Inorganic Chemistry
Article
pubs.acs.org/IC

1D to 3D Heterobimetallic Complexes Tuned by Cyanide Precursors: Synthesis, Crystal Structures, and Magnetic Properties

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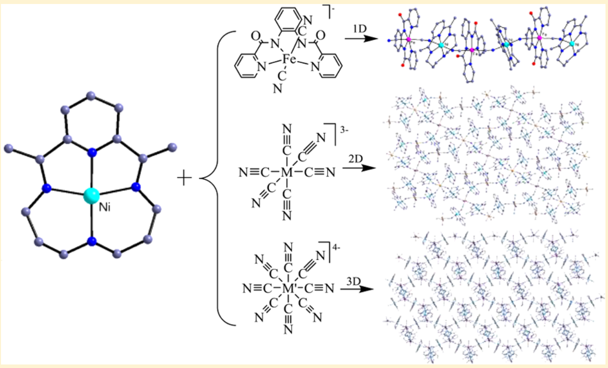
Supporting Information

ABSTRACT: Five new heterobimetallic complexes, namely, $\{[Ni(L)][Fe(bpb)(CN)_2]\}ClO_4$ (L = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate) (**1**), $\{[Ni(L)]_3[M(CN)_6]_2\}\cdot 7H_2O$ (M = Fe (**2**), Cr (**3**)), $\{[Ni(L)]_2[Mo(CN)_8]\}\cdot CH_3CN\cdot 13H_2O$ (**4**), and $\{[Ni(L)]_2[W(CN)_8]\}\cdot 16H_2O$ (**5**), were assembled from the polyaza macrocycle nickel(II) compound and five cyanidometalate precursors containing different numbers of cyanide groups. Single-crystal X-ray diffraction analysis reveals their different structure ranging from a cyanide-bridged cationic polymeric single chain for **1**, a two-dimensional network for **2** and **3**, and a three-dimensional network for **4** and **5**. In addition, a systematic investigation over the magnetic properties of **1**−**3** indicates the ferromagnetic magnetic coupling between neighboring Fe(III)/Cr(III) and Ni(II) ions through the bridging cyanide group. For complex **1**, the magnetic susceptibility has been simulated by the Seiden model using the Hamiltonian $H = -J\sum_{i=0}^{N} S_iS_{i+1}$, leading to the magnetic coupling constant of J = 3.67 cm^{-1}. The two-dimensional magnetic complexes exhibit three-dimensional magnetic ordering behavior with a magnetic phase transition temperature of T_C = 4.0 K for **2** and T_N = 6.0 K for **3**, respectively.



INTRODUCTION

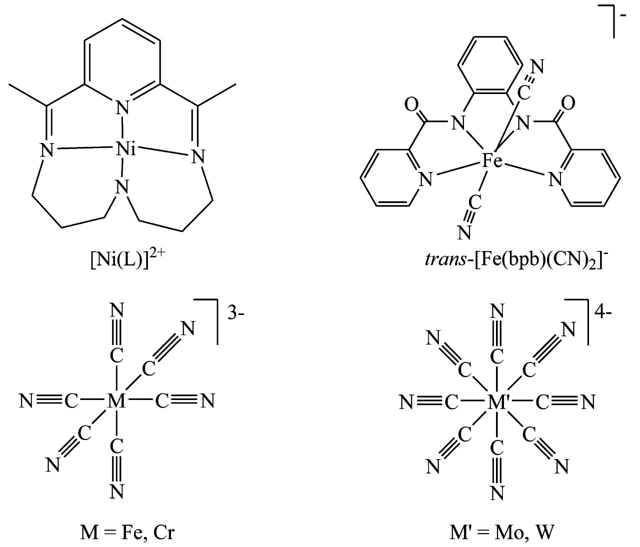
Due to the significant role of the cyanide group as a remarkable magnetic linker in mediating efficient ferro- or antiferromagnetic exchange interactions between paramagnetic centers depending on the electronic configuration of the magnetic centers and the structural parameters around them,[1,2] cyanide-based molecular materials including high-temperature magnetic order,[3,4] photoresponsive properties,[5−7] spin-crossover (SCO),[8,9] chirality,[10−14] single-molecule magnets (SMMs),[15−17] and single-chain magnets (SCMs)[18−20] have attracted intensive and extensive attention. Usually, the rational design of cyanide-bridged magnetic complexes can be achieved following a common assembly method by selecting appropriate cyanidometalates exhibiting targeted chemical (number and arrangement of cyanido groups, steric hindrance of the ligand, etc.) and physical properties (local anisotropy, spin state, etc.) as building blocks and various paramagnetic metal ions prepared with organic ligands as construction segments.[21−23]

It is well known that the ancillary ligands attached to the counterpart assembling metal cations play an important role in influencing the structure of the resulting complexes. As a result, many organic ligands with different size and structure have been employed to block the paramagnetic metal ions, targeting the tuning of the structure of the cyanide-bridged complexes formed. Similar to the polyimine macrocyclic ligands always containing flexible coordination positions with *cis* or *trans* configurations,[24−29] the polyaza macrocyclic ligands with some rigid character obtained by condensation of 2,6-diacetylpyridine and polyamine, which are usually coordinated to the equatorial plane of metal ions with only two *trans* replaceable sites weakly bonded to other ligands, were proved to be good ancillary ligands to assemble cyanide-bridged complexes. Some Ni(II), Mn(II), or Fe(II) complexes based on the above polyaza macrocyclic ligand with different structures and interesting magnetic properties have been reported.[30−34] Interest in this type of ligand also led to the report of several one-dimensional Mn(II) complexes starting from *trans*-dicyanide-containing precursor building blocks by this group.[35] As part of our continuous efforts in this direction, herein we describe the synthesis, structure, and magnetic properties of a series of new cyanide-bridged heterobimetallic complexes including one-dimensional $\{[Ni(L)][Fe(bpb)(CN)_2]\}ClO_4$ (**1**), two-dimensional $\{[Ni(L)]_3[M(CN)_6]_2\}\cdot 7H_2O$ [M = Fe (**2**), Cr (**3**)], and three-dimensional $\{[Ni(L)]_2[Mo(CN)_8]\}\cdot CH_3CN\cdot 13H_2O$ (**4**) and $\{[Ni(L)]_2[W(CN)_8]\}\cdot 16H_2O$ (**5**), Scheme 1, based on the Ni(II) polyaza macrocyclic complex $[Ni(L)](ClO_4)_2$ building block by using several cyanide precursors with different numbers of cyanide groups.

