Inorg. Chem. **2002**, *41*, 6887–6891

Inorganic Chemistry
Article

From One-dimensional Chain to Pentanuclear Molecule. Magnetism of Cyano-Bridged Fe(III)–Ni(II) Complexes

Hui-Zhong Kou,*,[†] Bei Chuan Zhou,[†] Dai-Zheng Liao,[‡] Ru-Ji Wang,[†] and Yadong Li[†]

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China,
Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

Received August 3, 2002

Two cyano-bridged Ni(II)–Fe(III) complexes $\{(H_3O)[Ni(H_2L)]_2[Fe(CN)_6]_2{\cdot}[Fe(CN)_6]{\cdot}6H_2O\}_n$ (**1**) and $[K(18\text{-}C\text{-}6)(H_2O)_2]$-$[Ni(H_2L)]_2[Fe(CN)_6]_3{\cdot}4(18\text{-}C\text{-}6){\cdot}20H_2O$ (**2**) (L = 3,10-bis(2-aminoethyl)-1,3,6,8,10,12-hexaazacyclotetradecane, 18-C-6 = 18-crown-6-ether) have been synthesized and characterized structurally and magnetically. Complex **1** has a zigzag one-dimensional structure, in which two *trans*-CN^- ligands of each $[Fe(CN)_6]^{3-}$ link two *trans*-$[Ni(H_2L)]^{4+}$ groups, and in turn, each *trans*-$[Ni(H_2L)]^{4+}$ links two $[Fe(CN)_6]^{3-}$ in a trans fashion. Complex **2** is composed of cyano-bridged pentanuclear molecules with moieties connected by the *trans*-CN^- ligands of $[Fe(CN)_6]^{3-}$. Magnetic studies show the existence of ferromagnetic Ni(II)–Fe(III) interactions in both complexes. The intermetallic magnetic coupling constant of both complexes was analyzed by using an approximate model on the basis of the structural features.

Introduction

Cyanide ligand has been used to construct molecular magnetic materials, and some interesting findings have been reported.[1-24] Among these interesting research, low-dimensional as well as polynuclear clusters have attracted special attention.[9-14] This is because such system can be used to investigate the intermetallic magnetic coupling quantitatively, whereas lack of an appropriate model for high-dimensional systems is the problem for quantitative magnetic analysis. Until now, a few cyano-bridged one-dimensional or polynuclear clusters were designed and synthesized. The synthetic method is to control the available coordination site around the metal ion. Starlike Mn_6M ($M = Fe^{III}$ or Fe^{II}) or Ni_6Fe complexes are prepared by this method. Also, controlling the coordination type of the leaving groups could lead to polynuclear clusters as shown by Dunbar et al.[11]

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* To whom correspondence should be addressed. E-mail: kouhz@mail.tsinghua.edu.cn. Fax: 86-10-62788765.

[†] Tsinghua University.

[‡] Nankai University.

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10.1021/ic025927+ CCC: $22.00

Four-coordinate macrocyclic nickel(II) complexes can accept two donor atoms at the trans positions to form cyano-bridged species.[15−24] A number of two-dimensional honeycomblike or brick-wall-like complexes, $[NiL']_3[M(CN)_6]_2 \cdot nH_2O$, (L′ = macrocyclic ligands, M = Fe^{III} or Cr^{III}) have been prepared by the reaction of $[M(CN)_6]^{3-}$ with four-coordinate macrocyclic nickel(II) complexes.[15−22] These 2D Ni_3M_2 complexes have been assembled on the basis of the charge ratio (2:3) of the cation and anion. Therefore, we infer that if a different charge ratio is involved, e.g., 4:3, a different molecular structure might occur. Along this end, a tetravalent hexaazamacrocyclic nickel(II) complex, $[Ni(H_2L)](ClO_4)_4$ (L = 3,10-bis(2-aminoethyl)-1,3,6,8,10,12-hexaazacyclotetradecane), was employed for the synthesis. In this paper, we report the synthesis, structure, and magnetic properties of one-dimensional chain **1** and pentanuclear complex **2**.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. The infrared spectroscopy was performed on a Magna-IR 750 spectrophotometer in the 4000−400 cm^{-1} region. Variable-temperature magnetic susceptibility measurements of **1** and **2** were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

