

Assembling Metal Ions Induced Cyanide-Bridged Heterometallic 1D and Ion-Pair Complexes: Synthesis, Crystal Structures and Magnetic Properties

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In the past three decades, the design and synthesis of molecular magnetic materials has attracted extensive interest in several scientific fields including chemistry, physics, materials, and biology. Among of all the molecular magnetism systems, for the well known reasons, cyanide-containing complexes have been widely employed as bridges to assemble homo/hetero-metallic molecular magnetic materials by using the cyanide bridge transferring magnetic coupling between the neighboring paramagnetic ions, in which some showed interesting magnetic properties, such as high-*T_c* magnets,¹ spin crossover materials,² single-molecule magnets (SMMs)³ and single-chain magnets (SCMs).⁴

Very recently, low-dimensional cyanide-bridged complexes attracted much attention due to the necessity for the full and clear elucidation of magneto-structural correlation and the preparation of some interesting molecular materials such as SMMs and SCMs.⁵⁻¹⁷ As has been known, several factors, including the number and the position of cyanide group, the number and the charge nature of the cyanide-containing building block, and the steric effect of the cyanide precursor, can put obvious influence on the structure types of the cyanide-bridged complexes. On the other hand, the ancillary ligands attached to the counterpart assembling segments also play a crucial role in influencing the structure of the resulting complexes. The magnetic assembling segments containing organic ligands with large steric effect, such as 1,10-phenanthroline or 2,2'-bipyridine, are very favor of forming polynuclear or low dimensional cyanide-bridged complexes.^{18,19} With these in mind, we report the synthesis, crystal structures, and magnetic properties of a cyanide-bridged one-dimensional complex $\{[\text{Mn}(\text{Phen})_2][\text{Ni}(\text{CN})_4] \cdot 3\text{H}_2\text{O}\}_n$ (**1**) and an ion-pair complex $\{[\text{Co}(\text{Phen})_2(\text{CN})_2]_2[\text{Ni}(\text{CN})_4]\} \cdot 4\text{H}_2\text{O}$ (**2**) based on tetracyanometallate $\text{K}_2[\text{Ni}(\text{CN})_4]$ and $[\text{M}(\text{Phen})_2\text{Cl}_2]$ ($\text{M} = \text{Mn}, \text{Co}$; Phen = 1,10-phenanthroline) acting as assemble segments in this paper.

Results and Discussion

Synthesis and General Characterization. The recent reports indicated that the assembling segment containing phen or bipy could efficiently lower the dimensionality of the cyanide-bridged complexes.^{18,19} As parts of our continuous efforts towards low-dimensional cyanide-bridged mag-

netic complexes, we investigated the reactions of $\text{M}(\text{Phen})_2\text{Cl}_2$ ($\text{M} = \text{Mn}, \text{Co}$) with tetracyanide-containing precursor $[\text{Ni}(\text{CN})_4]^{2-}$. By employing $\text{Mn}(\text{Phen})_2\text{Cl}_2$ as assemble segment, a one-dimensional cyanide-bridged single chain complex $\{[\text{Mn}(\text{Phen})_2][\text{Ni}(\text{CN})_4] \cdot 3\text{H}_2\text{O}\}_n$ (**1**) has been synthesized. The large phen molecules attached to the Mn(II) ion hindered the other two free cyanide groups of the $[\text{Ni}(\text{CN})_4]^{2-}$ to be coordinated further by Mn(II) ion, therefore preventing from forming two dimensional coordination polymer. The reaction of $[\text{Ni}(\text{CN})_4]^{2-}$ with $\text{Co}(\text{Phen})_2\text{Cl}_2$ resulted in an ion-pair complex $\{[\text{Co}(\text{Phen})_2(\text{CN})_2]_2[\text{Ni}(\text{CN})_4]\} \cdot 4\text{H}_2\text{O}$ (**2**) comprised by two free $[\text{Co}(\text{Phen})_2(\text{CN})_2]^+$ cation and $[\text{Ni}(\text{CN})_4]^{2-}$ anion, in which the initial Co(II) ion in $\text{Co}(\text{Phen})_2\text{Cl}_2$ was readily oxidized to more stable Co(III) ion. Due to the more stronger coordination ability of cyanide group than that for the chloride, the two chloride ion was substituted by two cyanide groups coming from the degradation of the $[\text{Ni}(\text{CN})_4]^{2-}$. The different structure types of these two complexes indicated that both the attached ligand to the metal ion and the property of the assembling metal ions can

