Cyanide-Bridged Cr^{III}Mn^{II} Binuclear Complexes Based on [Mn(phen)$_2$]$^{2+}$ and Dicyanidechromate(III) Building Blocks: Syntheses, Crystal Structures, and Magnetic Properties

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Three new cyanide-bridged Cr^{III}Mn^{II} binuclear complexes, [Mn(phen)$_2$Cl][Cr(bpmb)(CN)$_2$]·H$_2$O (**1**) (phen = 1,10-phenanthroline, bpmb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate), [Mn(phen)$_2$Cl][Cr(bpdmb)-(CN)$_2$]·H$_2$O (**2**) (bpdmb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4,5-dimethyl-benzenate), and [Mn(phen)$_2$Cl]-[Cr(bpClb)(CN)$_2$]·CH$_3$OH·H$_2$O (**3**) (bpClb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4-chloro-benzenate) were obtained based on Mn(phen)$_2$Cl$_2$ and a series of dicyanidechromate(III) building blocks. Single crystal X-ray diffraction analysis shows the structures of the three complexes are dimeric type with two different metal centers linked by a cyanide group from corresponding dicyanidechromate(III) building block. Magnetic investigations indicate the existence of relatively weak antiferromagnetic coupling between Cr(III) and Mn(II) ions with best-fit constants J_{CrMn} = −2.78(5) cm^{-1} for **1**, J_{CrMn} = −3.02(2) cm^{-1} for **2** and J_{CrMn} = −2.27(3) cm^{-1} for **3** based on the spin exchange Hamiltonian = $-2J_{CrMn}\hat{S}_{Cr}\hat{S}_{Mn}$. The magneto-structural correlation of cyanide-bridged Cr^{III}Mn^{II} complexes has been discussed at last.

Key Words : Cyanide-bridged, Binuclear complex, Crystal structure, Magnetic property, Magneto-structural correlation

Introduction

In the field of magnetic chemistry, cyanide-bridged metal complexes have continuously attracted considerable attention not only because they are one of the best kind of carriers for studying some interesting magnetic phenomena, the nature of the magnetic interactions and magneto-structural correlations, but also for their potential application in molecular-based functional materials.[1,2] Until now, numerous cyanide-bridged complexes with various topological structures, including molecular clusters, 1D chains and 2D or 3D networks, manifesting charming magnetic characteristics have been obtained through rational design.[3-6] Among them, cyanide-bridged low-dimensional complexes especially binuclear and trinuclear compounds have received particular attention because they can provide suitable models for the establishment of correct magneto-structural correlations.

Very recently, our group have developed a series of *trans*-dicyanideferrite(III), *trans*-dicyanidechromate(III), *trans*-dicyanidecobalt(III) and *mer*-tricyanideferrite(III) building blocks with relatively large in-plane tetradentate and tridentate pyridinecarboxamide ligands. These building blocks are suitable to be employed to assemble low-dimensional magnetic complexes, and the molecular structure of which can be skillful tuned through the control of the steric effect of outer ligands, the number and position of cyanide group and the charge number of these cyanide-containing blocks. Based on these cyanide-containing building blocks together

with the rational selection for the other unsaturated precursors, a series of cyanide-bridged magnetic complexes with various structures such as binuclear, trinuclear, tetranuclear, large wheel-like and one-dimensional molecules have been obtained successfully.[4a,5d,7-12] In this work, we report the syntheses, crystal structures, and magnetic properties of three cyanide-bridged Cr^{III}Mn^{II} binuclear complexes: [Mn(phen)$_2$-Cl][Cr(bpmb)(CN)$_2$]·H$_2$O (**1**), [Mn(phen)$_2$Cl][Cr(bpdmb)-(CN)$_2$]·H$_2$O (**2**) and [Mn(phen)$_2$Cl][Cr(bpClb)(CN)$_2$]·CH$_3$OH·H$_2$O (**3**), which were obtained by the reaction of *trans*-[Cr^{III}(L)(CN)$_2$]$^-$ [L = bpmb^{2-} (**1**), bpdmb^{2-} (**2**) or bpClb^{2-} (**3**)] building blocks with the bulky building block Mn(phen)$_2$Cl$_2$. To the best of our knowledge, cyanide-bridged Cr^{III}Mn^{II} binuclear and trinuclear complexes are very limited.