Received: November 27, 2013
Published: March 21, 2014

dx.doi.org/10.1021/ic4029386 | *Inorg. Chem.* 2014, 53, 3494−3502

Scheme 1. Starting materials used to prepare complexes 1−5



EXPERIMENTAL SECTION

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El (Supporting Information). The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000−400 $\mathrm{cm^{-1}}$ region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

General Procedures and Materials. All the reactions were carried out under an air atmosphere, and all chemicals and solvents used were reagent grade without further purification. $[\mathrm{NiL}](\mathrm{ClO_4})_2$ and $\mathrm{K[Fe^{III}(bpb)(CN)_2]}$ were synthesized as described in the literature.[36,37]

Caution! KCN is hypertoxic and hazardous. Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities with care.[38,39]

Synthesis of Complex 1. To a solution of $[\mathrm{NiL}](\mathrm{ClO_4})_2$ (51.1 mg, 0.10 mmol) in methanol (10 mL) was carefully added $\mathrm{K[Fe(bpb)(CN)_2]}$ (46.5 mg, 0.10 mmol) dissolved in methanol/water (4:1, v:v) (10 mL). The resulting mixture was filtered at once, and the filtrate was kept undisturbed at room temperature. After one week, dark brown block crystals were collected by filtration with a yield of 51.0 mg, 60.7%. Anal. Calcd for $\mathrm{C_{35}H_{34}FeClN_{10}NiO_6}$: C,50.00; H, 4.07; N, 16.67. Found: C, 50.21; H, 4.11; N, 16.78. Main IR bands ($\mathrm{cm^{-1}}$): 2123 (s, νC≡N), 1615, 1624 (vs, νC=N), 1098 (vs, νCl=O).

Synthesis of Complexes 2 and 3. A solution containing $\mathrm{K_3[Fe(CN)_6]}$ (32.9 mg, 0.10 mmol) or $\mathrm{K_3[Cr(CN)_6]}$ (32.5 mg, 0.10 mmol) dissolved in 5 mL of distilled water was laid in the bottom of a tube, upon which a solvent mixture of water, acetonitrile, and methanol with a ratio of 1:2:1 was carefully added. Then, a solution of $[\mathrm{NiL}](\mathrm{ClO_4})_2$ (76.7 mg, 0.15 mmol) in 5 mL of $\mathrm{CH_3CN}$ was carefully added to the top of the mixed solvent layer. Single crystals suitable for X-ray diffraction were obtained adhering to the tube wall from the mixture solvent layer about one week later, which were then collected by filtration and dried in air.

Complex 2. Yield: 41.2 mg, 54.9%. Anal. Calcd for $\mathrm{C_{57}H_{80}Fe_2N_{24}Ni_3O_7}$: C, 45.61; H, 5.37; N, 22.39. Found: C, 45.71; H, 5.31; N, 22.46. Main IR bands ($\mathrm{cm^{-1}}$): 2158, 2121 (s, νC≡N), 1634 (vs, νC=N).

Complex 3. Yield: 42.5 mg, 56.9%. Anal. Calcd for $\mathrm{C_{57}H_{80}Cr_2Ni_3N_{24}O_7}$: C, 45.84; H, 5.40; N, 22.50. Found: C, 46.00; H, 5.31; N, 22.61. Main IR bands ($\mathrm{cm^{-1}}$): 2158, 2122 (s, νC≡N), 1632 (vs, νC=N).

Synthesis of Complexes 4 and 5. $\mathrm{K_4[Mo(CN)_8]\cdot 2H_2O}$ (47.8 mg, 0.1 mmol) or $\mathrm{K_4[W(CN)_8]\cdot 2H_2O}$ (56.6 mg, 0.1 mmol) dissolved in distilled water (10 mL) was added to one arm of an H-type tube, and a $\mathrm{CH_3CN}$ solution (10 mL) containing $[\mathrm{NiL}](\mathrm{ClO_4})_2$ (102.2 mg, 0.2 mmol) was put in the other arm. The dark brown crystals generated suitable for X-ray diffraction were grown out in the middle of the H-type tube after one month.

Complex 4. Yield: 65.8 mg, 30.6%. Anal. Calcd for $\mathrm{C_{78}H_{116}Mo_2Ni_4N_{33}O_{13}}$: C, 43.56; H, 5.44; N, 21.49. Found: C, 43.64; H, 5.34; N, 21.66. Main IR bands ($\mathrm{cm^{-1}}$): 2156, 2121 (s, νC≡N), 1630 (vs, νC=N).

Complex 5. Yield: 71.2 mg, 30.4%. Anal. Calcd for $\mathrm{C_{76}H_{120}W_2Ni_4N_{32}O_{16}}$: C, 39.00; H, 5.17; N, 19.15. Found: C, 39.12; H, 5.11; N, 19.28. Main IR bands ($\mathrm{cm^{-1}}$): 2156, 2122 (s, νC≡N), 1632 (vs, νC=N).