Syntheses. All chemicals and solvents used in the synthesis were reagent grade. $[K(18\text{-}C\text{-}6)]_3[Fe(CN)_6]$ and $[Ni(H_2L)](ClO_4)_4$ were prepared according to the literature method.[25,26]

$\{(H_3O)[Ni(H_2L)]_2[Fe(CN)_6]_2 \cdot [Fe(CN)_6] \cdot 6H_2O\}_n$ (1): Platelike brown single crystals were obtained by slow evaporation of an aqueous solution (15 mL) of $[Ni(H_2L)](ClO_4)_4$ (0.1 mmol) and $K_3[Fe(CN)_6]$ (0.1 mmol) in a molar ratio of 1:1. Yield: 40%. Anal. Calcd for $C_{42}H_{83}Fe_3N_{34}Ni_2O_7$: C, 34.52; H, 5.73; N, 32.59. Found: C, 34.26; H, 5.83; N, 32.39. IR (cm^{-1}): 2146 s, 2118 vs, 2043 w ($\nu_{C\equiv N}$).

$[K(18\text{-}C\text{-}6)(H_2O)_2][Ni(H_2L)]_2[Fe(CN)_6]_3 \cdot 4(18\text{-}C\text{-}6) \cdot 20H_2O$ (2): Brown single crystals were obtained by slow evaporation of an aqueous solution (10 mL) of $[Ni(H_2L)](ClO_4)_4$, $[K(18\text{-}C\text{-}6)]_3[Fe(CN)_6]$, and an excess amount of 18-C-6 in a molar ratio of 1:1:3. Yield: 50%. Anal. Calcd for $C_{102}H_{232}Fe_3KN_{34}Ni_2O_{52}$: C, 39.63; H, 7.56; N, 15.41. Found: C, 39.23; H, 7.43; N, 15.72. IR (cm^{-1}): 2140 sh, 2112 vs ($\nu_{C\equiv N}$); 1102 vs (ν_{C-O}).

X-ray Structure Determination. The data collections of **1** and **2** were made on a Rigaku R-Axis RIPID IP (123 K) and a Nonius Kappa-CCD (293 K) diffractometer, respectively. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELEXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined by using a riding model. Weighted *R*-factors, *wR*, and all goodness of fit (*S*) are based on F^2, conventional *R*-factors are based on *F*, with *F* set to zero for negative F^2. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. The high *R*1 factors are due to the efflorescent nature of the crystals. Therefore, the temperature factors of the 18-C-6 molecules are high, which indicates that there is some extent of disorder present. The crystal data are summarized in Table 1.

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	2
formula	$C_{42}H_{83}Fe_3N_{34}Ni_2O_7$	$C_{102}H_{232}Fe_3KN_{34}Ni_2O_{52}$
fw	1461.3	3091.29
λ, Å	0.71073	0.71073
Space group	*P*-1	$P2_1/n$
A, Å	8.9283(8)	20.652(4)
B, Å	13.4802(10)	15.716(3)
C, Å	15.2995(19)	25.591(5)
α, deg	67.2407(57)	90.00
β, deg	87.4952(6)	103.09(3)
γ, deg	83.7363(21)	90.00
V, $Å^3$	1687.8(3)	8090(3)
Z	1	2
ρ_{calcd}, g cm^{-3}	1.438	1.269
μ(MoKα), mm^{-1}	1.246	0.602
independent reflections	7234	14207
data/restraints/parameters	7234/8/417	14207/16/895
*R*1 [$I > 2\sigma(I)$]	0.0964	0.0837
*wR*2 (all data)	0.2817	0.253

