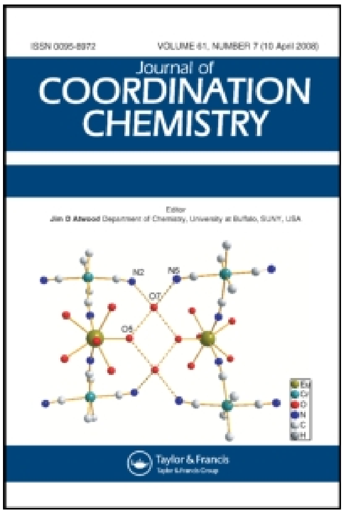

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Preparations, IR spectra and crystal structures of cyano-bridged bimetallic complexes of zinc(II) and cadmium(II) with tetracyanopalladate(II)

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Preparations, IR spectra and crystal structures of cyano-bridged bimetallic complexes of zinc(II) and cadmium(II) with tetracyanopalladate(II)

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The novel heteronuclear compounds [Zn(hydet-en)$_2$Pd(CN)$_4$] (**1**) and [Cd(hydet-en)$_2$Pd(CN)$_4$] (**2**) {hydet-en: *N*-(2-hydroxyethyl-ethylenediamine)} have been synthesized and characterized by elemental analyses and IR spectra. The crystal structures of **1** and **2** have been determined by X-ray diffraction. Structural analysis shows that both compounds have shown a polymeric chain, in which the Zn(II)/Pd(II) and Cd(II)/Pd(II) centres are linked by two CN groups. Both zinc and cadmium atoms are six coordinate with two *trans* cyanide–nitrogen and four hydet-en N atoms in a distorted octahedron arrangement; the palladium atoms in **1** and **2** are four coordinate with four cyanide-C atoms in a square planar arrangement. The chains in both compounds are connected through weak interchain hydrogen bonds, N–H $\cdots$ O, N–H $\cdots$ N and O–H $\cdots$ N, thereby forming a three-dimensional network.

Keywords: Heteronuclear Pd complexes; Polymeric chains; Cyano-bridged complexes; Crystal structures

1. Introduction

The coordination chemistry of cyanide-bridged metal complexes attracts interest because of their magnetic behaviour, unusual electronic states and photochemical properties [1–4]. The cyanide ion may coordinate either through the C atom, as a monodentate ligand, or through the C and N atoms as a bridging ligand, forming polymeric compounds with a one-, two- or three-dimensional networks. The construction of one-dimensional system can be achieved by the use of the 'brick and mortar' method [5, 6], where the metal cation forms the bricks and the cyano complex anion represents the mortar.

Zinc(II) and cadmium(II) ions, as the cationic central atom in cyano complexes, generally adopt a coordination number of six. Therefore, four vertices around the metal

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cation need to be coordinated by terminate ligands, and two form a chain structure [7]. Cyanocomplexes, especially tetracyanonickelate, have been systematically investigated [8–10], but very little has been published to date on the structures of tetracyanopalladate complexes [11–13]. As part of our ongoing research on cyanide-bridged complexes, we have synthesized compounds **1** and **2**; this article reports the syntheses, IR spectra and crystal structures of these one-dimensional heterometallic polymeric complexes, $[Zn(hydet\text{-}en)_2Pd(CN)_4]_n$, {catena-poly[$\mu$-cyano-$1:2\kappa^2C:N$-dicyano-$1\kappa^2C$-*trans*-*bis* [N-(2-hydroxyethyl)ethane-1,2-diamine-$2\kappa^2N,N'$] zinc(II)palladium(II)]-μ-cyano-$1:2'^2C:N$]}, and $[Cd(hydet\text{-}en)_2Pd(CN)_4]_n$, {catena-poly[$\mu$-cyano-$1:2\kappa^2C:N$-dicyano-$1\kappa^2C$-*trans*-*bis* [N-(2-hydroxyethyl) ethane-1,2-diamine-$2\kappa^2N,N'$]cadmium(II)palladium(II)]-μ-cyano-$1:2'\kappa^2C:N$]}. A mixed N/O-donor ligand with three donor sites [14–18] was used in this study.

