Extended Networks of Co\textsuperscript{2+} and Mn\textsuperscript{2+} Bridged by NCS\textsuperscript{-}/N\textsubscript{3} – Anions and Flexible Long Spacers: Syntheses, Structures, and Magnetic Properties

Xin-Yi Wang\textsuperscript{[a]} Bao-Long Li,*\textsuperscript{[b]} Xia Zhu\textsuperscript{[b]} and Song Gao*\textsuperscript{[a]}

Keywords: Thiocyanate / Azide / Cobalt / Manganese / 1,2-Bis(imidazol-1-yl)ethane / 1,2-Bis(1,2,4-triazol-1-yl)ethane / Magnetic properties

Four new metal-organic polymers with SCN\textsuperscript{-}/N\textsubscript{3} – anion bridges and flexible long spacers \( L \) [\( L = \text{bim} \) \( [1,2\text{-bis(imidazol-1-yl)ethane}] \) \( \) and \( \text{bte} \) \( [1,2\text{-bis(1,2,4-triazol-1-yl)ethane}] \), \( \text{[Co(SCN)]}_2(\text{bim}) \) ] \( ) \( 1\text{-Co} \), \( [\text{Co(SCN)}]_2(\text{bte}) \) ] \( ) \( 2\text{-Co} \), \( [\text{Mn(N}_3]_2(\text{bte}) \) ] \( ) \( 3\text{-Mn} \), and \( [\text{Mn(N}_3]_2(\text{bim}) \) ] \( ) \( 4\text{-Mn} \), were synthesized and characterized by single-crystal X-ray diffraction studies and their magnetic properties were investigated. Complex 1\text{-Co} is a triple-bridging chain complex with double end-to-end SCN\textsuperscript{-} anions and single gauche-bim spacers as bridges. Complexes 2\text{-Co} and 3\text{-Mn} both contain 1D chains bridged by double end-to-end SCN\textsuperscript{-} or N\textsubscript{3} – anions and these chains are further extended to 2D (4,4) layers by the anti-bte spacers. Complex 4\text{-Mn} has a topological 3D diamond structure constructed through 1D double end-on azide-bridged Mn\textsuperscript{II} chains and extended through the anti-bim spacers. Magnetic measurements reveal that 1\text{-Co} and 3\text{-Mn} remain paramagnetic; the dominant magnetic coupling between Co\textsuperscript{III} is weak ferromagnetic and that between Mn\textsuperscript{II} is strong antiferromagnetic. As for 2\text{-Co} and 4\text{-Mn}, they show metamagnetic behavior below \( T_S = 2.9 \) and 3.0 K, respectively. Our results show that a combination of the short anion bridges (SCN\textsuperscript{-}/ N\textsubscript{3} –) and flexible bidentate long spacers can be used to construct coordination polymers with novel topologies and interesting magnetic properties. (© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005)

Introduction

In the attractive field of supermolecular chemistry and crystal engineering, long bidentate spacers provide a useful approach to new functional materials with a variety of multi-dimensional arrays and networks. Because of the large separation and the inefficiency to transmit magnetic interactions, these long spacers were seldomly used to construct molecule-based magnetic materials with high magnetic-ordering temperatures. However, their abilities to form new architectures with novel topologies and interesting magnetic properties still attracts intensive attention, such as compounds constructed by rigid \( N,N' \)-bidentate spacers like 4,4’-bipyridine (4,4’-bpy), \( (E)\text{-1,2-bis(4-pyridinyl)ethene} \), pyrazine, and other related ligands. Very recently, we reported a series of compounds \( \text{M(CHOO)}_2(4,4'-\text{bpy})\cdot n\text{H}_2\text{O} \) \( (M = \text{Mn, Co, } n = 0; M = \text{Co, Ni, } n = 5) \) with all 3D structures and magnetically long-range ordering. As with its azide analog \( \text{M(N}_3]_2(4,4'-\text{bpy}) \) \( (M = \text{Mn, Fe}) \), the bidentate long spacer 4,4’-bpy efficiently tuned the topologies of these compounds and led to weak ferromagnetism. The design of coordination polymers is highly influenced by several factors such as the coordination geometry of the central atom, the structural characteristics of the ligand molecule, the solvent system and the counterion. When rigid bifunctional ligands are used as spacers to connect metal centers, the topology of the network is usually determined by the coordination geometry of the central metal preference. Contrary to rigid ligands, the flexible ligands with conformational flexibility induce a variety of structures and may lead to the formation of the supramolecular isomers. Some coordination polymers with flexible ligands have been investigated. For example two remarkable polyrotaxane-like polymers based on 1,4-bis(imidazol-1-yl-methyl)benzene (bix) were synthesized by Robson and co-workers. The flexible ligands 1,2-bis(imidazol-1-yl)-ethane (bim) and 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) can adopt either gauche (angular) or anti (linear) conformations (Scheme 1). We previously reported several coordination polymers in which the ligands also exhibit either gauche or anti conformations. Complex \( \text{[Mn(gauche-bte)]}_2(\text{NCS)}_2 \) \( \) contains both a double-stranded chain and a single chain in the same crystal and both gauche and anti conformations of the bte spacer.
Of course, the main approach to constructing molecule-based magnetic materials is to employ short bridging ligands, which are efficient to mediate the magnetic coupling, to connect paramagnetic transition metal ions. Among the widely used anion ligands, the pseudohalide azide has been demonstrated to be the all-important one, if not the most, due to the versatility and the ability to mediate strong magnetic coupling, either ferro- or antiferromagnetic. Most commonly, the azide ion can adopt two possible bridging modes: end-to-end (EE) associated with antiferromagnetic (AF) coupling, and end-on (EO) related with ferromagnetic exchange. In our previous reports,[2d,6] we explored another three-atom bridging ligand, the formate anion, which is a natural analog of azide, to construct new formate compounds with structures and magnetic properties similar to or different from those of azide. Furthermore, we investigated another pseudohalide anion: the thiocyanato ion (SCN). Like azide and formate, SCN can also mediate magnetic coupling between the metal ions, with the sign and the magnitude depending on the bridging modes and the localized structural details.[7a–7c] Owing to the two different donor groups (N and S) within it, the thiocyanate ion has less versatility and is less efficient as a magnetic coupler than the azide ligand. In contrast with the large number of azide-bridged compounds studied from a magnetic and structural point of view, there are fewer reports on the divalent first-row transition metal complexes bridged by SCN. Fully studied complexes are mainly compounds of NiII[8,9] and CuII[10–12] such as dimers[8,10] 1D chains,[9,11] and 2D layers.[12] For MnII and CoII compounds, the existing results are quite rare.[13,14] The 2D compounds [M(SCN)2(ROH)2] (M = Mn, Co; R = CH3, C2H5, C6H5)[13b,14] and the proposed 1D chain compounds M(SCN)2(2,2'-bipyridine) (M = Mn, Co) are rare examples that have been investigated thoroughly.[13a] New thiocyanato-bridged compounds, especially of CoII, are needed to be explored further.

