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Azide-bridged Cu(II), Mn(II) and Co(II) coordination polymers constructed with a bifunctional ligand of 6-(1H-tetrazol-5-yl)-2,2′-bipyridine

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Three new azide-bridged coordination polymers, [M(N₃)(tzbp)]ₖ (M = Cu, 1·Cu; Mn, 2·Mn; Co, 3·Co), were successfully synthesized by the introduction of a bifunctional tetrazolate/2,2′-bipyridine ligand, 6-(1H-tetrazol-5-yl)-2,2′-bipyridine (Htzbp), from the in situ [2+3] cycloaddition of 6-cyan-2,2′-bipyridine in the presence of an excess of sodium azide under hydrothermal conditions. Compounds 1·Cu-3·Co were characterized by X-ray crystallography, IR spectroscopy, thermogravimetry, and elemental analysis. With tzbp ligands acting in the chelating coordination mode, compound 1·Cu was comprised of a single end-on N₃ (EO-N₃) bridged one-dimensional (1D) zigzag structure. Both compounds 2·Mn and 3·Co adopt two-dimensional (2D) layered structures composed of a double EO-N₃ bridged dinuclear motif, [M₂(EO-N₃)₂], which are interlinked by tzbp ligands in the chelating/bridging mode. The layers of 2·Mn and 3·Co are stacked on each other in ⋯ABAB⋯ and ⋯AAAA⋯ fashions, respectively. Magnetic investigations revealed that intrachain antiferromagnetic interactions were dominant in compound 1·Cu, and both 2·Mn and 3·Co exhibited spin-canted antiferromagnetism behaviour with critical temperatures (Tₛ) of 3.0 and 18.4 K, respectively. Furthermore, below Tₛ, the field-induced magnetic transitions of spin-flop and metamagnetism were observed in 2·Mn and 3·Co, respectively.

Introduction

The design and synthesis of new coordination polymers (CPs) with paramagnetic metal ions that function as molecule-based magnets have attracted considerable attention and play important roles over recent years. Great progress has been made in our understanding of structure–property relationships, such as magneto-structural correlation, of molecular magnetic systems and constructing new magnetic materials with potential technological applications. Enormous efforts in this field have been focused on the design of suitable organic ligands and the ease of coordination of metal ions for the construction of various extended networks.

A variety of short bridging groups, such as azide and five-membered heterocyclic azoles, have been widely studied due to their versatility in both structural and magnetic aspects. They not only connect metal ions in various bridging modes with various dimensionality/topology, but also induce the magnetic exchange of different magnitudes and natures (ferromagnetic, FM, or antiferromagnetic, AF) leading to development of unusual magnetic properties, such as long-range magnetic ordering, metamagnetism, single-molecule magnets (SMMs), and single-chain magnets (SCMs). In addition, the rich structural and magnetic diversities of these magnetic systems can be evoked by introduction of different auxiliary organic co-ligands and/or ligands that contain short bridging groups as backbones. Encouraged by the success with tetrazolate-based ligands, a combination of two dissimilar groups as simultaneous bridges has been attempted in pursuit of new magnetic CPs.

In our previous studies, we designed a bridging ligand, 6,6′-bis(1H-tetrazol-5-yl)-2,2′-bipyridine (H₂btzbp), by the unitization of two tetrazolates at the terminal of a 2,2′-bipyridine for the construction of a Co(II) metamagnet. The designed btzbp ligand features a chelating/bridging coordination mode in which multiple metal ions are connected to a 2D structure and processes significant interlayer π–π interactions. This result suggests that ligands in combination with tetrazoyl and 2,2′-bipyridyl groups may represent a potential linker for the preparation of new magnetic CPs.

Scheme 1. Molecular structure of Htzbp ligand.

In a continuation of our research, we herein report on the synthesis and characterization of three new coordination polymers, [M(N₃)(tzbp)]ₖ (M = Cu, 1·Cu; Mn, 2·Mn; Co, 3·Co), by a bifunctional tetrazolate/2,2′-bipyridine ligand, 6-(1H-tetrazol-5-yl)-2,2′-bipyridine (Htzbp, Scheme 1), through in situ
[2-3] cycloaddition of 6-cyano-2,2’-bipyridine and in the presence of an excess of sodium azide under hydrothermal conditions. With tzbp ligands acting in the chelating coordination mode, compound 1-Cu assumes a single end-on N3− (EO-N3) bridged one-dimensional (1D) zigzag structure. Both compounds 2-Mn and 3-Co adopt two-dimensional (2D) layered structures comprised of double EO-N3 bridged dinuclear moieties, [Mn(EO-N3)2]n, which are interlinked by tzbp ligands in a chelating/bridging mode. The layers of 2-Mn and 3-Co are stacked on each in ...ABAB··· and ···AAAA··· fashions, respectively. Magnetic investigations revealed that intrachain antiferromagnetic interactions dominated in compounds 1-Cu, while 2-Mn and 3-Co exhibited spin-canted antiferromagnetism with critical temperatures (Tc) of 3.0 and 18.4 K, respectively. Furthermore, below the Tc, field-induced magnetic transitions of spin-flop and metamagnetism were observed in 2-Mn and 3-Co, respectively.