2. Experimental

2.1. *Materials and instrumentation*

Palladium(II) chloride ($PdCl_2$), zinc(II) chloride ($ZnCl_2$), cadmium(II) sulfate 8/3 hydrate ($CdSO_4 \cdot 8/3H_2O$), [*N*-(2-hydroxyethyl-ethylenediamine)($C_4H_{12}N_2O$)], potassium cyanide (KCN) were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were carried out by standard methods (TÜBİTAK Ankara Test and Analysis Laboratory, Turkey). The IR spectra were recorded on a Jasco 430 FTIR spectrophotometer using KBr pellets in the 4000–200 cm^{-1} range.

2.2. *Syntheses*

2.2.1. $[Zn(hydet\text{-}en)_2Pd(CN)_4]$ (1). KCN (0.147 g, 2.257 mmol) was added to 20 mL $PdCl_2$ (0.100 g, 0.564 mmol) solution in 1/4 ethanol–water mixture. Then, $ZnCl_2$ (0.077 g, 0.565 mmol) in ethanol (10 mL) was added to the solution which became a cloudy white mixture. *N*-(2-hydroxyethyl)-ethylenediamine (0.117 g, 1.123 mmol) in 10 mL ethanol was added to this mixture dropwise. The resultant solution was left to crystallize at room temperature and white crystals of **1** suitable for X-ray measurement formed by slow evaporation in a few days. Anal. Calcd For **1** (%): C, 29.7; H, 5.0; N, 23.1. Found: C, 29.9; H, 5.3; N, 23.1.

2.2.2. $[Cd(hydet\text{-}en)_2Pd(CN)_4]$ (2). A solution of $PdCl_2$ (0.100 g, 0.564 mmol) in an ethanol–water mixture (Ratio1/4; 20 mL) was added with stirring to solid KCN (0.147 g, 2.257 mmol). $CdSO_4 \cdot 8/3H_2O$ (0.145 g, 0.565 mmol) was then added slowly to the solution, which became a cloudy white mixture. This mixture was added slowly to *N*-(2-hydroxyethyl)-ethylenediamine (0.117 g, 1.123 mmol) with stirring. The solution was left to crystallize at room temperature and white crystals of **2**, suitable for X-ray analysis, formed by slow evaporation in a few days. Anal. Calcd For **2** (%): C, 27.1; H, 4.5; N, 21.1. Found: C, 27.4; H, 4.4; N, 21.2.

Table 1. Crystal data and structure refinement for $[ZnPd(CN)_4(C_4H_{12}N_2O_2)_2]$ and $[CdPd(CN)_4(C_4H_{12}N_2O_2)_2]$.

Compound	$[ZnPd(CN)_4(C_4H_{12}N_2O_2)_2]$	$[CdPd(CN)_4(C_4H_{12}N_2O_2)_2]$
Color	Colorless	Colorless
Empiricial formula	$C_{12}H_{24}N_8O_4PdZn$	$C_{12}H_{24}CdN_8O_4Pd$
Formula weight	484.16	531.19
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensional (Å, °)		
a	7.1950(8)	10.031(3)
b	7.9840(9)	11.3760(9)
c	9.3900(11)	17.830(3)
α	100.117(9)	90.00
β	101.551(9)	99.771(7)
γ	107.452(9)	90.00
V (Å^3)	487.86(10)	2005.1(7)
Z	1	4
Absorption coefficient (mm^{-1})	2.172	1.978
θ_{max} (° for data collection)	27.5	27.5
Reflections collected	1935	2301
Independent reflections	2238($R_{int} = 0.0607$)	2301($R_{int} = 0.047$)
Reflections with $I > 2\sigma(I)$	1935	1974
D_{Calcd} (Mg m^{-3})	1.648	1.760
Crystal size (mm^3)	0.300 × 0.240 × 0.170	0.330 × 0.240 × 0.130
Absorption correction	Integration	Integration
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Extinction coefficient	0.0196(15)	0.00325(16)
Final R indices [$F > 2(F^2)$]	$R_1 = 0.0225$, $wR_2 = 0.0512$	$R_1 = 0.0209$, $wR_2 = 0.0496$
Goodness-of-fit on F^2	0.997	1.016
Largest difference peak and hole (e Å^{-3})	0.674 and −0.970	0.367 and −0.492
CCDC deposition no.	294534	294535

