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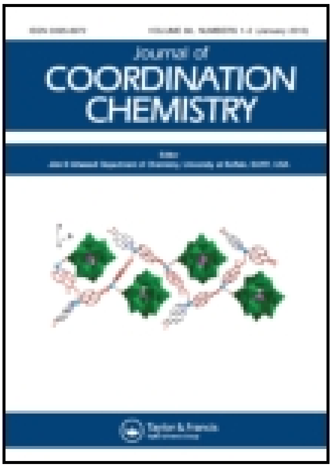

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Journal of Coordination Chemistry
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Synthesis, crystal structures, and magnetic properties of three K[M(bpb)(CN)$_2$]-based trinuclear sandwich-like heterobimetallic M(III)-Ni(II) (M=Fe, Cr, Co) complexes

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Accepted author version posted online: 25 Apr 2014.Published online: 21 May 2014.

To cite this article: Daopeng Zhang, Ping Wang, Zengdian Zhao & Xia Chen (2014) Synthesis, crystal structures, and magnetic properties of three K[M(bpb)(CN)$_2$]-based trinuclear sandwich-like heterobimetallic M(III)-Ni(II) (M=Fe, Cr, Co) complexes, Journal of Coordination Chemistry, 67:9, 1664-1672, DOI: 10.1080/00958972.2014.918266

To link to this article: http://dx.doi.org/10.1080/00958972.2014.918266

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Journal of Coordination Chemistry, 2014
Vol. 67, No. 9, 1664–1672, http://dx.doi.org/10.1080/00958972.2014.918266

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Synthesis, crystal structures, and magnetic properties of three K[M(bpb)(CN)$_2$]-based trinuclear sandwich-like heterobimetallic M(III)–Ni(II) (M = Fe, Cr, Co) complexes

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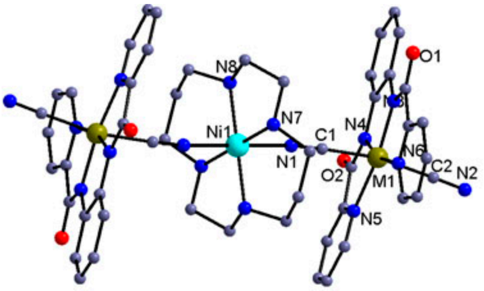
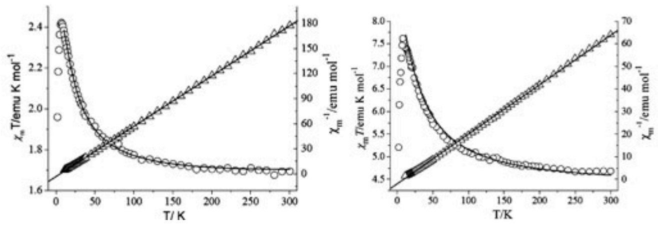
(*Received 29 January 2014; accepted 4 April 2014*)





Three trinuclear sandwich-type cyanide-bridged M^{III}–Ni^{II} complexes, {[Ni(cyclm)[Fe(bpb)(CN)$_2$]$_2$}·8H$_2$O (**1**), {[Ni(cyclm)[Cr(bpb)(CN)$_2$]$_2$}·2H$_2$O (**2**), and {[Ni(cyclm)[Co(bpb)(CN)$_2$]$_2$}·CH$_3$OH·2H$_2$O (**3**) (cyclm = 1,4,8,11-tetraazacyclotetradecane), have been synthesized using K[M(bpb)(CN)$_2$] (M = Fe, Cr, Co; bpb = 1,2-bis(pyridine-2-carboxamido)benzenate) as building block and one Ni(II) compound containing a 14-membered macrocycle ring as assembling segment. All the complexes have been characterized by elemental analysis, IR spectroscopy, and X-ray structure determination. Single X-ray diffraction analysis shows similar sandwich-like structures, in which the two cyanide-containing building blocks are monodentate through one of their two cyanides, coordinated face to face to the central Ni(II). Investigation of the magnetic properties of **1** and **2** reveals ferromagnetic magnetic coupling between the neighboring Fe(III)/Cr(III) and Ni(II) through the bridging cyanide. A best-fit to the magnetic susceptibilities of **1** and **2** based on the trinuclear M$_2$Ni model leads to magnetic coupling constants $J = 5.47(1)\,\mathrm{cm}^{-1}$ for **1** and $J = 6.37(2)\,\mathrm{cm}^{-1}$ for **2**.

