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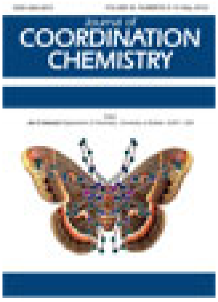

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Cyano-complexes and salts with tetracyanonickellate^{II} and N,N-bis(2-hydroxyethyl)-ethylenediamine: synthesis, IR spectra, magnetic properties, thermal analyses, and crystal structures

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Cyano-complexes and salts with tetracyanonickellate^{II} and *N*,*N*-bis(2-hydroxyethyl)-ethylenediamine: synthesis, IR spectra, magnetic properties, thermal analyses, and crystal structures

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Four cyano complexes, $[Ni(N\text{-}bishydeten)Ni(CN)_4]_n$ (**c1**), $[Cu(N\text{-}bishydeten)_2][Ni(CN)_4]$ (**c2**), $[Zn_2(N\text{-}bishydeten)_2Ni(CN)_4]_n$ (**c3**), and $[Cd(N\text{-}bishydeten)_2][Ni(CN)_4]$ (**c4**), have been synthesized and characterized by FT-IR, elemental, and thermal analyses. The structures of **c2** and **c4** were determined by single-crystal X-ray diffraction studies; both structures contain isolated cations and anions. The **c2** consists of $[Cu(N\text{-}bishydeten)_2]^{2+}$ with octahedrally coordinated Cu^{II} and diamagnetic $[Ni(CN)_4]^{2-}$, but **c4** consists of $[Cd(N\text{-}bishydeten)_2]^{2+}$, in which Cd^{II} is eight coordinate with two tetradentate *N-bishydeten* and diamagnetic $[Ni(CN)_4]^{2-}$. The value of the shape measure *S* (°) indicates that the coordination geometry around Cd^{II} lies along D_{2d} [dodecahedron; (dd)], C_{2v} [*b*icapped *t*rigonal *p*rism; (*btp*)], and D_{4d} [square *a*nti*p*rism; (*sap*)] but close to D_{2d} and D_{4d}. Variable temperature magnetic susceptibility measurements of **c1** and **c2** show the presence of little antiferromagnetic interaction below 20 K. Thermal analyses reveal that first neutral *N-bishydeten* and then cyano ligands were liberated from the complexes.

Keywords: Tetracyanonickellate^{II}; Bimetallic complexes; *N*,*N*-*Bis*(2-hydroxyethyl)-ethylenediamine; Eight-coordination; Thermal analysis; Magnetic properties

1. Introduction

Complexes containing cyano have attracted attention from different areas, ranging from chemistry to material science [1–4]. These compounds serve as models for the study of various physical properties associated with magnetism [5–9] and functional materials for catalysis [10, 11]. For instance, tetracyanonickellates are model

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compounds for magnetic studies at low temperatures, and $[Ni(CN)_4]^{2-}$ may bridge paramagnetic ions partially coordinated with amine ligands, forming 1-D, 2-D, and 3-D structures [12].

In general synthetic design of cyano-complexes can be based on the *brick* and *mortar* method. In this method, metals coordinated by suitable ligand(s) form *brick* and $[Ni(CN)_4]^{2-}$ forms *mortar* [13, 14]. Cationic Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} usually adopt a coordination number of six whereas Cd^{II} rarely adopts eight coordination in cyano complexes.

Complexes with tetracyanonickellate have been systemically studied. Paharová *et al.* [15] prepared 1-D $[Ni(L')(L'')Ni(CN)_4]_n$ (L′: diethylenetriamine (*dien*), L″: 2-aminoethanole (*mea*)), and ionic $[Ni(aepn)_2][Ni(CN)_4]\cdot H_2O$ (*aepn*: *N*-(2-aminoethyl)-1,3-propanediamine) cyanocomplexes. Karadağ and co-workers synthesized and characterized $[M(hydeten)_2Ni(CN)_4]$ {*hydeten*: *N*-(2-hydroxyethyl)-ethylenediamine M^{II}: Ni, Cu, Zn, and Cd)} [16, 17], $[Ni(edbea)Ni(CN)_4]\cdot 1/2H_2O$, $[Cu(\mu\text{-}edbea)(\mu\text{-}CN)_2Ni(CN)_2]\cdot H_2O$ {*edbea*: 2,2′-(ethylenedioxy)*bis*(ethylamine)} [18], $[M(bishydeten)Ni(CN)_4]$ {*bishydeten*: *N*,*N*′-*bis*(2-hydroxyethyl)-ethylenediamine M^{II}: Ni, Zn, and Cd)} [19], $[Zn(edbea)Ni(CN)_4]$ [19], and $[Cd(edbea)_2][Ni(CN)_4]\cdot 2H_2O$ [20] complexes. On the other hand, the $\{[Ni(hto)Ni(CN)_4]\cdot(i\text{-}C_3H_7OH)\cdot 2H_2O\}_n$ (*hto*: 1,3,6,9,11,14-hexaaza tricyclooctadecane) [21]; $[Cu(HL)]_2[Ni(CN)_4]$ (H_2L = 3,9-dimethyl-4,8-diazaundec-3, 8-diene-2,10-dionedioxime) [22]; $[\{Cu_2(L)_2Ni(CN)_4\}(ClO_4)_2\cdot xH_2O]_n$ (for 1, L: bis(3-aminopropyl) methylamine: *medpt* and $x = 2.5$, for 2, L = *N*-(2-aminoethyl)-1,3-propanediamine: *aepn* and *x*: 2; for 3, *L* = diethylene triamine: *dien* and $x = 1$) and $[Cu(medien)Ni(CN)_4]_n$ (*medien*: bis(2-aminoethyl)methylamine) were synthesized and characterized by single-crystal X-ray structure analysis [23] and the $[Ni(en)_2Ni(CN)_4]$ (*en* = ethylenediamine) [24], $[Ni(en)_2Ni(CN)_4]_2\cdot 2.16H_2O$ [25], $[Ni(hmtd)Ni(CN)_4]\cdot H_2O$ (*hmtd* = *N*-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) [26], $[Ni(bpy)_2Ni(CN)_4]$ (bpy = 2,2-bipyridine) [27], $[Ni(pn)_2Ni(CN)_4]\cdot H_2O$ (*pn* = 1,2-diaminopropane) [28], $[Cu(en)_2Ni(CN)_4]$ [29], 2-D structure of $[Cu(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$ [30], $\{[Ni(tren)][Ni(CN)_4]\}_n$ (*tren* = tris(2-aminoethyl)amine) [31], and $Zn(DMF)_2Ni(CN)_4$ [32] were also studied.

In this study, four coordination complexes of Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} with *N-bishydeten* and $[Ni(CN)_4]^{2-}$ have been synthesized. Complexes **c1**, **c2**, **c3**, and **c4** were by infrared (IR) spectra, elemental, and thermal analyses. The crystal structures of **c2** and **c4** were determined using X-ray diffraction analysis. In addition, the magnetic properties and electron paramagnetic resonance (EPR) spectra of **c1** and **c2** were also established.