Taking into account the above-mentioned aspects, we report here the syntheses, structures and the magnetic properties of four new coordination polymers: Co(L)(SCN)2 (L = bim (1-Co) and bte (2-Co)) and Mn(L)(N3)2 (L = bim (3-Mn) and bim (4-Mn)). All four of these polymers assemble through both the flexible-bidentate long spacers (bim/bte) and the short anion ligands (SCN/N3) as bridges. Among them, 1-Co is a triple-bridging 1D compound bridged by double EE-SCN− ligands and single gauche-bim spacers. 2-Co is a 2D metamagnet with double EE-SCN− ligands and anti-bte spacers as bridges. 3-Mn has a very similar structure to that of 2-Co and behaves as a magnetic AF chain. As for 4-Mn, the double EO-azides and the anti-bim spacers lead to a metamagnet with a distorted 3D diamondoid structure.

Results and Discussion

Crystal Structures

Single-crystal X-ray diffraction of 1-Co reveals that it crystallizes in the orthorhombic space group Pnma2, and the structure is presented in Figure 1. In 1-Co, each CoII center is octahedrally coordinated by two nitrogen atoms from two bridging bim ligands in trans positions, two nitrogen and two sulfur atoms from four bridging EE-SCN− groups. Lengthened along the S1–Co1–S2 axis, the octahedron is of an approximate D2h point group. The bond lengths are as follows: Co1–N1 2.083(2), Co1–N3 2.076(2), Co1–N5 2.127(2), Co1–N6 2.122(2), Co1–S1 2.660(2), and Co1–S2 2.635(1) Å. The bond angles of D–Co1–D (D represents N or S atoms) are in the range of 88–92°. The angles of Co1–S2–C10 and Co1A–S1A–C9 are ca. 98°, which are close to a right angle, and the angles of Co1–N5–C9 and Co1A–N6A–C10 are 160° or so. So the geometry of the Co2(SCN)2 ring is close to that of a rectangle although with poor coplanarity. The geometrical feature of Co2(SCN)2 has already been observed in other thiocyanato-containing metal complexes and it is believed to have a very important influence on the magnetic coupling between the transition metal ions, especially NiII.[7a–7c,9e] It is well demonstrated that, because of the orthogonality of the orbitals, the more rectangular the geometry, the greater the possibility of ferromagnetic coupling will be.[7a–7c]

Figure 1. Toothed chain structures and the 2D layer of 1-Co. Hydrogen atoms are omitted for clarity. The thin lines represent the π–π and C–H···π interactions between adjacent chains.

The SCN− anion is almost linear [S1A–C9–N5 and S2–C10–N6A are 179.2(2) and 178.8(2)°, respectively] and the bim ligand is of the gauche conformation (torsion angle of N2–C7–C8–N4 is 59.2(3)°). Both of these ligands act as bridges to connect adjacent CoII ions to form a triple-bridg-
ing 1D toothed chain along the [100] crystallographic direction. Parallel chains stack in the [010] direction such that the convex bim bow of one chain extends into the concave section of the neighboring chain. There are obvious C–H···π interactions between the hydrogen atoms of alkanes and imidazole rings of adjacent chains (C–H···π angles 110.1° and 109.5°, and C···π distances 3.294 and 3.294 Å). Also, there are π–π interactions between the imidazole rings of adjacent chains (perpendicular distance between centroids of the imidazole rings: 5.625(2) and 9.095(2) Å). Thus, the 2D layer parallel with the centroids of the imidazole rings: 4.054 Å, dihedral angle: 0.6°). Thus, the 2D layer parallel with the π···π interactions between the adjacent triazole rings (shortest perpendicular distance between centroids of the triazole rings: 5.691 Å, dihedral angle: 0°). But, obvious π–π interactions between the 2D networks can be found (perpendicular distance between centroids of the triazole rings: 3.886 Å, dihedral angle: 0°), and there are C–H···π interactions between the hydrogen atoms of alkane and triazole rings of adjacent 2D networks (C3–H···π angles 124.5°, C···π distances 3.811 Å (Table S2)). All these weak interactions stack the 2D layers along the [011] direction in the sequence “···A–B–C–A–B–···” with a slide of 4.55 Å (b/2) and the shortest Co–Co interlayer distance is about 8.170(2) Å.

