% (43.98%); DTA_{max} = 201 °C]. In the last stage between 334 and 366 °C temperature range, strong exothermic peak (DTA_{max} = 364 °C) is associated with the burning of the four cyanide ligands [found (calcd.): 15.59% (18.73%)]. The final solid products of thermal decompositions, CdO and NiO, were identified by FT-IR spectroscopy [found: 37.05%, calcd.: 36.55%].

The complex **2** exhibits two decomposition stages. The first stages of **2**, the 3aepy ligand decompose between 82 and 361 °C [found (calcd.): 27.44% (24.89%)]. In the last stage between 361 and 415 °C temperature range, strong exothermic peak (DTA_{max} = 406 °C) is associated with the burning of the four cyanide ligands [found (calcd.): 21.06% (23.38%)]. The final solid products of thermal

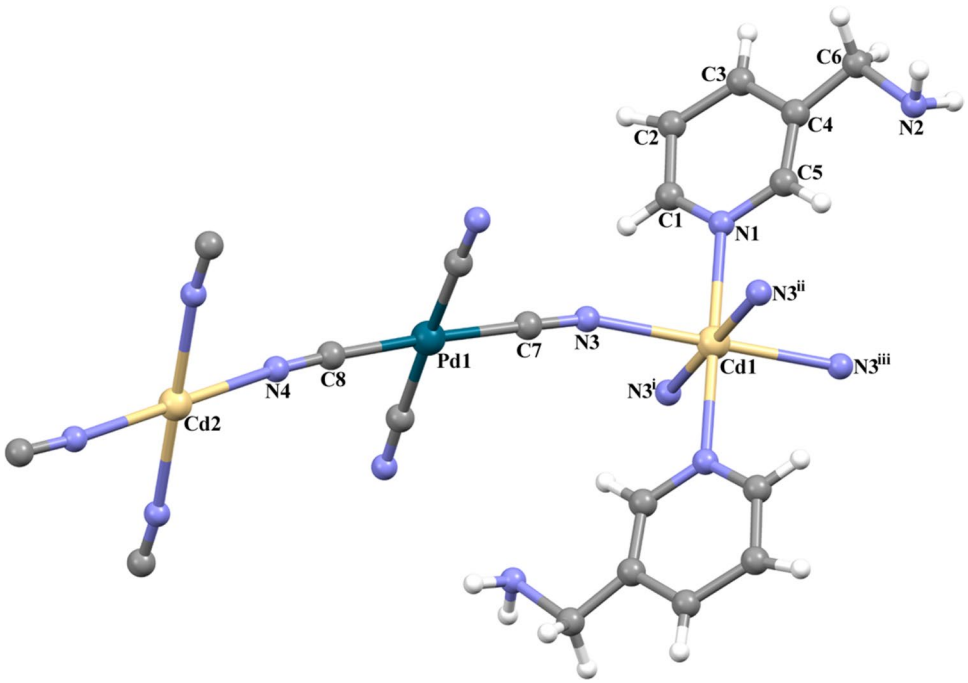


Fig. 4 The molecular structure of **2** showing the atom numbering scheme.[(i) − x + 2, − y + 1, − z + 1; (ii) x, − y + 1, z; (iii) − x + 2, y, − z + 1]