2. Experimental

2.1. *Materials and instrumentation*

$NiCl_2\cdot 6H_2O$ (Surchem), $CuCl_2\cdot 2H_2O$ (Merck), $ZnCl_2$ (Panreac), $CdSO_4\cdot 8/3H_2O$ (Sigma), KCN (Merck), and *N*,*N*-bis(2-hydroxyethyl)-ethylenediamine ($C_6H_{16}N_2O_2$) (Aldrich) were used as purchased without purification.

Elemental analyses (C, H, and N) were carried out by standard methods (Middle East Technical University, Central Laboratory, Research-Development Education,

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and Measure Center). IR spectra were taken by using a Jasco 430 FT-IR spectrophotometer on KBr pellets from 4000 cm^{-1} to 400 cm^{-1}. Thermal decomposition of approximately 5–10 mg of the complexes were realized under nitrogen at a heating rate of 10°C min^{-1} from 35°C to 1200°C and α-Al_2O_3 was used as a reference on a PYRIS Diamond TG/DTA (DSC) Thermal Analysis Instrument. EPR powder spectrum was recorded with a Bruker EMX X-band spectrometer (9.8 GHz) with about 20 mW microwave power and 100 kHz magnetic field modulation. The 10–300 K magnetization measurements were carried out on a Quantum Design PPMS system. χ–T graphs were recorded under constant magnetic field of 0.5 kOe.

2.2. *Syntheses*

2.2.1. [Ni(*N-bishydeten*)Ni(CN)$_4$]$_n$ (c1). For the first preparation step, KCN (0.22 g, 3.36 mmol) was added to $NiCl_2 \cdot 6H_2O$ (0.2 g, 0.84 mmol) in water (20 mL). Then, $NiCl_2 \cdot 6H_2O$ (0.2 g, 0.84 mmol) was added to the clear yellow solution and stirred for a few minutes. Finally, *N*,*N*-bis(2-hydroxyethyl)-ethylenediamine (0.156 g, 1.68 mmol) in ethanol (15 mL) was added dropwise. The resulting lilac precipitate was collected by filtration and then washed with ethanol and water, and dried in air. Yield: 57%. Anal. Calcd for **c1** (%): C, 32.49; H, 4.36; N, 22.73. Found (%): C, 32.71; H, 4.65; N, 22.53. IR (KBr disc, cm^{-1}): 3595, 3201 (ν_{OH}); 3305, 3278 (ν_{NH}); 2985, 2935, 2895, 2860 (ν_{CH}); 2164, 2129 ($\nu_{C\equiv N}$); 1625 (δ_{NH}); 1475, 1455 (δCH_2); 1203, 1016 (ν_{CN}); 1030 (ν_{CO}).

2.2.2. [Cu(*N-bishydeten*)$_2$][Ni(CN)$_4$] (c2). KCN (0.22 g, 3.36 mmol) was added to water/ethanol mixture (15 mL/5 mL) containing $NiCl_2 \cdot 6H_2O$ (0.2 g, 0.84 mmol). When the solution became clear yellow, an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.14 g, 0.84 mmol) was added slowly with continuous stirring. An ethanol solution of *N-bishydeten* (0.24 g, 1.68 mmol) was added dropwise to this green slurry. For dissolution, dilute aqueous solution of ammonia was added slowly to the cloudy blue solution. The resulting deep blue solution was filtered to avoid the presence of any solid impurities and blue single crystals suitable for X-ray diffraction were obtained on keeping at room temperature for a few weeks. They were collected by filtration. The yield was about 44%. Anal. Calcd for **c2** (%): C, 36.76; H, 6.17; N, 21.45. Found (%): C, 36.17; H, 5.86; N, 20.92. IR (KBr, cm^{-1}): 3385, 3147 (ν_{OH}); 3283, 3229 (ν_{NH}); 2979, 2946, 2912, 2889, 2822 (ν_{CH}); 2118 ($\nu_{C\equiv N}$); 1645 (δ_{NH}); 1468 (δCH_2); 1145 (ν_{CN}); 1059, 1010 (ν_{CO}).

2.2.3. [Zn$_2$(*N-bishydeten*)$_2$Ni(CN)$_4$]$_n$ (c3). The synthesis of **c3** was similar to **c1**. The yield of **c3** is about 40%; Anal. Calcd for **c3** (%): C, 32.57; H, 5.47; N, 18.99. Found (%): C, 32.82; H, 5.16; N, 18.95. IR (KBr disc, cm^{-1}): 3238 (ν_{OH}); 3126 (ν_{NH}); 2981, 2954, 2885, 2848, 2822 (ν_{CH}); 2156, 2133 ($\nu_{C\equiv N}$); 1581 (δ_{NH}); 1467 (δCH_2); 1149 (ν_{CN}); 1061, 1026 (ν_{CO}).

2.2.4. [Cd(*N-bishydeten*)$_2$][Ni(CN)$_4$] (c4). Complex **c4** was synthesized as for **c2** and the yield was about 71%; Anal. Calcd for **c4** (%): C, 33.62; H, 5.64; N,

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Table 1. Crystal data and structure refinement parameters for **c2** and **c4**.

Empirical formula	C_{16} $H_{32}N_8O_4NiCu$	C_{16} $H_{32}N_8O_4NiCd$
Formula weight	522.75	571.61
Temperature (K)	293	293
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	7.5415(5)	13.9735(9)
b	9.3542(6)	13.8142(9)
c	9.7128(6)	12.2527(9)
α	95.687(5)	90.00
β	111.834(4)	104.516(5)
γ	113.726(10)	90.00
Volume (Å^3), Z	556.78(6), 1	2289.7(3) 4
Calculated density (Mg m^{-3})	1.559	1.658
Absorption coefficient (mm^{-1})	1.839	1.789
F(000)	273	1168
Crystal size (mm^3)	0.480 × 0.413 × 0.310	0.61 × 0.40 × 0.26
θ range for data collection (°)	2.36–26.93	2.11–27.75
Limiting indices	$-9 \leq h \leq 9$; $-11 \leq k \leq 11$; $-12 \leq l \leq 12$	$-18 \leq h \leq 18$; $-17 \leq k \leq 17$; $-15 \leq l \leq 15$
Reflections collected	11,878	41,257
Independent reflection	2167	4086
Absorption correction	Multi-scan	Integration
Data/restraints/parameters	2393/1/144	5308/37/311
Goodness-of-fit on F^2	1.066	1.194
R indices (all data)	$R_1 = 0.026$, $wR_2 = 0.065$	$R_1 = 0.1029$, $wR_2 = 0.1957$
w	$1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.2420P]$ $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0000P)^2 + 35.6206P]$ $P = (F_o^2 + 2F_c^2)/3$
S, $\Delta\sigma_{max}$	1.08/0.000	1.190/0.000
Largest difference peak and hole (e Å^{-3})	0.336 and −0.293	2.144 and −3.898

19.60. Found (%): C, 33.96; H, 5.83; N, 19.47. IR (KBr, cm^{-1}): 3352 (ν_{OH}); 3298 (ν_{NH}); 2886, 2838 (ν_{CH}); 2124 ($\nu_{C\equiv N}$); 1643 (δ_{NH}); 1480, 1453 (δCH_2); 1246 (ν_{CN}); 1080, 1037 (ν_{CO}).

