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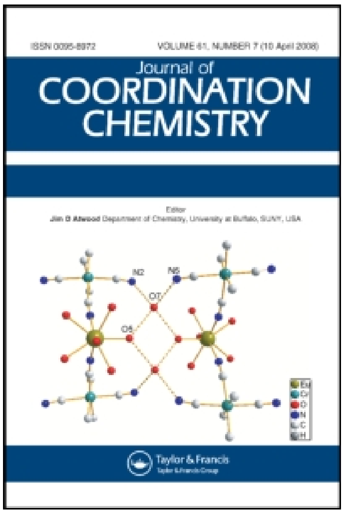

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Synthesis, crystal structures and magnetic properties of a series of new cyano-bridged complexes derived from templates $[Ni(CN)_4]^{2-}$ and $[Co(III)(CN)_6]^{3-}$

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Synthesis, crystal structures and magnetic properties of a series of new cyano-bridged complexes derived from templates $[Ni(CN)_4]^{2-}$ and $[Co(III)(CN)_6]^{3-}$

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Three new cyano-bridged complexes **1** $[Ni(tn)_2Ni(CN)_4]$ (tn = 1,3-diaminopropane), **2** $[Cu^{II}(dipn)Ni^{II}(CN)_4]$, and **3** $[Cu(dipn)]_6[Co(CN)_6]_4 \cdot 4H_2O$ (dipn = dipropylenetriamine) have been assembled by the templates $[Ni(CN)_4]^{2-}$ and $[Co(CN)_6]^{3-}$. **1** consists of a one-dimensional linear chain $–Ni(tn)_2–NC–Ni(CN)_2–CN–Ni(tn)_2–$ in which the Ni(II) centers are linked by two CN groups. One 1-D zigzag chain of **2** is formed with –Ni(2)–C–N–Cu(1)–N–C– linkages. A 2D structure of **3** is formed by an alternate array of $[Co(CN)_6]^{3-}$ and $[Co][Cu_6]$ units. For **1**, there is an overall weak antiferromagnetic interaction between Ni(II) ions through the –NC–Ni–CN– bridges of the diamagnetic $[Ni(CN)_4]^{2-}$ anions. **2** exhibits a weak antiferromagnetic exchange interaction between copper(II) ions mediated by $[Ni(CN)_4]^{2-}$ diamagnetic bridges. Complex **3** exhibits a weak ferromagnetic interaction between nearest Cu^{II} and Cu^{II} atoms through –NC–Co–CN– bridges.

Keywords: Cyano-bridged complexes; Crystal structures; Magnetic properties

1. Introduction

Research has been devoted to design and elaboration of new heterometallic molecular materials with extended structures which have intriguing properties and potential applications in catalysis, electrical conductivity, molecular-based magnetism, and host-guest chemistry [1, 2]. The general synthetic approach for metal assemblies is to utilize metal complexes as building blocks to react with transition metal cations. Very popular as a building block are $[M(CN)_n]^{m-}$ (M = Cr(III), Mn(III), Fe(III) and Fe(II)) complexes because cyanide is an ambidentate ligand capable of bridging two metal centers in an asymmetric mode. Recognition of the ability of the cyano group to bridge metal centers and to promote ferromagnetic interactions has led to the application of hexacyanometallates as building blocks for bimetallic assemblies with 1-D chain, 2-D sheet and 3-D lattice structures showing novel magnetic properties [3–10].

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Ohba *et al.* used $[Fe(II)(CN)_6]^{4-}$ as one building block to build a three-dimensional network $[Ni(L)_2]_3[Fe(CN)_6]X_2$ (L = ethylenediamine, trimethylenediamine; $X = PF_6^-$, ClO_4^-), showing a ferromagnetic interaction between the nearest Ni^{II} ions through the diamagnetic Fe^{II} ion [11]. Jiang and co-workers employed $[Ni(II)(CN)_4]^{2-}$ to assemble a 1D helical chain {*cis*-[Ni(*f*-*rac*-L)][Ni(CN)$_4$]}$_2$, with adjacent Ni(II) atoms antiferromagnetically coupled through bent –NC–Ni–CN– bridges [12]. Recently we initiated study of bimetallic assemblies derived from templates $[Fe(III)(CN)_6]^{3-}$ and $[M(CN)_4]^{2-}$ [13, 14]. We herein report the synthesis, structure, and magnetic properties of three new cyano-bridged complexes derived from $[Ni(CN)_4]^{2-}$ and $[Co(CN)_6]^{3-}$.

2. Experimental

$K_3[Co(CN)_6]$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, 1,3-diaminopropane, dipropylenetriamine, and KCN were purchased from commercial sources and used as received. $K_2Ni(CN)_4 \cdot 2H_2O$ was prepared according to the literature method [15].

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2.1. *Physical measurements*

Infrared spectra were recorded (4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. The electronic spectra both in solid and an aqueous solution were recorded on a Hitachi U-3010 (UV-Vis) spectrophotometer. Magnetic susceptibility data for powder samples were collected in the temperature range 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility.