Although 2-Co has a similar composition to 1-Co by replacing bim with bte, its structure and properties are different from 1-Co (Figure 2). 2-Co crystallizes in the triclinic space group P1 and the CoII atom is located in the symmetrical center. The cobalt atom in 2-Co is also in the same elongated octahedron of an approximate D4h point group formed by two trans-N atoms from bte, two trans-N and S atoms from four symmetry-related SCN– anions of an EE mode. The bond lengths and the angles of D–Co–D are close to those of 1-Co and the details can be found in the CIF file. Unlike 1-Co, the ring of Co2(SCN)2 is almost coplanar and results in an approximate rectangle where the angles of Co–S–C and Co–N–C are ca. 165° and 100°, respectively, slightly larger than those in 1-Co. Bridged by SCN– only, 2-Co forms 1D [Co(SCN)2]n chains along the a axis; and the adjacent octahedra align parallel to one another. Different from the gauche-bim spacer in 1-Co, the bte ligand in 2-Co is of the anti conformation with the torsion angle N1–C3–C3A–N1A of 180.0 (2)°. Through this linear conformation, bte links adjacent cobalt chains to form a 2D neutral (4,4) network, which is very similar to that in [Cd(NCS)2(bte)]n.[48] The 2D network in 2-Co is completely different from the 1D toothed chain in 1-Co only because bim in 1-Co is replaced by bte in 2-Co. This difference shows the subtle modulations of the bidentate spacers to construct novel topologies. The nearest Co–Co intrachain distance is 5.691(3) Å and that of the interchain is 12.014(56) Å. In the 2D network, there are no obvious π–π interactions between the adjacent triazole rings (shortest perpendicular distance between centroids of the triazole rings: 5.691 Å, dihedral angle: 0°). But, obvious π–π interactions between the 2D networks can be found (perpendicular distance between centroids of the triazole rings: 3.886 Å, dihedral angle: 0°), and there are C–H···π interactions between the hydrogen atoms of alkane and triazole rings of adjacent 2D networks (C3–H···π angles 124.5°, C···π distances 3.811 Å (Table S2)). All these weak interactions stack the 2D layers along the [011] direction in the sequence “···A–B–C–A–B–···” to form the whole architecture (Figure S1).

The structure of 3-Mn is very similar to that of 2-Co (Figure 3), except that the bridging ligand is the EE-N3– anion instead of SCN–. Also, this structure is very similar to that of [Mn(N3)2(bpa)]n[3ml] except that the flexible bte spacer is present instead of the flexible bpa spacer. The 1D [Mn(N3)2]n chain is linked by bte to form a two-dimensional (4,4) layer and the layers stack along the [011] direction also in the “···A–B–C···” mode (Figure S2). There are no π–π interactions between the adjacent triazole rings in the 2D networks (shortest perpendicular distance between centroids of the triazole rings: 5.236 Å). Different from 2-Co, the π–π interactions between adjacent 2D layers are negligibly weak (perpendicular distance between centroids of the triazole rings: 4.334 Å, dihedral angle: 0°). The coordination octahedron of MnII is more regular than that of 1-Co. The bond lengths of Mn–N are in the range of 2.21–2.27 Å and the bond angles are from 87.0 to 93.0°. The metal–metal distance of 5.236(5) Å within the chain is shorter than that of 5.691(3) Å in 2-Co, originating from the short length of the N3– ion as compared to SCN– [2.348(8) and 2.799(10) Å for N3– and SCN–, respectively]. The interchain M–M distance [11.948(56) Å] is similar to that of 2-Co due to the same bridging ligand anti-bte.
Figure 3. Two-dimensional (4,4) layer bridged by double end-to-end N$_3^-$ and anti-bte ligands of 3-Mn.

The crystal structure of 4-Mn has some interesting characteristics. The change from the bte ligand in 3-Mn to bim in 4-Mn leads to very different crystal structures, which shows the importance that ancillary ligands play in tuning the crystal structure. As can be seen from Figure 4a, every Mn$^{II}$ atom in 4-Mn is also coordinated by six nitrogen atoms, two from the cis-imidazole rings of the bim ligand and the others from four EO-azide anions. The octahedron is largely distorted with the Mn–N bond lengths from 2.223(5) to 2.299(3) Å and N–Mn–N bond angles from 74.03(11) to 100.17(11)°. The Mn–N bond lengths do not vary much but the N–Mn–N angles deviate much from 90°, especially those of the N$_3^-$–Mn–N$_3^-$ angles [e.g., N5–Mn1–N5a = 74.03(11)°, N8–Mn1–N8a = 77.44(11)°, and N5–Mn1–N8 = 100.17(11)°]. The detailed bond lengths and bond angles can be found in the CIF file.