Results and Discussion

Synthesis and Physical Characterization. The 1D complex (**1**) was synthesized by the reaction of $[Ni(H_2L)](ClO_4)_4$ with $K_3[Fe(CN)_6]$ in an aqueous solution. A pentanuclear complex (**2**) was obtained with a synthetic procedure similar to that for the extended chain complex **1,** except that $[K(18\text{-}C\text{-}6)]_3[Fe(CN)_6]$ was used instead of $K_3[Fe(CN)_6]$. This probably results from the supramolecular interaction between the 18-C-6 and the macrocyclic ligands (vide infra). It is worth mentioning that we found that using $[Bu_4N]_3[Fe(CN)_6]$ in place of $[K(18\text{-}C\text{-}6)]_3[Fe(CN)_6]$ produces complex **1** rather than complex **2**, which indicates that large counteractions are not the key factor in forming the pentanuclear molecule. Not forming the common honeycomblike Ni_3Fe_2 complexes is due to the fact that many counteranions were needed and consequently much more space was required. Therefore, it is understandable that using neutral cyano-containing building blocks, e.g., $(tacn)M(CN)_3$ (tacn = 1,4,7-triazacyclononane, M = Cr or Mo)[27−30] and $Fe(phen)_2(CN)_2$ (phen = 1,10-phenanthroline),[31,32] could generate polynuclear or 1D coordination compounds.

The IR spectra of **1** and **2** in the range 2000−2200 cm^{-1} ($\nu_{C\equiv N}$) exhibit splitting peaks, suggesting the presence of bridging and nonbridging cyano ligands in $[Fe(CN)_6]^{3-}$. The intense band at 1102 cm^{-1} can be assigned to the C−O stretching vibration of 18-crown-6.[33]

Crystal Structures. ORTEP drawings of complexes **1** and **2** are shown in Figures 1 and 3, respectively. Figure 2 shows

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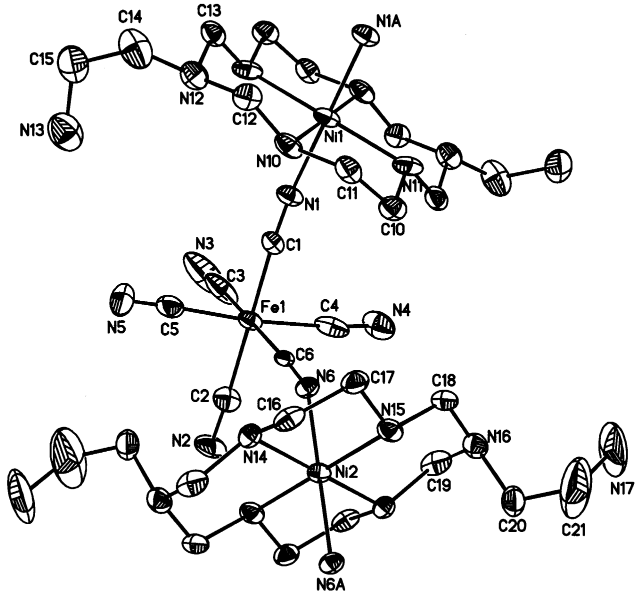

Figure 1. ORTEP plot of the polymeric cation of **1** drawn at 30% probability thermal ellipsiod.