2.2. *Synthesis of complexes*

2.2.1. Complex 1 $[Ni(tn)_2(Ni(CN)_4]$. A solution of 1,3-diaminopropane (0.3 g, 4 mmol) in water (2 mL) was added to a solution of $NiCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) in water (5 mL). The mixture was stirred for 2 min before addition of $K_2Ni(CN)_4 \cdot 2H_2O$ (0.55 g, 2 mmol) dissolved in a minimum of water. After stirring for 10 min at room temperature and filtering, the solution was left standing for several days, which led to violet needles. They were collected by filtration and dried in air (0.44 g, 58.7%). The elemental analysis results (Found: C, 32.87; H, 5.40; N, 29.97. $C_{10}H_{20}Ni_2N_8$ requires C, 32.45; H, 5.41; N, 30.29) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2149(s), 2111(s) cm^{-1} (ν_{CN}).

2.2.2. Complex 2 $[Cu^{II}(dipn)][Ni^{II}(CN)_4]$. A solution of dipropylenetriamine (0.52 g, 4 mmol) in water (6 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.68 g, 4 mmol) in water (5 mL). The mixture was stirred for 2 min before addition of $K_2Ni(CN)_4 \cdot 2H_2O$ (1.11 g, 4 mmol) dissolved in a minimum of water. After stirring for 10 min at room temperature and filtering, the solution was left standing for several days, producing blue pellets which were collected by filtration and dried in air (0.94 g, 67%). The elemental analysis results (Found: C, 33.87; H, 4.72; N, 27.25. $C_{10}H_{17}CuN_7Ni$ requires C, 33.56;

H, 4.75; N, 27.41) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2151(s), 2114(s) cm^{-1} (ν_{CN}).

2.2.3. Complex 3 $[Cu(dipn)]_6[Co(CN)_6]_4 \cdot 4H_2O$. To an aqueous solution of $CuCl_2 \cdot 2H_2O$ (2 mmol, 0.341 g) in water (5 cm^3) was added dipropylenetriamine (dipn) (6 mmol); after stirring for 2 min, $K_3[Co(CN)_6]$ (2 mmol, 0.665 g) in water (8 cm^3) was added with stirring at room temperature. The resulting blue mixture produced blue pellets which were collected by filtration and dried in air (0.587 g, 83.9%). The elemental analysis results (Found: C, 34.65; H, 5.11; N, 27.68. $C_{60}H_{110}Co_4Cu_6N_{42}O_4$ requires C, 34.27; H, 5.24; N, 28.00) were in agreement with the formula of the sample used for X-ray analysis. IR (KBr pellet): 2180(vs), 2130(vs) cm^{-1} (ν_{CN}).

2.3. *X-ray crystallography*

Data were collected with a Bruker SMART CCD area detector and a Siemens P4 automatic four-circle diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied by using the SADABS program [16]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system [17]. Details of the crystal parameters, data collection and refinement for **1**, **2**, and **3** are listed in table 1 and selected bond distances and angles are given in tables 2–4.

Table 1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_{10}H_{20}N_8Ni_2$	$C_{10}H_{17}CuN_7Ni$	$C_{60}H_{110}Co_4Cu_6N_{42}O_4$
Formula weight	369.76	357.56	2100.86
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic	Rhombohedral
Space group	*P42/m*	*P21/n*	*R*-3
a (Å)	10.0781(14)	11.4035(13)	14.1568(11)
b (Å)	10.0781(14)	10.0638(12)	14.1568(11)
c (Å)	7.287(2)	13.7289(16)	40.125(7)
α (°)	90	90	90
β (°)	90	108.3350(10)	90
γ (°)	90	90	120
V (Å^3)	740.1(2)	1495.6(3)	6964.4(15)
Z	2	4	3
D_c (Mg m^{-3})	1.659	1.588	1.503
F(000)	384	732	3234
Data/restraints/parameters	911/0/57	3400/0/176	3570/0/189
Goodness-of-fit on F^2	1.084	1.055	0.962
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0235$, $wR_2 = 0.0581$	$R_1 = 0.0262$, $wR_2 = 0.0609$	$R_1 = 0.0360$, $wR_2 = 0.0920$
R indices (all data)	$R_1 = 0.0307$, $wR_2 = 0.0637$	$R_1 = 0.0351$, $wR_2 = 0.0646$	$R_1 = 0.0621$, $wR_2 = 0.0974$