2.3. *X-ray crystallography*

Crystals suitable for data collection were mounted on a glass fiber and data collections were performed on a STOE IPDS 2 diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 273 K. Details of crystal data, data collections, and refinements are given in table 1. The structures were solved by direct-methods using SHELXS-97 [33] and refined by full-matrix least-squares on F^2 using SHELXL-97 [34]. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in calculated positions (C–H 0.97 Å and N–H 0.90 Å) and refined isotropically using a riding model with $U = 1.2U$ of the parent atom. The coordinates of the hydroxyl hydrogen atoms were obtained from difference map and refined isotropically with U 1.5 times that of attached oxygen atoms. CH_2 groups of one *N-bishydeten* ligand were disordered over two sites with occupation factor of 0.37(2) and 0.63(2).

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3. Results and discussion

3.1. *FT-IR spectra*

Characteristic IR absorptions of *N-bishydeten* are observed at 3400–3250 (2948, 2876, and 2832), 1570, 1471, 1148, and 1036 cm^{-1} from $\nu_{O–H}$–$\nu_{N–H}$, $\nu_{C–H}$, $\delta_{N–H}$, δ_{CH2}, $\nu_{C–N}$, and $\nu_{C–O}$, respectively [35].

Absorptions of cyano complexes can be easily identified since they exhibit sharp $\nu_{C\equiv N}$ at 2200–2000 cm^{-1}. The stretching frequency of free cyanide is 2080 cm^{-1} in aqueous solution and when it coordinates to a metal, $\nu_{C\equiv N}$ shifts to higher frequency [36]. For instance, in free tetracyanonickellate this absorption is observed at 2128 cm^{-1} [37].

The positions of the relevant IR bands are listed in section 2. Complex formations were proved by determining the characteristic peaks of cyano and *N-bishydeten* ligands in the complexes. The presence of two cyano stretching vibrations is important evidence for formation of cyano-bridged complexes with bridged cyano group at higher frequency and the other to terminal cyano. Vibration assignments were given for all the observed bands and the spectral features supported the structures of **c1** and **c3** as polymeric complexes. Absorptions in **c1** (2129 cm^{-1} and 2164 cm^{-1}) and **c3** (2156 cm^{-1} and 2133 cm^{-1}) result from the presence of both bridging and terminal cyano in the structures. Only one absorption of ionic **c2** and **c4** was observed at 2118 cm^{-1} and 2124 cm^{-1}, respectively, because there was no bridging cyano. These results were verified by X-ray analysis. The presence of the N- and O-donors in all four complexes was disclosed by various absorptions due to vibrations of CH_2, OH, and NH_2. In these complexes, $\nu_{O–H}$ shifted to lower frequencies showing that *N-bishydeten* coordinates to Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} with oxygen. While $\nu_{O–H}$ at 3595 cm^{-1} was due to the presence of free OH in **c1**, the $\nu_{O–H}$ at 3147 cm^{-1} is attributed to the formation of O–H···N type hydrogen bond in **c2**. IR spectra of $[Cd(\mathit{edbea})_2][Ni(CN)_4]\cdot 2H_2O$ and $[Cd(\mathit{edbea})_2][Pd(CN)_4]$ [20] were similar to **c4**. All the other bands appear more or less at their usual positions.

3.2. *Structures of c2 and c4*

The molecular structure of **c2** is ionic (complex salt) and is made of isolated [Cu(*N-bishydeten*)$_2$]$^{2+}$ which are six-coordinate ($S = 1/2$) and planar diamagnetic $[Ni(CN)_4]^{2-}$. The structure of the cation is similar to that reported previously for [Cu(*N-bishydeten*)$_2$][Pd(CN)$_4$] and [Ni(*N-bishydeten*)$_2$][Pt(CN)$_4$] [20]. The ORTEP of the complex indicating the atom-numbering schemes is shown in figure 1. The copper of the cation is six-coordinate with two *N-bishydeten* ligands. The coordination sphere is completed by four nitrogen atoms at equatorial position and two oxygen atoms at axial positions from *N-bishydeten*. *N-bishydeten* is tridentate in this complex. The coordination environment of the Cu^{II} ion can be described as distorted octahedral, whereas Ni^{II} is square-planar by four CN^{-} which are all terminal. Selected bond distances and angles for **c2** are listed in table 2.

The bond distances of axial positions in the cation are longer than equatorial because of Jahn–Teller distortion at Cu^{II} (d^9). Both *N-bishydeten* molecules have identical coordination environments. The bond between the tertiary amine nitrogen and Cu^{II} is longer than that with the primary amine nitrogen, attributed to the steric constraints arising from the shape of the ligand. Cu–N distances are similar to Ni–N distances in

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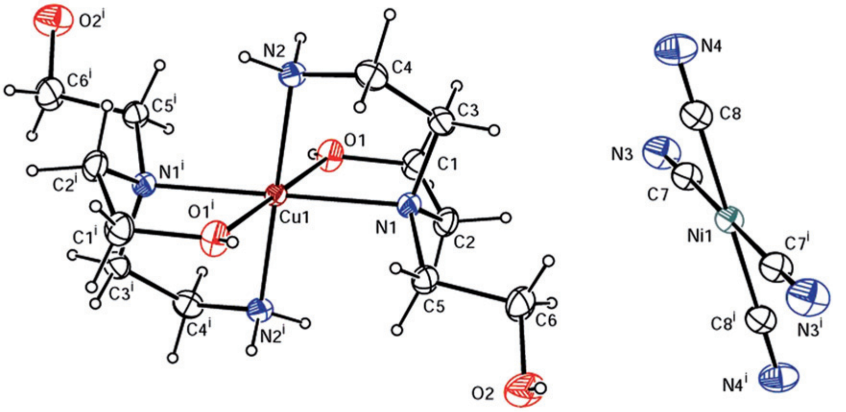

Figure 1. An ORTEP illustration of **c2**, [*trans-bis*[(*N*,*N*-bis(2-hydroxyethyl)-ethylenediamine-2κ^3*N*,*N′*,*O*)-*copper*^{II}][(*tetracyano-κC*)-*nickellate*^{II}] {Symmetry code: ^{i} $1-x$, $1-y$, $1-z$}.

Table 2. Selected bond lengths (Å) and angles (°) for **c2**.