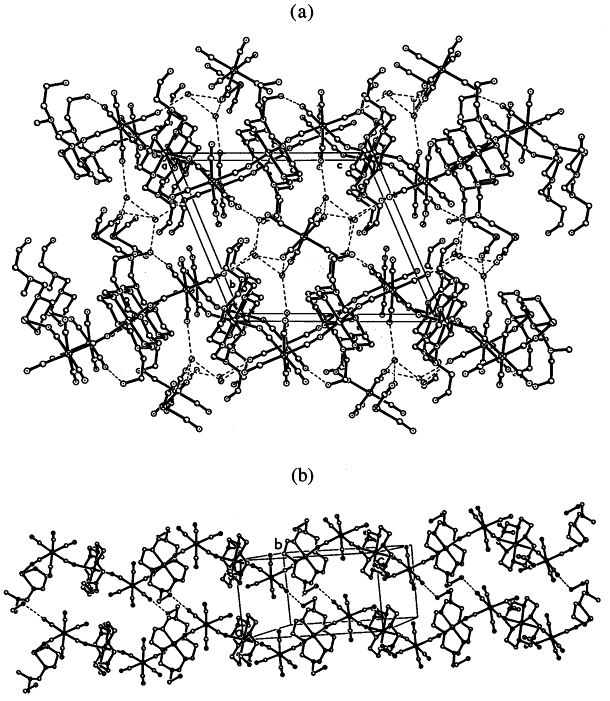

Figure 2. Cell packing of **1** showing hydrogen-bonded chains.

the cell packing diagram of **1**. Selected bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

X-ray crystallography of **1** reveals that the structure consists of an alternating one-dimensional cationic polymer $\{[Ni(H_2L)]_2[Fe(CN)_6]_2\}_n^{2n+}$, with free $[Fe(CN)_6]^{3-}$ as counteranions (Figure 1). Due to the charge balance of the complex, a cation is required. ICP measurements clearly show the absence of a K^+ ion, therefore a protonated water molecule is assumed. The zigzag chain is made of a cyano-bridged alternating $[Fe(CN)_6]^{3-}$−$[Ni(H_2L)]^{4+}$ fragment. In the chain, $[Fe(CN)_6]^{3-}$ uses two *cis*-CN^- groups to connect with two $[Ni(H_2L)]^{4+}$ groups, whereas each $[Ni(H_2L)]^{4+}$ group is linked to two $[Fe(CN)_6]^{3-}$ ions in trans positions. Two nitrogen atoms of the bridging C≡N ligands coordinate to the Ni(II) ions with the Ni−N contacts of 2.065(8) Å for Ni(1) and 2.103(7) Å for Ni(2). The bridging cyanide ligands coordinate to the nickel(II) ions in a bent fashion with Ni−N≡C bond angles of 153.4(7)° and 169.2(7)°. The adjacent Fe---Ni distances are 5.085(2) Å for Fe(1)---Ni(1) and 5.005(2) Å for Fe(1)---Ni(2). The Fe−C distances range from 1.886(10) to 1.972(15) Å for Fe(1). The shortest