4-Mn is different from 3-Mn in that there are two symmetrically independent azide anions (N5–N6–N7 and N8–N9–N10) and they both act as EO bridges, linking Mn$^{II}$ ions to form a 1D zigzag [Mn(N$_3$)$_2$]$_n$ chain along the a direction (Figure 4b). The bond angles of Mn–N5–Mn and Mn–N8–Mn are 105.97(13) and 102.56(12)°, respectively, giving rise to two metal–metal intrachain distances, 3.614(5) and 3.535(5) Å, respectively. These kinds of double EO-azide-bridged Mn$^{II}$ ions form a ferromagnetic chain in 4-Mn as in two reported compounds.[2e,15]

The bim ligands in the anti conformation all act as bridges to expand the [Mn(N$_3$)$_2$]$_n$ chains into a 3D architecture. No obvious weak interactions can be found in 4-Mn as the bim ligands are sufficiently separated from each other. Along the chain, the bim ligands of the Mn$^{II}$ ions point in four different directions alternatively (Figure 4c), leading to an interesting shape of a “molecular windmill”, with bim...
ligands in four directions as four arms. As a result of this connection mode, every MnII atom is a four-connected node, and thus the topology of 4-Mn is a distorted 3D diamond, as can be seen in Figure 4d. If a dimer MnII bridged by azide is considered as one node, the structure can also be viewed as a simple cubic topology. The distance between the MnII ions bridged by bim is 11.460(14) Å, and such a long distance leads to porous channels along the a direction.

Magnetic Properties

1-Co

The plots of $\chi_M T$ versus $T$ and $\chi_M^{-1}$ versus $T$ measured from 2 to 300 K in 1 kOe are displayed in Figure 5. At 300 K, the $\chi_M T$ value is 3.10 cm$^3$Kmol$^{-1}$ and decreases to a minimum of 1.71 cm$^3$Kmol$^{-1}$ at 8 K, then it increases abruptly to 5.78 cm$^3$Kmol$^{-1}$ at 2 K. Fitting the data above 30 K using the Curie–Weiss law, $\chi_M = C/(T - \theta)$, gives a Curie constant $C = 3.31$ cm$^3$Kmol$^{-1}$, significantly larger than the spin-only value of 1.875 cm$^3$Kmol$^{-1}$ for Co$^{2+}$, and a negative Weiss constant $\theta$ of –18.8 K. Commonly, this kind of behavior of $\chi_M T$ and the negative $\theta$ value may indicate the occurrence of a dominant antiferromagnetic coupling between the spin carriers. However, because the spin-orbit coupling itself can lead to a negative $\theta$ value and a decrease of $\chi_M T$ at high temperatures, caution must be paid concerning those spins with large spin-orbit coupling, such as the Co$^{2+}$ ion in an octahedral ligand field. Actually, the increase of $\chi_M T$ below 8 K indicates the possibility of ferromagnetic coupling. Although difficult, some efforts have been made to calculate the spin-orbit coupling parameter $\lambda$ ($\lambda = -170$ cm$^{-1}$ for the free ion), the axial splitting parameter $A$ (and then the axial zero-field splitting parameter $D$), and/or the exchange coupling parameter $J$ for some mononuclear CoII ions in the octahedral field.\cite{16-18} In the case of 1-Co, we fitted the susceptibility data by considering a mononuclear Co$^{2+}$ ion with spin-orbit coupling parameter $\lambda$ ($H = -\lambda LS$) in a molecular-field approximation. The $\chi_{\text{mono}}$ for a mononuclear Co$^{2+}$ in an octahedral environment can be calculated from Equation (1)\cite{16} with $x = \lambda J/k_B T$.

The parameter $A$ gives a measure of the crystal field strength relative to the interelectronic repulsions and is equal to 1.5 for a weak crystal field, 1.32 for a free ion, and 1.0 for a strong field. Considering the molecular-field theory with $J$ as the total exchange parameter, we can fit our experimental data above 30 K with Equation (2).\cite{19}

$$\chi = \frac{\chi_{\text{mono}}}{1 - (2zJ/Ng^2)\beta\chi_{\text{mono}}}$$

(2)

In Equations (1) and (2), $N$, $g$, $\beta$, $k_B$, and $T$ have their usual meanings. The best fit (Figure 5) gives $\lambda = -117$ cm$^{-1}$ = –168 K, $A = 1.24$, and $zJ = 0.42$ cm$^{-1}$ = 0.61 K with $R = 1.3 \times 10^{-5}$ $[\chi = \chi_{\text{obsd.}} - \chi_{\text{calcd.}}]/\chi_{\text{obsd.}}]^2$.

Although our results are semi-quantitative due to the imprecision of the molecular-field theory, the evaluated positive $zJ$ shows the possibility of the ferromagnetic interaction between CoII neighbors. It is also evidenced by the isothermal magnetization measurement at 1.8 K (inset of Figure 5). The magnetization increases very fast from zero to about 0.7 $\mu_B$ at 2 kOe, which indicates the occurrence of ferromagnetic coupling and might suggest the occurrence of a phase transition. After a slow increase to about 1.0 $\mu_B$ at 20 kOe, the magnetization increases faster again to 2.43 $\mu_B$ at 70 kOe. To clarify the occurrence of a phase transition, the temperature dependence of the susceptibility $\chi_M$ from 1.8 to 8 K, and the ac susceptibility under $H_{ac} = 0$ Oe and $H_{ac} = 3$ Oe from 1.8 to 4 K were measured, and the results are presented in Figure S3. All these results show no sign of long-range ordering at the lowest temperature limit of 1.8 K of our SQUID system.