Cu(1)–N(1)	2.1113(16)	Ni(1)–C(8)	1.861(2)
Cu(1)–N(2)	2.0292(16)	N(3)–(7)	1.139(3)
Cu(1)–O(1)	2.3154(16)	N(4)–C(8)	1.139(3)
Ni(1)–C(7)	1.859(2)		
N(1)–Cu(1)–N(1)	180.00(6)	C(7)–Ni(1)C(7)	180.00(1)
N(2)–Cu(1)–N(2)	180.0	C(8)–Ni(1)–C(8)	180.0
N(2)–Cu(1)–N(1)	83.24(7)	C(7)–Ni(1)–C(8)	89.55(9)
O(1)–Cu(1)–O(1)	180.00(9)	N(1)–Cu(1)–O(1)	77.46(6)
Ni(1)–C(7)–N(3)	178.8(2)	N(2)–Cu(1)–O(1)	87.87(7)
Ni(1)–C(8)–N(4)	178.50(19)		

[Ni(*aepn*)$_2$][Ni(CN)$_4$]$\cdot$H$_2$O and [Ni(*N-bishydeten*)$_2$][Pt(CN)$_4$] complexes with a few differences from ion radii [15]. The Cu–N and Cu–O bond distances of **c2** are comparable to [Cu(*N-bishydeten*)$_2$][Pd(CN)$_4$] with the equatorial and axial bond lengths [Cu1–N1: 2.003(4) Å, Cu1–N2: 2.110(4) Å (equatorial); Cu1–O1: 2.403(3) Å (axial)]. The Ni–C bond distances of 1859–1866 Å are similar to those found in [Cd(*edbea*)$_2$][Ni(CN)$_4$]$\cdot$2H$_2$O [20] [Ni(*aepn*)$_2$][Ni(CN)$_4$]$\cdot$H$_2$O, [Cu(*N-Eten*)$_2$Ni(CN)$_4$] [38], [Cu(*dpt*)Ni(CN)$_4$] [13], [Zn(*en*)$_2$Ni(CN)$_4$]$_n$, and [Cd(*en*)$_2$Ni(CN)$_4$]$_n$ [39].

Crystal packing and stability are achieved by intra- and intermolecular conventional and non-conventional hydrogen bonds, HBs. These HBs are observed between NH$_2$, OH, and CH$_2$ of *N-bishydeten* and nitrogen atoms of the cyanides (table 3). The O(2)–H(2)$\cdots$N(3)^{ii} HB-chains cations and anions, and forms a 1-D structure (figure 2a). This 1-D structure is changed by O(1)–H(1)$\cdots$N(4)^i and a 2-D structure forms (figure 2b); all of the HBs are effective in forming a layered structure (figure 2c). The shortest distance between inter-centers Cu$\cdots$Cu distances in the 2-D structure is 9.360 Å, as the largest inter-centers distance between Ni$\cdots$Ni in the 2-D structure is 14.342 Å. The neighbor Ni$\cdots$Cu distance in the 1-D structure composed by HB-chains is 10.281 Å, whereas the nearest Ni$\cdots$Cu distance in the 2-D is 6.400 Å.

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Table 3. Hydrogen bonds (Å, °) for **c2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1)–H(1)···N(4)^{i}	0.77	2.09	2.849(3)	168
O(2)–H(2)···N(3)^{ii}	0.82	2.03	2.745(4)	145
N(2)–H(2C)···N(4)^{iii}	0.90	2.46	3.300(4)	155
N(2)–H(2D)···N(3)^{iv}	0.90	2.49	3.301(3)	151
C(5)–H(5A)···O(2)^{v}	0.97	2.58	3.364(3)	138

Symmetry codes: ^{i} $1-x, 1-y, 1-z$; ^{ii} $2-x, 1-y, -z$; ^{iii} $-1+x, y, z$; ^{iv} $1-x, -y, -z$; ^{v} $2-x, 2-y, 1-z$.

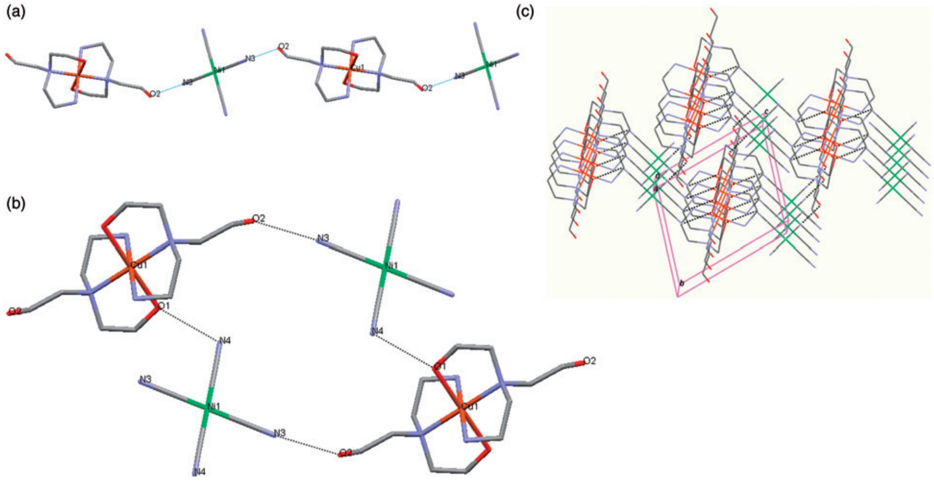

Figure 2. (a) The 1-D, (b) 2-D, and (c) layered unit cell structure of **c2** (intermolecular HBs shown as black dashed line).

As can be seen in figure 3(a), the structure of **c4** results from [Cd(*N-bishydeten*)$_2$]$^{2+}$ cationic unit in which Cd^{II} is eight-coordinate, bound to four nitrogen atoms [Cd1–N1, 2.444(9); Cd1–N2, 2.294(11); Cd1–N3, 2.435(9); Cd1–N4, 2.299(10)] and four oxygen atoms [Cd1–O1, 2.588(9); Cd1–O2, 2.649(9); Cd1–O3, 2.604(10); Cd1–O4, 2.597(10)] from two tetradentate *N-bishydeten* and [Ni(CN)$_4$]$^{2-}$. The selected bond lengths and angles of **c4**, [*trans-bis[(N,N-bis(*2-hydroxyethyl)-ethylenediamine-2κ^4*N,N′,O,O′*) cadmium^{II}] [(*tetracyano-κC*)*nickellate*^{II}], are given in table 4.

The geometry of the eight-coordinate cadmium (figure 3b) is rather complicated since the closest idealized polyhedron is not usually straightforward. Burdett *et al.* [40] have presented a systematic molecular orbital analysis of eight-coordinate molecules in all possible geometries; dodecahedron (dd), square antiprism (*sap*), bicapped trigonal prism (*btp*), cube (*cb*), hexagonal bipyramid (*hbp*), square prism (*sp*), bicapped trigonal antiprism (*btap*). Muetterties and Wright [41] reported that the structures with dd, *sap*, and *btp* geometry were low-energy structures. Haigh has advised a simple criterion for distinguishing the types of low-energy structures. The 16th, 17th, and 18th lowest L–M–L′ angles in the Cd^{II} cation are 112.39°, 102.87°, and 99.32°. Thus, we cannot satisfactorily classify the structure as dd, *sap* or *btp* but rather as somewhat distorted structure. Since the symmetry of the complex deviates significantly from an idealized