Table 1. Crystallographic data for complexes **1** and **2**

	1	2
chemical formula	$\text{C}_{28}\text{H}_{22}\text{MnN}_8\text{NiO}_3$	$\text{C}_{56}\text{H}_{40}\text{Co}_2\text{N}_{16}\text{NiO}_4$
Fw	632.19	1177.61
Crystal system	Orthorhombic	Triclinic
Space group	Pbca	P-1
<i>a</i> /Å	18.506(2)	10.7749(6)
<i>b</i> /Å	12.6652(15)	10.9407(6)
<i>c</i> /Å	23.882(3)	12.0618(7)
α /deg	90	86.418(3)
β /deg	90	74.661(3)
γ /deg	90	84.894(3)
<i>V</i> /Å ³	5597.5(11)	1364.69(13)
<i>Z</i>	8	1
completeness	100.0%	99.4%
<i>F</i> (000)	2584	602
<i>q</i> /deg	1.71 to 25.01	1.75 to 25.01
GOF	0.963	1.074
<i>R</i> ₁ [<i>I</i> > 2 <i>s</i> (<i>I</i>)]	0.0406	0.0501
<i>wR</i> ₂ (all data)	0.1053	0.1494

markedly affect the structure of the complex.

These two cyanide-bridged heterometallic complexes have been characterized by IR spectroscopy. In the IR spectra of complex **1**, two sharp peaks due to the cyanide-stretching vibration were observed at about 2120 and 2160 cm^{-1} , respectively, indicating the presence of bridging and non-bridging cyanide groups in these complexes. For the IR spectra of complex **2**, only a sharp peak at about 2155 cm^{-1} can be found, giving information that the only existing of the non-bridging cyanide group.

Crystal Structures of Complexes 1 and 2. Some important structural parameters for complexes **1** and **2** are collected in Table 2. The neutral binuclear structure of complex **1**, its 1D single chain structure and cell packing diagram are shown in Figures 1-3, respectively. For complex **2**, its crystal structure and 3D supramolecular structure are given in Figures 4 and 5, respectively.

Complex **1** crystallizes in orthorhombic space group *Pbca* containing eight independent units in the cell. As can be found, complex **1** possess neutral one-dimensional single chain structures with zigzag conformation consisting of alternating units of $[\text{Mn}(\text{Phen})_2]^-$ and $[\text{Ni}(\text{CN})_4]^{2-}$. Each $[\text{Ni}(\text{CN})_4]^{2-}$ ion acting as a bidentate ligand through its two cyanide groups with a *trans* position connects the Mn(II) ions of two independent $[\text{Mn}(\text{Phen})_2]$ units. The Mn(II) ion is six-coordinated by a N_6 unit, forming a slightly distorted octahedron coordination geometry, in which four positions are occupied by N_4 unit coming from two Phen ligands and the other two ones coordinated by two N atoms of cyanide groups. The distances between Mn ion and N atoms of phen ligands are 2.277(3), 2.269(3), 2.282(3) and 2.246(3) Å, respectively, which are slight longer than the Mn- $\text{N}_{\text{cyanide}}$ bond lengths 2.169(3) and 2.194(4) Å, demonstrating further the octahedron around the Mn(II) ion is slightly distorted. The Mn...Mn separation bridged by $[-\text{NC}-\text{Ni}-\text{CN}-]$ unit is 9.968 Å, which is markedly shorter than the Mn...Mn distance 12.386 Å between the different chains.