Keywords: Cyanide-bridged; Sandwich-like; Crystal structure; Magnetic property

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1. Introduction

Molecular magnetic materials have received much attention in various scientific fields including chemistry, physics, materials science, and catalysis [1–5]. Due to the significant role of cyanide as a remarkable magnetic linker between paramagnetic centers, cyanide-bridged magnetic complexes have always been given intensive and extensive attention. Thus, far, a great deal of cyanidometallate-based molecular magnetic materials with diverse architectures from 0-D clusters to 3-D networks [6–15] and interesting properties, including spin cross-over, photomagnetic materials, single-molecule magnets, and single-chain magnets, have been reported.

One strategy to prepare new cyanide-bridged magnetic complexes is to design new cyanide-containing precursors by blocking the paramagnetic metal ions with organic ligand(s) with different structures and steric effects. A number of decorated polycyanidoiron building blocks, including $[Fe(L)(CN)_5]^{2-}$ (L = 1-methylimidazole), $[M(L)(CN)_4]^-$ (L = bipy, phen, bpym, M = Fe, Cr), *fac*-$[M(L)(CN)_3]^-$ (L = Tp, Tp*, pzTp, tach, M = Fe, Cr), and *mer*-$[Fe(L)(CN)_3]^-$ (L = bpca, pzcq, mpzcq, qcq, pcq) [16–23], have been employed to synthesize cyanide-bridged magnetic complexes. Our group has also developed a series of cyanide-containing building blocks $[Fe(L)(CN)_2]^-$ (L = bpb derivatives, bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate) with relatively large equatorial in-plane ligands and two *trans* cyanide groups, which are good for assembling low-dimensional, cyanide-bridged heterometallic complexes [24]. To gain further information on reactions of $[Fe(bpb)(CN)_2]^-$, and also to enrich the members of the cyanide-bridged family, we investigated the reactions of these types of precursors with $[Ni(cyclm)][ClO_4]_2$ (scheme 1). In this article, we present our recent work which concerns the synthesis, crystal structures, and magnetic properties of three trinuclear sandwich-like heterometallic cyanide-bridged M(III)–Ni(II) complexes $\{[Ni(cyclm)[Fe(bpb)(CN)_2]_2\}\cdot 8H_2O$ (**1**), $\{[Ni(cyclm)[Cr(bpb)(CN)_2]_2\}\cdot 2H_2O$ (**2**), and $\{[Ni(cyclm)[Co(bpb)(CN)_2]_2\}\cdot CH_3OH\cdot 2H_2O$ (**3**).

2. Experimental

2.1. *Physical measurements*

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

2.2. *General procedures and materials*

All chemicals and solvents used for the synthesis were reagent grade used without purification. $K[Fe^{III}(bpb)(CN)_2]$ was synthesized as described in the literature [25], and the two analogous complexes $K[Cr^{III}(bpb)(CN)_2]$ and $K[Co^{III}(bpb)(CN)_2]$ were similarly prepared.

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.

