Synthesis, crystal structures and magnetic properties of cyanide-bridged macrocyclic complexes

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Three cyanide-bridged dodecanuclear macrocyclic wheel-like complexes [Cr(bpmb)(CN)$_2$]$_6$[Mn(5-Brsalpn)]$_6$·12H$_2$O (1), [Co(bpmb)(CN)$_2$]$_6$[Mn(5-Brsalpn)]$_6$·12H$_2$O (2) and [Co(bpmb)(CN)$_2$]$_6$[Mn(5-Clsalpn)]$_6$·24H$_2$O·8CH$_3$CN (3) [bpmb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4-methylbenzenate dianion; 5-Brsalpn^{2-} = N,N'-propylenebis(5-bromosalicylideneaminato) dianion; 5-Clsalpn^{2-} = N,N'-propylenebis(5-chlorosalicylideneaminato) dianion] have been synthesized and their crystal structures and magnetic properties have been investigated. The three compounds are structurally isomorphous and consist of alternating Mn(Ⅲ)-Schiff base cations and [M(bpmb)(CN)$_2$]$^-$ anions, generating cyanide-bridged nanosized dodecanuclear macrocyclic structures with an approximate diameter of 2 nm. The study of the magnetic properties of complex 1 reveals an antiferromagnetic interaction between the Cr(Ⅲ) and Mn(Ⅲ) ions through the cyanide bridges. A best-fit to the magnetic susceptibility of the complex leads to a magnetic coupling constant of $J_{CrMn} = -2.65(6)$ cm^{-1} on the basis of a one-dimensional alternating chain model with the Hamiltonian $H = -J_{CrMn} \sum_{i=0}^{N} S_i \cdot S_{i+1}$.

polynuclear complex, crystal structure, magnetic property, cyanide, chromium, manganese

1 Introduction

In recent years, molecule-based magnetic materials have been one of the most active research topics in coordination chemistry. Molecular magnets have attracted the continuous interest of chemists, physicists and material scientists because of their unambiguous structure, good transparency and facile preparation[1]. The cyanide ligand has been employed extensively in the synthesis and assembly of molecular magnets because it can transmit relatively strong magnetic coupling, and the nature of the magnetic coupling between neighboring metal ions through the cyanide bridge can be readily predicted[2]. The magnetic phase transition temperature (T_c) of some molecular magnets, for example the cyanide-bridged heterobimetallic complex VCr(CN)$_6$, is higher than room temperature, suggesting possible practical applications

of these materials[3]. Recently, zero-dimensional cyanide-bridged polynuclear complexes have attracted much attention because of the appearance of single-molecule magnets (SMMs)[4,5]. Several strategies have been developed in the past decade for the preparation of cyanide-bridged polynuclear compounds with different molecular structures[6]. Many reports involve the precursors *fac*-[Fe(L)(CN)$_3$]$^-$ (where L$^-$ represents a tridentate ligand) with three *facial*-cyanide groups and cubic cage-like, tetranuclear square-like and trigonal bipyramidal complexes have been constructed based on such cyanide-containing building blocks. Some of these manifest SMM

behavior[6]. In addition, there have been some reports of the use of [M(phen)(CN)$_4$]$^-$ (M = Fe, Cr) complexes with four cyanide groups as building blocks, however, complexes based on these precursors are usually one-dimensional[7,8]. Compounds prepared from [Fe(phen)$_2$(CN)$_2$]$^+$, with two *cis*-cyanide ligands, usually have planar square structural units[9].