X-ray Data Collection and Structure Refinement. Data were collected on an Oxford Diffraction Gemini E diffractometer with Cu Kα radiation (λ = 0.71073 Å) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling; and SCALE3 ABSPACK for absorption correction. The structures were

Table 1. Crystallographic Data for Complexes 1−5

	1	2	3	4	5
chemical formula	$\mathrm{C_{35}H_{34}FeNiClN_{10}O_6}$	$\mathrm{C_{57}H_{80}Fe_2\ Ni_3N_{24}O_7}$	$\mathrm{C_{57}H_{80}Cr_2Ni_3N_{24}O_7}$	$\mathrm{C_{78}H_{116}Mo_2\ Ni_4N_{33}O_{13}}$	$\mathrm{C_{76}H_{120}W_2\ Ni_4N_{32}O_{16}}$
fw	840.73	1501.28	1493.58	2150.76	2340.58
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$
a/Å	11.217(3)	11.2260(16)	11.2803(8)	26.11(5)	26.2457(15)
b/Å	17.405(5)	16.255(2)	16.4227(11)	13.91(3)	13.9671(8)
c/Å	20.125(5)	19.936(3)	20.3742(14)	29.55(6)	29.8116(17)
α/deg	90	98.772(2)	98.2400(10)	90	90
β/deg	99.431(5)	91.718(2)	91.1160(10)	94.27(4)	95.3110(10)
γ/deg	90	105.780(2)	105.4670(10)	90	90
V/Å^3	3876.3(18)	3450.1(8)	3593.5(4)	10704(36)	10881.3(11)
Z	4	2	2	4	4
F(000)	1732	1564	1556	4460	4752
GOF	1.004	1.025	1.035	1.024	1.032
$R_1[I > 2\sigma(I)]$	0.0711	0.0630	0.0688	0.0775	0.0493
wR_2 (all data)	0.2145	0.1964	0.2231	0.2612	0.1538

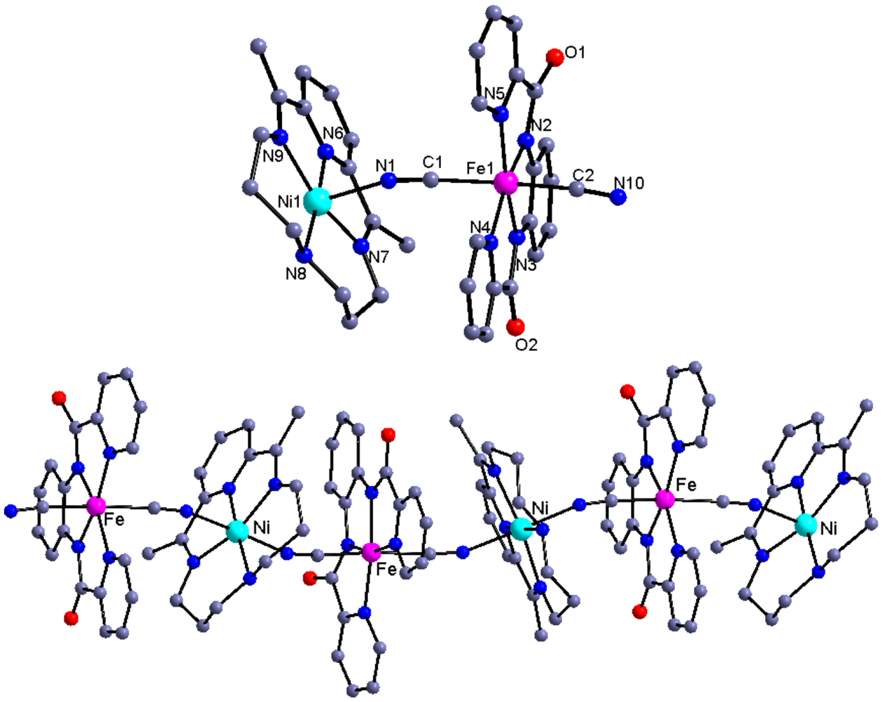


Figure 1. Asymmetric cationic unit and one-dimensional cationic infinite structure of complex **1**. All the hydrogen atoms and the free ClO_4^- have been omitted for clarity.

solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2.[40] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Selected bond distances and bond angles for complexes **1**−**5** with their estimated standard deviation are listed in Table 1. CCDC 972364−972368 for complexes **1**−**5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ RESULTS AND DISCUSSIONS

Synthesis and General Characterization. As shown in Scheme 1, the 14-membered polyaza macrocycle (L) has been found to adopt a planar conformation, imposing a tetragonal-based geometry on the central metal ion with different electronic configuration, leading to the stabilization of six-coordinated species. Due to the two replaceable *trans* positions, this compound is a good precursor to prepare cyanide-bridged complexes.[30a−c] It has been proven by the previous reports[16d,41] that dicyanide-containing iron complex $[Fe(bpb)(CN)_2]^-$, with a relatively large planar equatorial pyridinecarboxamido ligand and two *trans* cyanide groups, is a good building block for synthesizing low-dimensional cyanide-bridged complexes. As a result, employment of $[Fe(bpb)(CN)_2]^-$ as linker with the $[Ni(L)](ClO_4)_2$ building block might construct complexes with expected one-dimensional structure. This is indeed verified by the isolation of complex **1** from the reaction between $K[Fe(bpb)(CN)_2]$ and $[Ni(L)](ClO_4)_2$ with 1:1 molar ratio with an infinite cyanide-bridged single cationic chain structure as detailed below.