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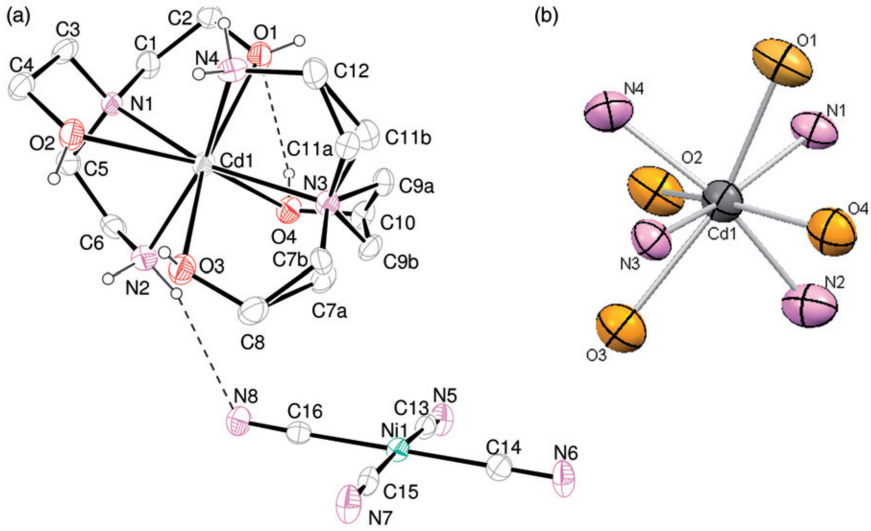

Figure 3. (a) An ORTEP drawing of **c4** with the atom-numbering scheme (the hydrogen atoms of CH$_2$ are omitted for the sake of clarity); (b) coordination polyhedron in the [Cd(*N-bishydeten*)$_2$]$^{2+}$.

Table 4. Selected bond lengths (Å) and angles (°) for **c4**.

Cd(1)–O(1)	2.588(9)	Cd(1)–N(3)	2.435(9)
Cd(1)–O(2)	2.649(9)	Cd(1)–N(4)	2.299(10)
Cd(1)–O(3)	2.604(10)	Ni(1)–C(13)	1.875(14)
Cd(1)–O(4)	2.597(10)	Ni(1)–C(14)	1.856(12)
Cd(1)–N(1)	2.444(9)	Ni(1)–C(15)	1.874(14)
Cd(1)–N(2)	2.294(11)	Ni(1)–C(16)	1.877(12)
C(14)–Ni(1)–C(15)	89.5(5)	N(4)–Cd(1)–O(4)	126.6(3)
C(13)–Ni(1)–C(14)	89.6(5)	N(3)–Cd(1)–O(4)	69.5(3)
C(13–Ni(1)–C(15)	176.6(5)	N(1)–Cd(1)–O(4)	99.3(3)
C(14)–Ni(1)–C(16)	179.8(6)	O(1)–Cd(1)–O(4)	69.1(3)
C(15)–Ni(1)–C(16)	90.4(5)	N(2)–Cd(1)–O(3)	76.2(4)
C(13)–Ni(1)–C(16)	90.5(5)	N(4)–Cd(1)–O(3)	90.2(3)
N(2)–Cd(1)–N(4)	159.8(4)	N(3)–Cd(1)–O(3)	69.9(3)
N(2)–Cd(1)–N(3)	112.8(3)	N(1)–Cd(1)–O(3)	128.2(3)
N(4)–Cd(1)–N(3)	75.1(3)	O(1)–Cd(1)–O(3)	160.4(3)
N(2)–Cd(1)–N(1)	75.4(3)	O(4)–Cd(1)–O(3)	112.4(3)
N(4)–Cd(1)–N(1)	102.8(3)	N(2)–Cd(1)–O(2)	88.2(4)
N(3)–Cd(1)–N(1)	161.9(3)	N(4)–Cd(1)–O(2)	73.0(3)
N(2)–Cd(1)–O(1)	121.4(4)	N(3)–Cd(1)–O(2)	127.7(3)
N(4)–Cd(1)–O(1)	74.8(4)	N(1)–Cd(1)–O(2)	66.8(3)
N(3)–Cd(1)–O(1)	93.6(3)	O(1)–Cd(1)–O(2)	116.1(3)
N(1)–Cd(1)–O(1)	68.7(3)	O(4)–Cd(1)–O(2)	159.3(3)
N(2)–Cd(1)–O(4)	73.0(4)	O(3)–Cd(1)–O(2)	69.9(3)

geometry, it was decided to analyze the geometry using all the dihedral angles (one for each pair of adjacent triangular planes) in the polyhedron as suggested by Xu *et al.* [42],

$$S = \min\left[\frac{1}{m}\sqrt{\sum_{i=1}^{m}(\delta_i - \theta_i)^2}\right]$$

Table 5. Atomic coordinates used for shape measure.

Atom	*x*	*y*	*z*
O1	0.3776(6)	0.5829(8)	0.8556(8)
O2	0.0998(6)	0.4145(8)	0.8125(8)
O3	0.1302(7)	0.3669(7)	0.5838(8)
O4	0.3099(7)	0.6250(7)	0.6131(7)
N1	0.1738(6)	0.6040(7)	0.8486(7)
N2	0.1035(8)	0.5832(9)	0.6061(9)
N3	0.3354(6)	0.4188(7)	0.6133(8)
N4	0.3124(8)	0.3770(8)	0.8361(8)

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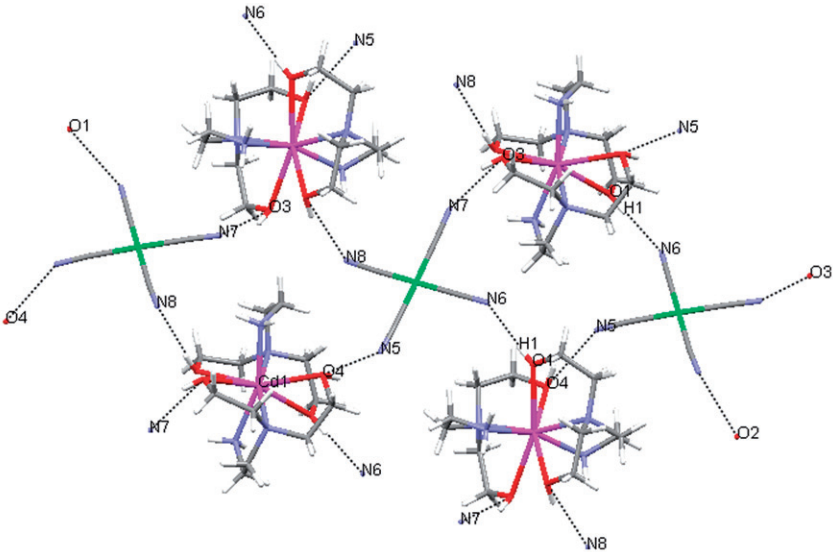

Figure 4. The 1-D structure of **c4** in the *bc*-plane connected through H-bonds.

where $m =$ number of edges, $\delta =$ angle between normals of adjacent faces, $\delta_{\mathrm{I}} =$ observed dihedral angle along the *i*th edge of δ, and θ same angle of corresponding ideal polytonal shape θ. The smallest S value is the one closest to describing the coordination geometry. We have used the Matlab® code developed by Xu *et al*. to calculate shape. Atomic coordinates used for shape measure calculation are given in table 5. The shape measure S $(^{\mathrm{o}})$ is given below for dd ($D_{2\mathrm{d}}$), *btp* ($C_{2\mathrm{v}}$), and *sap* ($D_{4\mathrm{d}}$): S ($D_{2\mathrm{d}}$), 15.5°; S ($C_{2\mathrm{v}}$), 18.9°; S ($D_{4\mathrm{d}}$), 15.4°. These values of S indicate that the coordination geometry around Cd$^{\mathrm{II}}$ lies along $D_{2\mathrm{d}}$, $C_{2\mathrm{v}}$, and $D_{4\mathrm{d}}$ but it is closer to $D_{2\mathrm{d}}$ and $D_{4\mathrm{d}}$. The Ni$^{\mathrm{II}}$ is essentially planar with *rms* (*r*oot *m*ean *s*quare) deviation of 0.0706 Å.