2.3. *X-ray crystallography*

A suitable single crystal was mounted on a glass fiber and data collection performed on a STOE IPDSII image plate detector using Mo-Kα radiation ($\lambda = 0.71019$ Å). Details of crystal structures are given in table 1. Data collection: Stoe X-AREA [19]. Cell refinement: Stoe X-AREA [19]. Data reduction: Stoe X-RED [19]. The structure was solved by direct-methods using SIR97 [20] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [21]. Hydrogen atoms (on C and O atoms) were placed at calculated positions (C–H = 0.97 Å; O–H = 0.82 Å) and were allowed to ride on the parent atom [$U_{iso}(H) = 1.2U(C)$; $U_{iso}(H) = 1.5U(O)$]. The amine H atoms were placed from the difference map and were refined with N–H distance restrained to be 0.87(2) Å in 1 and freely refined in 2 with N–H distances in the range 0.81(4)–0.86(3) Å. All non-hydrogen atoms of the complexes were refined anisotropically. Molecular drawings were obtained using ORTEP-III [22].

3. Results and discussion

3.1. *The FT–IR spectra*

The spectra of free hydet-en (a), complex **1** (b) and complex **2** (c) are illustrated in figure 1. The hydet-en ligand shows infrared bands at 3355–3210 ν(OH)–ν(NH),

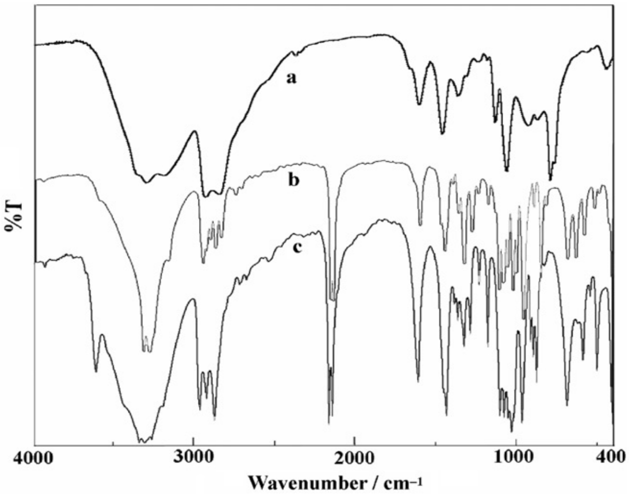

Figure 1. The FT–IR spectra of hydet-en (a), **1** (b) and **2** (c).

(2949, 2868) ν(CH), 1616 δ(NH), 1469 δ(CH) and 1067 cm^{-1} ν(CO). The stretching vibration of OH of **2** is observed at 3606 cm^{-1}, while the stretching vibrations of OH for **1** is observed at 3328 cm^{-1}. The ν(NH) vibrations of **1** and **2** are observed at 3288, 3172 and at 3338, 3303, 3259 cm^{-1}, respectively, due to splitting of the ν(NH) bands of the both complexes.

One of the interesting points in the cyano metal complexes is the bonding mode of ligand since both the carbon and the nitrogen atoms may be bonded to the metal ion. 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 a ligand field strength lower than ammonia [23]. The bridging systems are intermediate and this behaviour can be influenced by other coordinated ligands. Bridging of two metal ions in the form M–CN–M′, is well known, while alternate types of bridging are possible [24]. The cyano stretching wavenumber indicates the type of coordination shifting to higher wavenumbers than free cyano {2078 cm^{-1} in KCN, 2143 cm^{-1} in $K_2[Pd(CN)_4]$, 2150 cm^{-1} in $K_2[Pt(CN)_4]$} [24]. It has been observed that bridging (–CN–) cyano bands generally appear above 2150 cm^{-1}. Apart from that the cyano complexes also exhibit stretching and bending, M–C(N), bands in the low wavenumber region.

Two strong and sharp absorption bands at 2164 and 2141 cm^{-1} in the IR spectrum of complex **2** can easily be attributed to bridging cyano and terminal cyano bands, respectively, and the bands at 2160 and 2144 cm^{-1} in the IR spectrum of complex **1** correspond to bridging cyano and terminal cyano bands, respectively. The observed differences in these two cyano stretching vibrations are important evidence for formation of cyano-bridged complexes with the bridging cyano wavenumber higher than the terminal cyano. This shift was attributed to the kinematic coupling placing a mechanical constraint upon the bridging cyano by the second metal [18, 25].