Complexes based on *trans*-dicyanide building blocks are relatively scarce[10−12]. Lau and coworkers investigated magnetic complexes formed by using the *trans*-[Ru^{III}(acac)$_2$(CN)$_2$]$^-$ building block and found that this precursor can be employed to construct linear trinuclear, and two- and three-dimensional network complexes[10,11]. Very recently, our group developed *trans*-[Fe^{III}(bpb)(CN)$_2$]$^-$ (H$_2$bpb = 1,2-bis(pyridine-2-carboxamido)-benzene) as the starting reactant to assemble cyanide-bridged binuclear, trinuclear and one-dimensional complexes[13−15]. A series of novel Mn$_6$Fe$_6$ dodecanuclear macrocyclic complexes have been synthesized based on *trans*-[Fe^{III}(bpmb)(CN)$_2$]$^-$ (H$_2$bpmb = 1,2-bis(pyridine-2-carboxamido)-4-methylbenzene) and Mn(III)-Schiff base compounds ([Mn(SB)]$^+$), one of which has been shown to be a SMM[16,17]. These results have shown that methyl group substituents on the benzene ring play a decisive role in the formation of macrocyclic structures. In this work, we extend the Fe(III) system to Cr(III) and Co(III) compounds containing two *trans*-cyanide groups, and have obtained three cyanide-bridged dodecanuclear macrocyclic wheel-like complexes.

2 Experimental

2.1 Materials

Picolinic acid, 4,5-dimethyl-1,2-diaminobenzene, triphenyl phosphate, CrCl$_3$·6H$_2$O and KCN were obtained commercially, and the solvents used in the syntheses were reagent grade and used without further purification. K[Cr(bpmb)(CN)$_2$] was synthesized as described below, using a modification of the method reported previously for the synthesis of K[Cr(bpb)(CN)$_2$][18]. K[Co(bpmb)-(CN)$_2$], [Mn(5-Brsalpn)]ClO$_4$ and [Mn(5-Clsalpn)]ClO$_4$ 5-Brsalpn^{2-} = *N,N'*-propylenebis(5-bromosalicylideneaminato) dianion; 5-Clsalpn^{2-} = *N,N'*-propylenebis(5-chlorosalicylideneaminato) dianion] were prepared according to the literature methods[19,20].

2.2 Physical measurements

Infrared spectroscopy using the KBr disc method was performed on a Nicolet 7199B Fourier transform spectrophotometer, and elemental analyses for carbon, hydrogen and nitrogen were carried out with an Elementar Vario El analysis system. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The crystal data of complexes **1−3** were collected on Rigaku R-Axis RAPID IP diffractometer. The structures were solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package and refined anisotropically by full-matrix least squares calculations on F^2.

2.3 Preparation of complexes 1−3

Synthesis of H$_2$bpmb   Based on the synthesis of H$_2$bpb[21], H$_2$bpmb was prepared as follows: To a pyridine solution (10 mL) of picolinic acid (24.8 g, 200 mmol) at 40 ℃ was added a pyridine solution (50 mL) of 4-methyl-1,2-diaminobenzene (13.4 g, 100 mmol), and then triphenyl phosphate (62.0 g, 200 mmol) was added. The mixture was heated in a water bath for 5 h, and then cooled to room temperature. The white solid formed was collected by filtration, washed with water and ether, and dried in air. Yield: 70%.

Preparation of [Cr^{III}(bpmb)(Cl)]·xH$_2$O   CrCl$_3$·6H$_2$O (13.4 g, 50 mmol) was dissolved in DMF (300 mL), and the water from the solvent and CrCl$_3$·6H$_2$O were removed by distillation. After H$_2$bpmb (16 g, 50 mmol) was added to the solution formed above, the mixture was refluxed for 6 h. Water (500 mL) was poured into the cooled red-brown solution to afford a red-brown precipitate, which was filtered and dried at room temperature. Yield: 70%.

Preparation of K[Cr(bpmb)(CN)$_2$]   After excess KCN (15 g, 310 mmol) was added to a methanol suspension of [Cr^{III}(bpmb)(Cl)]·xH$_2$O (14 g, 30 mmol), the mixture was stirred for about 20 h, and then the solid was collected by filtration. The solid was dissolved in DMF, and KCl and the unreacted KCN were removed by suction filtration. The red product was obtained after the DMF was removed by distillation under reduced pressure. Yield: 60%. Anal. % Found (Calcd. for KCrC$_{21}$H$_{14}$N$_6$O$_2$). C, 52.88 (53.27); H, 3.08 (2.98); N, 16.46 (17.75). IR (cm^{-1}): ν_{CN} 2129.