The packing favors formation of an H-bonding scheme attained through N5, N6, N7, and N8 atoms of $[\mathrm{Ni(CN)_4}]^{2-}$ with the Hs of O(1)–H(1), O(2)–H(2), O(3)–H(3), and O(4)–H(4) of [Cd(*N-bishydeten*)$_2$]$^{2+}$ (figure 4). As is seen in table 6, other interactions are viable between O(4)–H(4) $\cdots$ O(1), N(2)–H2NA $\cdots$ N(8), N(2)–H2NB $\cdots$ N(8)$^{\mathrm{ii}}$, N(4)–H4NA $\cdots$ N(6), and N(4)–H4NB $\cdots$ N(7)$^{\mathrm{iii}}$ giving a 3-D network.

Table 6. Hydrogen bonds (Å, °) for **c4**.

D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	∠(DHA)
O(4)–H(4) ··· O(1)	0.86(9)	2.48(15)	2.942(13)	115(13)
O(1)–H(1) ··· N(6)^{i}	0.79(9)	2.05(9)	2.844(13)	176(18)
O(2)–H(2) ··· N(8)^{ii}	0.82(8)	2.12(11)	2.872(14)	152(15)
O(3)–H(3) ··· N(7)^{iii}	0.82(9)	2.03(10)	2.793(16)	156(16)
O(4)–H(4) ··· N(5)^{iv}	0.86(9)	2.08(12)	2.793(15)	140(14)
N(2)–H2NA ··· N(8)	0.90	2.61	3.455(15)	157.1
N(2)–H2NB ··· N(8)^{ii}	0.90	3.11	3.917(17)	150.9
N(4)–H4NA ··· N(6)	0.90	2.67	3.522(16)	159.3
N(4)–H4NB ··· N(7)^{iii}	0.90	2.75	3.472(17)	138.2

Symmetry codes: ^{i} $1-x, 1-y, 1-z$; ^{ii} $-x, 1-y, 1-z$; ^{iii} $x, 1/2-y, 1/2+z$; ^{iv} $x, 1.5-y, 1/2+z$.

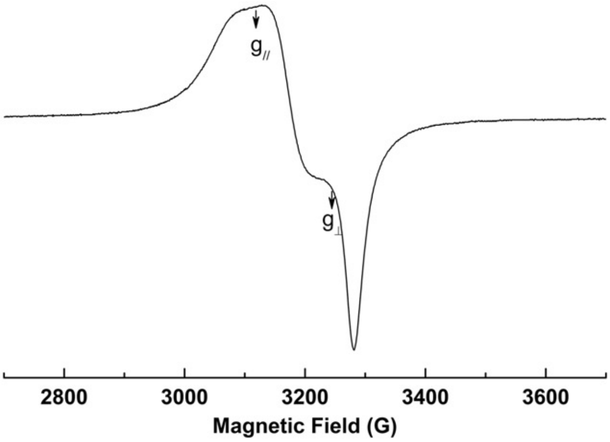

Figure 5. The powder EPR spectrum of **c2** at room temperature.

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The shortest distances between Ni···Ni and Cd···Cd are 9.559 and 9.610 Å, respectively, while the largest distances are 10.139 and 10.100 Å, respectively. When distances in adjacent Ni ··· Cd centers are compared, the distances between Ni···Cd inter-centers are 7.052, 6.989, 6.850, and 6.985 Å.

3.3. *Magnetic susceptibility*

The Ni^{II} ions in the complexes with the square-planar coordination are low spin ($S=0$), diamagnetic. For **c1** with octahedral coordination, Ni^{II} can have short relaxation times at room temperature. Because of these reasons, an EPR spectrum for the Ni^{II} ions was not observed.

Figure 5 shows the powder EPR spectrum of **c2** at room temperature. This spectrum is from Cu^{II} ($S=1/2$, $I=3/2$). Two components, one parallel and the other perpendicular, are observed in this spectrum. Hyperfine splitting could not be resolved due to line broadening from spin-exchange and spin–orbital interactions because of the excess spin concentration. The principal values of *g*-factor were $g_{\parallel}=2.183$ and

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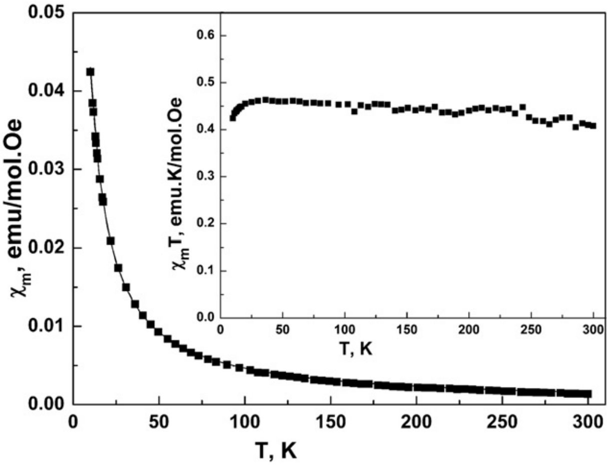

Figure 6. The temperature dependence of the molar magnetic susceptibility χ_m for **c2**. Solid line represents a fit by the Curie−Weiss law. Inset: The temperature dependence of $\chi_m T$.

$g_{\perp} = 2.088$ from the powder EPR spectrum at room temperature. The g parameters indicate the paramagnetic center is axially symmetric. From the order of $g_{\parallel} > g_{\perp} > g_e$ (free electron g value, $g_e = 2.0023$), Cu^{II} is located in tetragonal distorted octahedral sites (D_{4h}), elongated along the z-axis and the ground state of the paramagnetic electron is d_{x2-y2} ($^2B_{1g}$ state) [43–46].

The magnetic susceptibilities of **c1** and **c2** were obtained from 10 to 300 K. The temperature dependence of the molar magnetic susceptibility (χ_m) and $\chi_m T$ are shown in figure 6 for **c2**. The variable temperature dependence of χ_m was fitted by the relation of $C/(T-\theta)$, where C is the Curie constant and θ is the Weiss constant [47]. From this fitting process, $C = 0.47 \pm 0.0002$ emuK mol^{-1}. Oe and $\theta = -0.934 \pm 0.006$ K were determined. The effective magnetic moment, μ_{eff}, was calculated to be 1.79 using the relation $\mu_{eff} = 2.83(\chi T)^{1/2}$ in Bohr magneton (μ_B) at room temperature. The value of μ_{eff} for **c2** seems to be above the spin-only value due to mixing of some spin–orbital angular momentum through the excited states *via* spin–orbit coupling [48].