In addition to cyano stretching bands, **1** and **2** exhibit Pd–C stretching and Pd–C–N bending bands in the regions of 600–350 cm^{-1}. The absorption bands observed at 515 and 480 cm^{-1} in **1** and in **2** at 499 and 463 cm^{-1} can be attributed to these stretching and bending vibrations, respectively.

3.2. *Structure of [Zn(hydet-en)$_2$Pd(CN)$_4$] (1)*

In the polymeric unit Pd(II) is coordinated by four cyanide ligands in a square-plane, as shown in figure 2. Two of the four cyano groups in *trans* positions bridge, whereas other cyano groups are terminal. The Pd–C bond lengths and C–Pd–C, N≡C–Pd bond angles (see table 2 for details) in the $[Pd(CN)_4]^{2-}$ anion are comparable with those found in previously reported $[Cu(dimen)_2Pd(CN)_4]$ [13] and $[Cu(en)_2Pd(CN)_4]$ [12] complexes. In **1**, like $Cu(dimen)_2^{2+}Pd(CN)_4^{2-}$ and $Cu(en)_2^{2+}Pd(CN)_4^{2-}$ complexes, the bridging cyano groups in both cation and anion are *trans*, classified as a 2,2-TT type chain. The zinc(II) ion has an octahedral coordination with four amine N atoms from two symmetry-related bidentate hydet-en ligands and two N atoms from the cyano groups. All the ligands show a *trans* arrangement of the donor atoms around the zinc(II) atom. The basal plane is constructed by the coordination of four N atoms of bidentate hydet-en ligands, and two N atoms of CN-groups occupy axial positions. In the basal plane, the Zn–N distances are in the range 2.138(2)–2.178(2) Å, while the axial Zn–N bond distance is 2.215(2) Å. The Zn–N (secondary amine) bond length is slightly longer than Zn–N (primary amine); this may be a consequence of steric differences between the N atoms. The angle subtended at the Zn(II) metal ion by the hydet-en ligand is 81.63(7)°, which is significantly greater than that of complex **2**. The C5≡N1–Zn bond angle is 168.70(2)°, resulting in a one-dimensional chain being formed while the Pd–C5≡N1 angle [178, 6(2)°] is essentially linear. This angle is comparable with those found previously {C≡N–Cd: 167.30(12)° [7]}. This deviation

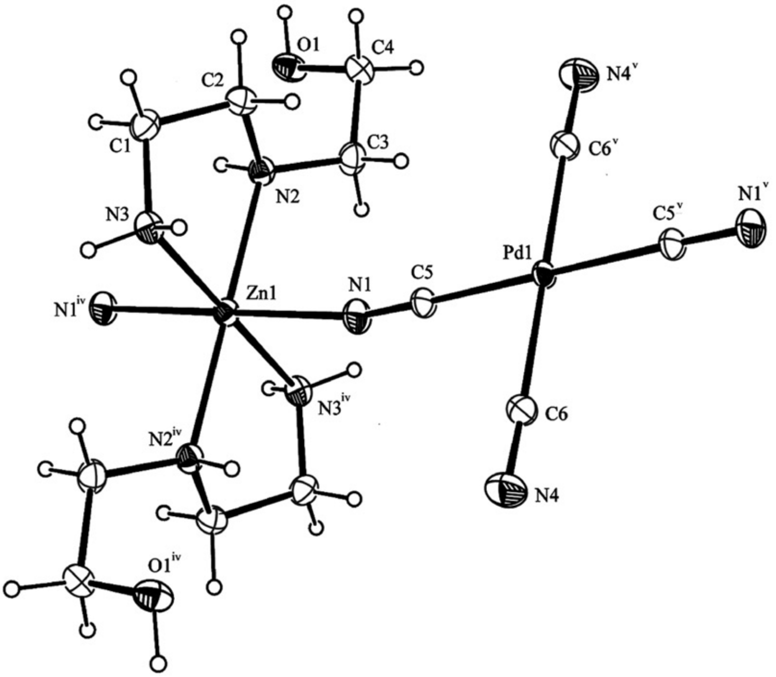

Figure 2. The molecular structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (iv) $1-x$, $2-y$, $1-z$ (v) $-x$, $2-y$, $-z$.]