Preparation of [Cr(bpmb)(CN)$_2$]$_6$[Mn(5-Brsalpn)]$_6$·

12H₂O (1), [Co(bpmb)(CN)₂]₆[Mn(5-Brsalpn)]₆·12H₂O (2) and [Co(bpmb)(CN)₂]₆[Mn(5-Clsalpn)]₆·24H₂O· 8CH₃CN (3) [Mn(5-Clsalpn)(H₂O)₂]ClO₄ or [Mn(5-Brsalpn)(H₂O)₂] ClO₄ (0.15 mmol) was dissolved in 6 mL of a MeOH/ MeCN mixture (1/1, *V/V*). *trans*-K[Cr-(bpmb)(CN)₂] or *trans*-K[Co(bpmb)(CN)₂] (0.15 mmol) dissolved in 5 mL of MeOH/H₂O (4/1, *V/V*) was carefully added to the former solution, and the mixture was immediately filtered and then left to stand undisturbed for 3 days at room temperature to yield well shaped dark brown single crystals suitable for X-ray diffraction. Yield: 60%.

3 Results and discussion

3.1 IR spectra of complexes 1－3

The elemental analysis and important IR frequencies of complexes **1－3** are shown in Table 1. The IR spectra in the range 2110－2160 cm^{-1} each exhibit a single moderately strong peak, which can be assigned to cyanide stretching absorptions.

3.2 Crystal structures of complexes 1－3

Crystal data and structure refinement details for com-

plexes **1－3** are listed in Table 2, selected bond lengths and angles are given in Table 3 and their crystal structures are shown in Figure 1.

X-ray diffraction showed that the three complexes are isostructural, and can be described as cyanide-bridged dodecanuclear molecular wheels composed of six M(Ⅲ) ions and six Mn(Ⅲ) ions. In these complexes, the substituents on the benzene ring of bpmb^{2-}, which are very prone to induce large steric effects, point towards the inside of the macrocycle, while the Cl or Br substituents on the Schiff base ligands 5-Clsalpn^{2-} and 5-Brsalpn^{2-} are all located on the two sides of the equatorial plane of the macrocycle.

Table 1 Elemental analysis and IR spectra of complexes **1－3**

	Formula	Anal (%): Found (Calcd.)			IR υ$_{CN}$ (cm^{-1})
		C	H	N	
1	Cr₆Mn₆C₂₂₈H₁₉₈ Br₁₂N₄₈O₃₆	47.78 (47.32)	3.55 (3.45)	12.01 (11.62)	2151
2	Co₆Mn₆C₂₂₈H₁₉₈ Br₁₂N₄₈O₃₆	47.25 (46.99)	3.52 (3.42)	11.95 (11.54)	2138
3	Co₆Mn₆C₂₄₄H₂₃₈ Cl₁₂N₅₆O₄₈	50.54 (50.26)	4.18 (4.11)	13.82 (13.45)	2136