2.3. *Preparation of 1–3*

All three target complexes were prepared using a similar procedure, therefore only the synthesis of **1** is detailed as a typical representative. K$[Fe(bpb)(CN)_2]\cdot CH_3OH$ (93 mg, 0.20 mM) dissolved in methanol and distilled water 10 mL (4 : 1, v : v) was added to a methanol solution (10 mL) formed by $[Ni(ClO_4)_2]\cdot 6H_2O$ (36.6 mg, 0.1 mM) and cyclam (20 mg, 0.1 mM). The mixture was stirred for a few minutes at room temperature and filtered to remove insoluble material (if any), and then the filtrate was allowed to evaporate slowly without disturbance for one week. The dark brown crystals suitable for X-ray diffraction were collected by filtration, washed with cool methanol, and dried in air. Yield 67.1 mg, 53.6%. Anal. Calcd for $C_{50}H_{64}Fe_2N_{16}NiO_{12}$: C, 47.98; H, 5.15; N, 17.90. Found: C, 47.82; H, 5.01; N, 18.12. Main IR bands (cm^{-1}): 2158, 2123 (s, νC≡N), 1616, 1625 (vs νC=N).

Complex **2**: 63.7 mg, 56.1%. Anal. Calcd for $C_{50}H_{52}Cr_2N_{16}NiO_6$: C, 52.88; H, 4.61; N, 19.73. Found: C, 52.65; H, 4.44; N, 19.98. Main IR bands (cm^{-1}): 2158, 2124 (s, νC≡N), 1617, 1628 (vs νC=N).

Complex **3**: 72.8 mg, 59.8%. Anal. Calcd for $C_{51}H_{60}Co_2N_{16}NiO_9$: C, 50.30; H, 4.97; N, 18.40. Found: C, 50.14; H, 4.71; N, 18.64. Main IR bands (cm^{-1}): 2160, 2124 (s, νC≡N), 1618, 1625 (vs νC=N).

2.4. *X-ray data collection and structure refinement*

Single crystals of all the complexes for X-ray diffraction analyses with suitable dimensions were mounted on a glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube ($\lambda = 0.71073$ Å) at 293 K, using a ω scan mode. The structures were solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, while hydrogens were introduced as fixed contributors. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogens were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C), and their coordinates were allowed to ride on their respective carbons using SHELXL97, except some hydrogens of

Table 1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Chemical formula	$C_{50}H_{64}Fe_2N_{16}NiO_{12}$	$C_{50}H_{52}Cr_2N_{16}NiO_6$	$C_{51}H_{60}Co_2N_{16}NiO_9$
Fw	1251.58	1135.79	1217.72
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P-1*
a (Å)	11.2542(7)	15.0155(15)	13.344(5)
b (Å)	22.5398(16)	12.2840(12)	14.159(3)
c (Å)	11.6850(8)	13.3720(13)	16.688(3)
α (°)	90	90	111.716(3)
β (°)	105.1970(10)	93.618(2)	104.920(4)
γ (°)	90	90	95.331(4)
V (Å^3)	2860.4(3)	2461.6(4)	2767.5(13)
Z	2	2	2
Completeness (%)	97.5	99.9	99.0
$F(0\,0\,0)$	1304	1176	1264
θ (°)	1.81–27.55	2.14–25.01	1.38–25.01
GOF	1.048	1.042	1.046
$R_1[I > 2\sigma(I)]$	0.0464	0.0445	0.0366
wR_2 (all data)	0.1454	0.1300	0.1077

solvent molecules, which were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameters. Details of the crystal parameters, data collection, and refinement are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and general characterization*

Our recent studies [26] have proven that *trans*-dicyanidemetalate building blocks were good candidates for synthesizing low-dimensional, cyanide-bridged magnetic complexes. Based on the consideration that polyimine macrocyclic complexes were suitable to assemble cyanide-bridged complexes [27–32], the reactions of *trans*-[M(bpb)$(CN)_2$]$^-$ with [Ni(cyclm)] $[ClO_4]_2$ have been investigated, resulting in three trinuclear heterobimetallic cyanide-bridged complexes with sandwich-like structures. The structures of the complexes here are different from those obtained by reactions of polyaza Ni(II) compounds also containing a 14-membered ring with *trans*-[Fe(bpb)$(CN)_2$]$^-$ [24(b)], clearly indicating that the assembly could obviously influence the structure of the cyanide-bridged complex formed.