Experimental

Elemental analyses (C, H and N) were carried out on an Elementar Vario El. The infrared spectra of solid samples on KBr pellets were recorded on a Nicolet 7199B FT-IR spectrophotometer in the regions of 4000-400 cm^{-1}. Variable-temperature magnetic susceptibilities of powdered samples were measured on a Quantum Design MPMS SQUID magnetometer in the applied field of 1000 Oe. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascal's constants.

All of the reactions were performed under air condition and all chemicals used were purchased from commercial

sources without any purication. The precursors $Mn(phen)_2Cl_2$,[13] $K[Cr(L)(CN)_2]$[14] (L = $bpmb^{2-}$, $bpdmp^{2-}$ or $bpClb^{2-}$) were synthesized as reported in the literatures.

Preparation of Complexes 1-3. Black block single crystals of **1**, **2** and **3** were prepared at room temperature by carefully mixing a methanol/aqueous solution of $Mn(phen)_2Cl_2$ (0.1 mmol, 48.6 mg) and methanol solution of $K[Cr^{III}(L)$-$(CN)_2]$ [L = $bpmb^{2-}$ (**1**), $bpdmp^{2-}$ (**2**) or $bpClb^{2-}$ (**3**)] (0.1 mmol) for about 2 days.

Complex 1: Yield: 0.049 mg, 54.4%. Anal. Calcd for $CrMnC_{45}H_{32}N_{10}O_3Cl$ (**1**): C, 59.84; H, 3.57; N, 15.51. Found: C, 59.53; H, 3.44; N, 15.25. Main IR frequencies (KBr disk, cm^{-1}): 2145 (m, $\nu C\equiv N$), 2138 (m, $\nu C\equiv N$).

Complex 2: Yield: 0.043 mg, 46.5%. Anal. Calcd for $CrMnC_{47}H_{38}N_{10}O_4Cl$ (**2**): C, 59.47; H, 4.03; N, 14.76. Found: C, 59.26; H, 3.93; N, 14.50. Main IR frequencies (KBr disk, cm^{-1}): 2142 (m, $\nu C\equiv N$), 2137 (m, $\nu C\equiv N$).

Complex 3: Yield: 0.049 mg, 52.8%. Anal. Calcd for $CrMnC_{44}H_{29}N_{10}O_3Cl_2$ (**3**): C, 57.22; H, 3.16; N, 14.17. Found: C, 56.97; H, 3.21; N, 13.99. Main IR frequencies (KBr disk, cm^{-1}): 2147 (m, $\nu C\equiv N$), 2136 (m, $\nu C\equiv N$).