2-Co

The temperature dependence of the susceptibility $\chi_M$ of 2-Co was measured in a magnetic field of 5 kOe from 2 to 300 K and the result is plotted as $\chi_M T$ versus $T$ and $\chi_M^{-1}$ versus $T$ in Figure 6. After decreasing slowly upon cooling to a minimum of 3.49 cm$^3$Kmol$^{-1}$ at 40 K (inset of Figure 6), $\chi_M T$ increases abruptly to a peak at 4.5 K, and then
drops again until 2 K. The data in the range of 30–300 K obeys the Curie–Weiss law with $C = 3.79 \text{cm}^3\text{K}^{-1}\text{mol}^{-1}$ and a negative $\theta$ value of $-3.50 \text{K}$. As discussed for 1-Co, the small negative $\theta$ value does not necessarily come from the AF coupling through the EE-SCN$^-$ ion but from the spin-orbit coupling. Similar to that of 1-Co, the $\chi_M/T$ data above 30 K can also be fitted by Equations (1) and (2) with a small temperature-independent paramagnetic constant $\chi_{\text{TIP}} = 0.0003 \text{cm}^3\text{mol}^{-1}$. The best fit (Figure 6) gives $\lambda = -85.6 \text{cm}^{-1} = -124 \text{K}$, $A = 1.45$ and $\Delta J = 2.43 \text{cm}^{-1} = 3.51 \text{K}$ with $R = 5 \times 10^{-6}$ [$R = \Sigma (\chi_{\text{obsd.}} - \chi_{\text{calcld.}})^2/\Sigma (\chi_{\text{obsd.}})$]. The $A$ value shows the weak ligand field and the positive $\Delta J$ clearly indicates the existence of the dominant ferromagnetic coupling between the adjacent Co$^{II}$ ions, consistent with the result of 1-Co.

To prove the long-range ordering of 2-Co, suggested by the peak of $\chi_M/T$ at 4.5 K, we performed other measurements at low temperatures. The isothermal magnetization at 1.8 K with the field up to 50 kOe shows a pronounced sigmoid behavior of a metamagnet. The magnetization first increases slowly with increasing field strength, then shows a sharp transition to a ferromagnetic state (or a paramagnetic one) (Figure 7). At 50 kOe, the magnetization value is $2.80 \mu_B$, close to the expected saturated value of high-spin Co$^{II}$. The critical field is ca. $0.65 \text{kOe}$ at 1.8 K, estimated from the sharp peak of $\text{d}M/\text{d}H$, which is the field strength of the steepest point of the $M(H,T)$ curve. We also measured the ac isothermal magnetization at $H_{\text{ac}} = 3 \text{Oe}$ with a dc field from $-6$ to $+6 \text{kOe}$ and a frequency of 666 Hz (Figure S4) and the FCM from 2 to 6 K at different fields (200, 400, 500, 600 and 800 Oe) (inset of Figure 7). The sharp peak of $\chi_M'$ is consistent with that of $\text{d}M/\text{d}H$; and the peak of $\chi_M$ in the FCM shifts to low temperatures with increasing external fields and finally disappears when the field is larger than the critical field. Also, the temperature-dependent ac susceptibility under $H_{\text{dc}} = 0 \text{Oe}$ and $H_{\text{ac}} = 3 \text{Oe}$ with frequencies of 277, 666, 1633, and 4111 Hz was measured from 2 to 6 K (Figure 8). The in-phase signal shows a sharp peak at ca. 2.9 K, and no detectable out-of-phase signal or frequency dependence was observed.

Figure 6. Plots of $\chi_M T$ versus $T$ and $\chi_M^{-1}$ versus $T$ from 2 to 300 K of 2-Co. The line across $\chi_M^{-1}$ is the fit using the Curie–Weiss law and that along $\chi_M T$ represents the best fit using the model mentioned in the text. Inset: the expansion of the minimum of $\chi_M T$.

Figure 7. Field-dependent isothermal magnetization $M(T,H)$ for 2-Co at 1.8 K. The low-field region is expanded for clarity. Inset: field-cooled magnetization from 2 to 6 K at different fields.

Figure 8. Ac susceptibilities from 2 to 6 K in zero applied dc field and an ac field of 3 Oe at different frequencies (277, 666, 1633, 4111 Hz) for 2-Co.

All of the measured data indicates that 2-Co is a metamagnet below the critical temperature 2.9 K, and the critical field for the metamagnetic transition is ca. 650 Oe at 1.8 K. Considering the structure, the metamagnetism of 2-Co can be rationalized as a result of the competition between the weak antiferromagnetic coupling among the ferromagnetic [Co(SCN)$_2$]$_n$ chains and the external field. External fields larger than 650 Oe overcome the antiferromagnetic stacking of the chains and turn the AF ground state into a paramagnetic one.

3-Mn

The magnetic susceptibility $\chi_M$ of 3-Mn measured at 10 kOe from 2 to 300 K shows a broad peak at about 50 K (Figure S5), which is typical for an AF-coupled system. As can be seen from Figure 9, the $\chi_M T$ value at 300 K is 3.61 cm$^3$K mol$^{-1}$, which is significantly lower than the spin-only value of 4.375 cm$^3$K mol$^{-1}$, and decreases continuously to 0.0387 cm$^3$K mol$^{-1}$ at 2 K. Fitting of the data above 130 K with the Curie–Weiss law gives $C = 4.94 \text{cm}^3\text{K}^{-1}\text{mol}^{-1}$ and $\theta = -108 \text{K}$, indicating a strong antiferromagnetic coupling between the Mn$^{II}$ ions bridged by the $EE$-N$_3$$^-$ anion. At 1.8 K, the isothermal magnetization $M(T,H)$ increases almost linearly from 0 to 50 kOe and reaches $0.2 \mu_B$ per Mn$^{II}$ atom at 50 kOe, far from the saturation value $M_S = 5 \mu_B$ for a spin-only Mn$^{II}$ ion, confirming the antiferromagnetic coupling between the Mn$^{II}$ ions. Considering the
low-dimensional structure of 3-Mn, we can fit the susceptibility data $\chi T$ above 30 K using Equation (3) based on the molecular-field theory.\cite{10} $\chi_{\text{chain}}$ is the susceptibility of the Fisher model of a 1D equally spaced Heisenberg chain for a classical spin ($S = 5/2$) with the Hamiltonian $H = -2J\sum_{<i,j>}S_iS_j$ ([Equation (4)]\cite{11} with $u$ represented by Equation (5)).