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

Ni(1)–N(2)#1	2.096(2)	Ni(1)–N(2)	2.096(2)
Ni(1)–N(1)#2	2.1100(15)	Ni(1)–N(1)#1	2.1100(15)
Ni(1)–N(1)#3	2.1100(15)	Ni(1)–N(1)	2.1100(15)
Ni(2)–C(3)#4	1.871(2)	Ni(2)–C(3)	1.871(2)
Ni(2)–C(4)	1.882(3)	Ni(2)–C(4)#4	1.882(3)
N(2)#1–Ni(1)–N(2)	180.0	N(1)#2–Ni(1)–N(1)#3	180.0
N(1)#1–Ni(1)–N(1)	180.0	C(3)#4–Ni(2)–C(3)	180.0
C(3)#4–Ni(2)–C(4)	91.16(10)	C(3)–Ni(2)–C(4)	88.84(10)
C(4)–Ni(2)–C(4)#4	180.0	N(2)–C(3)–Ni(2)	179.5(2)
N(3)–C(4)–Ni(2)	178.7(2)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y$, $-z$; #2: x, y, $-z$; #3: $-x+1$, $-y$, z; #4: $-x+2$, $-y$, $-z$.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Ni(2)–C(10)	1.863(2)	Ni(2)–C(7)	1.866(2)
Ni(2)–C(9)	1.868(2)	Ni(2)–C(8)	1.875(2)
Cu(1)–N(3)	2.013(2)	Cu(1)–N(1)	2.0209(17)
Cu(1)–N(4)	2.0238(19)	Cu(1)–N(2)	2.0450(18)
Cu(1)–N(5)#1	2.1998(19)	N(4)–C(7)	1.141(3)
N(5)–C(8)	1.137(3)	N(5)–Cu(1)#2	2.1998(19)
N(6)–C(9)	1.140(3)	N(7)–C(10)	1.140(3)
C(10)–Ni(2)–C(7)	89.22(9)	C(10)–Ni(2)–C(9)	90.69(10)
C(7)–Ni(2)–C(9)	178.55(11)	C(10)–Ni(2)–C(8)	177.99(10)
C(7)–Ni(2)–C(8)	91.95(9)	C(9)–Ni(2)–C(8)	88.10(9)
N(4)–Cu(1)–N(5)#1	100.02(8)	N(2)–Cu(1)–N(5)#1	99.13(8)
C(7)–N(4)–Cu(1)	176.92(19)	C(8)–N(5)–Cu(1)#2	141.03(18)
N(4)–C(7)–Ni(2)	177.0(2)	N(5)–C(8)–Ni(2)	175.00(19)
N(6)–C(9)–Ni(2)	177.4(2)	N(7)–C(10)–Ni(2)	178.7(2)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1/2$, $y+1/2$, $-z+1/2$; #2: $-x+1/2$, $y-1/2$, $-z+1/2$.

Table 4. Selected bond distances (Å) and angles (°) for **3**.

Cu(1)–N(2)	2.002(3)	Cu(1)–N(3)	2.019(3)
Cu(1)–N(5)	2.025(3)	Cu(1)–N(1)	2.060(3)
Cu(1)–N(4)	2.195(3)	Co(1)–C(7)	1.890(3)
Co(2)–C(8)	1.887(4)	Co(2)–C(9)	1.894(4)
Co(3)–C(10)	1.891(3)	N(4)– C(7)	1.148(4)
N(2)–Cu(1)–N(5)	85.42(13)	N(3)–Cu(1)–N(5)	83.40(14)
N(2)–Cu(1)–N(4)	99.26(11)	N(3)–Cu(1)–N(4)	94.18(15)
N(5)–Cu(1)–N(4)	107.99(13)	N(1)–Cu(1)–N(4)	96.35(12)
C(7)–Co(1)–C(7)#4	180.00(15)	C(7)#3–Co(1)–C(7)#4	89.06(13)
C(7)#1–Co(1)–C(7)#5	89.06(13)	C(7)#2–Co(1)–C(7)#5	180.00(15)
C(7)–Co(1)–C(7)#5	90.94(13)	C(7)#3–Co(1)–C(7)#5	90.94(13)
C(7)#4–Co(1)–C(7)#5	89.06(13)	C(8)–Co(2)–C(9)	90.27(15)
C(6)–N(3)–Cu(1)	122.6(3)	C(7)–N(4)–Cu(1)	153.4(3)
C(8)–N(5)–Cu(1)	151.2(3)	N(4)–C(7)–Co(1)	177.2(3)
N(5)–C(8)–Co(2)	175.4(3)	N(6)–C(9)–Co(2)	176.7(4)
N(7)–C(10)–Co(3)	178.1(3)		

Symmetry codes are as follows: 1: $y-1$, $-x+y$, $-z$; #2: $x-y+1$, $x+1$, $-z$; #3: $-y+1$, $x-y+2$, z; #4: $-x$, $-y+2$, $-z$; #5: $-x+y-1$, $-x+1$, z; #6: $-y+1$, $x-y+1$, z; #7: $-x+y$, $-x+1$, z; #8: $x-y+2/3$, $x+1/3$, $-z+1/3$; #9: $y-1/3$, $-x+y+1/3$, $-z+1/3$; #10: $-x+2/3$, $-y+4/3$, $-z+1/3$.