Table 2 Crystal data of complexes **1－3**

	1	2	3
Formula	Cr₆Mn₆C₂₂₈H₁₉₈ Br₁₂N₄₈O₃₆	Co₆Mn₆C₂₂₈H₁₉₈ Br₁₂N₄₈O₃₆	Co₆Mn₆C₂₄₄H₂₃₈ Cl₁₂N₅₆O₄₈
Fw	5786.90	5828.48	5831.52
Crystal system	hexagonal	hexagonal	hexagonal
Space group	*P*-3	*P*-3	*P*-3
a (Å)	25.450(4)	25.053(4)	25.0669(10)
b (Å)	25.450(4)	25.053(4)	25.0669(10)
c (Å)	12.735(4)	12.666(3)	12.5333(7)
V (Å^3)	7144(3)	6884.8(19)	6820.2(5)
Z	*1*	1	1
ρ_{calcd} (g·cm^{-1})	1.345	1.406	1.420
Absorption coefficient (mm^{-1})	2.218	2.426	0.820
F(000)	2904	2922	2994
Crystal size (mm)	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Limiting indices	0⩽*h*⩽26, 0⩽*k*⩽26, −14⩽*l*⩽14	−29⩽*h*⩽29, −29⩽*k*⩽29, 0⩽*l*⩽15	0⩽*h*⩽25, 0⩽*k*⩽25, −14⩽*l*⩽14
Independent reflections	8024	8027	7942
Reflections [*I*>2σ(*I*)]	1297	2257	5584
Goodness-of-fit on *F*^{2}	0.897	0.783	0.981
Data/restraints/parameters	8024/0/510	8027/0/494	7942/0/554
*R*1[*I*>2σ(*I*)]	0.0734	0.0797	0.0992
w*R*2 (all data)	0.1484	0.1437	0.2257
Largest diff. peak/hole (e. A^{-3})	0.333/−0.209	0.405/−0.408	1.137/−0.491

Table 3 Selected bond lengths (Å) and angles (°) of complexes **1–3**

	1	2	3
Mn(1)–N(1)	2.238(10)	2.259(4)	2.281(7)
Mn(1)–N(2)#1	2.240(11)	2.279(7)	2.242(8)
Mn(1)–N(7)	1.95(2)	1.947(8)	1.973(8)
Mn(1)–N(8)	2.01(3)	1.976(7)	2.018(8)
Mn(1)–O(3)	1.925(10)	1.976(7)	1.891(6)
Mn(1)–O(4)	1.895(12)	1.858(6)	1.861(6)
M(1)–C(1)	2.116(12)	1.928(10)	1.912(8)
M(1)–C(2)	2.133(12)	1.892(9)	1.890(9)
M(1)–N(3)	1.98(3)	1.934(8)	1.962(8)
M(1)–N(4)	1.92(4)	1.819(11)	1.900(7)
M(1)–N(5)	1.983(17)	1.856(11)	1.883(7)
M(1)–N(6)	2.107(15)	1.926(8)	1.962(7)
M(1)－M(1)#2	19.993	19.571	19.541
Mn(1)－Mn(1)#2	20.639	20.111	20.208
Mn(1)–N(1)–C(1)	160.5(15)	151.2(7)	159.3(6)
Mn(1)#3–N(2)–C(2)	146.5(16)	160.4(6)	148.1(7)
M(1)–C(1)–N(1)	174.3(16)	175.6(7)	177.9(8)
M(1)–C(2)–N(2)	176.7(19)	177.2(7)	178.4(9)

Symmetry code: #1 $y+1$, $-x+y+1$, $-z$ (**1**); y, $-x+y$, $-z$ (**2**); $y-1$, $-x+y$, $-z$ (**3**). #2 $-x$, $-y+2$, $-z$ (**1**); $-x$, $-y$, $-z$ (**2**); $x-y+1$, $x+1$, $-z$ (**3**). #3 $x-y$, $x-1$, $-z$ (**1**); $x-y$, x, $-z$ (**2**); $-x$, $-y+2$, $-z$ (**3**).
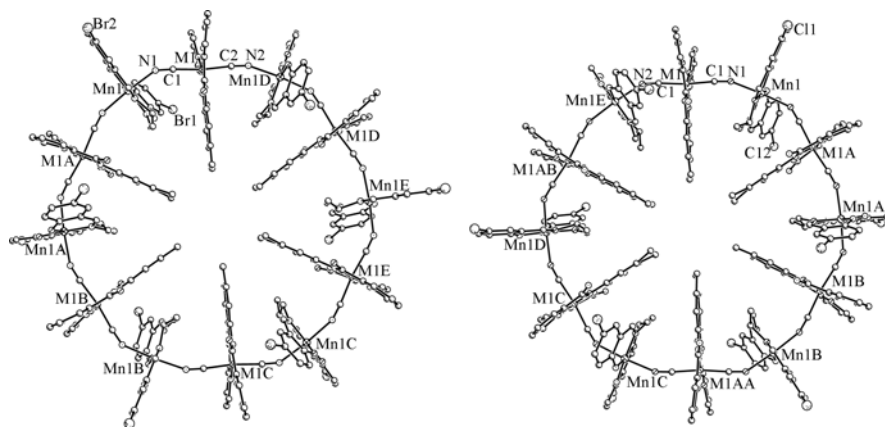

Figure 1 The crystal structures of dodecanuclear Mn_6M_6 (left: M = Cr (**1**), Co (**2**)) or Mn_6Co_6 (right: M = Co (**3**)) complexes.