$$
\chi = \frac{\chi_{\text{chain}}}{1 - (2zJ/Ng^2)^2\chi_{\text{chain}}}
$$

(3)

$$
\chi_{\text{chain}} = \frac{Ng^2(S(S + 1))}{3kT} \left[ \frac{1 + u}{1 - u} \right]
$$

(4)

$$
u = \coth \left( \frac{JS(S + 1)}{kT} \right) - \left[ \frac{kT}{JS(S + 1)} \right]^2
$$

(5)

In Equations (3)–(5), $S = 5/2$; $J$ and $zJ$ represent the magnetic coupling constants of the intra- and interchains. The best fit (Figure 9) gives $J = -8.08(3) \text{ cm}^{-1} = -11.7 \text{ K}$, $zJ = -0.9(1) \text{ cm}^{-1} = -1.3 \text{ K}$, and $g = 2.057$ with $R = 4.7 \times 10^{-5}$ [$R = \Sigma(\chi_{\text{obsd}} - \chi_{\text{calcld}})^2/\Sigma(\chi_{\text{obsd}})^2$]. The negative $J$ and $zJ$ values show that an AF interaction exists both within and between the chains.

### 4-Mn

As can be seen from the plots of $\chi_M T$ versus $T$ and $\chi_M^{-1}$ versus $T$ measured from 2 to 300 K in 10 kOe displayed in Figure S6, the value of $\chi_M T$ increases gradually with decreasing temperature and shows a peak at 10 K. This behavior suggests intrachain ferromagnetic coupling: the decrease of $\chi_M T$ below 10 K may be due to interchain antiferromagnetic coupling or saturation effect of the field. Fitting of the data above 100 K with the Curie–Weiss law gives $C = 4.16 \text{ cm}^3 \text{ K mol}^{-1}$ and a positive $\theta$ value of +23.5 K, also indicating the dominant ferromagnetic coupling between Mn$^{3+}$ ions transmitted by the EO-azide anion.

To further clarify the nature of the low-temperature phase, we have measured the FCM in different fields (200, 500, 1500 Oe) (inset of Figure 10) and the ac susceptibility under $H_{dc} = 0 \text{ Oe}$ and $H_{ac} = 2 \text{ Oe}$ from 2 to 15 K (Figure 11). The FCM at low fields of 200 and 500 Oe shows peaks at about 3.0 K but the peak disappears in the high-field region (1.5 kOe). This behavior is quite similar to that of 2-Co and indicates a phase transition from an antiferromagnetic state to a ferromagnetic one above some critical field. Actually, the ac susceptibility under zero dc field is typical for an antiferromagnet; the in-phase signal shows a sharp peak at 3.0 K, and no detectable out-of-phase signal nor frequency dependence was observed. In order to investigate the phase transition with increasing field, the isothermal magnetization $M(T,H)$ with fields up to 70 kOe at 1.8 K (Figure 11) was measured. As a whole, the magnetization increases fast at low fields and almost reaches saturation at about 10 kOe. At the highest field of 70 kOe, the saturation value is 5.1 $\mu_B$ very close to the saturated value of 5 $\mu_B$ for $S = 5/2$. Careful examination of the low-field range between 0 and 3 kOe reveals two obvious abrupt steps, with $H_{c1} = 0.23 \text{ kOe}$ and $H_{c2} = 0.82 \text{ kOe}$, defined as the $H$ values with the steepest slopes of the $M(T)$ curve (inset of Figure 11). The plateau region at 1.8 K is presumably associated with the familiar spin-flop state at the intermediate field values $H_{c1} < H < H_{c2}$. The ac isothermal magnetization under a field of $H_{ac} = 2 \text{ Oe}$ with $H_{dc}$ from 0 to 3 kOe and a frequency of 666 Hz at 1.8 K (Figure S7) supports these two transitions. Two obvious peaks, $\chi_M^I$ and $\chi_M^F$, are consistent with the peaks of $dM/dH$.

**Figure 9.** Plots of $\chi_M T$ versus $T$ and $\chi_M^{-1}$ versus $T$ from 2 to 300 K of 3-Mn. The line across $\chi_M^{-1}$ is the fit using the Curie–Weiss law and that along $\chi_M T$ represents the best fit using the chain model mentioned in the text. Inset: field-dependent isothermal magnetization $M(T,H)$ for 3-Mn at 1.8 K.

**Figure 10.** Ac susceptibilities from 2 to 6 K in the zero applied dc field and an ac field of 2 Oe at different frequencies (277, 666, 1633, 4111 Hz) for 4-Mn. Inset: field-cooled magnetization at different fields.

**Figure 11.** Field-dependent isothermal magnetization $M(T,H)$ for 4-Mn at 1.8 K. Inset: expansion of the low-field region.