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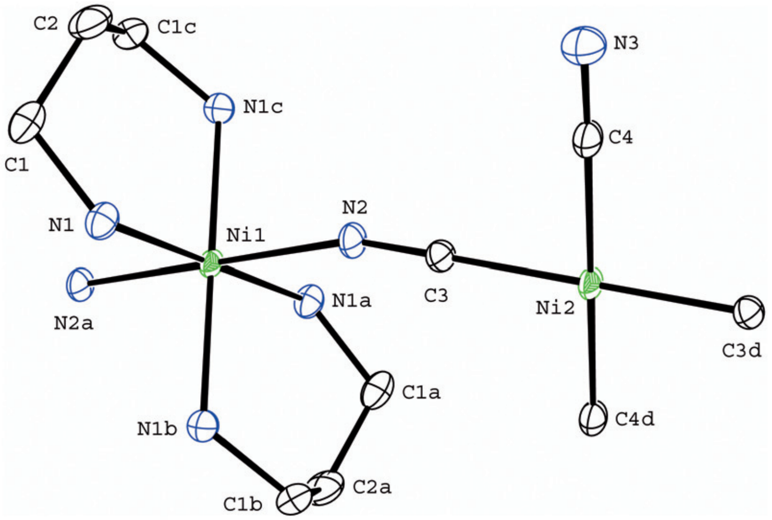

Figure 1. An ORTEP plot of **1**.

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3. Results and discussions

3.1. *Synthesis and general properties*

Cyano-bridged **1** was obtained as violet crystals by reaction of $NiCl_2 \cdot 6H_2O$, 1,3-diaminopropane, and $K_2Ni(CN)_4 \cdot 2H_2O$ in 1 : 2 : 1 molar ratio in an aqueous solution. The reaction system of $CuCl_2 \cdot 2H_2O$, dipn, and $K_2Ni(CN)_4 \cdot 2H_2O$ with molar ratio set of 1 : 1 : 1 gave cyano-bridged **2**. The reaction of $K_3[Co(CN)_6]$, $CuCl_2 \cdot 2H_2O$, and *bis*(3-aminopropyl)-amine in 1 : 1 : 3 molar ratio led to the formation of **3**.

The formation of cyanide bridges in the polynuclear complex was shown by the stretching vibration of the cyanide ligands. The IR spectrum of **1** $[Ni(tn)_2Ni(CN)_4]$ shows two bands at 2149 and 2111 cm^{-1}, assigned to the intermetallic $Ni^{II}–C≡N–Ni^{II}$ bond (νC≡N(b)) and the terminal CN group, respectively. A similar pattern was seen for ν(CN) band at 2169, and 2129 cm^{-1} of **2** $[Ni^{II}(CN)_4Cu^{II}(dipn)]$. The band at 2151 cm^{-1} is assigned to the intermetallic C≡N stretch and the band at 2114 cm^{-1} to terminal C≡N stretch. The presence of cyanide bridges in **3** was also verified by two CN stretching bands in the infrared spectrum at 2169 and 2129 cm^{-1}, corresponding to the bridging CN and the terminal CN ligands.

3.2. *Structure of 1*

An ORTEP drawing of **1** is shown in figure 1. The crystallographically asymmetric unit of **1** consists of one *trans*-$[Ni(tn)_2]^{2+}$ cation and one $[Ni(CN)_4]^{2-}$ anion. There are two independent Ni–N distances in each $[Ni(tn)_2]^{2+}$ cation with the N–Ni–N bond angles (N(2)#1–Ni(1)–N(2), N(1)#2–Ni(1)–N(1)#3) being exactly 180°. Similarly, there are two independent Ni–C distances in each $[Ni(CN)_4]^{2-}$ anion with the *trans* C–Ni–C bond angles (C(3)#4–Ni(2)–C(3) and C(4)–Ni(2)–C(4)#4) also being exactly 180°. The geometry of the ligand field of Ni(1) is distorted-octahedral; the Ni(1)–N bond

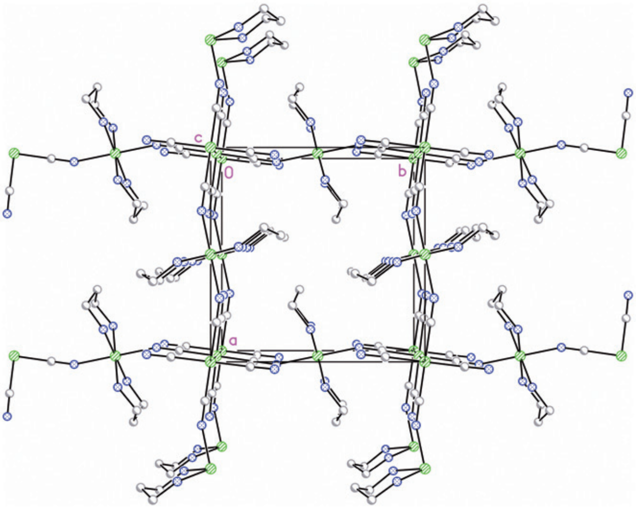

Figure 2. Crystal packing diagram of **1**.

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lengths range from 2.096(2) to 2.110(15) Å. Ni(2) is in a quadrilateral planar coordination sphere, connected with four cyanide C atoms. Nitrogen atoms of cyanides (N(2), N(2A)) coordinate with the adjacent $[Ni(tn)_2]^{2+}$ in *trans* positions. The 1-D chain is formed with the –Ni(1)–C–N–Ni(2)–N–C– linkages, the shortest distance of Ni(1) and Ni(2) is 3.643 Å.