The geometries of the units $[M(bpmb)(CN)_2]^-$ (M = Cr(III), Co(III)) in complexes **1－3** are very similar to that of $[Fe(bpmb)(CN)_2]^{-}$ [16,17]. The Cr(III) or Co(III) ions are surrounded by CrN_4C_2 or CoN_4C_2 units formed by four equatorial N atoms of bpmb^{2-} and C atoms of the two cyanide ligands in the axial positions, yielding a distorted octahedral geometry. The two Cr—C bond lengths in complex **1** are 2.116(12) Å and 2.133(12) Å, significantly longer than the Fe—C bond lengths (1.924(8)－1.984(6) Å) in $[Fe(bpmb)(CN)_2]^-$, while the

Co—C bond lengths (1.890(9)－1.928(10) Å) in complexes **2** and **3** are slightly shorter than the Fe—C bond lengths in $[Fe(bpmb)(CN)_2]^-$.

The average Mn—$N_{cyanide}$ bond lengths in complexes **1－3** are located in the range 2.238(10)－2.281(7) Å. The Mn—N≡C bond angles (Table 3) all deviate markedly from a linear conformation and have average values of 153.5(16)° (**1**), 155.8(7)° (**2**) and 153.7(7)° (**3**).

The distances between the opposite Mn(III), Cr(III) or Co(III) ions of the macrocycle are close to one another,

with the values of 19.993 Å and 20.639 Å (**1**), 19.571 Å and 20.111 Å (**2**) and 19.541 Å and 20.208 Å (**3**), indicating that these three complexes are nanosized metallomacrocycles.

Due to the high symmetry of complexes **1**−**3** (hexonal), the cyclic molecules in the crystal cell are packed regularly. The molecules are packed and linked together by the intermolecular Cl—Cl interactions, the hydrogen bonding interactions of water and the hydrogen bonding interactions between the O atom of water and that of the ligand, forming a supramolecular nanotube structure, as shown in Figure 2.
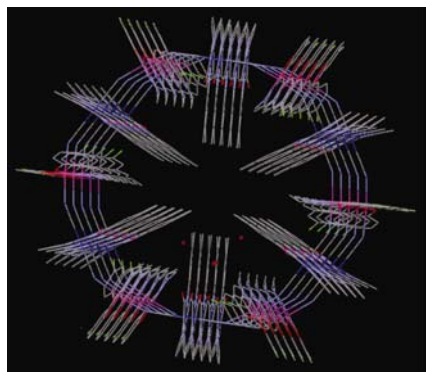

Figure 2   The supramolecular nanotube structure of complexes **1**−**3**.

3.3　Magnetic properties of complexes 1 and 3

The temperature dependence of the magnetic susceptibility of complex **1** measured in the temperature range 5−300 K under an external magnetic field of 1000 Oe is illustrated in Figure 3. The x_mT value at room temperature is 26.9 emu·K·mol^{-1}, slightly lower than the expected theoretical value of 29.25 emu·K·mol^{-1}. The value of x_mT decreases slowly on decreasing the temperature from 300 K to about 75 K. Below 75 K, the x_mT value starts to decrease rapidly and reaches its lowest value of 5.66 emu·K·mol^{-1} at 5 K. These results indicate that the magnetic coupling between Cr(III) and Mn(III) ions through cyanide bridges in complex **1** is antiferromagnetic. The magnetic susceptibility for the complex obeys the Curie-Weiss law in the range 15−300 K and gives a negative Weiss constant $\theta = -13.0$ K and Curie constant $C = 28.0$ emu·K·mol^{-1}. The large negative Weiss constant confirms that the complex is antiferromagntic.