For **c1**, the temperature dependence of the molar magnetic susceptibility (χ_m) and $\chi_m T$ are shown in figure 7. The temperature dependence of χ_m was fitted by the same relation as for **c2** with $C = 1.221 \pm 0.001$ emuK mol^{-1}.Oe and $\theta = -1.65 \pm 0.001$ K. The effective magnetic moment (μ_{eff}) was calculated to be 3.12 in Bohr magneton (μ_B).

There might be very little antiferromagnetic interactions in these complexes, as seen in figures 6 and 7 (insets). For these complexes, when temperature goes down, $\chi_m T$ (C) does not change until 20 K. Below this temperature the trend in $\chi_m T$ (C) decreased. This magnetic interaction might be between and within the chains through CN bridges and HBs.

3.4. *Thermal analysis*

Thermal behaviors of the complexes were studied by TG, DTG, and differential thermal analysis (DTA) in nitrogen atmosphere. TG and DTG curves are presented in

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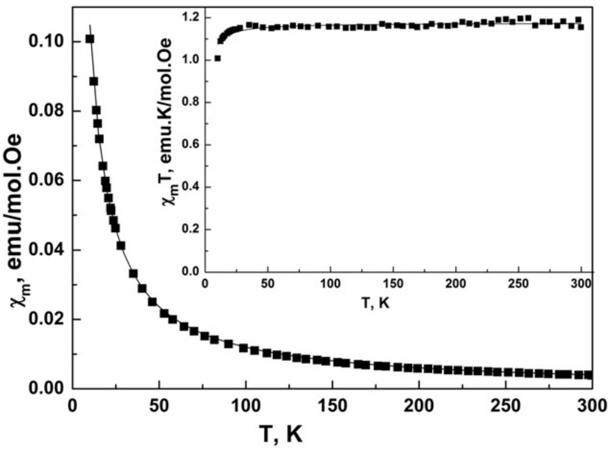

Figure 7. The temperature dependence of the molar magnetic susceptibility χ_m for **c1**. Solid line represents a fit by the Curie–Weiss law. Inset: The temperature dependence of $\chi_m T$.

"Supplementary material." The general thermal decomposition of cyano complexes is loss of N-donor ligand and then all cyano groups [49–53]. The **c1**, **c2**, **c3**, and **c4** are thermally stable to 225°C, 125°C, 211°C, and 107°C, respectively. The **c1** decomposes in two steps. At the first step 225–428°C which is accompanied by endothermic DTA peak at 344°C, the mass loss of 54.38% is observed, consistent with calculated mass loss of a *N-bishydeten* and two cyanides (54.17%). At the following stage, two remaining cyano groups decompose between 428°C and 647°C. The remaining mass loss of **c1** points to 2Ni as end product.

Thermal decomposition of **c2** consists of four degradation stages from 125°C to 178°C, 178°C to 292°C, 292°C to 451°C, and 451°C to 856°C corresponding to release of two *N-bishydetens* and four cyanides. The temperature between 211°C and 1340°C for **c3** corresponds to release of two neutral ligands, four cyanides, and 60% Zn, accompanied by endothermic DTA peaks at 273°C, 383°C, 420°C, 721°C, and 1350°C. Complex **c4** decomposed at 107–1200°C in three stages with Cd liberated at 735–1196°C. Simultaneous DTA signal featured with TG/DTA was automatically converted to DSC signal and the enthalpies (ΔH, $J\,g^{-1}$) of the complexes were determined. Thermal analyses data for **c1**, **c2**, **c3**, and **c4** are given in table 7.

4. Conclusion

We have synthesized one homonuclear and three heteronuclear complexes obtained through $[Ni(CN)_4]^{2-}$ connected to $[M(N\text{-}bishydeten)_2]^{2+}$($M = Ni^{II}$, Cu^{II}, Zn^{II}, and Cd^{II}). Crystal structures of **c2** and **c4** are solved using single-crystal X-ray diffraction data. X-ray studies confirmed tri- and tetra-dentate coordination of *N-bishydeten* to Cu^{II} and Cd^{II}, respectively. $\{[Cu(N\text{-}bishydeten)_2][Ni(CN)_4]\}$ exhibits distorted octahedral geometry forming chromophores of the CuN4O2 type. Cd^{II} in **c4** forms an eight-coordinate (CdN4O4). The shape of the eight-coordinate Cd^{II} complex may be

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Table 7. Thermal analyses data for *N-bishydeten*, **c1**, **c2**, **c3**, and **c4**.

					Mass loss, Δm (%)		Residue (%)	
Compound	Stage	Temperature range (°C)	$DTG_{max.}$ (°C)	ΔH (J g^{-1})	Obs.	Calcd	Obs.	Calcd
N-bishydeten	1	45–245	233	9515.82	99.39	99.99		
c1	1	225–428	344	26,460.13	54.38	54.17	45.62	45.83
MW: 369.66 g mol^{-1}	2	428–647	519	–9820.87	15.58	15.20	57.04	30.63 2Ni
c2	1	125–178	156	1492.05	28.42	28.36	71.58	71.64
MW: 522.72 g mol^{-1}	2	178–292	268	−14,479.85				
	3	292–451	326	2786.65	25.3	25.3	46.28	46.34
	4	451–856	681	30,303.84	20.53	19.91	25.75	26.43 Ni + Cu
c3	1	211–338	273	3236.15	25.43	25.12	74.57	74.88
MW: 589.95 g mol^{-1}	2	338–404	383	85.59				
	3	404–540	420	971.67	42.99	42.76	31.58	32.12
	4	540–875	721	5495.34				
	5	875–1350	1339	−220,100	17.80	17.73	13.78 Ni + 0.40% Zn	14.39
c4	1	107–305	253	4266.3	51.65	51.86	48.35	48.14
MW: 571.61 g mol^{-1}	2	305–550	416	894.64				
	3	550–735	630	1695.51	17.94	18.12	30.41	30.02
	4	735–1196	889	3418.25	19.00	19.67	11.41 Ni	10.35

described as a transition form between the dodecahedron (D_{2d}) and the *s*quare *a*nti*p*rism (D_{4d}). The EPR spectrum of **c1** was not obtained due to the short relaxation times of Ni^{II}, whereas the parallel and perpendicular components were observed in the EPR spectrum of **c2**. The **c1** and **c2** exhibit very weak antiferromagnetic properties below 20 K.