Complex **2**, containing a free $[\text{Ni}(\text{CN})_4]^{2-}$ anion and two $[\text{Co}(\text{Phen})_2(\text{CN})_2]^+$ cations, crystallizes in monoclinic space group *C2/c*. The Ni-C bond lengths and the Ni-CN bond angles in $[\text{Ni}(\text{CN})_4]^{2-}$ are almost equal to those correspond-

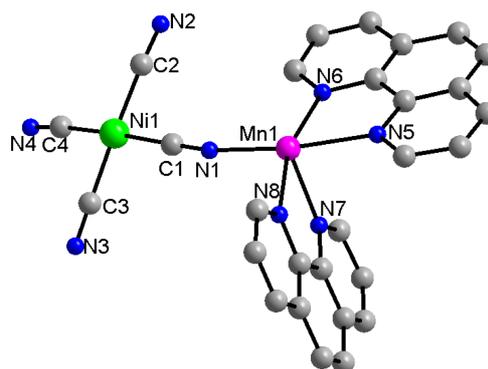


Figure 1. The binuclear molecular structure of complex **1**. The solvent water molecules and all the hydrogen atoms have been omitted for clarity.

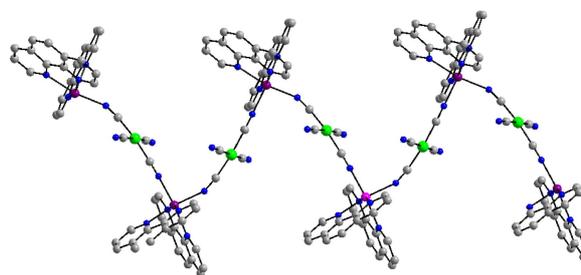


Figure 2. The 1D zigzag single chain structure for complex **1**. The solvent water molecules and all the hydrogen atoms have been omitted for clarity.

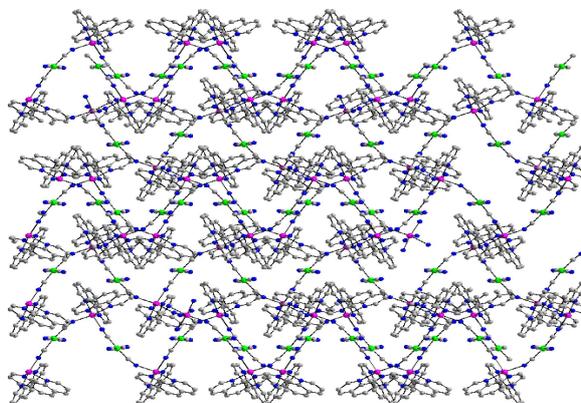


Figure 3. The cell packing for complex **1** along *c* axis. The solvent water molecules and all the hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for complexes **1** and **2**

1		2	
Mn1-N1	2.169(3)	Co1-C1	1.894(3)
Mn1-N4	2.194(4)	Co1-C2	1.870(3)
Mn1-N5	2.277(3)	Co1-N5	1.937(2)
Mn1-N6	2.269(3)	Co1-N6	1.977(2)
Mn1-N7	2.282(3)	Co1-N7	1.941(2)
Mn1-N8	2.246(3)	Co1-N8	1.981(2)
		N1-C1-Co1	175.1(3)
C1-N1-Mn1	167.3(4)	N2-C2-Co1	179.2(3)
N1-Mn1-N4#1	93.61(13)	C1-Co1-N5	92.99(12)
C4#1-N4#1-Mn1	154.3(3)	C2-Co1-N5	89.18(12)

ing parameters in complex **1**, indicating that the coordinating or non-coordinating of the N atom to the metal atom has no obvious influence on the geometry of the cyanide precursor. In the $[\text{Co}(\text{Phen})_2(\text{CN})_2]^+$, the Co(III) ion is six coordinates with the six positions occupied by N_4C_2 unit, in which four N atoms come from two phenanthroline ligands and the two C atoms from the two coordinated cyanide groups. The Co- N_{phen} bond lengths 1.937(2), 1.977(2), 1.941(2) and 1.981(2) Å are obvious longer than the Co- $\text{C}_{\text{cyanide}}$ 1.894(3) and 1.870(3) Å, giving further information that the Co(III) ion is involved in a slightly distorted octahedron. All the bond