Based on the structure of 4-Mn and the magnetic data, we rationalize that this phenomenon is a metamagnetic...
transition coexisting with a spin-flop transition. The metamagnetic transition originates from competition between the external field and the AF coupling among ferro- or ferrimagnetic chains or layers. And the spin-flop transition is quite common for many antiferromagnets with weak anisotropy (for MnII, the S ground state makes it one of the weakest anisotropic ions). The moment orientation switches from the easy axis to an orientation perpendicular to the applied field only when the fields are larger than a critical field \( H_{c1} \). From the magnetic point of view, 4-Mn can be considered as a 1D ferrimagnetic chain because of the very large interchain Mn–Mn distances \( 11.46(14) \text{Å} \) as compared to the short intrachain distances of 3.614(5) and 3.535(5) Å. The intrachain coupling transferred by the EO-N3 anion is ferrimagnetic since the angles of Mn–N azide–Mn are about 103° and 106°, and there are numerous reports concluding that this kind of bridging azide favors the ferrimagnetic coupling between MnII ions. With the weak AF coupling between the chains, these ferrimagnetic chains are aligned in an anti-parallel fashion to each other at low external fields. As the field increases to a spin-flop field \( H_{c1} \) \( \approx 0.23 \text{kOe} \), 4-Mn transfers from the AF state to a spin-flop one and the antiparallel magnetizations of the two sub-lattices flop from the direction of the easy axis to that perpendicular to it. Further increase of the external field to a critical field \( H_{c2} \approx 0.82 \text{kOe} \) can totally overwhelm the interchain AF coupling and the state turns into a ferromagnetic one. Similar behavior was also observed in a compound where MnII and NiII ions were ferromagnetically bridged by NO2– anions to form a ferrimagnetic chain.

**Conclusions**

By using two flexible long ligands \( 1,2\)-bis\{1,4-triazol-1-yl\}ethane (bte) and \( 1,2\)-bis\{imidazol-1-yl\}ethane (bim), and two short anion bridges SCN– and single \( \text{N}_3 \), we successfully synthesized four new coordination polymers formulated as \([\text{Co(SCN)}_2(bim)] \) \((1-\text{Co})\), \([\text{Co(SCN)}_2(bte)] \) \((2-\text{Co})\), \([\text{Mn(N}_3)_2(bte)] \) \((3-\text{Mn})\), and \([\text{Mn(N}_3)_2(bim)] \) \((4-\text{Mn})\). 1-\text{Co} crystallizes as a triple-bridging chain compound with double \( EE-\text{SCN}^- \) and single \( \text{N}_3 \) anions, and 3-\text{Mn} have similar 2D (4,4) layer structures with an \( \text{anti} \)–bte ligand connecting \([\text{Co(SCN)}_2]_n \) or \([\text{Mn(N}_3)_2]_n \) chains bridged by double \( EE-\text{SCN}^-/\text{N}_3^- \) anions. 4-\text{Mn} forms a distorted diamondoid structure due to double \( EO-\text{N}_3^- \) and \( \text{anti} \)-bim bridging ligands. Magnetic measurement reveals that the dominant magnetic coupling between the CoII ions in 1-\text{Co} and 2-\text{Co} is ferrimagnetic. 1-\text{Co} remains paramagnetic up to 1.8 K and 2-\text{Co} is a metamagnet below \( T_N \approx 2.9 \text{K} \) with a critical field \( H_{c1} = 650 \text{Oe} \) at 1.8 K. For 3-\text{Mn}, the strong AF coupling leads to an AF chain compound without long-range ordering above 1.8 K. For 4-\text{Mn}, the AF ground state exists below \( T_N \approx 3.0 \text{K} \) and a metamagnetic transition coexisting with a field-induced spin-flop transition was observed with the \( H_{c1} \approx 0.23 \text{kOe} \) and \( H_{c2} \approx 0.82 \text{kOe} \). Our results show that a combination of short anion bridges (\( \text{SCN}^-/\text{N}_3^- \)) and flexible-bidentate long spacers can be used to construct coordination polymers with novel topologies and interesting magnetic properties.

**Experimental Section**

**General Remarks**

All starting materials were commercially available, reagent grade, and used as purchased without further purification. The ligands bim and bte were prepared according to a literature method. Elemental analyses of C, H, N were carried out with a Perkin–Elmer 240C analyzer. FTIR spectra were obtained for KBr pellets with a Nicolet 170SX FTIR spectrophotometer in the 4000–400 cm–1 region. Variable-temperature magnetic susceptibility, zero-field ac magnetic susceptibility measurements, and field dependence of magnetization were performed with an Oxford Maglab 2000 System or a Quantum Design PPMS XL-5 SQUID system. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal’s tables).

**Synthesis**

\[ [\text{Co(SCN)}_2(bim)] \) \((1-\text{Co})\): \( \text{Co(NO)}_3_2 \cdot 6\text{H}_2\text{O} \) (0.146 g, 0.5 mmol), KSCN (0.097 g, 1.0 mmol) and bim (0.081 g, 0.5 mmol) in 14 mL of water were heated in a Teflon-lined autoclave (20 mL) at 180 °C for 4 d. After slow cooling to room temperature, purple prismatic crystals suitable for single-crystal X-ray crystallographic analysis were obtained. The crystals were filtered from the mother liquor and washed with ethanol. Yield: 0.110 g (65%).