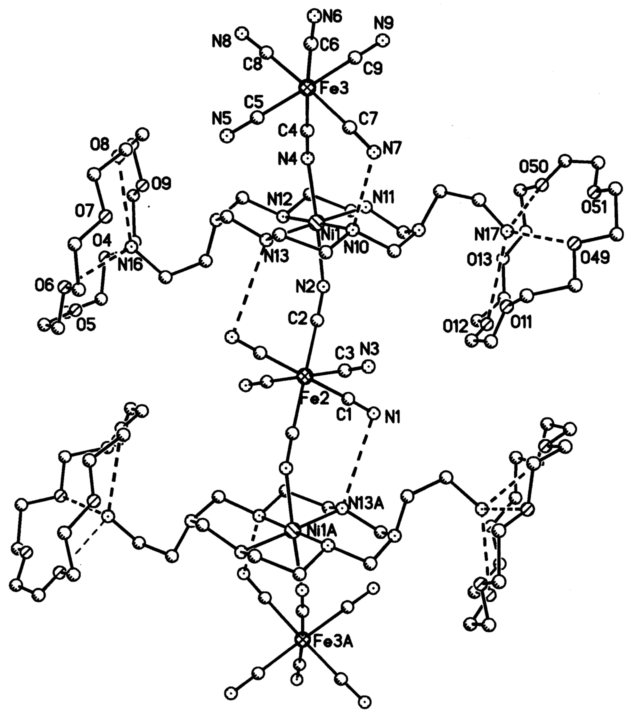

Figure 3. Structure of **2**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Ni(1)−N(11)	2.063(8)	Ni(1)−N(10)	2.083(8)
Ni(1)−N(1)	2.065(8)	Ni(2)−N(6)	2.103(7)
Ni(2)−N(14)	2.056(8)	Ni(2)−N(15)	2.069(8)
Fe(1)−C(1)	1.886(10)	Fe(1)−C(2)	1.926(11)
Fe(1)−C(3)	1.920(12)	Fe(1)−C(4)	1.972(15)
Fe(1)−C(5)	1.967(14)	Fe(1)−C(6)	1.950(10)
Fe(2)−C(7)	1.950(7)	Fe(2−)−C(8)	1.932(8)
Fe(2)−C(9)	1.948(7)	N(1)−C(1)	1.170(12)
N(2)−C(2)	1.183(13)	C(3)−N(3)	1.138(14)
C(4)−N(4)	1.136(14)	C(5)−N(5)	1.165(15)
N(6)−C(6)	1.125(10)	C(7)−N(7)	1.149(5)
N(8)−C(8)	1.144(5)	C(9)−N(9)	1.158(5)
C(1)−N(1)−Ni(1)	169.2(7)	C(6)−N(6)−Ni(2)	153.4(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Ni(1)−N(2)	2.125(7)	Ni(1)−N(4)	2.122(6)
Ni(1)−N(10)	2.071(5)	Ni(1)−N(11)	2.041(6)
Ni(1)−N(12)	2.071(5)	Ni(1)−N(13)	2.066(6)
Fe(2)−C(1)	1.924(10)	Fe(2)−C(2)	1.928(8)
Fe(2)−C(3)	1.937(8)	Fe(3)−C(4)	1.932(8)
Fe(3)−C(5)	1.937(8)	Fe(3)C(6)	1.923(9)
Fe(3)−C(7)	1.974(10)	Fe(3)−C(8)	1.930(10)
Fe(3)−C(9)	1.940(8)	K(1)−O(1)	2.776(6)
K(1)−O(2)	2.739(6)	K(1)−O(3)	2.875(6)
K(1)−O(15W)	2.993(7)	C(1)−N(1)	1.156(10)
N(2)−C(2)	1.149(8)	C(3)−N(3)	1.130(9)
N(4)−C(4)	1.146(8)	N(5)−C(5)	1.137(9)
C(6)−N(6)	1.159(9)	N(7)−C(7)	1.128(9)
C(8)−N(8)	1.146(10)	N(9)−C(9)	1.139(9)
C(2)−N(2)−Ni(1)	147.1(6)	C(4)−N(4)−Ni(1)	150.5(6)

Table 4. Hydrogen Bonds in **2** with H···A < *r* (Å) + 2.000 Å and ∠DHA > 110°

DH	∠DHA	*d*(D···A)	A	symmetry operation of A
N(13)−H(13C)	143.92	3.337	N(1)	[$-x, -y+2, -z$]
N(11)−H(11C)	131.39	3.016	O(11W)	[$-x+1/2, y-1/2, -z+1/2$]
N(12)−H(12C)	130.76	3.274	O(15W)	[$-x, -y+1, -z$]
N(10)−H(10C)	149.39	3.305	N(7)	
N(17)−H(17A)	164.63	2.918	O(49)	
N(17)−H(17B)	164.05	2.876	O(50)	
N(17)−H(17E)	153.32	3.151	O(12)	
N(16)−H(16A)	156.38	2.985	O(6)	
N(16)−H(16B)	150.71	2.984	O(4)	
N(16)−H(16E)	147.62	3.009	O(8)	

interchain metal−metal distance is 7.64 Å for Fe---Ni. Figure 2 shows the H-bonding interaction between the interstitial water molecules and the cyano nitrogen atoms (Figure 2a) and the intermolecular contacts (N---N = 2.873 Å) between the cyano nitrogen atoms of one chain and the NH_3^+ of $[Ni(H_2L)]^{4+}$ of adjacent chains (Figure 2b).