All three complexes have been characterized by IR spectroscopy. In IR spectra of **1–3**, two sharp peaks due to the cyanide-stretching vibrations were observed at 2125 and 2160 cm^{-1}, respectively, indicating the presence of bridging and non-bridging cyanides in these complexes.

3.2. *Crystal structures of 1–3*

Selected bond lengths and angles for **1–3** are given in table 2. Representative crystal structure of the three complexes and their cell packing diagram are shown in figures 1 and 2, respectively.

Complexes **1–3**, which crystallize in monoclinic space group *P2(1)/c* for **1** and **2** and triclinic space group *P-1* for **3**, possess similar trinuclear sandwich-like structures comprising of two *trans*-[M(bpb)$(CN)_2$]$^-$ units with the [Ni(cyclm)]$^{2+}$ in the middle. In these three complexes, two [M(bpb)$(CN)_2$]$^-$ units, monodentate through one cyanide, connect Ni(II)

Table 2. Selected bond lengths and angles for **1–3**.

	1	**2**	**3**
Ni1–N1	2.122(2)	2.133(3)	2.122(2)
Ni1–N7	2.051(3)	2.061(3)	2.072(3)
Ni1–N8	2.060(3)	2.058(3)	2.075(3)
M1–C1	1.967(3)	1.924(4)	1.920(3)
M1–C2	1.966(3)	1.917(4)	1.921(3)
M1–N3	1.886(2)	1.881(3)	1.994(2)
M1–N4	1.878(2)	1.885(3)	1.979(2)
M1–N5	1.999(2)	1.981(3)	1.897(2)
M1–N6	1.997(2)	1.987(3)	1.895(2)
Ni1–N1–C1	172.1(2)	168.6(3)	164.5(2)
C1–M1–C2	167.65(11)	177.09(17)	178.96(11)
M1–C1–N1	173.7(2)	172.6(3)	174.3(2)
M1–C2–N2	178.2(3)	177.4(4)	178.9(3)

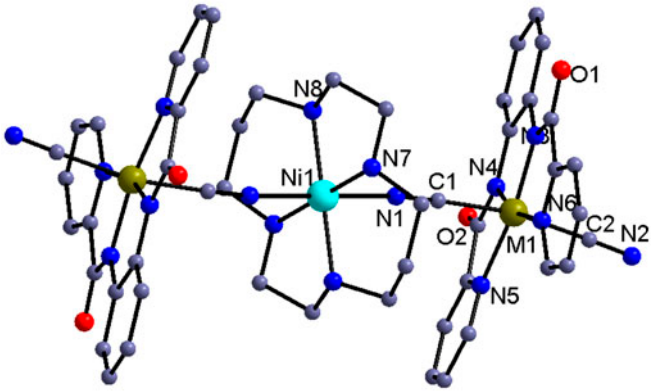


Figure 1. The trinuclear structure of **1–3**. Solvent molecules and all hydrogens have been omitted for clarity.