A view of the crystal cell $[Ni(tn)_2Ni(CN)_4]_n$ is shown in figure 2. The Ni atoms of the $[Ni(CN)_4]^{2-}$ anions lie at the eight corners of the tetragonal cell and at the midpoints of the four edges perpendicular to the ab face, consistent with two $[Ni(CN)_4]^{2-}$ units per cell. As a result, the planar $[Ni(CN)_4]^{2-}$ anions are stacked along the *c*-axis and separated by a distance of 3.643 Å, which corresponds to half the *c*-lattice length. The chains that are separated by this distance are oriented perpendicular to one another.

3.3. *Structure of 2*

A labeled diagram of the asymmetric unit of **2** is shown in figure 3. The structure of **2** consists of one $[Cu(dipn)]^{2+}$ and one $[Ni(CN)_4]^{2-}$. Nitrogen atoms of cyanide (N(4A), N(5A)) coordinate the adjacent $[Cu(dipn)]^{2+}$ *cis*, different from **1**. Nitrogen of cyanide N(4) coordinates with the adjacent $[Cu(dipn)]^{2+}$ in a bond angle 176.8(2)° for C7–N4–Ni2.

The tridentate dipn (dipropylenetriamine) ligand occupies three basal sites of a pseudo square-pyramidal coordination environment about Cu with the remaining basal and apical sites occupied by two *cis*-cyano groups provided by $[Ni(CN)_4]^{2-}$. The average value for the Cu(1)–$N_{triamine}$ distance is 2.028(2) Å, and Cu(1)–$N_{cyanide}$ distance is 2.024(2) Å.

Ni(2) is in a quadrilateral planar coordination sphere, connected with four cyanide C atoms. Among the bond distances between Ni(2) and cyano-carbon atoms, two

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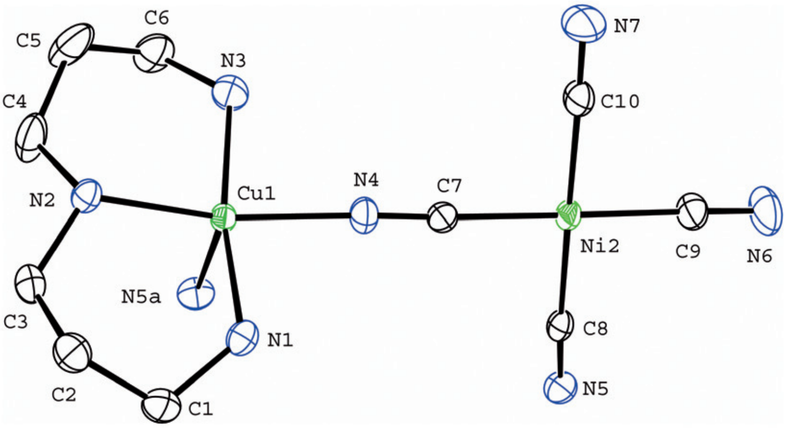

Figure 3. An ORTEP plot of **2**.

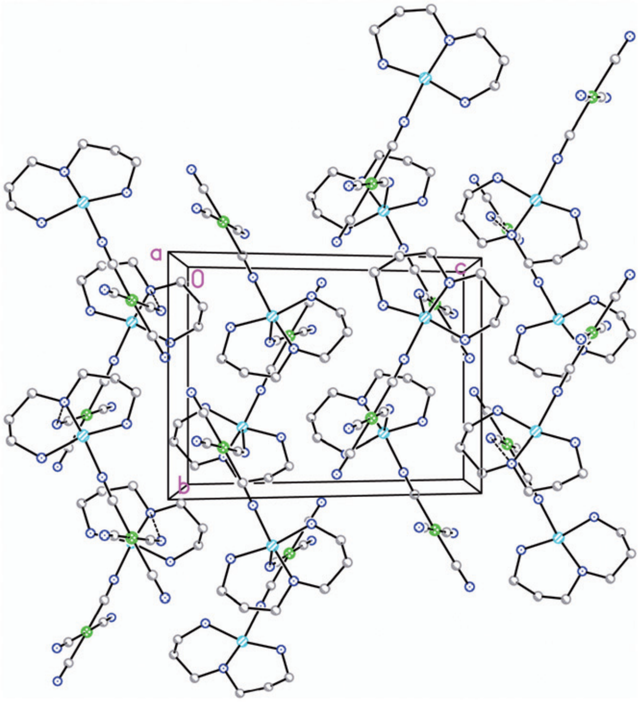

Figure 4. Crystal packing diagram of **2**.

bridging cyano groups form an average distance of 1.866(3) Å, similar to the 1.864 Å found in [Ni(pn)$_2$Ni(CN)$_4$] [14], whereas the other two non-bridging cyano groups show an average distance of 1.873(3) Å. The 1-D zigzag chain is formed with the –Ni(2)–C–N–Cu(1)–N–C– linkages (figure 4) and the shortest Ni^{II}–Cu^{II} separation is 4.870 Å.