X-Ray Data Collection and Structure Renement. Single crystals of complexes **1-3** with suitable size for X-ray diffraction were obtained as depicted above. Structural measurement were performed on a Bruker APEX II CCD based on graphite-monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å) and the ω-scan technique. The structures were solved by direct methods with the SHELXS-97 computer program,[15] and refined by full-matrix least-squares methods.
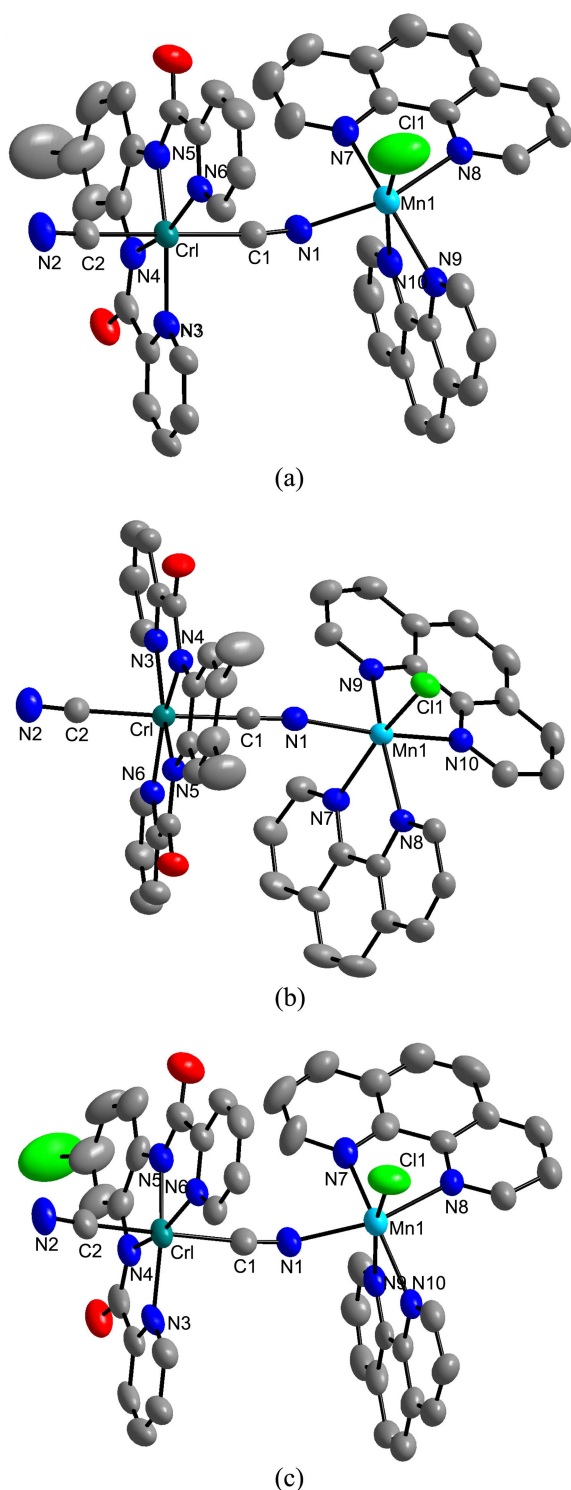
All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the water molecules were found from difference Fourier maps and normalised to O-H distances of 0.85 Å. Hydrogen atoms bound to carbon atoms and methanol oxygen atom for **2** were placed using the HFIX commands in SHELXL-97 program.[15] Images were created by using the DIAMOND program.[16] The structures of complexes **1** and **3** contain the solvent accessible volumes of 365 and 354 Å[3], respectively, which may be the release of solvent such as methanol molecule. CCDC numbers for complexes **1-3** are 860673, 860674 and 860675, respectively, which can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) or at www.ccdc.cam.ac.uk/conts/ retrieving.html. The crystal and structure refinement parameters as well as the conditions for data collection are listed in Table 1.

Results and Discussion

Synthesis and General Characterization. All the binuclear complexes reported in this paper were obtained by reaction of equivalent molar $Mn(phen)_2Cl_2$ with $K[Cr(L)$-$(CN)_2]$ [L = $bpmb^{2-}$ (**1**), $bpdmb^{2-}$ (**2**) or $bpClb^{2-}$ (**3**)], and these products are single crystals and can be reproduced. The formation of dimeric structure is normal due to the existence of relatively strong steric hindrance in both $[Mn(phen)_2]^{2+}$ and dicyanidechromate(III) building blocks. The results are constant with our previous works[17] and further illustrate these pyridinecarboxamide *trans*-dicyanide-

Table 1. Crystal data and structure refinement parameters for complexes **1-3**

	1	**2**	**3**
Empirical formula	$CrMnC_{45}H_{32}N_{10}O_3Cl$	$CrMnC_{47}H_{38}N_{10}O_4Cl$	$CrMnC_{44}H_{29}N_{10}O_3Cl_2$
Formula weight	903.200	949.26	923.61
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	11.805(11)	11.684(2)	11.91(2)
b(Å)	13.776(12)	14.542(3)	13.69(3)
c(Å)	16.130(16)	15.665(3)	16.11(3)
α(°)	112.43(3)	114.92(3)	113.21(4)
β(°)	100.34(2)	102.38(3)	99.49(4)
γ(°)	103.02(3)	101.38(3)	103.21(4)
Volume (Å^3)	2257(4)	2229.6(12)	2252(7)
Z	2	2	2
$\rho_{Calcd.}$ (g m^{-3})	1.329	1.414	1.362
μ(Mo-$K\alpha$) (mm^{-1})	0.630	0.643	0.690
F(000)	924	976	940
θ (°)	3.19-25.00	2.24-26.36	2.38-26.67
Measured reflections	7834	7721	7676
Unique reflections [R_{int}]	7834 [0.0000]	7721[0.0189]	7676 [0..0000]
Reflections ($I > 2\sigma(I)$)	4597	6931	3399
GOF on F^2	1.123	1.120	0.938
R_1 [$I > 2sigma(I)$]	0.0734	0.0440	0.0719
wR_2 (all data)	0.2312	0.1268	0.2150
ρ_{max}/ρ_{min}(e Å^{-3})	1.409/–0.838	0.409/–0.93	1.288/–0.557