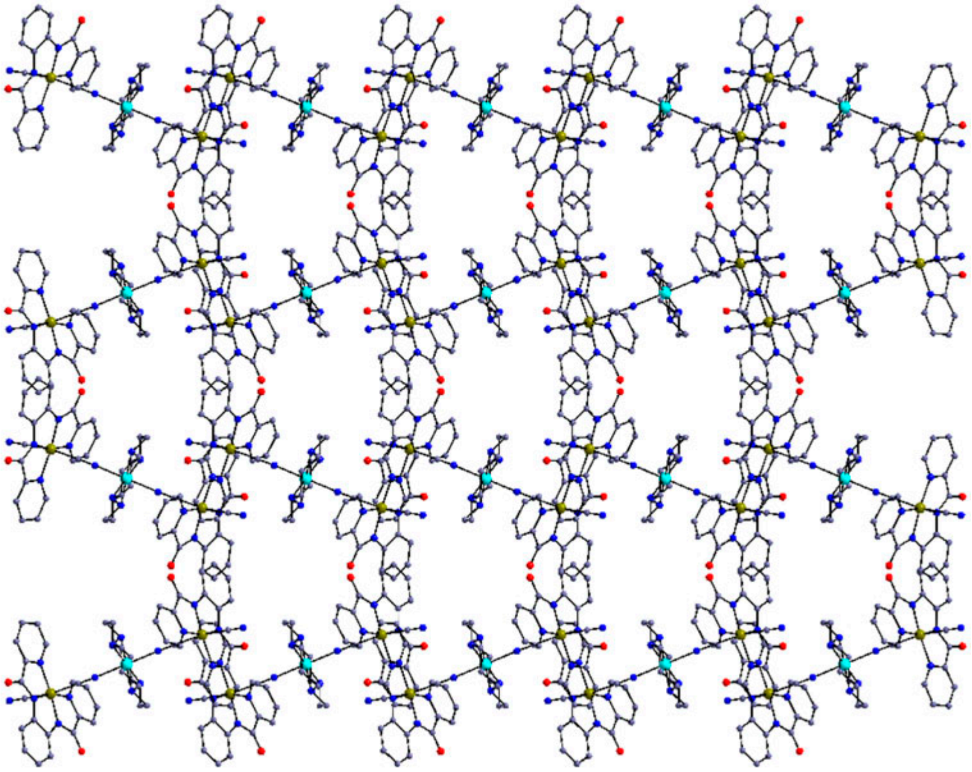


Figure 2. Cell packing along the *c* axis for **1–3**. Solvent molecules and all hydrogens have been omitted for clarity.

coordinated by cyclam. M is coordinated by an equatorial N_4 unit from bpb and two carbons of cyanide in the *trans* position, forming a slightly distorted octahedral geometry. The average M–N bond lengths in **1–3** are 1.94, 1.93, and 1.94 Å, respectively, slightly shorter than the M–C$_{cyanide}$ bond length of 1.917(4)–1.966(3) Å. As listed in table 2, the bond angles of M–C≡N very close to 180° clearly indicate that the three atoms are linear.

The coordination sphere for Ni(II) in these three complexes is also an octahedron, in which four equatorial positions are occupied by four nitrogens of cyclam and the axial positions by nitrogen of the bridging cyanides. As tabulated in table 2, the average distances between Ni and N of cyclam are 2.05, 2.06, and 2.07 Å in **1–3**, while the Ni–N$_{cyanide}$ bond lengths are 2.122(2), 2.133(3), and 2.122(2) Å, respectively, clearly showing the distorted octahedral geometry of Ni(II). The angles of C≡N–Ni in these three complexes are 172.1(2), 168.6(3), and 164.5(2)°, respectively, indicating that these three atoms deviate from linear. The intramolecular M^{III}–Ni^{II} separation through bridging cyanide are 5.199, 5.164, and 5.111 Å for **1–3**, respectively, while the shortest intermolecular metal–metal distance is obviously longer than the above separation with values of 6.632, 6.419, and 6.560 Å. It is worth noting that all three complexes can be constructed into 3-D supramolecular networks with abundant intermolecular O–H···N and O–H···O hydrogen bond interactions.

3.3. *Magnetic properties of 1 and 2*

The magnetic properties of **1** and **2** were investigated, while that of **3** was not studied due to the diamagnetic nature of Co(III). The temperature dependence of the $\chi_m T$ product per M$_2$Ni unit from 2 to 300 K for **1** and **2** is shown in figure 3. The changing tendency of $\chi_m T$ for these two complexes is similar. The $\chi_m T$ value at room temperature is 1.69 and 4.68 emu K M^{-1} for **1** and **2**, respectively, which is slightly lower than the spin only value of 1.75 and 4.75 emu K M^{-1} for uncoupled Ni(II) ($S = 1$) and two low-spin Fe(III) ($S = 1/2$) or two Cr(III) ($S = 3/2$) based on $g = 2.00$. Upon lowering the temperature, the $\chi_m T$ value increases slowly until about 100 K, then increases rapidly and reaches the highest peak with the value of 2.42 emu K M^{-1} for **1** at 7 K and 7.61 emu K M^{-1} for **2** at 8.0 K, and then the $\chi_m T$ value begins to decrease sharply from this point and attains their lowest value of 1.95 emu K M^{-1} for **1** and 5.20 emu K M^{-1} for **2** with the temperature decreasing to 2 K. The decrease in the $\chi_m T$ value at very low-temperature is probably due to the integrated operation of the saturation effect, the intermolecular antiferromagnetic interaction, and/or the zero-field splitting effect of the Ni(II) ions. The magnetic susceptibilities for these two complexes conform well to the Curie–Weiss law in the range of 10–300 K and give the negative Weiss constant $\theta = 5.42$ K and Curie constant $C = 1.67$ emu K M^{-1} for **1** and $\theta = 9.14$ K, $C = 4.56$ emu K M^{-1} for **2**, respectively. These data, together with the changing tendency of