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

1		**2**	
C5–N1	1.139 (3)	C5–N3	1.130(3)
C6–N4	1.133(3)	C6–N4	1.136(3)
C5–Pd1	1.9880(19)	C5–Pd1	1.987(2)
C6–Pd1	1.990(2)	C6–Pd1	1.989(3)
N3–Zn1	2.138(2)	N3–Cd1	2.328(2)
N1–Zn1	2.2150(19)	N1–Cd1	2.360(3)
N2–Zn1	2.1782(18)	N2–Cd1	2.3983(19)
C5–N1–Zn1	168.7(2)	N3–C5–Pd1	179.2(2)
N3–Zn1–N2	81.63(7)	N4–C6–Pd1	178.4(3)
N3–Zn1–N1	90.46(8)	N3–Cd1–N1	85.94(9)
N2–Zn1–N1	91.59(7)	N3–Cd1–N2	158.74(8)
N1–C5–Pd1	178.6(2)	N1–Cd1–N2	74.29(8)
N4–C6–Pd1	178.0(2)	C5–N3–Cd1	167.9(2)
N3–C5–Pd1	179.2(2)	C5–Pd1–C6	89.96(10)

Table 3. Hydrogen bonds (Å, °) for **1**[a] and **2**[b].

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	∠(DHA)
1				
N3–H1 ··· N4^{i}	0.845(17)	2.52(2)	3.329(3)	160(3)
N3–H2 ··· O1^{ii}	0.843(16)	2.27(2)	3.028(3)	149(2)
O1–H4 ··· N4^{iii}	0.82	2.02	2.799(3)	157.3
N2–H3 ··· O1	0.845(16)	2.50(3)	2.830(2)	104(2)
2				
N1–H1 ··· N4^{i}	0.81(4)	2.57(4)	3.306(4)	150(3)
N1–H2 ··· O1^{ii}	0.86(3)	2.35(3)	3.087(3)	143(3)
N2–H3 ··· O1	0.83(3)	2.44(3)	2.800(3)	108(2)
O1–H4 ··· N4^{iii}	0.82	2.04	2.848(3)	168

Symmetry codes: [a](i) x, y, $1+z$; (ii) $x-1$, y, z; (iii) $1-x$, $1-y$, $-z$.
[b](i) $1/2+x$, $1/2+y$, z; (ii) $1/2+x$, $y-1/2$, z; (iii) $-x$, $1+y$, $1/2-z$.

from linearity is greater than observed in related structures [26, 27]. However, in Cu(en)$_2^{2+}$Pd(CN)$_4^{2-}$ and Cu(dimen)$_2^{2+}$Pd(CN)$_4^{2-}$ complexes, the C≡N–Cu angles are 121.6(2)° and 123.1(2)°, respectively; these angles suggest some degree of ionic character of the Cu–N bond which is found to be smaller than the corresponding bound value of **1**. The Pd–C6≡N4 angle [178.0(2)°] is also almost linear, as expected.

The one-dimensional chains are linked to form a three-dimensional network *via* N–H ··· N, N–H ··· O, and O–H ··· N weak hydrogen bonds (see table 3 for details). NH, NH$_2$, and OH groups are involved in interchain hydrogen bonding, forming a layered structure (figure 3). The intramolecular Zn ··· Zn^{vi} [symmetry code (vi): $x-1$, y, $z-1$] distance is 10.625(7) Å, whereas the first and second shortest interchain Zn ··· Zn^{ii}, Zn ··· Zn^{vii} [symmetry code (ii): $x-1$, y, z, (vii): x, $y-1$, z] distances are 7.1950(5) and 7.9840(5) Å, respectively.

3.3. *Structure of [Cd(hydet-en)$_2$Pd(CN)$_4$] (2)*

The X-ray crystal structure determination of **2** reveals that Pd(II) is coordinated by four cyanide ligands (two cyano groups are terminal, whereas two *trans* cyano groups constitute the bridges) in a square-planar arrangement, as shown in figure 4. The Pd–C