(a)

(b)

(c)

Figure 1. The binuclear structure of complexes **1**(a), **2**(b), **3**(c). The solvent molecules and all the hydrogen atoms have been omitted for clarity.

metalate building blocks are suitable to assemble low-dimensional compounds.

In the IR spectra of complexes **1-3**, two sharp peaks at around 2136 cm^{-1} and 2145 cm^{-1} caused by the cyanide stretching vibration were observed, indicating the presence of both bridging and non-bridging cyanide ligands in these

**Table 2.** Selected bond distances [Å] and angles [°] of complexes **1-3**

	1	2	3
Mn-N(1)	2.197(18)	2.211(2)	2.189(7)
Mn-N(7)	2.29(2)	2.244(2)	2.266(7)
Mn-N(8)	2.252(18)	2.300(2)	2.250(6)
Mn-N(9)	2.269(19)	2.315(2)	2.324(8)
Mn-N(10)	2.35(2)	2.255(2)	2.260(7)
Mn-Cl	2.329(15)	2.4613(12)	2.413(5)
Cr-C(1)	2.11(2)	2.094(3)	2.090(9)
Cr-C(2)	2.06(2)	2.086(3)	2.074(9)
Mn···Cr	5.371(18)	5.440(3)	5.357(8)
C(1)-N(1)-Mn	167.2(18)	171.08(19)	165.3(6)
N(1)-Mn-Cl	93.2(7)	93.56(6)	93.0(2)
N(1)-C(1)-Cr	174.(2)	179.2(2)	174.7(7)
N(2)-C(2)-Cr	177.(2)	176.7(2)	176.5(7)
C(2)-Cr-C(1)	172.6(8)	170.69(10)	171.7(3)

compounds. Moreover, the absorbed frequency of bridging cyanide groups is usually higher than the frequency of non-bridging groups.

Crystal Structures of Complexes 1-3. X-ray crystal analysis shows the structures of complexes **1-3** are dimeric type which are composed of a [Mn(phen)$_2$]$^{2+}$ unit and a [Cr(L)(CN)$_2$]$^-$ [L = bpmb^{2-} (**1**), bpdmb^{2-} (**2**) or bpClb^{2-} (**3**)] unit linked by a cyanide group from the dicyanidechromate (III) building blocks. The labeling schemes for the crystal structures of complexes **1-3** are shown in Figure 1, and the main structural parameters are presented in Table 2.

All the three complexes crystallized in the triclinic P$\bar{1}$ group. Each chromium(III) ion in these complexes is coordinated by four nitrogen atoms from pyridinecarboxamide ligands on the equatorial plane and two cyanide carbon atoms on the two axial positions, forming a slightly distorted octahedral geometry. The Cr(1)-C(1) (bridging cyanide) and Cr(1)-C(2) (non-bridging cyanide) bond distances are 2.11(2) and 2.06(2) Å for **1**, 2.094(3) and 2.086(3) Å for **2**, 2.090(9) and 2.074(9) Å for **3**, respectively. The Cr-C≡N bond angles for both bridging and terminal cyanide linkages in complexes **1-3** are almost collinear with the angles ranging from 174.0(2)° to 179.2(2)°. The C(1)-Cr(1)-C(2) bond angles in these complexes are similar, locating within 170.69(10)-172.6(8)°.