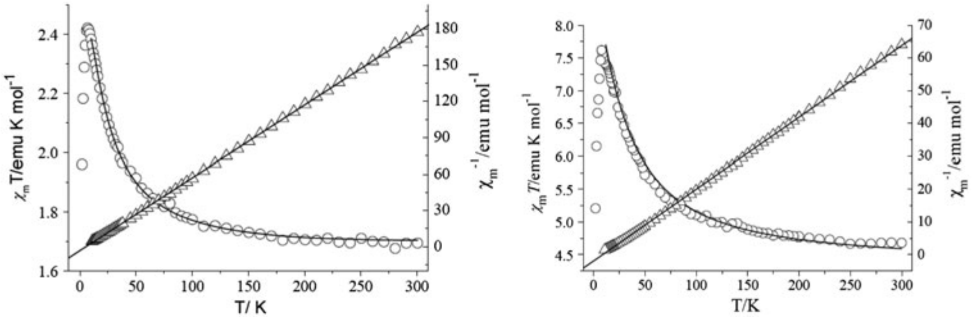
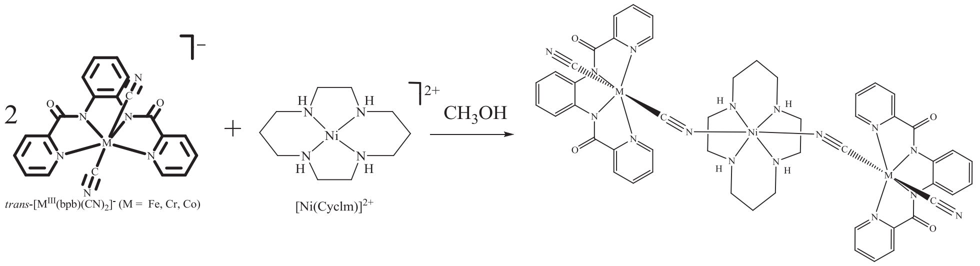


Figure 3. Temperature dependences of $\chi_m T$ and $\chi_m{}^{-1}$ for **1** (left) and **2** (right) (the solid line for $\chi_m T$ represents the best-fit based on the parameters discussed in the text).



Scheme 1. The synthesis of the target complexes.

$\chi_m T - T$ considered, result in the primary conclusion that the magnetic coupling between Fe (III)/Cr(III) and Ni(II) bridged by the cyanide group in **1** and **2** is ferromagnetic.

These magnetic behaviors are also consistent with an intramolecular Fe(III)–Ni(II) ferromagnetic interaction, which can be rationalized in terms of the strict orthogonality of the magnetic orbitals of the low-spin Fe(III) [d^5, $t_{2g}{}^5e_g{}^0$], Cr(III) [d^3, $t_{2g}{}^3e_g{}^0$] and Ni(II) [d^8, $t_{2g}{}^6e_g{}^2$] centers, an arrangement which normally gives ferromagnetic coupling. On the basis of the trimeric model, the magnetic susceptibilities can be fitted accordingly by the following expression derived from the exchange spin Hamiltonian $H = -2JS_{Ni}(S_M(1) + S_M(2))$ [33]:

Complex **1**: $\chi_m = \dfrac{2Ng^2\beta^2}{kT} \cdot \dfrac{1 + 5\exp(4J/kT) + \exp(2J/kT)}{3 + 5\exp(4J/kT) + \exp(-2J/kT) + 3\exp(2J/kT)}$

Complex **2**: $\chi_m = \dfrac{Ng^2\beta^2}{kT}\left[\dfrac{A}{B}\right]$ (χ_m: molar magnetic susceptibility; g: Lande factor; k: Boltzmann constant; β: Bohr magneton; J: coupling constant between the cyanide-bridged Fe(III)–Mn(II)).

$$\begin{aligned} A = {} & 60 + 28\exp(-8J/kT) + 10\exp(-14J/kT) + 28\exp(-2J/kT) + 10\exp(-8J/kT) \\ & + 2\exp(-12J/kT) + 10\exp(-4J/kT) + 2\exp(-8J/kT) + 2\exp(-6J/kT) \end{aligned}$$

$$\begin{aligned} B = {} & 9 + 7\exp(-8J/kT) + 5\exp(-14J/kT) + 7\exp(-2J/kT) + 5\exp(-8J/kT) \\ & + 3\exp(-12J/kT) + 5\exp(-4J/kT) + 3\exp(-8J/kT) + 3\exp(-6J/kT) \\ & + \exp(-10J/kT) \end{aligned}$$

By using the above model, the susceptibilities from 10 to 300 K for **1** and **2** were simulated, giving the best-fit parameters $J = 5.47(1)$, $g = 2.02(2)$, $R = \sum(\chi_{obsd}T - \chi_{cald}T)^2/\sum(\chi_{obsd}T)^2 = 2.37 \times 10^{-5}$ for **1** and $J = 6.37(2)$, $g = 1.98(6)$, $R = 2.67 \times 10^{-5}$ for **1**, respectively, which are slightly smaller than those found in the reported cyanide-bridged Fe/Cr^{III}–Ni^{II} complexes [24(b), 34].

The magnetic properties of the cyanide-bridged MNi (M = Fe, Cr) complexes reveals ferromagnetic coupling between the cyanide-bridged M^{III}–Ni^{II}. As reported previously, the strict orthogonality of the magnetic orbitals in the cyanide-bridged system could result in ferromagnetic coupling between the paramagnetic metal ions. The electronic configurations of low-spin Fe(III) and Cr(III) are $t_{2g}{}^5e_g{}^0$ and $t_{2g}{}^3e_g{}^0$, respectively. Meanwhile, the electronic configuration for Ni(II) in the octahedral coordination field is $t_{2g}{}^6e_g{}^2$. Therefore, the ferromagnetic coupling caused by the strict orthogonality of the magnetic orbitals between

t_{2g} and e_g can be expected, which have also been proven by examples reported previously [24(b), 34] and the result of this paper.

4. Conclusion

Three *trans*-dicyanide precursors K[M(bpb)$(CN)_2$] (M = Fe, Cr, Co) and a polyimine macrocyclic nickel compound were used as building blocks to assemble three trinuclear cyanide-bridged heterometallic M(III)–Ni(II) complexes with sandwich-like structures. Investigation of the magnetic properties of the cyanide-bridged Fe–Ni and Cr–Ni complexes reveals an overall ferromagnetic interaction between Fe(III)/Cr(III) and Ni(II) ions bridged by a cyanide. The present results and those reported previously [24, 26] indicate further that $[M(bpb)(CN)_2]^-$ types of cyanide precursors are suitable building blocks with potential for assembling low-dimensional, cyanide-bridged complexes with various molecular structures.

Supplementary material

CCDC 983779–983781 contain the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

Funding

This work was supported by the National Natural Science Foundation of China [grant number 21171107]; the Natural Science Foundation of Shandong Province [grant number ZR2011BM008]; the Science and Technology Project of High Education, Shandong Province [grant number J11LB09].

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