Nevertheless, utilization of $K_3[M(CN)_6]$ (M = Fe, Cr) as construction segments to react with $[Ni(L)](ClO_4)_2$ through a diffusion method in a molar ratio of 2:3 led to the isolation of two cyanide-bridged two-dimensional M^{III}−Ni^{II} coordination polymers containing neutral Ni_3M_2 core **2** and **3**, indicating the obvious influence of the number and the arrangement of the cyanide groups in the cyanide precursor on the dimensionality of the cyanide-bridged complexes generated. Enlightened by this result and also inspired by our very recent findings that the structure of the products from the reactions of $K_4[W(CN)_8]$ and $[Ni(L)](ClO_4)_2$ can be rationally controlled by the quantity of the water used,[42] the reactions between $K_4[M'(CN)_8]$ (M′ = Mo, W) containing the maximum number of cyanide groups in the polycyanide metalate family and $[Ni(L)](ClO_4)_2$ were carried out in an H-type tube, leading to the isolation of two three-dimensional networks, **4** and **5**. It is worth noting that their 3D structures are revealed to be different from that for the reported two 3D coordination polymers,[42] giving further information on the effect of increasing the cyanide groups on increasing the dimensionality of the cyanide-bridged complexes for the reaction system herein.

The whole series of new cyanide-bridged complexes have been characterized by IR spectroscopy. In the IR spectra of complex **1**, the single peak at about 2125 cm^{-1} can be assigned to the bridging cyanide groups. Observation of a strong broad peak centered at ca. 1090 cm^{-1} suggests the presence of ClO_4^- anions. For the IR spectra of **2**−**5**, two sharp peaks due to the cyanide-stretching vibration were observed in the range of 2120 and 2160 cm^{-1}, respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes.

Crystal Structure of Complexes 1−5. Some important structural parameters for complexes **1**−**5** are collected in Tables S1 and S2 (Supporting Information). The asymmetry cationic unit, the one-dimensional cationic structure, and the cell packing diagram for complex **1** are depicted in Figures 1 and S1 (Support information), respectively. As can be found, this compound possesses a perfect one-dimensional cationic infinite structure comprising a repeating [-NC-Fe(bpb)-CN-Ni(L)-] unit with the positive charge balanced by a ClO_4^- anion. Each

$[Fe(bpb)(CN)_2]^-$ unit, acting as a bidentate ligand through its two cyanide groups, connects the Ni(II) ions of two independent macrocyclic nickel units. The Fe atom is coordinated by four N atoms of a cyanide-containing precursor located in the equatorial plane and two C atoms of cyanide groups in *trans* position, forming a slightly distorted octahedral geometry.

The Ni(II) ion in **1** is six-coordinated, also forming a slightly distorted octahedral coordination geometry, in which the four equatorial positions are occupied by a N_4 unit coming from the polyaza macrocyclic ligand and two axial ones coordinated by two N atoms of cyanide groups. The $Ni-N_{cyanide}$ bond lengths in complex **1** are 2.107(8) and 2.085(9) Å, respectively, slightly longer than $Ni-N_{equatorial}$ bond lengths with an average value of 2.025 Å. The bond angle of N1−Ni1−N2 is 178.3(3)°, indicating the good linear configuration of these three atoms. However, the $Ni-N\equiv C$ bond angle is somewhat bent, with values of 162.2(7)° and 162.3(8)°, respectively. The intramolecular $Fe^{III}-Ni^{II}$ separation through bridging cyanide is 5.130 Å, while the shortest intermolecular metal−metal distance, 7.966 Å, is obviously longer than this value.

Complexes **2** and **3**, crystallizing in triclinic space group $P\overline{1}$, are isostructural. The representative neutral molecular structure containing an M_2Ni_3 core and the two-dimensional network containing the solvent molecules are shown in Figures 2 and 3, respectively. In these two complexes, the coordination sphere for both Fe/Cr and Ni ions is octahedron. Among which, the one for the Ni(II) ion is slightly distorted, with the average $Ni-N_{cyanide}$ bond length of 2.139 Å and $Ni-N_{equatorial}$ 2.011 Å, respectively [with Ni(1) in complex **2** as representative]. Different from the reported cyanide-bridged Ni−M (M = Fe, Cr) complexes with polyimine macrocyclic ligands as starting materials, in which the $[M(CN)_6]^{3-}$ ions use three C_3 rotational symmetry related *cis* C≡N groups to connect with three Ni^{2+}, giving rise to $M-C\equiv N-Ni$ linkages with the three remaining symmetry-related *cis* C≡N groups monodentate,[24a−c] the $[M(CN)_6]^{3-}$ in **2** and **3** act as tetradentate ligands. Four $[Ni(L)]^{2+}$ units are coordinated to the central $[M(CN)_6]^{3-}$ through two pairs of cyanide groups located in *trans* positions to each other, resulting in a 2D layer sheet containing a repeating cyclic $[(\text{-Ni-NC-M-CN-})]_6$ unit with solvent water molecules in the interlayer space. The two $Ni-N\equiv C$ bond angles for each Ni(II) ion are close to each other, with values of 156.1(3)° and 152.3(4)° in **2** and 154.0(4)° and 156.9(5)° in **3**. The intramolecular M−Ni distance through the bridging cyanide group is about 5.05 Å.