The Mn(II) ion in the three complexes also displays octahedral coordinated sphere with a chloride anion and a bridging cyanide nitrogen atom from [Cr(L)(CN)$_2$]$^-$ and four nitrogen atoms from two phen ligands. The Mn-Cl bond distances in the three complexes are ranging from 2.329(15) Å to 2.4613(12) Å, which can be compared with those in their precursor Mn(phen)$_2$Cl$_2$.[13] The Mn-N$_{cyanide}$ bond length is 2.197(18) Å for **1**, 2.211(2) Å for **2**, and 2.189(7) Å for **3**, which are shorter than the Mn-N$_{phen}$ bond distances in the three complexes ranging from 2.244(2) Å to 2.35(2) Å. The Mn-N≡C linkages deviate from linearity with angles range of 165.3(6)-171.08(19)°. The intramolecular Cr---Mn separation
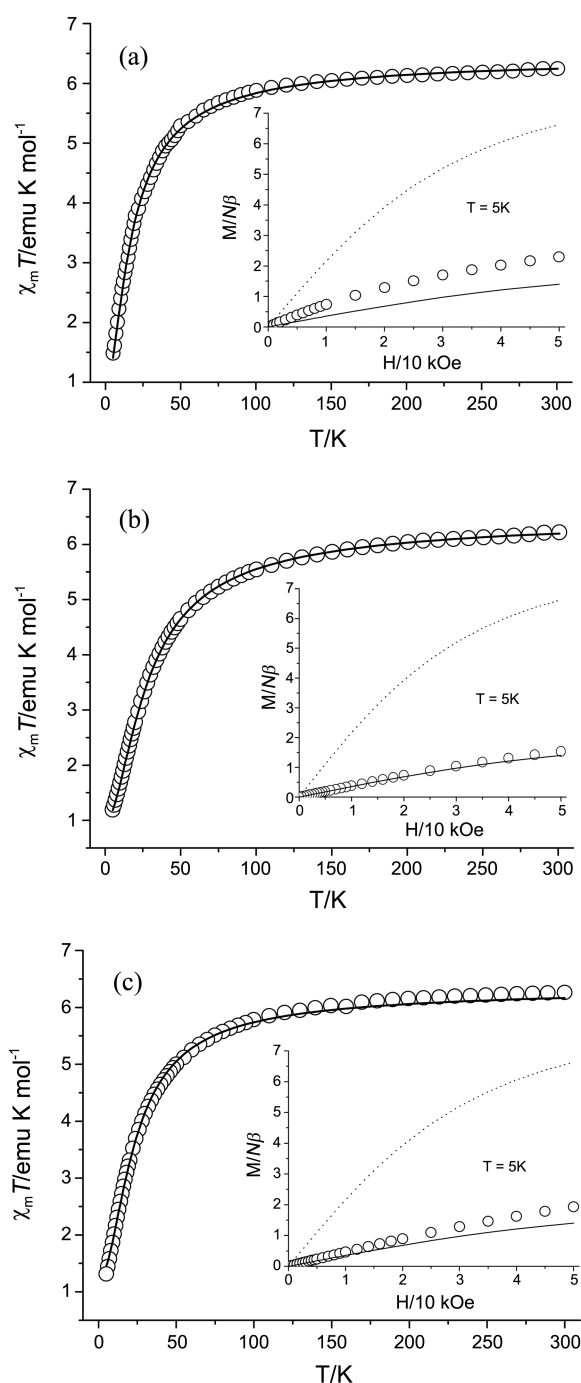
Figure 2. Temperature dependence of $\chi_m T$ for complex **1** (a), **2** (b), **3** (c) measured under an applied field of 1000 Oe (Inset: Field dependences of magnetization, the line and the broken line represent the Brillouin function that correspond to $S = 2/2$ and $S = 3/2 + 5/2$, respectively, based on g = 2.0).

through cyanide linkage is 5.371(18) Å for **1**, 5.440(3) Å for **2** and 5.357(8) Å for **3**. All the bond distances and angles in complexes **1-3** are similar to those of their analogue [Cr-(bpb)(CN)₂][Mn(phen)₂Cl]·2H₂O reported previously by our group.[17]