Results and Discussion

Syntheses.

Hydrothermal reactions of 6-cyano-2,2’-bipyridine (bpCN) and different metal salts in the presence of an excess sodium azide resulted in the formation of various coordination polymers with bifunctional a tetrazolate/2,2’-bipyridine ligand (tzbp). It is noteworthy that the tzbp anions in compounds 1-Cu, 2-Mn and 3-Co are generated through [2 + 3] cycloaddition and hydrolysis reactions with the cyano-groups changed to tetrazolate. The IR spectra of 1-Cu, 2-Mn and 3-Co were consistent with the characteristics of their structures. The absence of peaks corresponding to a cyano group in the 2200 cm−1 region, indicate that a cyano group is no longer present in the product, and the emergence of a peak at 1400–1500 cm−1 indicates the formation of the tetrazole group, consistent with previous reports.12 Meanwhile, the strong peaks around 2050–2070 cm−1 are assigned to the bridging coordination mode of the azide group.

To examine the thermal stabilities of the compounds, thermogravimetric analyses (TGA) were carried out (Supporting Information, Fig. S1). Compounds 1-Cu, 2-Mn and 3-Co were found to be thermally stable without weight loss at temperatures lower than 260°C, 320°C and 300°C, respectively. The structures of 1-Cu, 2-Mn and 3-Co begin to decompose and a rapid weight loss was observed when the temperature reached 280°C, 340 °C and 320 °C, respectively, which can be attributed to the elimination of the tzbp and azido groups. X-ray powder diffraction (XRPD) patterns were also carried out for compounds 1-Cu, 2-Mn and 3-Co. The measured XRPD patterns of the three compounds are in good agreement with patterns simulated from the respective single-crystal data for the compounds, thus confirming the bulk purity of the three samples (Figs. S2-S4).

Structure description.

Single crystals of compounds 1-Cu, 2-Mn and 3-Co suitable for single-crystal X-ray crystallography were obtained. Labelled plots of crystal structures are shown in Figs. 1–5 and the selected bond distances and angles are listed in Table S1.

Structure of Compound 1-Cu. Compound 1-Cu crystallizes in the monoclinic space group P21/c and the asymmetric unit contains one crystallographically independent Cu2+ ion, one tzbp ligand and one azido anion. As shown in Fig. 1, compound 1-Cu has a covalently bonded zigzag chain structure, in which the Cu2+ ions are singly bridged by the EO-N3 ligands. Each Cu2+ ion in 1-Cu is penta-coordinated with a distorted square pyramidal geometry (r = 0.27).13 Three nitrogen atoms (N1–N3) of the tzbp ligand and a nitrogen donor (N7) of the azido ligand comprise the basal plane, and the axial coordination sites are occupied by one nitrogen atom (N7A) of the azide group. The bridging EO azido anions are bound asymmetrically to Cu2+ with Cu–N distances of 2.048 and 2.880 Å, and the Cu–N3–Cu angle is 121.26°. The two transoid angles in the basal plane are 156.23° and 160.65°, while the cisoid angles are in the range 73.65°–98.86°. The small bite angles are mainly due to the five-membered ring chelating of tzbp ligands. The Cu···Cu distance of 4.314 Å in the chain is rather large compared to that observed in Cu2+ compounds with azido anions bridging in an EO mode at the two equatorial positions.14

Fig. 1. ORTEP drawing of the uniform chain of 1-Cu with thermal ellipsoids set at a 50% probability. The H atoms are omitted for clarity.