Supplementary material

Crystallographic information is available (CCDC ID: 808036 for **c2**; CCDC ID: 764239 for **c4**) from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] R.K. Kumar, I. Goldberg. *Angew. Chem., Int. Ed. Engl.*, **37**, 3027 (1998).
[2] S.W. Keller, S. Lopez. *J. Am. Chem. Soc.*, **121**, 6306 (1999).
[3] W. Lin, O.P. Evans, R.G. Xiong, Z. Wang. *J. Am. Chem. Soc.*, **120**, 13272 (1998).
[4] R.H. Groeneman, L. MacGillvray, L. Atwood. *Chem. Commun.*, 2735 (1998).
[5] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain. *Coord. Chem. Rev.*, **192**, 1023 (1999).
[6] J. Černák, M. Orendáč, I. Potočňák, J. Chomič, A. Orendáčová, J. Skoršepa, A. Feher. *Coord. Chem. Rev.*, **224**, 51 (2002).
[7] D.W. Knoeppel, J.P. Liu, E.A. Meyers. *Inorg. Chem.*, **37**, 4828 (1998).
[8] J. Černák, J. Skoršepa, K.A. Abboud, M.W. Meisel, M. Orendáč, A. Orendáčová, A. Feher. *Inorg. Chim. Acta*, **326**, 3 (2001).
[9] I. Escorihuela, L.R. Falvello, M. Tomás. *Inorg. Chem.*, **40**, 636 (2001).
[10] M.L. Merlau, M.P. Mejia, S.T. Nguyen, J.T. Hupp. *Angew. Chem. Int. Ed.*, **40**, 4239 (2001).
[11] R.V. Slone, K.D. Benkstein, S. Belanger, J.T. Hupp, I.A. Guzei, A.L. Rheingold. *Coord. Chem. Rev.*, **171**, 221 (1998).
[12] Z. Smékal, Z. Trávníček, J. Mroziński, J. Marek. *Inorg. Chem. Commun.*, **6**, 1395 (2003).
[13] R.D. Willet, Z. Wang, S. Molnar, K. Brewer, C.P. Landee, M.M. Turnbull, W. Zhang. *Mol. Cryst. Liq. Cryst.*, **233**, 277 (1993).
[14] O. Kahn. *Molecular Magnetism*, Verlag Chemie, New York (1993).
[15] J. Paharová, J. Černák, R. Boča, Z. Žák. *Inorg. Chim. Acta*, **346**, 25 (2003).
[16] A. Karadağ. *Z. Kristallogr.*, **222**, 39 (2007).
[17] A. Karadağ, H. Paşaoğlu, G. Kaştaş, O. Büyükgüngör. *Acta Cryst.*, **C60**, m581 (2004).
[18] A. Şenocak, A. Karadağ, Y. Yerli, Ö. Andaç, E. Şahin. *J. Inorg. Organomet. Polym.*, **20**, 628 (2010).
[19] A. Şenocak, Supervisor: A. Karadağ. Investigation of synthesis, structure and properties of new cyano-bridged polymeric transition metal complexes. PhD thesis, University of Gaziosmanpaşa (2010).
[20] A. Karadağ. TUBİTAK (Scientific and Technical Research Council of TURKİYE), Grant No: 104T205 (2010).
[21] H.B. Zhou, W. Dong, L.N. Zhu, L.H. Yu, Q.L. Wang, D.Z. Liao, Z.H. Jiang, S.P. Yan, P. Cheng. *J. Mol. Struct.*, **703**, 103 (2004).
[22] A. Ray, D. Dutta, P.C. Mondal, W.S. Sheldrick, H. Mayer-Figge, M. Ali. *Polyhedron*, **26**, 1012 (2007).
[23] D. Ghoshal, A.K. Ghosh, T.K. Maji, J. Ribas, G. Mostafa, E. Zangrando, N.R. Chaudhuri. *Inorg. Chim. Acta*, **359**, 593 (2006).
[24] J. Černák, J. Chomič, D. Baloghová, M. Dunaj-Jurčo. *Acta Crystallogr., Sec. C*, **44**, 1902 (1988).
[25] J. Černák, J. Chomič, P. Domiano, O. Ori, G.D. Andreetti. *Acta Crystallogr., Sec. C*, **46**, 2103 (1990).
[26] G.J. Gainsford, N.F. Curtis. *Aust. J. Chem.*, **37**, 1799 (1984).
[27] J. Černák, K.A. Abboud. *Acta Crystallogr., Sect. C*, **56**, 783 (2000).
[28] S.Z. Zhan, D. Guo, X.Y. Zhang, C.X. Du, Y. Zhu. *Inorg. Chim. Acta*, **298**, 57 (2000).
[29] J. Lokaj, K. Gyerová, A. Sopková, J. Sivý, V. Kettmann, V. Vrábel, *Acta Cryst.* **C47**, 2447 (1991).
[30] T. Miyoshi, T. Iwamoto, Y. Sasaki. *Inorg. Chim. Acta*, **7**, 97 (1973).
[31] A. Panja. *J. Coord. Chem.*, **64**, 987 (2011).
[32] R. Lu, H. Zhou, Y. Chen, J. Xiao, A. Yuan. *J. Coord. Chem.*, **63**, 794 (2010).
[33] G.M. Sheldrick. Direct methods. *Acta Cryst.*, **A46**, 467 (1990).
[34] G.M. Sheldrick. *SHELXL-97*, *Program for Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[35] Ş. Aslan, Supervisor: A. Karadağ. Synthesis and investigation of spectroscopic, voltammetric and thermal properties of bimetallic cyano complexes constituting *N*,*N*-bis(2-hydroxyethyl)ethylenediamine. Master thesis, University of Gaziosmanpaşa (2008).
[36] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, pp. 272–273, Wiley-Interscience, New York (1978).
[37] A.G. Sharpe. *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London (1976).
[38] T. Akitsu, Y. Einaga. *Inorg. Chim. Acta*, **360**, 497 (2007).
[39] H. Yuge, T. Iwamoto. *J. Chem. Soc., Dalton Trans.*, 1237 (1994).
[40] J.K. Burdett, R. Hoffmann, R.C. Fay. *Inorg. Chem.*, **17**, 2553 (1978).
[41] E.L. Muetterties, C.M.Q. Wright. *Rev. Chem. Soc.*, **21**, 109 (1967).
[42] J. Xu, E. Radkov, M. Ziegler, K.N. Raymond. *Inorg. Chem.*, **39**, 4156 (2000).
[43] R.J. Dudley, B.J. Hathaway. *J. Chem. Soc. A*, **12**, 2799 (1970).
[44] E.D. Mauro, S.M. Domiciano. *J. Phys. Chem. Solids*, **60**, 1849 (1999).
[45] Y. Yerli, S. Kazan, O. Yalçın, B. Aktas. *Spectrochim. Acta, Part A*, **64**, 642 (2006).
[46] Y. Yerli, F. Köksal, A. Karadağ. *Solid State Sci.*, **5**, 1319 (2003).

[47] J.J. Earney, C.P.B. Finn, B.M. Najafabadi, V. Vleck. *J. Phys. C: Solid State Phys.*, **4**, 1013 (1971).
[48] B.J. Hathaway, D.E. Billing. *Coord. Chem. Rev.*, **5**, 143 (1970).
[49] J. Černák, J. Chomič, I. Potočňák. *J. Therm. Anal.*, **35**, 2265 (1989).
[50] J. Černák, I. Potočňák, J. Chomič. *J. Therm. Anal.*, **39**, 849 (1993).
[51] J. Černák, J. Skoršepa, J. Chomič, I. Potočňák, J. Hoppan. *J. Therm. Anal.*, **41**, 91 (1994).
[52] V.T. Yılmaz, A. Karadağ. *Thermochim. Acta*, **348**, 121 (2000).
[53] F. Yakuphanoğlu, A. Karadağ, M. Şekerci. *J. Therm. Anal.*, **86**, 727 (2006).

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