Magnetic Properties of Complexes 1-3. The magnetic properties of complexes **1-3** have been investigated since the magnetic coupling strength of binuclear complexes is relative-

ly accurate and binuclear complexes are the best carries for illustrating the magneto-structural correlations. The magnetic properties of complexes have been measured in the temperature range of 5-300 K under an applied field of 1000 Oe, and the temperature dependences of the magnetic susceptibilities for them are presented in Figure 2. The magnetic behaviors of the three complexes are very similar. The room temperature $\chi_m T$ value is 6.24 emu K mol⁻¹ for **1**, 6.20 emu K mol⁻¹ for **2** and 6.26 emu K mol⁻¹ for **3**, which are almost equal to the spin-only value of 6.25 emu K mol⁻¹ anticipated for the isolated spin dimeric systems of Cr^{III} ($S = {}^3/_2$) and high-spin Mn^{II} ($S = {}^5/_2$) based on g = 2.00. As the temperature is decreased, the $\chi_m T$ values decrease slowly until about 100 K, and then they decrease quickly to 1.41 emu K mol⁻¹ for **1**, 1.19 emu K mol⁻¹ for **2** and 1.46 emu K mol⁻¹ for **3**, respectively. The changing tendency of these $\chi_m T$ curves reveals that the magnetic exchange between the cyanide-bridged Cr(III) and Mn(II) ions is overall antiferromagnetic in the three complexes. The magnetic susceptibilities of these compounds in the whole temperature range obey the Curie-Weiss law with the Weiss constant $\theta = -14.76$, Curie constant $C = 6.583$ K mol⁻¹ for **1**, $\theta = -19.48$, $C = 6.70$ K mol⁻¹ for **2**, and $\theta = -24.62$ K, $C = 6.79$ K mol⁻¹ for **3**. These negative Weiss constants also indicate the occurrence of overall antiferromagnetic coupling in the three complexes. The field dependence of the magnetization of complexes **1-3** measured in the field range of 0-50 kOe at 5.0 K (Insert in Figure 2) is almost in agreement with their corresponding Brillouin curve for the $S = 2/2$ spin state with g = 2.00, this feature gives further evidence of the $S = 2/2$ ground state and the presence of overall antiferromagnetic coupling in these compounds.

Based on the dimeric $Cr^{III}Mn^{II}$ model, the magnetic susceptibilities of complexes **1-3** can be fitted according to the following expressions derived from the isotropic exchange spin Hamiltonian $\hat{H} = -2J_{CrMn}\hat{S}_{Cr}\,\hat{S}_{Mn}$:

$$\chi_d = \frac{Ng^2\beta^2}{kT}\frac{2+10\exp(8J/kT)+28\exp(20J/kT)+60\exp(36J/kT)}{3+5\exp(8J/kT)+7\exp(20J/kT)+9\exp(36J/kT)}$$

$$(1)$$

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

The best-fit parameters are $J_{CrMn} = -2.78(5)$ cm⁻¹, $zJ' = -0.05(4)$ cm⁻¹, g = 2.00(1), and $R = \Sigma(\chi_{obsd.}T - \chi_{cald.}T)^2/\Sigma(\chi_{obsd.}T)^2 = 2.39 \times 10^{-5}$ for **1**, $J_{CrMn} = -3.02(2)$ cm⁻¹, $zJ' = 0.09(1)$ cm⁻¹, g = 2.03(1), and $R = 5.38 \times 10^{-5}$ for **2** and $J_{CrMn} = -2.27(3)$ cm⁻¹, $zJ' = -0.008(8)$ cm⁻¹, g = 2.03(1), and $R = 5.74 \times 10^{-5}$ for **3**.

These magnetic parameters of complexes **1-3** can be compared with those of other complexes containing Cr^{III}-C≡N-Mn^{II} unit. The magnetic coupling between Cr(III) [d³, t_{2g}^3] and Mn(II) [d⁵, $t_{2g}^3 e_g^2$] through bridging cyanide group in these complexes is antiferromagnetic,[17-21] which can be attributed to a net overlap of the magnetic orbitals through the π t_{2g}-t_{2g} pathways. In fact, for cyanide-bridged Cr^{III}-Mn^{II}

Table 3. Structural and magnetic parameters for compared cyanide-bridged binuclear Cr^{III}Mn^{II} and trinuclear Cr$^{III}_2$Mn^{II} complexes