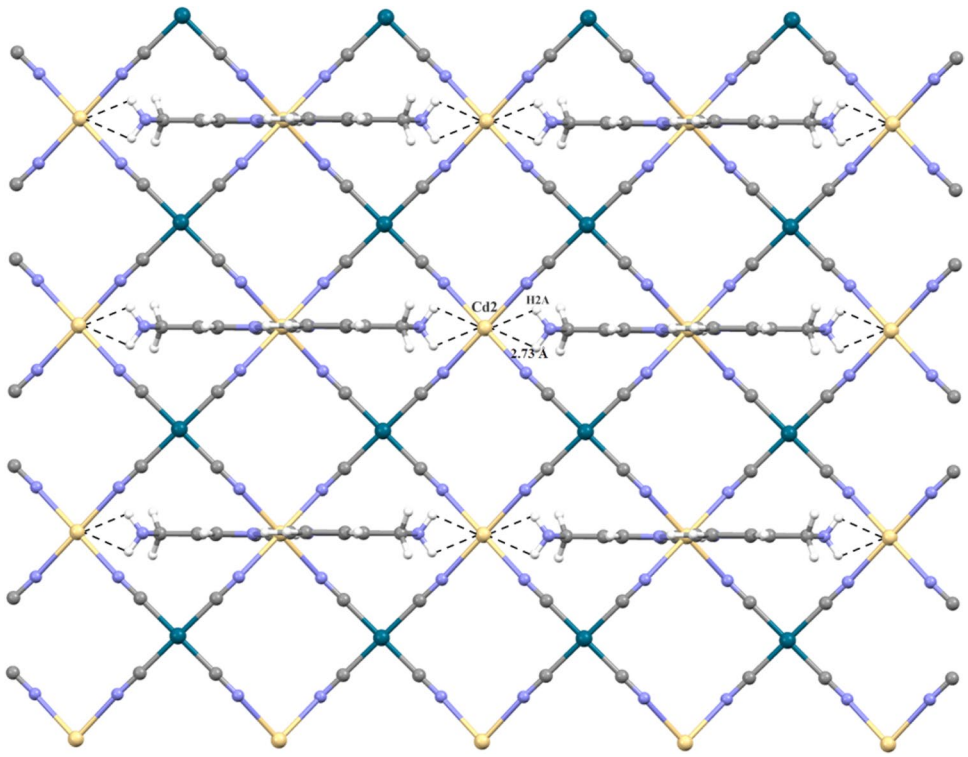


Fig. 5 An infinite 2D layer and N–H···Cd interactions in **2**

decompositions, CdO and PdO, were supported by FT-IR spectroscopy [found: 54.05%, calcd.: 56.35%]. A similar pattern of decomposition was observed in the thermal analyses of $[Cd(pyr)_2Ni(\mu\text{-}CN)_4]_n$ [45], $\{[Cd(pdz)Ni(CN)_4]\cdot H_2O\}_n$ [46], $[Zn(NH_3)_2(\mu\text{-ampy})Pd(\mu\text{-}CN)_2(CN)_2]_n$ [22] complexes. In literature, TGA results for $[Cd(pyr)_2Ni(\mu\text{-}CN)_4]_n$ appeared at $DTA_{max} = 377$ °C a weight loss between 307 and 384 °C [45], for $[Zn(NH_3)_2(\mu\text{-ampy})Pd(\mu\text{-}CN)_2(CN)_2]_n$ TGA results appeared at $DTA_{max} = 398$ °C a weight loss between 377 and 421 °C, for $[Cu(hepH)_2Pd(\mu\text{-}CN)_2(CN)_2]_n$ complex, TGA results appeared at $DTA_{max} = 405$ °C a weight loss between 363 and 412 °C [47].

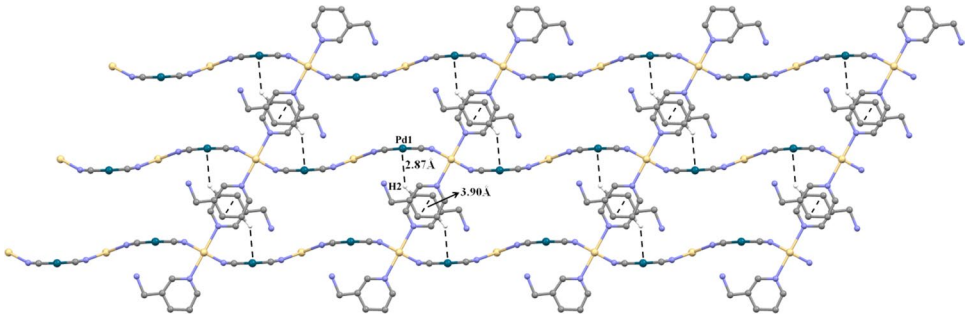


Fig. 6 C–H···Pd and π···π interactions in **2**

Table 4 The wavenumbers of the $[M(CN)_4]^{2-}$ (M = Ni(II) or Pd(II)) vibrations in the complexes (cm^{-1})

Assignments [41, 42]	$K_2[Ni(CN)_4]$	$K_2[Pd(CN)_4]$	**1**	**2**
A_{1g}, ν(C≡N)	(2160) vs	(2169) vs	(2163) s	(2188) s
B_{1g}, ν(C≡N)	(2137) m	(2159) s	(2137) vs	(2173) vs
E_u, ν(C≡N)	2120 vs	2135 vs	2150 vs	2163 vs, 2152 vs
E_u, ν($C^{13}N$)	2084 w	2096 w	2095 vw	2129 vw
E_u, ν(M–C)	540 w	486 w	544 m	491 w
A_{2u}, π(M–CN)	443 w	-	422 vs	-
A_{1g}, ν(M–C)	(374)	(436) m	(413) m	(451) m
E_u, δ(M–CN)	298	374	293 w	397 vs

s strong, *m* medium, *w* weak, *sh* shoulder, *v* very. The symbols ν, δ and π refer to valence, in-plane and out-of-plane vibrations, respectively

Raman bands are given in parentheses

4 Conclusion

In this study, two heteronuclear complexes, $\{[Cd(\mu\text{-}3aepy)_2Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O\}_n$ (**1**) and $[Cd(3aepy)Pd(\mu_4\text{-}CN)_4]_n$(**2**), were synthesized and characterized. The approaches given in this paper are thought to be useful in the preparation of other single crystal types to develop new chemical and physical properties. The results reported here offer meritorious information for the rational design in coordination chemistry with various structural types and using as catalyst such as the Suzuki–Miyaura and the Heck–Mizoroki coupling reactions cyanide complexes containing palladium central. The Cd(II) and M(II) ions are bridged by cyanide ligands, generating corrugated rectangular grid-like 2D sheets in complexes. The Cd1 ions are coordinated by six nitrogen atoms from two 3aepy and four cyanide ligands, whereas Cd2 ions are coordinated by four nitrogen atoms from cyanide ligands to form a square-planar geometry. In the complexes, the presence of intramolecular C–H···M (M = Ni(II) or Pd(II)) interactions with distance values of 2.92–2.87 Å are found, respectively. The C–H···M interactions among M and H atoms of the 3aepy ligands are the most important properties of the obtained complexes.

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