The magnetic properties of the ring-like complex **1** can be approximately simulated on the basis of an alternating one-dimensional chain model. This method is
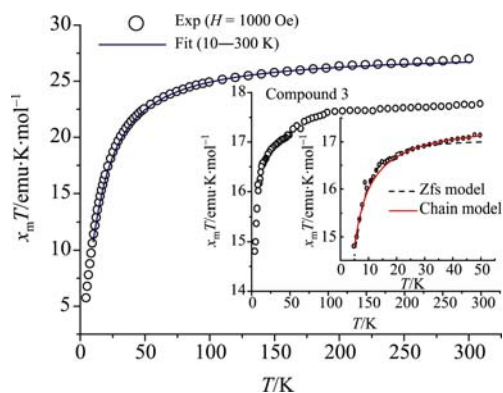

Figure 3 x_mT vs. T curves for complexes **1** and **3** (inset). The lines represent the best-fit curves.

especially applicable to classical systems with large spin quantum number[22]. The expression for the Mn(III)-Cr(III) complex based on the Hamiltonian $H = -J\sum_{i=0}^{N} S_i \cdot S_{i+1}$ is shown as eqs. 1 and 2, taking into account the intermolecular magnetic interactions.

$$x_{chain} = \frac{2N\beta^2}{3kT}\left[M^2\frac{1+P}{1-P} + (\delta M)^2\frac{1-P}{1+P}\right],\qquad(1)$$

where $P = \coth(J_{eff}/kT) - (kT/J_{eff})$,

$$M = g_{Mn}\sqrt{S_{Mn}(S_{Mn}+1)} + g_{Cr}\sqrt{S_{Cr}(S_{Cr}+1)},$$
$$\delta M = g_{Mn}\sqrt{S_{Mn}(S_{Mn}+1)} - g_{Cr}\sqrt{S_{Cr}(S_{Cr}+1)},$$
$$J_{eff} = J\sqrt{S_{Mn}(S_{Mn}+1)S_{Cr}(S_{Cr}+1)}.$$

$$x_M = 6\cdot\frac{x_{chain}}{1 - x_{chain}\left(2zJ'/Ng^2\beta^2\right)}.\qquad(2)$$

The best-fit parameters in the temperature range 10−300 K are $J = -2.65(6)$ cm^{-1}, $g = 1.94(1)$, and $zJ' = -0.027(7)$ cm^{-1}. The value of J is comparable to that (−1.6 to −12.6 cm^{-1}) for previously reported cyanide-bridged Cr(III)-Mn(III) complexes[23−26]. It has been suggested that the magneto-structural correlation is $J = -33 + 0.18\theta$, in which J represents the magnetic coupling constant (cm^{-1}) and θ is the Mn—N≡C bond angle[26]. According to this formula, the values of J for complex **1** should be −6.63 and −4.11 cm^{-1} for two Mn—N≡C bond angles; the average value of −5.37 cm^{-1}, is slightly higher than the experimental value.

All the cyanide-bridged Cr(III)-Mn(III) complexes reported to date are antiferromagnetic, which can be reasonably explained by orbital orthogonality theory[27].

The electronic configuration for the octahedral Cr(III) ion is $d_{xy}{}^1 d_{xz}{}^1 d_{yz}{}^1$. The three unpaired electrons are located in the three degenerate orbitals with t_{2g} symmetry. However, for the elongated octahedral Mn(III) ion the four unpaired electrons are, in increasing order in energy, in the $(d_{xz}{}^1 d_{yz}{}^1) d_{xy}{}^1 d_{z^2}{}^1$ orbitals. According to group theory, the π type orbitals (d_{xy}, d_{xz}, d_{yz}) of the same symmetry should overlap, which favors the antiferromagnetic interaction. There is no orbital overlap between the σ type magnetic orbital of Mn(III) (d_{z^2}) and the π type orbitals of Cr(III) ion, generating ferromagnetic interactions. Therefore, the overall magnetic coupling is determined by the competition between ferromagnetic and antiferromagnetic interactions. Because the antiferromagnetic contributions are generally stronger than the ferromagnetic contributions, the overall magnetic interactions for cyanide-bridged Cr(III)-Mn(III) complexes are usually antiferromagnetic. However, Cr(III)-Mn(III) complexes with ferromagnetic properties are also possible, because the ferromagnetic coupling contribution could be stronger than the antiferromegnetic contribution in certain cases.