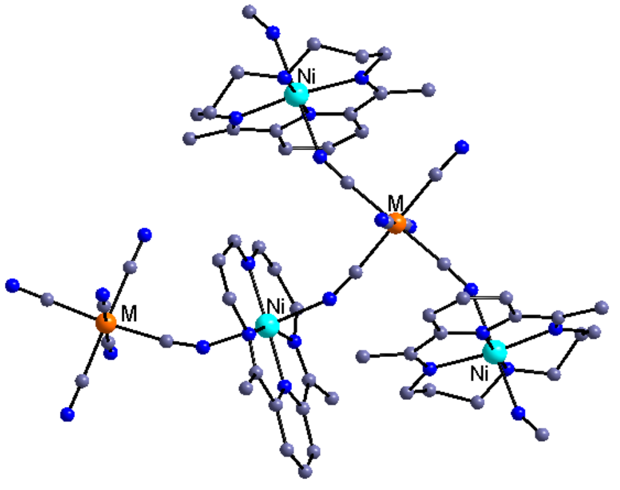


Figure 2. Representative neutral molecular structure containing an M_2Ni_3 core for complexes **2** and **3**. All the H atoms and the solvent molecules have been omitted for clarity.

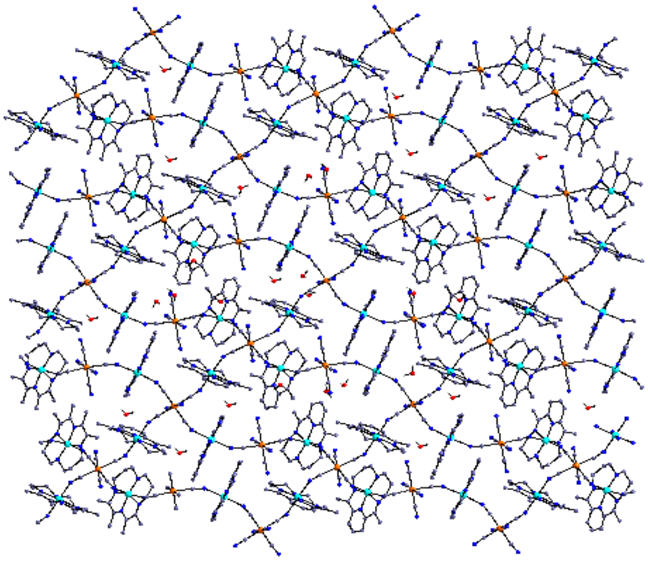


Figure 3. Representative 2D network structure of complexes **2** and **3**. All the nonsolvent H atoms have been omitted for clarity.

Complexes **4** and **5** crystallizing in monoclinic space group $P2(1)/n$ are also isostructural. The representative coordination geometry and the cell-packing diagram containing the solvent molecules along the *b* axis for these two complexes are shown in Figure 4. The cell packing along the *a* and *c* axes are given in Figures S2 and S3 (Supporting Information). The coordination sphere of the M′ atom is distorted square antiprism involving eight cyanide groups. Each $[M'(CN)_8]^{4-}$ ion acting as a tetradentate ligand connects four $[Ni(L)]^{2+}$ units, in which three cyanide bridges come from one tetragonal pyramid and the additional one from another tetragonal pyramid. The four $[Ni(L)]^{2+}$ units can be further bridged by the cyanide groups of another $[M'(CN)_8]^{4-}$ with the same coordination mode as mentioned above, therefore forming the 3D network structure.

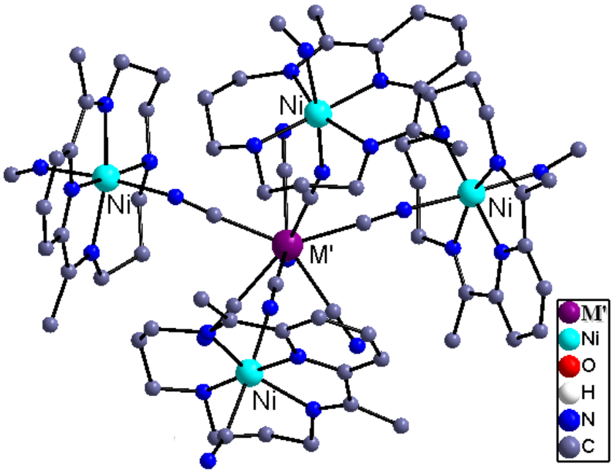


Figure 4. Representative coordination geometry for complexes **4** and **5**. All the H atoms and the solvent molecules have been omitted for clarity.

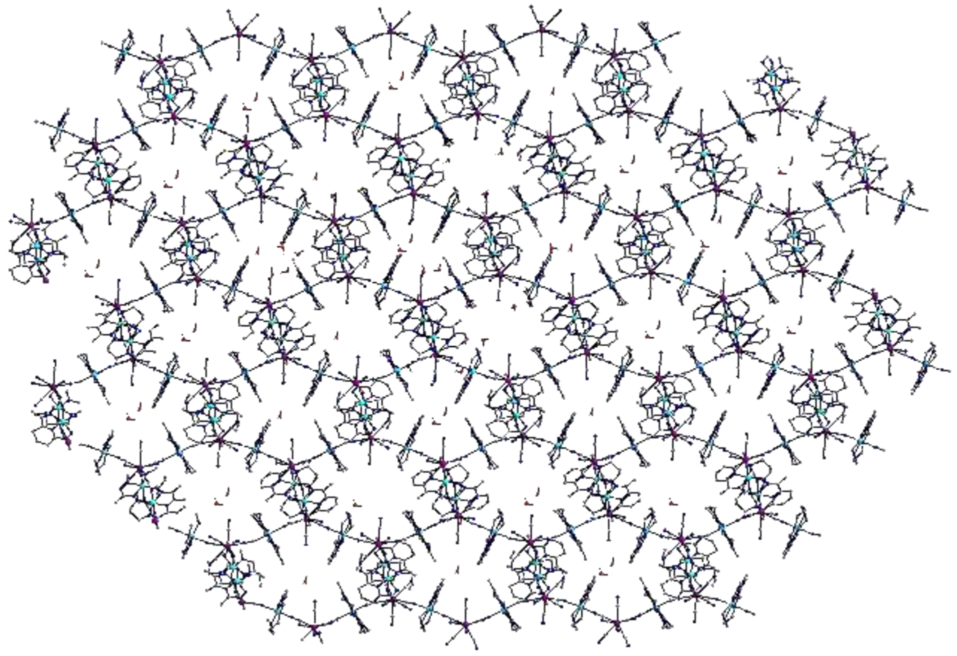


Figure 5. Cell-packing diagram containing the solvent molecules along the *b* axis for complexes **4** and **5**. All the nonsolvent H atoms have been omitted for clarity.