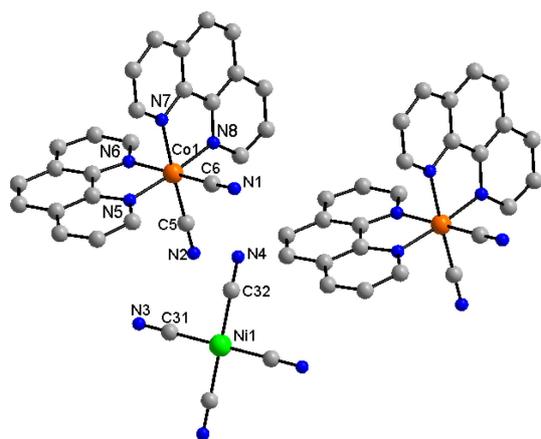


Figure 4. The crystal structure of complex **2**. The solvent water molecules and all the hydrogen atoms have been omitted for clarity.

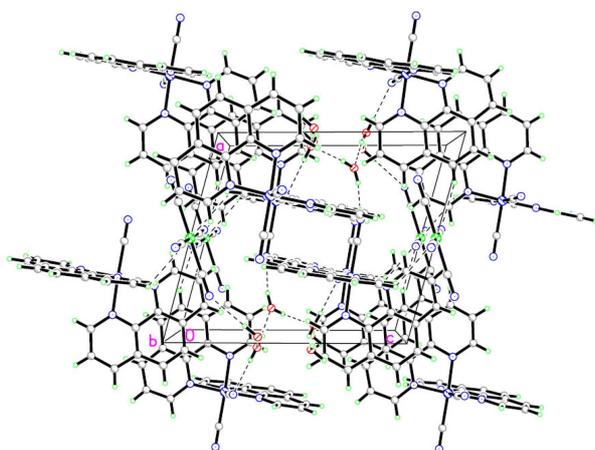


Figure 5. The cell packing diagram of complex **2** along *b* axis constructed by intermolecular hydrogen bond interactions (grey: C; blue: Co (big), N (small); green: Ni (big), H (small)).

parameters around the center Co(III) ions are consistent with the corresponding ones found in $\{[\text{Co}(\text{Phen})_2][\text{Co}(\text{Phen})(\text{CN})_4]_2\} \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$.²² As shown in Figure 4, under the help of the abundant intermolecular hydrogen bond interactions between the complex ions and the solvent water molecules, complex **2** was linked into a three-dimensional supramolecular network structure.

Magnetic Properties of Complex 1. The temperature dependence of magnetic susceptibilities for complex **1** measured in the range of 2–300 K under the external magnetic field of 2000 Oe is illustrated in Figure 6. The $\chi_m T$ value at room temperature is $4.34 \text{ emu K mol}^{-1}$, slightly lower than the spin only value of $4.375 \text{ emu K mol}^{-1}$ for the isolated high spin Mn(II) ($S = 5/2$). With the temperature decreasing, the $\chi_m T$ value remains almost constant from 300 to about 70 K. After this, the $\chi_m T$ value starts to decrease rapidly and reaches their lowest peak with the value of $1.75 \text{ emu K mol}^{-1}$ at 2 K. The magnetic susceptibility for complex **1** conforms well to Curie-Weiss law in a range of 2–300 K and gives the negative Weiss constant $\theta = -1.37 \text{ K}$ and Curie constant $C =$

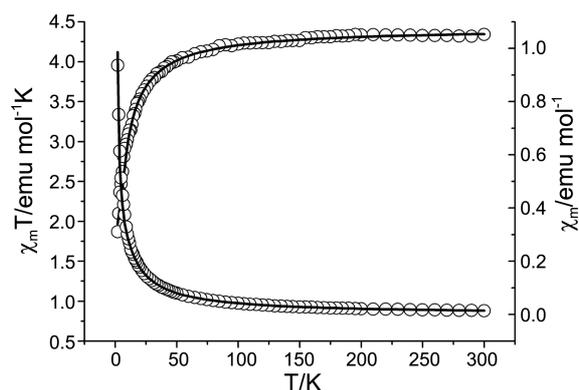


Figure 6. χ_m vs *T* and $\chi_m T$ vs *T* curve for complex **1**. The lines represent to the best fit curves.