Structure of Compound 2-Mn. Single-crystal X-ray diffraction analysis revealed that compound 2-Mn crystallizes in orthorhombic space groups Pbcn and the asymmetric unit of compound 2-Mn contains one crystallographically independent Mn2+ ion, one tzbp ligand and one azido anion. As depicted in Fig. 2, the Mn2+ ion displays an distorted octahedral coordination sphere, in which the equatorial positions are occupied by the tridentate NNN atoms from the tzbp ligand and a nitrogen donor (N7) and one nitrogen atom from an azide anion (N7), and the axial positions are occupied by one azido nitrogen (N7A) atom and one tetrazolate nitrogen atom from the tzbp ligand (N6B) with Mn–N distances in the range 2.196–2.318 Å. The distortion of the metal polyhedron is mainly due to the small bite angles of the five-membered chelating ring (N1–Mn1–N2, N2–Mn1–N3 and N7–Mn1–N7A) at 70.55, 71.79 and 76.73°, respectively. Two neighboring Mn2+ ions related by an inversion center are doubly linked by two EO-N3 bridges (N7 and N7A) resulting a dinuclear [Mn2(EO-N3)2] unit, in which the Mn–N–Mn bridging angle and Mn–Mn distance are 103.27° and 3.461 Å, respectively (Fig. 3a). Each Mn2 unit is further connected to four identical neighboring Mn2 units by four µ-N,N'-tetrazolate from four tzbp ligands and results a 6-hcub 2D polymeric layer that is parallel to the ab crystal plane (Fig. 3b). The metal coordination spheres of each Mn2 moiety in the layer display two alternately orientations, in which the dihedral angle of the equatorial planes and the Mn···Mn distance between two tetrazolate-bridged Mn2+ ions are
65.89° and 6.444 Å, respectively. Closely related, the dihedral angle of the \( \text{Mn}_2\text{N}_2 \) plane between each \( \text{Mn}_2 \) moiety is 31.32°. As shown in Fig. 3b, the layers are stacked alternately, so that the \( \text{Mn}_2 \) units of neighboring 2D layers are directly above the mesh units of another layer (i.e., an ABAB mode). There are some interdigitations between the pyridyl groups that protrude from different sheets through supramolecular π-π stacking (the nearest interlayer \( \text{Mn}^{2+} \cdot \cdot \cdot \text{Mn}^{2+} \) distance is 8.832 Å). The separations between the pyridyl rings of \( \text{tzbp}^- \) ligands are 3.75 Å for the centroid-centroid distance and 3.34 Å for the interplane distance (Fig. S5).

Structure of Compound 3·Co. X-ray analysis reveals that compound 3·Co crystallizes in the \( P2_1/c \) space group and the asymmetric unit contains one crystallographically independent \( \text{Co}^{2+} \) ion, one \( \text{tzbp}^- \) ligand and one azido anion. Similar to compound 2·Mn, compound 3·Co adopts a 2D layered structure with a \([\text{Co}_2(\text{EO}-\text{N}_3)_2]^-\). As shown in Fig. 4, the \( \text{Co}^{2+} \) center is coordinated in a distorted octahedral sphere occupied by four nitrogen atoms (N1, N2, N3 and N5B) from two \( \text{tzbp}^- \) ligand and two nitrogen atom (N7 and N7A) from two EO-N_3 group with the Co–N distances in the range 2.086–2.297 Å. The distorted metal polyhedron is mainly due to the small bite angles of the five-membered chelating ring (N1–Co1–N2 and N2–Co1–N3 are 75.39° and 76.45°, respectively). Two neighboring \( \text{Co}^{2+} \) ions related by an inversion center are linked by two EO-N_3 bridges (N5 and N5A) forming a dinuclear, \([\text{Co}_2(\text{EO}-\text{N}_3)_2]^-\), unit. In the unit, the Co–N–Co bridging angle is 101.89° and the Co⋯Co distance is 3.362 Å. Each Co_2 unit is connected to four neighboring identical Co_2 units through four \( \mu^+\text{N}^1 \cdot \cdot \cdot \text{N}^4 \)-tetrazolate bridges from four \( \text{tzbp}^- \) ligands, generating a 6\(^{3+}\)-\text{hcb} layer that is orientated parallel to the bc crystal plane (Fig. 5a), where the Co⋯Co distance spanned by the \( \mu^+\text{N}^1 \cdot \cdot \cdot \text{N}^4 \)-tetrazolate group is 6.370(2) Å. In the layer, the \( \text{Co}^2 \) moiety shows a systematic alternation of two different orientations, where the dihedral angle of the \( \text{Co}_2\text{N}_2 \) planes is 88.18°. The 3D packing of structure in 3·Co is unlike that in 2·Mn, the adjacent layers are packed together in a cavity-above-cavity (⋯AABB⋯) fashion by supramolecular π-π interactions with the nearest interlayer Co⋯Co distance being 8.25 Å (Fig. 5b). The separations between the pyridyl rings of the \( \text{tzbp}^- \) ligands are 3.81 Å for the centroid-centroid distance and 3.24 Å for the interplane distance (Fig. S6).