The $C_{bridge\text{-}CN}-M'-C_{bridge\text{-}CN}$ angles (with Mo(1) in complex **4** as representative) are 142.1(3)°, 116.2(3)°, 74.2(3)°, 84.5(3)°, 84.8(3)°, and 70.6(3)°, respectively. Comparison of the $M'-C_{bridge\text{-}CN}$ bond lengths with those of other M′−C ones found no conspicuous difference, indicating no obvious influence of the coordinated Ni−N bonds on the geometry of the $[M'(CN)_8]^{4-}$ ion. The coordination geometry of the Ni(II) ion is a slightly distorted octahedron, in which the four equatorial positions are occupied by the four N atoms of the macrocyclic ligand, and the other two axial ones come from the N atoms of the bridged cyanide groups. The $Ni-N_{cyandie}$ bond lengths are 2.053(4) and 2.106(7) Å [with Ni(1) in complex **4** as representative], respectively, slightly longer than the $Ni-N_{polyaza}$ distance with the average value of 2.039 Å. Analyzing the structure of these two coordination polymers reveals a cavity ratio as high as 31.6% and 30.1% for **4** and **5**, indicating their potential application as a good hole material for gas storage.

Magnetic Property of Complex 1. The magnetic properties for complexes **1**−**5** were investigated. The temperature dependence of magnetic susceptibility for complex **1** was measured in the range 2−300 K under an external magnetic field of 2000 Oe. The $\chi_M T$ product per $Fe^{III}Ni^{II}$ unit for **1** is illustrated in Figure 6. The room-temperature value of $\chi_M T$ is 1.56 emu K mol^{-1}, slightly higher than the spin-only value of 1.375 emu K mol^{-1} for high-spin Ni(II) ($S = 1$) and low-spin Fe(III) ($S = 1/2$) with $g = 2.0$. With the temperature lowering, the $\chi_M T$ value increases very slowly until about 50 K, then increases rapidly to the value of 6.36 emu K mol^{-1} at 2.7 K, and then decreases to 5.61 emu K mol^{-1} at 2 K. The magnetic susceptibility obeys Curie−Weiss law in the range 2−300 K and affords positive Weiss constant θ☐ = 4.95 K and Curie constant $C = 1.52$ emu K mol^{-1}, primarily indicating the ferromagnetic coupling between the cyanide-bridged Ni(II)−Fe(III) in complex **1**.

As can be found from the crystal data, the two Fe(III)−CN−Ni(II) linkages are almost equal, with the two Ni−N≡C bond angles of 162.3(8)° and 162.3(7)°, respectively. Therefore, a Seiden chain model based on the following spin Hamiltonian is suitable for evaluating the intrachain coupling,[43,44] for which the equation used is given in the Supporting Information.

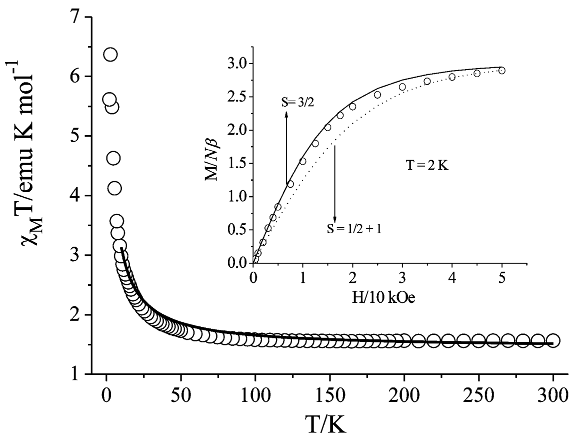


Figure 6. Temperature dependence of $\chi_M T$ of complex **1** (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the solid or dotted line is the Brillouin curve for $S = 3/2$ or for uncoupled $S_{Fe} = 1/2$ and $S_{Ni} = 1$ with $g = 2.0$).

$$H = -J \sum_{i=0} N S_i S_{i+1}$$

Considering that the effects resulted from the intermolecular interaction and the zero-field splitting of the Ni(II) ion are relatively small and can therefore be safely neglected at comparable high temperature, the data of the experimental $\chi_M T$ value of 10−300 K were used for fitting, giving the best-fit parameters $J = 3.67$ cm^{-1}, $g = 2.02$, and $R = 2.28 \times 10^{-5}$. The result is basically comparable to those found in the reported cyanide-bridged Fe−Ni complexes (Table S3, Supporting Information).