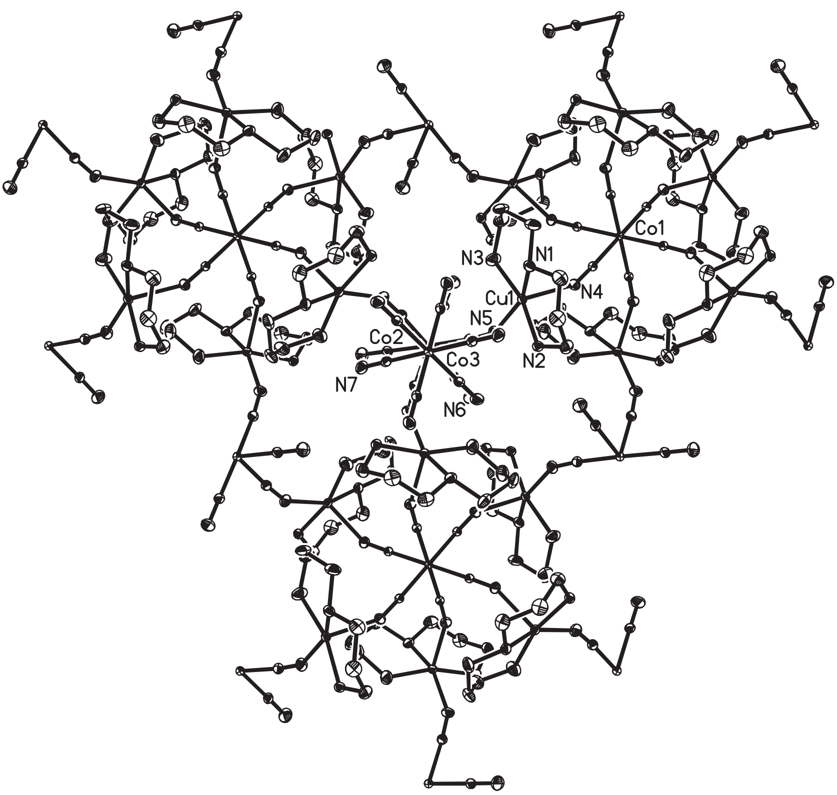

Figure 5. The ORTEP view of **3**.

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3.4. *Structure of 3*

Complex **3** consists of one $\{[Cu(dipn)]_6[Co(CN)_6]_3\}^{3+}$ cation, one $[Co(CN)_6]^{3-}$ anion and four water molecules. There are three types of Co sites (Co1, Co2, and Co3) in **3**, which all have an octahedral environment. The Co(1) unit ($[Co(CN)_6]^{3-}$) coordinates to six $[Cu(dipn)]^{2+}$ cations through all of its cyano nitrogens, forming a 3-D network extended by Co^{III}–CN–Cu^{II} linkages (figure 5). The Co1–C, C–N, and N–Cu1 bond distances in the linkage are 1.890(3), 1.148(4), and 2.195(3) Å, respectively. The Co(2) unit ($[Co(CN)_6]^{3-}$) is surrounded by three $[Cu(dipn)]^{2+}$ moieties through cyanide bridges. The Co2–C8, C8–N5, and N5–Cu1 bond distances in the linkage are 1.887(5), 1.137(4), and 2.025(3) Å, respectively. The Co(3) has an octahedral surrounding with Co–C bond distances from 1.891(3) Å.

The tridentate dipn (dipropylenetriamine) ligand occupies three basal sites of a pseudo trigonal-bipyramidal coordination environment about the Cu atom with the remaining basal and apical sites occupied by two *trans*-cyano groups provided by $[Co(CN)_6]^{3-}$. The Cu–N(triamine) distances range from 2.002(3) to 2.060(3) Å, and Cu(1)–$N_{cyanide}$ distances are 2.025(2) and 2.195 (3) Å.

In the lattice, a 2D structure is formed by the alternate array of $[Co(CN)_6]^{3-}$ and $[Co][Cu_6]$ units (figure 6). The bridging Cu(1)–NC–Co are non-linear with Cu(1)–N(5)–C(8) and Cu(1)–N(4)–C(7) angles of 151.2(3) and 177.2(3)°. The shortest Cu(1) $\cdots$ Co(1), Cu(1) $\cdots$ Co(2) distances are 5.080(6) and 4.867(7) Å, respectively.

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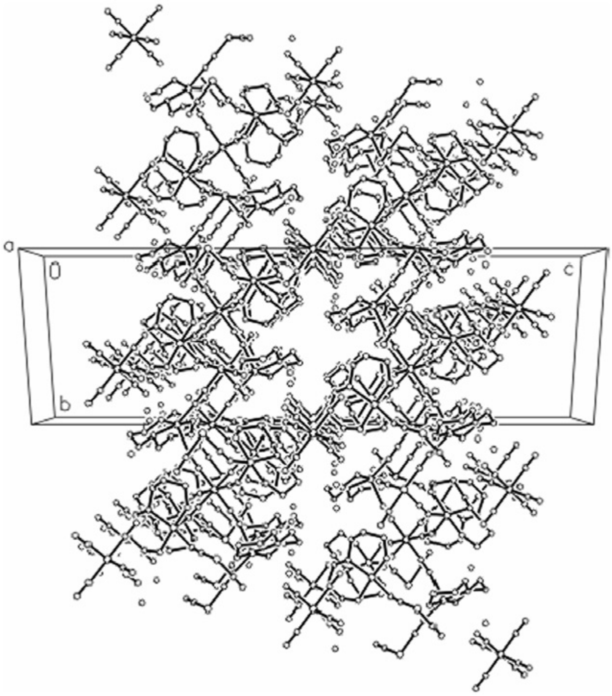

Figure 6. The infinite 2D structure of **3**.