The structure of **2** reveals that the complex is a pentanuclear anion with two macrocyclic $[Ni(H_2L)]^{4+}$ ions linked by three $[Fe(CN)_6]^{3-}$ moieties (Figure 3). One $[Fe(CN)_6]^{3-}$ lying at the reversion center bridges two Ni(II) ions in a bent fashion (Ni−N≡C = 147.1(6)°) using two trans cyano ligands, and the coordination sphere of two Ni(II) ions is completed by the bridging cyano nitrogen atoms of two terminal $[Fe(CN)_6]^{3-}$ groups (Ni−N≡C = 150.5(6)°), yielding a snakelike Ni_2Fe_3 complex. This bridging coordination angle is unexpectedly low. The Fe−C bond distances and most of the Fe−C−N bond angles are in the normal range. The K^+ ion in *trans*-$[K(18\text{-}C\text{-}6)(H_2O)_2]^+$ is coordinated by eight oxygen atoms of one 18-C-6 and two water molecules with the K−O distances ranging from 2.739(6) to 2.993(7) Å. The *trans*-$[K(18\text{-}C\text{-}6)(H_2O)_2]^+$ ions are situated in the vicinity of the Ni_2Fe_3 molecule (see supporting information). Interestingly, three oxygen atoms of each uncoordinated 18-C-6 are hydrogen bonded to the nitrogen atom (NH_3^+) of the pendent of the coordinated macrocyclic ligand with the N---O contacts ranging from 2.876(9) to 3.151(16) Å (Table 4). Another significant supramolecular interaction is present within the pentanuclear entity between the nonbridging cyano nitrogen atoms (N7 and N1), which are H-bonded to the adjacent N atoms (N10 and N13) of the macrocyclic ligands with the contacts of 3.337(9) for N13---N1A and 3.305(9) Å for N10---N7. The presence of the N10---N7 H-bonding may be responsible for the bent bridging mode between the terminal $[Fe(CN)_6]^{3-}$ and $[Ni(H_2L)]^{4+}$ (Figure 3).

Magnetic Properties. Magnetic studies of **1** and **2** were performed (H = 5000 G) on a SQUID magnetometer. The plots of $\chi_m T$ vs T (per Ni_2Fe_3 unit) for **1** and **2** confirm the ferromagnetic interactions between adjacent Ni(II)···Fe(III) ions (Figures 4 and 5). The ferromagnetic interaction between the low-spin Fe(III) and Ni(II) ions is due to the strict orthogonality of the magnetic orbitals of the low-spin Fe(III) (d^5, t_{2g}^5) and Ni(II) [d^8, $t_{2g}^6e_g^2$] ions.

To analyze the magnetic data of **1**, we tried to use an approximate approach similar to that previously used for 2-D and quasi-2-D complexes.[34−37] On the basis of the crystal data, the Fe−CN−Ni likages were unequal. Therefore, the 1-D chain can be treated as alternating uniform FeNi dimers with the different intradimeric and intrachain exchange constant (J_d vs J_c).

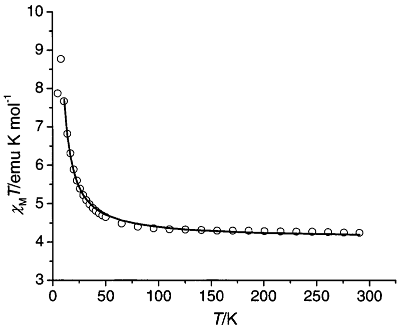

Figure 4. Temperature dependence of $\chi_m T$ for **1**. The solid line is the best fit with the parameters in the text.