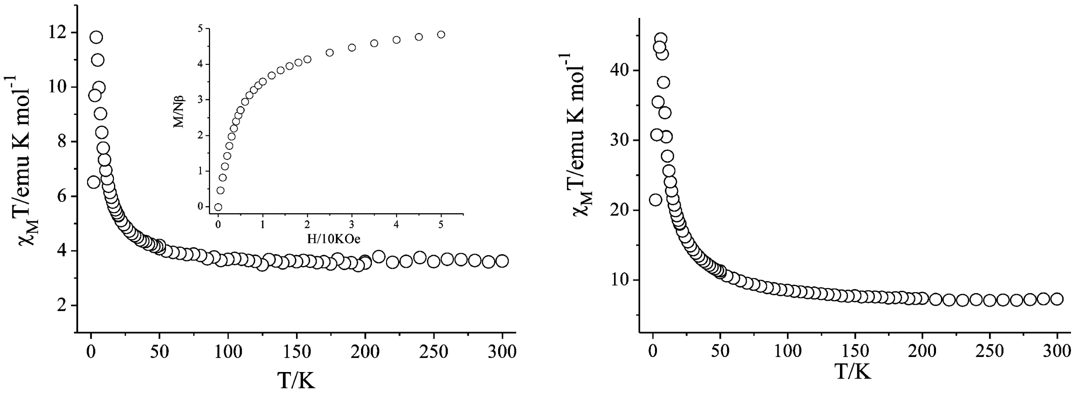


Figure 7. Temperature dependence of $\chi_M T$ of **2** (left) and **3** (right). Left inset: Field dependence of magnetization of **2** at 2 K.

The field dependence of magnetization measured up to 50 kOe at 2 K (inset of Figure 6) for **1** shows no obvious abnormity, indicative of the paramagnetic properties of this complex. The experimental data are basically consistent with the calculated Brillouin function that corresponds to ferromagnetic coupled low-spin Fe(III) ions and high-spin Ni(II) ions ($S_T = 3/2$) with $g = 2.0$ at 2 K. The value of saturation magnetization is about 2.92 *Nβ*, which is close to the expected value 3.0 *Nβ*. These data give further information about the existence of a ferromagnetic coupling interaction between Fe(III) and Ni(II) ions.

Magnetic Properties of Complexes 2 and 3. Figure 7 shows the temperature dependence of magnetic susceptibilities for complexes **2** and **3** measured in the range of 2−300 K under the external magnetic field of 2000 Oe, where χ_M is the magnetic susceptibility/Ni_3M_2 unit. The temperature dependence of the magnetic susceptibility of complexes **4** and **5** is given in Figure S4 (Supporting Information). The $\chi_M T$ values at room temperature are about 3.62 and 7.26 emu K mol^{-1} for **2** and **3**, respectively, which are basically consistent with 3.75 and 6.75 emu K mol^{-1} for three high-spin Ni(II) ($S = 1$) and two low-spin Fe(III) ($S = 1/2$) ions or two Cr(III) ($S = 3/2$) ions. With the temperature decreasing to about 50 K, the $\chi_M T$ value increases smoothly and then sharply reaches the maximum value of 11.82 and 44.5 emu K mol^{-1} for **2** and **3**, respectively. The maximum values are obviously larger than the spin-only value of 10.0 emu K mol^{-1} for $S_T = 4$ and 21 emu K mol^{-1} for $S_T = 6$ resulting from the ferromagnetic coupling of three nickel(II) ions and two low-spin iron(III) ions, respectively, clearly suggestive of the occurrence of magnetic ordering. Below 4.0 K for **2** and 6.0 K for **3**, the $\chi_M T$ values decrease rapidly, which is due to the presence of an interlayer magnetic interaction, the field saturation of the magnetization, and/or the zero-field splitting effect of the nickel(II) ions in axially elongated octahedral surroundings.

The field dependence of the magnetization (0−5 T) measured at 2.0 K is shown in the inset of Figures 7 and 9 in the form of $M/N\beta$ (per Ni_3M_2 unit) vs H, where M, N, β, and H are the magnetization, Avogadro's constant, the electron Bohr magneton, and applied magnetic field, respectively. The magnetization shows a rapid increase at the low field, then reaches with a relatively slow speed the values 4.93 and 11.3 *Nβ* at 5 T for **2** and **3**, respectively, which are close to their expected values of 8 *Nβ* ($S = 4$, Ni_3Fe_2) and 12 *Nβ* ($S = 6$, Ni_3Cr_2), indicating the presence of ferromagnetic interaction between the adjacent M(III) ion and Ni(II) ion bridged by a cyanide group.

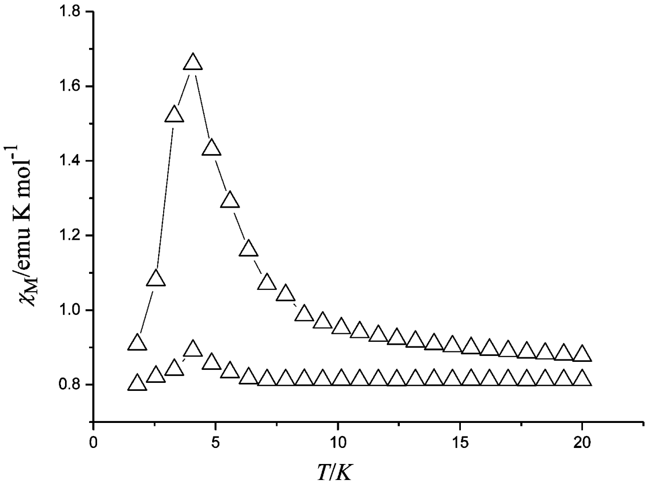


Figure 8. Temperature dependence of ac susceptibility of complex **2** in a zero-static field and an ac field of 3 Oe at frequencies of 411 Hz.