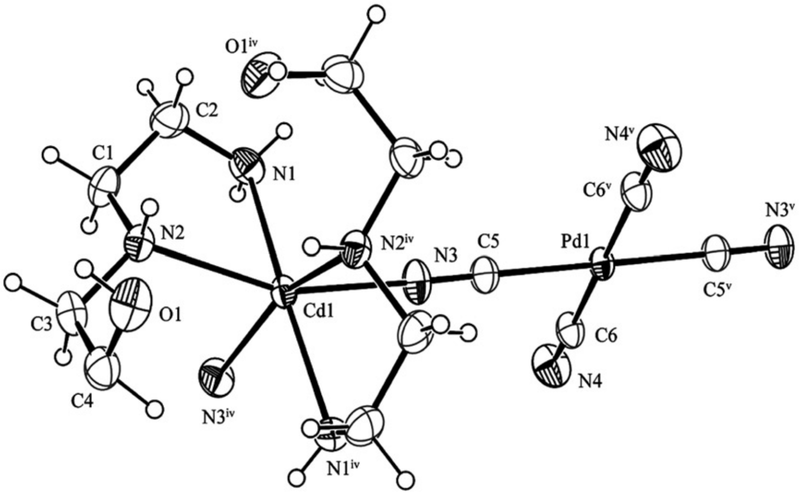

Figure 3. ORTEP III drawing of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (iv) $-x$, y, $0.5-z$; (v) $-x$, $-y$, $1-z$.].

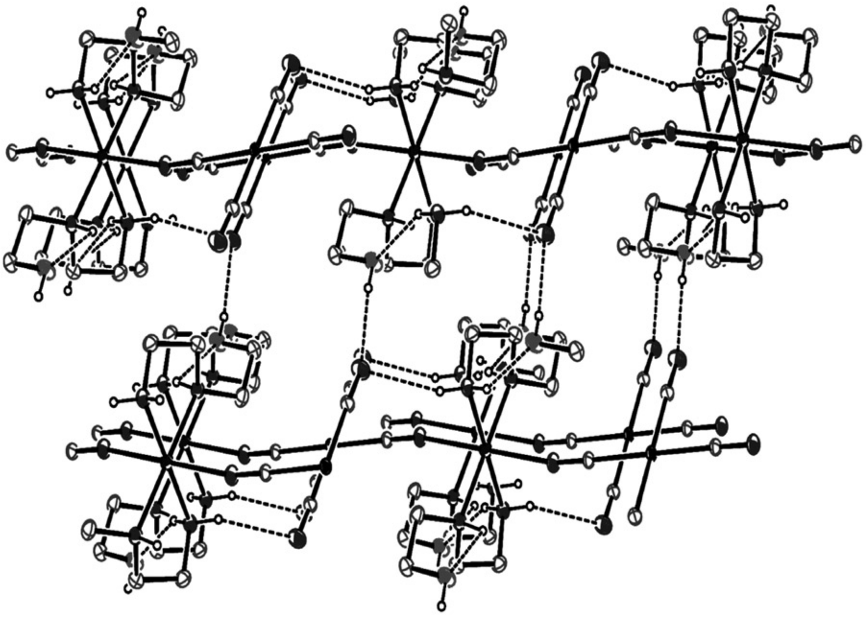

Figure 4. The zigzag chain structure of **1**, with intra- and interchain interactions shown as dashed lines.

bond lengths and C–Pd–C and N–C–Pd bond angles (table 2) in $[Pd(CN)_4]^{2-}$ are comparable with those found in previously reported heteronuclear $[Cu(en)_2^{2+}][Pd(CN)_4^{2-}]$ (en: ethylenediamine) [12] and $[Cu(dimen)_2^{2+}][Pd(CN)_4^{2-}]$ (dimen: dimethylethylenediamine) complexes [13] of the two bridging cyano groups in **2**, one is in a mutually *trans* position at the Pd atom and the other is *cis* at the Cd atom; the resulting chain can be classified as a 2,2-CT type. There are only a few examples of zigzag chain structures [28], and no Pd coordination polymer exhibiting a 2,2-CT type zigzag chain. The reason that two types of chains are observed, although the same ligands are used, can be attributed to ionic radius of Cd^{2+} ion which makes the N–Cd distance [2.328(2)] slightly bigger than that of N–Zn [2.215(2)]. This slight change may affect the orientation of CH_2CH_2OH groups. In $[Cu(en)_2Pd(CN)_4]$, $[Cu(dimen)_2^{2+}$ $Pd(CN)_4^{2-}]$, and $[Ni(en)_2Pd(CN)_4]$ [29], the bridging cyano groups in both cation and anion are *trans*. Therefore, these compounds are 2, 2-TT type chains.