\[ [\text{Mn(N}_3)_2(bim)] \) \((4-\text{Mn})\): A methanolic solution (20 mL) of bte \((0.082 \text{ g, 0.5 mmol})\) was added to one side of a H-shaped tube, and 20 mL of an \( \text{H}_2\text{O}/\text{EtOH} \) solution \((1: 1, \text{v/v})\) of bte \((0.082 \text{ g, 0.5 mmol})\) was added to the other side of the H-shaped tube. After approximately 3 months, purple crystals suitable for X-ray analysis were obtained. Yield: 0.090 g (53%).

\[ [\text{Mn(N}_3)_2(bim)] \) \((3-\text{Mn})\): A methanolic solution \((0.163 \text{ g, 2.5 mmol})\) of \( \text{Mn(NO)}_3_2 \cdot 6\text{H}_2\text{O} \) \((0.146 \text{ g, 0.5 mmol})\) was slowly added to an aqueous solution \((20 \text{ mL})\) of \( \text{MnSO}_4 \cdot 7\text{H}_2\text{O} \) \((0.085 \text{ g, 0.5 mmol})\) and excess NaN3 \((0.163 \text{ g, 2.5 mmol})\) while stirring. The mixtures were stirred at room temperature and the resultant solution was filtered. The filtrate was allowed to stand in the air for 1 week, well-shaped pale yellow crystals were obtained. Yield: 0.126 g (83%).

**Acknowledgements**

X.-Y. Wang, B.-L. Li, X. Zhu, S. Gao
Table 1. Crystallographic data for compounds 1–4.

<table>
<thead>
<tr>
<th></th>
<th>1-Co</th>
<th>2-Co</th>
<th>3-Mn</th>
<th>4-Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₈H₁₀CoN₆S₂</td>
<td>C₈H₄CoN₈S₂</td>
<td>C₈H₆MnN₁₂</td>
<td>C₈H₆MnN₁₀</td>
</tr>
<tr>
<td>M[gmol⁻¹]</td>
<td>337.29</td>
<td>339.27</td>
<td>303.18</td>
<td>301.20</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>a [Å]</td>
<td>11.249(3)</td>
<td>5.691(3)</td>
<td>5.236(5)</td>
<td>5.234(5)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>9.095(2)</td>
<td>6.432(4)</td>
<td>6.419(6)</td>
<td>6.214(2)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>12.585(3)</td>
<td>8.840(5)</td>
<td>8.760(8)</td>
<td>18.984(5)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90</td>
<td>94.753(10)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>90</td>
<td>100.220(9)</td>
<td>94.551(13)</td>
<td>90</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90</td>
<td>94.753(10)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V[Å³]</td>
<td>1287.6(6)</td>
<td>308.3(3)</td>
<td>286.2(4)</td>
<td>1224.6(5)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>ρcalcd [g cm⁻³]</td>
<td>1.740</td>
<td>1.827</td>
<td>1.759</td>
<td>1.634</td>
</tr>
<tr>
<td>Crystal size [mm⁻¹]</td>
<td>0.12 ± 0.16 ± 0.4</td>
<td>0.11 ± 0.20 ± 0.2</td>
<td>0.3 ± 0.3 ± 0.4</td>
<td>0.1 ± 0.2 ± 0.2</td>
</tr>
<tr>
<td>μ(Mo Kα) [mm⁻¹]</td>
<td>1.650</td>
<td>1.728</td>
<td>1.163</td>
<td>1.083</td>
</tr>
<tr>
<td>Meas. reflections</td>
<td>13604</td>
<td>3464</td>
<td>2120</td>
<td>11816</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2935</td>
<td>1391</td>
<td>1212</td>
<td>2166</td>
</tr>
<tr>
<td>Observed reflections[a]</td>
<td>2819</td>
<td>1264</td>
<td>1196</td>
<td>2056</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>173</td>
<td>88</td>
<td>88</td>
<td>172</td>
</tr>
<tr>
<td>F(000)</td>
<td>684</td>
<td>171</td>
<td>153</td>
<td>612</td>
</tr>
<tr>
<td>GOF</td>
<td>1.177</td>
<td>1.070</td>
<td>0.989</td>
<td>1.242</td>
</tr>
<tr>
<td>Max/min [e Å⁻³]</td>
<td>0.293/–0.354</td>
<td>0.286/–0.336</td>
<td>0.330/–0.237</td>
<td>0.227/–0.366</td>
</tr>
<tr>
<td>Tmin/Tmax/Tmin</td>
<td>0.827/0.731</td>
<td>0.829/0.714</td>
<td>0.705/0.661</td>
<td>0.901/0.802</td>
</tr>
<tr>
<td>R [b]</td>
<td>0.0277</td>
<td>0.0306</td>
<td>0.0231</td>
<td>0.0535</td>
</tr>
<tr>
<td>wR₂[w]</td>
<td>0.0586</td>
<td>0.0696</td>
<td>0.0605</td>
<td>0.1169</td>
</tr>
</tbody>
</table>

[a] Observation criterion: I > 2σ(I). [b] R₁ = Σ|F₁| – |F₂|/Σ|F₁|, I > 2σ(I). [c] wR₂ = (Σ[w(Fo₂² – Fc₂²)²]/Σ[w(Fo₂²)²])¹/², for all data.

Acknowledgments

We acknowledge support from the National Science Fund for Distinguished Young Scholars (20125104), NSFC Nos. 20221101, 20490210, and the Natural Science Foundation of the University of Jiangsu Province (No. 03KJB150118), and the Funds of The Key Laboratory of Organic Synthesis of Jiangsu Province, P. R. China. We also acknowledge Mr. Zhang Yong for the single-crystal structural determination.