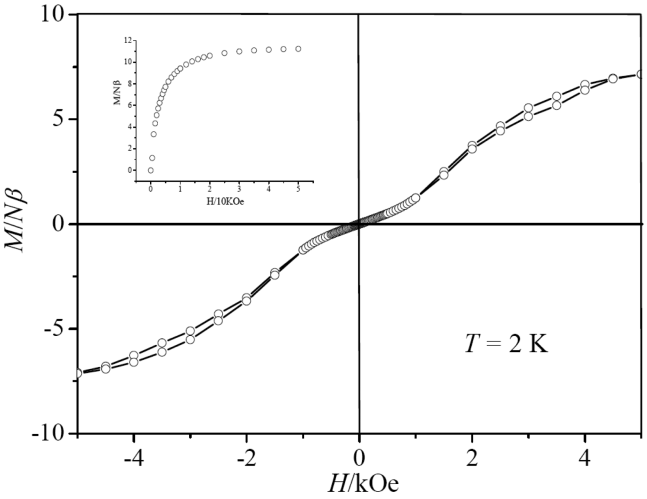


Figure 9. Magnetic hysteresis loop for complex **3** at 2 K. Inset: Field dependence of magnetization at 2 K.

The onset of a magnetic phase transition is further confirmed by the temperature dependence of the ac molar magnetic susceptibility displayed in Figure 8. For complex **2**, both the real and the imaginary part of the zero field ac magnetic susceptibility, $\chi_M(T)$, have a maximum at ca. 4.0 K for a frequency of 411 Hz, suggesting that T_C of **2** is ca. 4 K (Figure 8).[24a] Also, the long-range ferromagnetic ordering can be further proved by the field-cooled magnetization (FCM) curve obtained by cooling the sample from 30 K to 2 K under a weak magnetic field of 0.1 kOe (Figure S5, Supporting Information). However, no obvious hysteresis loop could be found for this complex due probably to the low magnetic phase transition temperature.

The field-cooled magnetization for complex **3** was measured under the magnetic fields of 0.1, 0.5, 1.5, 3, and 10 kOe in the range 2−30 K (Figure S6, Supporting Information). The FCM curves show a peak at about 6.0 K, which can be considered as the antiferromagnetic phase transition temperature for this complex. Also, the absence of a peak for the 1.5 kOe curve shows the metamagnetic property, suggesting also the critical field of about 1.5 kOe. In the real part of the ac magnetic susceptibility measurement carried out at a frequency of 411 Hz with a zero dc field (Figure S7, Supporting Information), a maximum of the in-phase susceptibility (χ_M') was observed at about 6.0 K, and no signal was observed in the imaginary part of the ac magnetic susceptibility measurement, confirming again the 3D antiferromagnetic ordering for complex **3** with the Néel temperature (T_N) at about 6.0 K.[24b] Furthermore, the hysteresis loop for complex **3** at 2 K (Figure 9) shows a sigmoid curve, typical of a metamagnetic behavior. It has been known that, as far as the 2D layered cyanide-bridged Ni_2M_3 system is concerned,[24] the combination of the intralayer ferromagnetic and the interlayer ferromagnetic/antiferromagnetic interactions is responsible for the occurrence of the magnetic ordering behavior. The magnetic ordering temperature usually depends on the intensity of the interlayer magnetic interaction, which is always related to the interlayer separation and the number and the position of the lattice solvent water.[24,45] The comparatively low magnetic phase transition temperature for the reported complexes here is probable due to the long interlayer separation of about 11.3 Å.

Investigation of the magnetic properties of the three cyanide-bridged MNi (M = Fe, Cr) complexes always reveals the ferromagnetic coupling between the M^{III} and Ni^{II} bridged by a cyanide group. It has been shown that the observed ferromagnetic coupling between nearest paramagnetic neighbors in linear cyanide-bridged systems is due to the strict orthogonality of the magnetic orbitals even if the bending of the A−N−C unit introduces some orbital overlap and weakens the ferromagnetic interaction. The electronic configurations of low-spin Fe(III) and Cr(III) are $t_{2g}^5e_g^0$ and $t_{2g}^3e_g^0$, respectively, while that for the Ni(II) ion involved in the octahedral coordination field is $t_{2g}^6e_g^2$. Therefore, the ferromagnetic coupling observed in the present work can be interpreted by the orthogonality of the t_{2g} magnetic orbitals of Fe(III) and Cr(III) with the e_g ones of Ni(II) (Figure S8, Supporting Information), as in examples reported previously (see Table S3, Supporting Information).

CONCLUSION

In summary, a series of new heterobimetallic cyanide-bridged complexes structurally characterized as 1D, 2D, and 3D coordination polymers have been synthesized with a polyaza macrocyclic Ni(II) compound as the assembly segment as a result of the rational selection of five polycyanide metalates with different cyanide group numbers and arrangements. The two 3D complexes were revealed to exhibit a cavity ratio as high as 31.6% and 30.1%, implying their potential application as hole material for gas storage. Nevertheless, systematic and comparative studies over the magnetic properties of complexes **1**−**3** show the ferromagnetic coupling between neighboring Fe(III)/Cr(III) and Ni(II) ions through the bridging cyanide group and reveal the three-dimensional magnetic ordering character for **2** and **3**.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. The cell-packing diagram for complex **1**. The cell-packing diagram along the *a* and *c* axes for complexes **4** and **5**. Field-cooled magnetization of complex **2** in applied fields of 0.1 kOe. Field-cooled magnetization of complex **3** in applied fields of 0.1, 0.5, 1.5, 3, and 10 kOe. Temperature dependence of ac magnetization of complex **3** in a zero-static field and an ac field of 3 Oe at frequencies of 411 Hz. The temperature dependence of the magnetic susceptibility of complexes **4** and **5**. The graphic for the strict orthogonality of the magnetic orbitals through a cyanide bridge. Selected bond lengths (Å) and angles (deg) for complexes **1**−**5**. Structure and magnetic property of previously reported cyanide-bridged $Fe^{III}Ni^{II}$ complexes and the references therein. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China (21171107) and the Natural Science Foundation of Shandong Province (ZR2011BM008) and China Postdoctoral Special Foundation.

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