The coordination environment of the Cd atom in **2** can be best described as distorted octahedral. The basal plane is constructed from three N atoms of the bidentate hydet-en ligand and $N3^{iv}$ of the cyanide group [symmetry code (iv): $-x$, y, $1/2-z$ $[Cu(en)_2Pd(CN)_4]$ [12], $[Cu(dimen)_2Pd(CN)_4]$ [13] whereas atoms N2 and N3 occupy the axial positions. The Cd–N distances reveal a small tetragonal distortion of the Cd–N_4 plane (r.m.s. deviation 0.1187 Å), with the Cd–N bonds to the secondary amines [2.398(2) Å] being slightly longer than the Cd–N bonds to the primary amines [2.360(3) Å]. The largest deviation from the basal plane is 0.1541(14) Å for atom $N1^{iv}$, and the Cd atom is 0.0004(9) Å out of this mean plane.

All the N–Cd–N bond angles deviate significantly from 90° or 180°, presumably the result of steric constraints. The angle subtended at the Cd atom by the hydet-en ligand is 74.29(8)°, in agreement with previously reported values for hydet-en-containing Cd(II) complexes [14, 16]. The C5≡N3–Cd1 bond angle is 167.9(2)°, resulting in the formation of a one-dimensional zigzag chain, while the Pd–C5≡N3 angle [179.2(2)°] is essentially linear. This angle is comparable with that found in our previously reported heteronuclear $[Ni(CN)_4Cd(hydet\text{-}en)_2]$ complex (C≡N–Cd 167.30(12)°) [16] and with the corresponding angle in **1**.

The crystal packing in **2** is formed by NH, NH_2 and OH groups, which are involved in interchain hydrogen bonding (figure 5). Each polymeric unit is linked

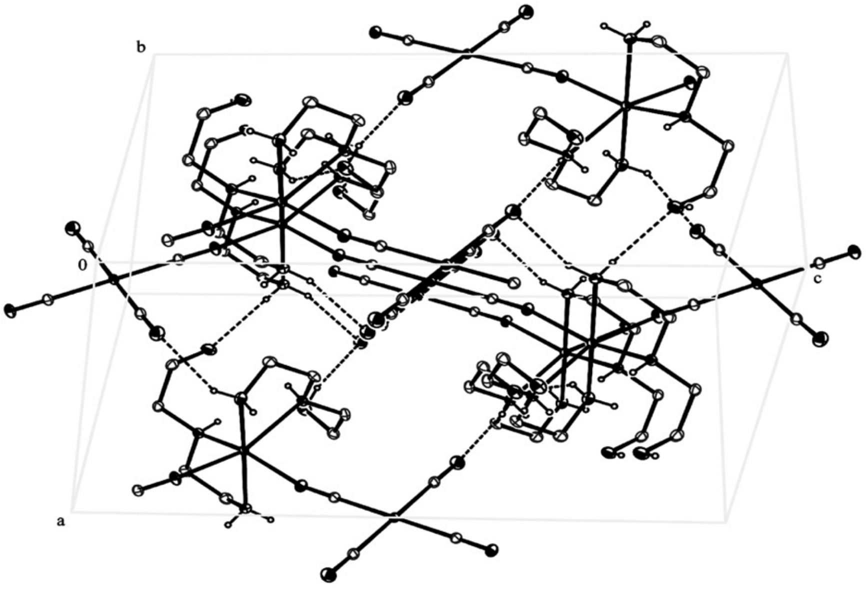

Figure 5. Three dimensional structure of **2**, with intra- and interchain interactions shown as dashed lines.

to a second unit via weak interchain N–H···N, N–H···O and O–H···N hydrogen-bonding interactions. These interactions are also effective in forming a layered structure, and the geometry of the interactions is given in table 3. The intramolecular Cd1···Cd1^{v} distance is 10.828(5) Å, whereas the shortest interchain Cd1···Cd1^{vi} distance is 7.583(2) Å [symmetry codes: (v) $-x$, $-y$, $1-z$; (vi) $x-1/2$, $y-1/2$, z].

4. Conclusions

One-dimensional cyano-bridged **1** and **2** coordination polymers have been prepared by the brick and mortar method and characterized. The most striking feature of these complexes is that these structures exhibit a 2,2-TT type chain for **1** and a 2,2-CT type zigzag chain for **2** in a repeated periodic fashion which is, to our knowledge, not reported before.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 294534 for $[ZnPd(CN)_4(C_4H_{12}N_2O)_2]$ and CCDC 294535 for $[CdPd(CN)_4(C_4H_{12}N_2O)_2]$. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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