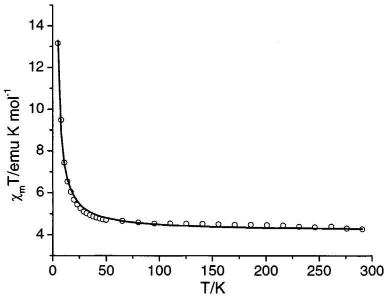

Figure 5. Temperature dependence of $\chi_m T$ for **2**. The solid line is the best fit with the parameters in the text.

$$\chi_d = \frac{Ng^2\beta^2}{4kT}\frac{10 + \exp(-3J_d/kT)}{3 + \exp(5J_d/kT)} \qquad (1)$$

$$\chi_d = \frac{Ng^2\beta^2}{3kT}S_d(S_d + 1) \qquad (2)$$

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\frac{1 + u}{1 - u}S_d(S_d + 1) \qquad (3)$$

where $u = \mathrm{cth}(J_cS_d(S_d + 1)/kT) - kT/J_cS_d(S_d + 1)$

$$\chi_m = \chi_{chain} + \frac{Ng^2\beta^2}{3kT}S_{Fe}(S_{Fe} + 1) \qquad (4)$$

$$\chi_M = \frac{\chi_m}{1 - \chi_m(2zJ'/Ng^2\beta^2)} \qquad (5)$$

Using this rough model, the susceptibility above 10 K was simulated, giving the best fit with parameters J_c = +2.4 cm^{-1}, J_d = +1.9 cm^{-1}, zJ' = −0.4 cm^{-1}, g = 2.29. The $Ni^{II}-Fe^{III}$ exchange coupling parameter is comparable to that

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of the cyano-bridged pentanuclear $[Ni(bmp)_2]_3[Fe(CN)_6]_2\cdot 7H_2O$ (bpm = bis(1-pyrazolyl)methane, $J = +5$ cm^{-1}).[9] The small J_d value might be attributed to the more bent C≡N−Ni linkages, which has an unfavorable effect on magnetic interaction. This result also supports the fact that a wide range of angles could stabilize ferromagnetic Ni^{II}−Fe^{III} coupling through the CN$^-$ bridge.[38]

According to the crystal structure data, complex **2** is a pentanuclear Ni_2Fe_3 entity, which can be described by the following Hamiltonian for an Fe3−Ni2−Fe1−Ni1−Fe2 arrangement:

$$\hat{H} = -2J_{FeNi}(\hat{S}_{Fe1}(\hat{S}_{Ni1} + \hat{S}_{Ni2}) + \hat{S}_{Fe2}\hat{S}_{Ni1} + \hat{S}_{Fe3}\hat{S}_{Ni2})$$

No appropriate model for such a system could be used. To estimate the rough exchange constant, we tried to use an approximate model, i.e., first to consider the central Ni_2Fe trimer and calculate the possible spin states and then estimate the coupling between each spin state and the two terminal $S = 1/2$ spins. The final eigenvalue could be calculated by using the following equation:

$$\chi_m = \Sigma \chi_m{}^{i} P_{(S^i)}$$

where $\chi_m{}^{i}$ represents every molar magnetic susceptibility deduced by the above method and $P_{(Si)}$ the partition factor of every possible spin state.

The partition of each coupling state of the central Ni_2Fe cluster is

$$P_i = \frac{(2S_i + 1)e^{-E_i/kT}}{\Sigma(2S_i + 1)e^{-E_i/kT}} \qquad (6)$$

among them, $S_i = 5/2, 3/2, 1/2$.

The magnetic susceptibilities of the systems containing the two uttermost Fe(III) spins and each spin state derived from the central Ni_2Fe cluster can be calculated as follows.