Compound	θ (°)	Mn-N$_{cyanide}$ (Å)	Cr---Mn (Å)	J (cm^{-1})	refs.
2	171.1	2.211	5.404	−3.02	this work
[{Cr(bipy)(CN)$_4$}$_2$Mn(H$_2$O)$_4$][a]	168.9	2.251	5.364	~ −3.1	17
[Mn(bpy)$_2$][Cr(bpy)(CN)$_4$]$_2$·5H$_2$O[a]	167.8	2.200	5.4	~ −2.6	18a
1	167.2	2.197	5.571	−2.78	this work
[Mn(phen)$_2$Cl][Cr(bpb)(CN)$_2$]·2H$_2$O	166.4	2.211	5.404	−2.39	15
{[Mn(bpy)(dca)(H$_2$O)$_2$][Cr(bpy)(CN)$_4$]}·CH$_3$OH[a]	165.3	2.226	5.353	~ −2.6	18b
3	165.3	2.189	5.357	−2.27	this work
[Cr(salen)(CN)$_2$]$_2$[Mn(phen)$_2$]·2H$_2$O	163.3	2.177	5.343	−2.02	19

[a]The J value has been halved because the employment of different Hamiltonian operators.
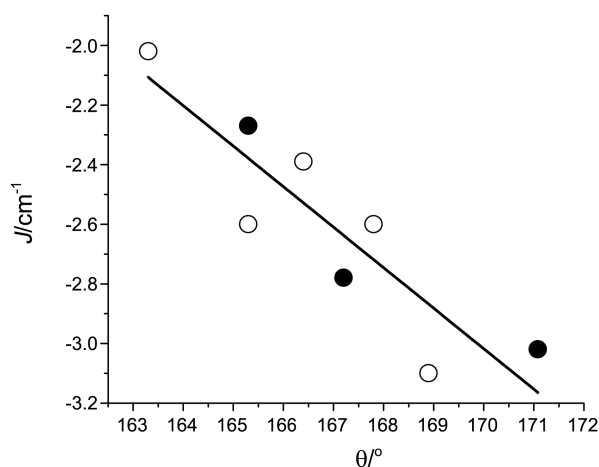
Figure 3. The coupling constant (*J*) plotted against the angle of Mn-N≡C (*θ*). The open symbols stand for the data in this work and the solid ones for the reported data in the literature. The line corresponds to the linear fitting.

complexes, ferromagnetic and antiferromagnetic interactions coexist and the competition between ferromagnetic and antiferromagnetic interactions is very sophisticated. However, the antiferromagnetic interactions are usually dominated in the competition, therefore, nearly all the cyanide-bridged Cr^{III}-Mn^{II} complexes exhibit overall antiferromagnetic interactions. The final magnetic coupling is determined by several factors such as bond angles, bond distances and coordination surrounding. In order to evaluate the magneto-structural correlation of cyanide-bridged Cr^{III}-Mn^{II} system more reliably and exactly, binuclear Cr^{III}Mn^{II} and trinuclear Cr$^{III}_2$Mn^{II} complexes should be selected as the experimental examples because they can provide relatively more correct magnetic coupling parameters. The bond parameters and the magnetic coupling constants of cyanide-bridged binuclear Cr^{III}Mn^{II} and trinuclear Cr$^{III}_2$Mn^{II} complexes are listed in Table 3 and the plot of magnetic coupling constant (*J*) *vs.* Mn-N≡C bond angle (*θ*) is illustrated in Figure 3. It can be seen, the antiferromagnetic coupling strength increases with *θ* increasing in the range of 163.3-171.1°, obeying an approximate relationship: J(cm^{-1}) = 20.1-0.135 θ. The result is different from those for cyanide-bridged Cr^{III}-Mn^{II} complexes reported by Julve's group and Gao's group.[20a,22] The magneto-structural investigation is a very complicated process and the

final full establishment of magneto-structural correlation for Cr^{III}-Mn^{II} complexes and other cyanide-bridged systems needs more experimental examples and further deep theoretical investigation.

Conclusions

In this work, three new cyanide-bridged binuclear Cr^{III}Mn^{II} complexes based on Mn(phen)$_2$Cl$_2$ and three *trans*-dicyanidechromate(III) building blocks have been synthesized and characterized by single X-ray diffraction analysis. Magnetic investigations indicate the occurrence of overall antiferromagnetic interactions in the three cyanide-bridged binuclear Cr^{III}Mn^{II} complexes. The study of magneto-structural correlation for cyanide-bridged Cr^{III}-Mn^{II} complexes suggests that the larger the Mn-N≡C bond angle the stronger is the antiferromagnetic interaction between Cr(III) and Mn(II) ions.

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