$4.29 \text{ emu K mol}^{-1}$. These results primarily show the antiferromagnetic magnetic coupling between the two Mn(II) centers bridged by $[-\text{NC}-\text{Ni}-\text{CN}-]$ unit.

The magnetic data are analyzed by using the Hamiltonian: $\hat{H} = -2\sum J\hat{S}_i\hat{S}_{i+1}$. The temperature dependence of the magnetic susceptibility is given by the equation:²³

$$\chi_M^{\text{chain}} = N g^2 \beta^2 \{S_{Mn}(S_{Mn} + 1)/3KT\} \{(1 + \mu)/(1 - \mu)\}$$

(Fisher's infinite chain model) with:

$$\mu = \coth[JS_{Mn}(S_{Mn} + 1)/KT] - [KT/JS_{Mn}(S_{Mn} + 1)].$$

χ_M : molar magnetic susceptibility; *g*: Lande factor; *K*: Boltzmann constant; β : Bohr magneton; *J*: coupling constant between the adjacent Mn(II) ions bridged cyanide precursor).

The least-squares fit to the data leads to $J = -0.058 \text{ cm}^{-1}$, $g = 1.998$, $R = 1.34 \times 10^{-5}$. The small *J* value, which is comparable to those found in other Mn(II) complexes bridged antiferromagnetic cyanide-containing precursors,^{24,25} suggests the overall very weak magnetic coupling between the Mn(II) ions with a long separation.

Conclusion

In summary, we obtained a heterobimetallic one-dimensional cyanide-bridged Mn(II)-Ni(II) complex and an Co(III)-Ni(II) ion-pair complex with $[\text{Ni}(\text{CN})_4]^{2-}$ as building block and M(II)-phenanthroline (*M* = Mn, Co) compounds as assembling segment. The different structural types of complexes **1** and **2** indicate that the property of the metal ions the assembling segment contained have obvious influence on the structure of the cyanide-bridged complex. Investigation over the magnetic properties of complex **1** reveals an overall weak antiferromagnetic coupling between the adjacent Mn(II) ions bridged by the antiferromagnetic $[-\text{NC}-\text{Ni}-\text{CN}-]$ unit.

Experimental

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectro-

scopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000-400 cm^{-1} region. Variable-temperature magnetic susceptibility was 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 in the synthesis were reagent grade without further purification. $\text{Mn}(\text{Phen})_2\text{Cl}_2$ and $\text{Co}(\text{Phen})_2\text{Cl}_2$ were prepared according to the previous reports.^{20,21}

Caution! KCN is hypertoxic and hazardous and should be handled in small quantities with care.

The preparation of complexes **1** and **2**: $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.1 mmol, 28.8 mg) dissolved in distilled water 10 mL was added to a methanol and water solution 10 mL (4:1, v:v) of $\text{Mn}(\text{phen})_2\text{Cl}_2$ (0.1 mmol, 48.8 mg) or $\text{Co}(\text{phen})_2\text{Cl}_2$ (0.1 mmol, 49.2 mg). The mixture was stirred for several minutes at room temperature and filtered to remove any insoluble material, and then the filtrate was allowed to evaporate slowly without disturbance for about one week in air. The single crystals generated suitable for X-ray diffraction were collected by filtration, washed with cool methanol, and dried in air.

Complex 1: Yield 46.1 mg, 72.9%. Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{MnN}_8\text{NiO}_3$: C, 53.20; H, 3.51; N, 17.73. Found: C, 53.01; H, 3.41; N, 17.86. Main IR bands (cm^{-1}): 2158, 2120 (s, $\text{nC}\equiv\text{N}$).

Complex 2: Yield 51.2 mg, 43.5%. Anal. Calcd. for $\text{C}_{56}\text{H}_{40}\text{Co}_2\text{N}_{16}\text{NiO}_4$: C, 57.12; H, 3.42; N, 19.03. Found: C, 57.01; H, 3.31; N, 19.20. Main IR bands (cm^{-1}): 2153, 2158 (s, $\text{nC}\equiv\text{N}$).

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Supporting Information. The powder XRD pattern of complex **1**.

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