3.5. *Magnetic properties of 1, 2, and 3*

The magnetic properties of **1**, **2** and **3** were investigated in the temperature range 2–300 K for molar susceptibility. The magnetic behavior of **1** is shown in figure 7 in the form of $\chi_M T$ *versus* T. From room temperature down to 60 K, the $\chi_M T$ remains constant at 0.993 $cm^3\,K\,mol^{-1}$ (2.82 μ_B), which is close to the value of 1.0 $cm^3\,K\,mol^{-1}$ (2.83 μ_B) of an isolated Ni(II) ion ($S = 1$). Below 60 K, the $\chi_M T$ decreases, reaching a value of 0.5 $cm^3\,K\,mol^{-1}$ at 2 K. This variation is indicative of weak antiferromagnetic behavior of **1**. Since the Ni(II) ions interact through one diamagnetic $[Ni(CN)_4]^{2-}$ unit, the coupling between them is expected to be very weak.

The magnetic property of **2** is shown in the form of $\chi_M T$ *versus* T plot (figure 8). From room temperature to 40 K, the $\chi_M T$ remains constant at 0.374 $cm^3\,K\,mol^{-1}$ (1.73 μ_B), close to the value of 0.375 $cm^3\,K\,mol^{-1}$ (1.73 μ_B) of isolated Cu(II) ($S = 1/2$). Below 40 K, the $\chi_M T$ decreases, reaching a value of 0.188 $cm^3\,K\,mol^{-1}$ at 2 K. As a consequence, there is a weak antiferromagnetic exchange interaction between copper(II) ions mediated by $[Ni(CN)_4]^{2-}$ diamagnetic bridges.

The magnetic behavior of **3** is shown in figure 9 in the form of $\chi_M T$ *versus* T. The room temperature value of $\chi_M T$ for **1** is 1.92 $cm^3\,K\,mol^{-1}$ (3.92 μ_B per Cu_6Co_4) which is smaller than the expected for six Cu(II) ($S = 1/2$) ions (4.24 μ_B) and slightly increases with decreasing temperature to a maximum value of 2.25 $cm^3\,K\,mol^{-1}$ (4.24 μ_B) at 2 K. The $1/\chi_M$ *versus* T plot in the range from 300–2 K obeys the Curie–Weiss Law with a positive Weiss constant of $\Theta = +1.9$ K. The magnetic behavior in the range 2.0–300 K means a weak ferromagnetic interaction between the nearest

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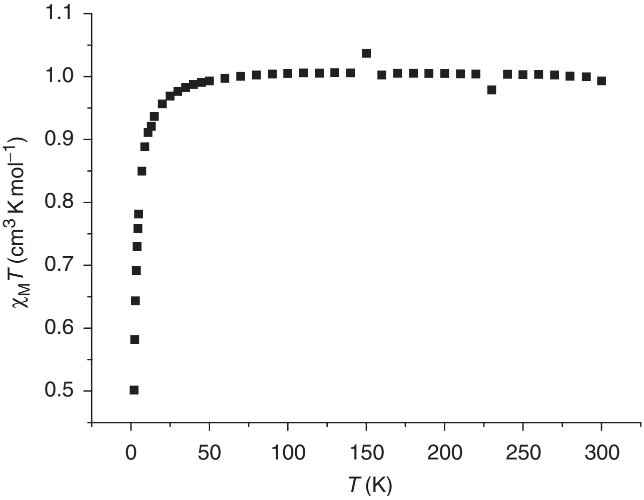

Figure 7. Temperature dependence of $\chi_M T$ for **1**.

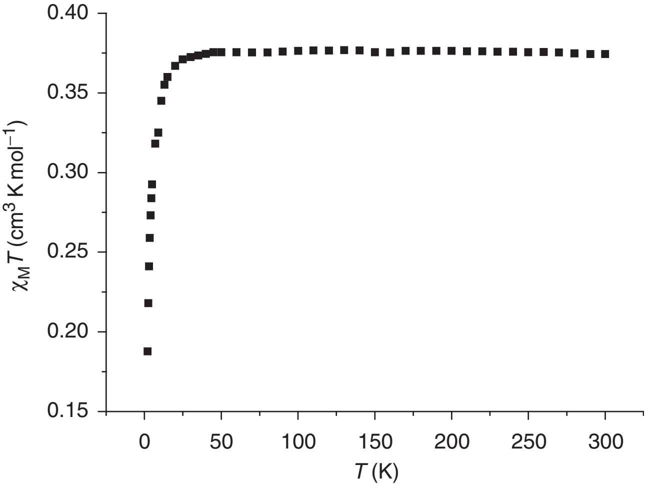

Figure 8. Temperature dependence of the $\chi_M T$ for **2**.