The $x_m T$-T curve of complex **3** measured in the temperature range 5－300 K and an external field of 1000 Oe is shown in the inset of Figure 3. The value of $x_m T$ is 17.75 emu·K·mol^{-1}, very close to the expected value of 18.0 emu·K·mol^{-1} ($6 S_{Mn}$ with $S_{Mn} = 2$), on the basis of $g = 2.0$. The $x_m T$ value decreases gradually with decreasing temperature until 75 K, and then decreases rapidly to reach 14.75 emu·K·mol^{-1} at 5 K. The Curie-Weiss law over the whole range gives $\theta = -1.48$ K and $C = 17.08$ emu·K·mol^{-1}.

$$x_m = 6 x_{zfs} = 6 \times (2 x_\perp + x_{//})/3, \quad (3)$$

where,
$$x_{//} = \frac{N g^2 \beta^2}{kT} \cdot \frac{2 e^{-x} + 8 e^{-4x}}{1 + 2 e^{-x} + 2 e^{-4x}},$$

$$x_\perp = \frac{N g^2 \beta^2}{kT} \cdot \frac{\dfrac{6}{x}\left(1 - e^{-x}\right) + \dfrac{4}{3x}\left(e^{-x} - e^{-4x}\right)}{1 + 2 e^{-x} + 2 e^{-4x}},$$

$$x = D/kT.$$

$$x_m = \frac{6 N g^2 \beta^2}{k} \frac{2 + 71.938 \left(J/kT\right)^2}{1 + 10.482 \left(J/kT\right) + 955.56 \left(J/kT\right)^3}. \quad (4)$$

Complex **3** is a good model for the magnetic properties of polynuclear Mn(III) compounds because the Co(III) ion is diamagnetic. Complex **3** can be simplified as six isolated Mn(III) ions, if the zero-field splitting (zfs) of the Mn(III) ion is considered. The best fit to the data in the temperature range 5－50 K on the basis of eq. 3 gives $g = 1.97(1)$, and $|D| = 5.2(2)$ cm^{-1}. Alternatively, if the zfs of the Mn(III) ion is neglected, the magnetic properties of complex **3** can be fitted by considering only the Mn(III)–Mn(III) superexchange magnetic coupling through the Mn—NC—Co—CN—Mn linkage. Complex **3** can be accordingly thought as a uniform one-dimensional Mn(III) system from the magnetic viewpoint. According to the one-dimensional model for $S = 2$ (eq. 4)[28], the best fit to the magnetic susceptibility in the range 5－50 K gives the parameters $g = 1.97(1)$, and $J = -0.073(2)$ cm^{-1}. The small J value indicates that the magnetic coupling through the —NC—Co—CN— pathway is very weak[29,30].

4 Conclusions

The structures of three new cyanide-bridged dodecanuclear heterometallic macrocyclic complexes have been determined. The employment of *trans*-dicyanide Cr(III) or Co(III) precursors can effectively facilitate the formation of ring-like complexes, and methyl group substituents on the benzene ring play an important role in the formation of the macrocyclic structures. The cyanide-bridged macrocyclic Cr(III)–Mn(III) compound manifests weak antiferromagnetic coupling, which is different from the ferromagnetic coupling frequently found in cyanide-bridged Fe(III)-Mn(III) complexes. The supramolecular nanotube array of dodecanuclear ring-like complexes has the potential to be applied as a host for the storage of small guest molecules.

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