For the 1/2−5/2−1/2 system:

$$\chi_1 = \frac{Ng^2\beta^2}{4kT} \frac{84\exp(5J/kT) + 35\exp(-2J/kT) + 10\exp(-7J/kT) + 35}{4\exp(5J/kT) + 3\exp(-2J/kT) + 2\exp(-7J/kT) + 3} \qquad (7)$$

For the 1/2−3/2−1/2 system:

$$\chi_2 = \frac{Ng^2\beta^2}{4kT} \frac{35\exp(3J/kT) + 10\exp(-2J/kT) + \exp(-5J/kT) + 10}{2\exp(3J/kT) + 2\exp(-2J/kT) + \exp(-5J/kT) + 2} \qquad (8)$$

For the 1/2−1/2−1/2 system:

$$\chi_3 = \frac{Ng^2\beta^2}{4kT} \frac{\exp(-2J/kT) + 10\exp(-J/kT) + 1}{\exp(-2J/kT) + 2\exp(-J/kT) + 1} \qquad (9)$$

The total magnetic susceptibility can be calculated by the following equation:

$$\chi_m = P_{5/2}\chi_1 + (P_{3/2} + P_{3/2}{}')\chi_2 + (P_{1/2} + P_{1/2}{}')\chi_3 \qquad (10)$$

If a molecular field term is taken into account, the final magnetic susceptibility can be obtained:

$$\chi_M = \frac{\chi_m}{1 - \chi_m(2zJ'/Ng^2\beta^2)}, \text{ where } z = 2 \qquad (11)$$

The corresponding expressions eqs 6−10 together with a molecular field term eq 11 are used to fit the experimental data giving the following results: $J = +2.1$ cm^{-1}, $g = 2.26$, and $zJ' = +0.17$ cm^{-1}. The result indicates the presence of weak ferromagnetic interaction between Ni(II)−Fe(III) ion through cyano bridges and intercluster ferromagnetic coupling. It should be mentioned that not taking into consideration the intermolecular interaction gave a bad fit at low temperatures, and the considerably high $\chi_m T$ value at low temperatures might reflect the presence of strong intermolecular magnetic coupling. The J value is similar to that of complex **1**, which is understandable considering that both complexes are involved in bent Ni−NC−Fe bridging linkages.

The field dependence of the magnetization (0−50 kOe) of **1** and **2** measured at 5.0 K shows the regular increase of the magnetization reaching 6.0 μ_B for **1** and 5.8 Nβ for **2**. The magnetizations at the highest field (50 kOe) approach the expected value of 7.0 μ_B for ferromagnetic Ni_2Fe_3. The experimental curves lie above the Brillouin curve corresponding to noninteracting two S_{Ni} and three S_{Fe} spins, suggesting the presence of intermetallic ferromagnetic coupling (See supporting information). This indicates the $S = 7/2$ ground state for the complexes.

Conclusions

The self-assembly of the tetravalent hexaazacyclic $[Ni(H_2L)]^{4+}$ cation and $K_3[Fe(CN)_6]$ results in formation of the cyano-bridged one-dimensional complex $\{(H_3O)[Ni(H_2L)]_2[Fe(CN)_6]_2\cdot[Fe(CN)_6]\cdot 6H_2O\}_n$ (**1**). When the reaction of $[Ni(H_2L)]^{4+}$ with $[Fe(CN)_6]^{3-}$ was performed in the presence of 18-C-6, a novel pentanuclear complex $[K(18\text{-}C\text{-}6)(H_2O)_2][Ni(H_2L)]_2[Fe(CN)_6]_3\cdot 4(18\text{-}C\text{-}6)\cdot 20H_2O$ (**2**) was obtained. Variable-temperature magnetic susceptibility measurements show that both complexes exhibit ferromagnetic Ni(II − Fe(III) coupling with small exchange constants (<10 cm^{-1}). The present research highlights that the structure of cyano-bridged species (so-called Prussian blue analogues) can be fine-tuned and may be further enriched.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (project No.: 20201008 & 50272034). H.Z.K. thanks Tsinghua University for supporting this work.

Supporting Information Available: Field dependence of magnetic susceptibilities of complexes **1** and **2** at 5 K, crystal cell packing plot of complex **2,** and **a**n X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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