Cu(II) ions through –NC–Co–CN– bridge. If one takes into consideration the electronic configurations of Cu(II) ($t_{2g}{}^6e_g{}^3$) and Co(III) ($t_{2g}{}^6$), a σ-superexchange pathway is proposed between the nearest Cu(II) ions through the empty dσ orbital of Cu(II).

The magnetic analysis was carried out using the Bleaney–Bowers equation based on the Heisenberg mode $H = -2J\mathbf{S_1S_2}$ [equation 1] [18], where p is the fraction of monomeric impurity and χ_M is the magnetic susceptibility. The magnetism of **1** is well reproduced by the Bleaney–Bowers equation using the magnetic parameters $g = 1.9$, $J = +0.30\,\text{cm}^{-1}$, $N_\alpha = -9.2 \times 10^{-3}\,\text{mol}^{-1}$ and $p = 0.042$. As a consequence, there is a

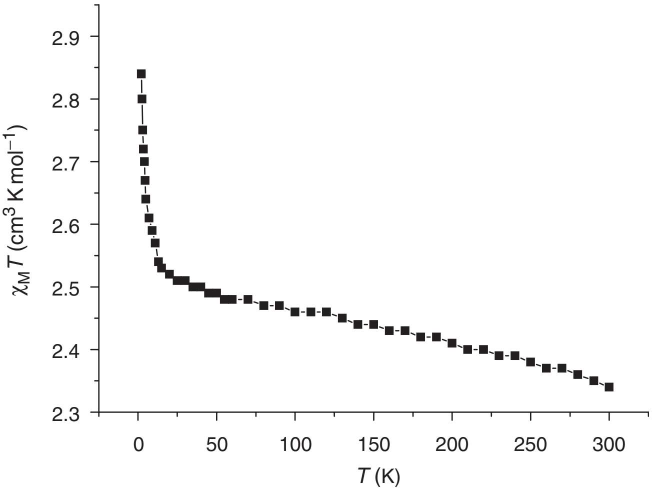

Figure 9. Temperature dependence of $\chi_M T$ for **3**.

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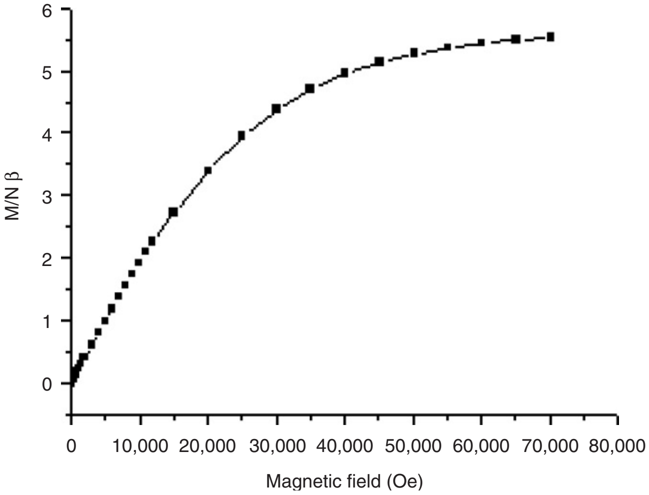

Figure 10. Field dependence of the magnetization at 2 K for **3**.

weak ferromagnetic interaction between adjacent Cu^{II} and Cu^{II} ions through the cyanide bridge.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{1-p}{3+\exp(-2J/KT)} + \frac{0.45p}{T} + N_\alpha \qquad (1)$$

The field dependence of the magnetization (0–70,000 Oe) measured at 2 K is shown in figure 10 in the form of $M/N\mu_B$ *versus* H. The magnetization curve showed a gradual increase with applied field reaching a value of 6.21 $N\mu_B$ at 70,000 Oe, which is smaller than the expected $S = 3$ value of 6.93 NμB for the Cu_6Co_4 system, suggesting that not all the spins in the Cu(II) ions aligned parallel at high field.

4. Conclusions

A rational strategy for synthesis of polynuclear species based on tetracyanonickel(II) center surrounded by Ni^{II} ion and hexacyanocobaltate(III) center surrounded by Cu^{II} ion is described herein. Three new cyano-bridged complexes **1**, **2**, and **3** were synthesized and characterized. For **1**, there is an overall weak antiferromagnetic interaction between Ni(II) ions through the –NC–Ni–CN– bridges of the diamagnetic $[Ni(CN)_4]^{2-}$ anions. **2** exhibits a weak antiferromagnetic exchange interaction between copper(II) ions mediated by $[Ni(CN)_4]^{2-}$ diamagnetic bridges. **3** exhibits a weak ferromagnetic interaction between the nearest Cu(II) ions through a –NC–Co–CN– bridge. It should be possible to extend the synthetic strategy to other metallic polycyanometalates.

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Supplementary data

CCDC-299697, CCDC-621684, and CCDC-297325 contain the supplementary crystallographic data of **1**, **2**, and **3**, respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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