**Fig. 2.** ORTEP drawing of the local coordination environment of dimeric unit of 2·Mn with thermal ellipsoids set at a 50% probability. The H atoms are been omitted for clarity.

**Fig. 3.** (a) View of the tetrazole-Mn\(_2\) layer parallel to the ab plane in 2·Mn. (b) The packing of 6\(^{3+}\)-hcb net topology of 2·Mn with Mn ion as the node.

**Fig. 4.** ORTEP drawing of the local coordination environment of dimeric unit of 3·Co with thermal ellipsoids set at a 50% probability. The H atoms are been omitted for clarity.

**Fig. 5.** (a) View of the tetrazole-Mn\(_2\) layer parallel to the bc plane in 3·Co. (b) The packing of 6\(^{3+}\)-hcb net topology of 3·Co with Co ion as the node.

**Magnetic Properties.**

**Compound 1·Cu.** The temperature-dependent magnetic susceptibility of a powder sample of 1·Cu in 2.0–300 K under an applied field of 1.0 kOe is shown in Fig. 6. The \( \chi_MT \) value at room temperature is 0.406 cm\(^3\) mol\(^{-1}\) K, slightly larger than the theoretical value of spin-only Cu\(^{2+}\) ions (0.375 cm\(^3\) mol\(^{-1}\) K). Upon cooling, the \( \chi_MT \) value decreases slightly until 30 K and then rapidly decreases, reaching 0.145 cm\(^3\) mol\(^{-1}\) K at 2.0 K indicating the presence of antiferromagnetic coupling. The magnetic susceptibility above 30 K obeys the Curie–Weiss law very well (Fig. S7), giving a Curie constant \( C \) of 0.41 cm\(^3\) mol\(^{-1}\) K and a Weiss constant, \( \theta \), of −0.75 K. The negative Weiss constant indicates the existence of antiferromagnetic coupling between the Cu\(^{2+}\) ions. For the isotropic Heisenberg antiferromagnetic system with an \( S = 1/2 \), the molar susceptibility can be expressed as follows based on \( H = -JS_S\mu_1 \):
where $x = |J|/kT$. The best fitting for the data from 8 to 300 K gives $J = -0.60 \text{ cm}^{-1}$, $g = 2.10$ with $R = 3.5 \times 10^{-6}$, and $R = [\Sigma \chi_{\text{obsd}} - \chi_{\text{calc}}]^{2}/\Sigma \chi_{\text{obsd}}^{2}$. The negative $J$ values suggest the existence of antiferromagnetic interactions between the Cu$^{2+}$ ions through the single EO-N$_3$, which is consistent with literature values, both empirically and theoretically. A magneto-structural correlation based-on several EO-N$_3$ bridged Cu$^{2+}$ complexes was reported by Thompson et al., in which the magnetic interaction changes from ferromagnetic to antiferromagnetic at Cu–N–Cu angle of 108°. The interaction is found to be ferromagnetic for lower angle values and antiferromagnetic for higher angle values. A reported density functional study for an EO azido-bridged Cu$^{2+}$-binuclear model complex also confirms this empirical conclusion, in which the critical Cu–N–Cu angle was found to be 104°. In the present case, for 1-Cu, it is clear that the weak antiferromagnetic interaction results from the large Cu–N–Cu angle (121.2°), which is much larger than the critical value of 108°, and the long Cu–N bond distance.

**Compound 2-Mn.** The temperature-dependent $\chi_M T$ of 2-Mn in 2.0–300 K under an applied field of 1.0 kOe is shown in Fig. 7. The $\chi_M T$ value at 300 K is 4.74 cm$^3$ mol$^{-1}$ K, which is higher than that expected value of 4.38 cm$^3$ mol$^{-1}$ K for an isolated Mn$^{2+}$ ion ($S = \frac{5}{2}$ and $g = 2.0$). The $\chi_M T$ value increases gradually upon cooling, reaching a smooth maximum of 5.57 cm$^3$ mol$^{-1}$ K at 26 K, indicating the ferromagnetic interaction. The $\chi_M$ data above 100 K obeys the Curie–Weiss law with a Curie constant $C = 4.56$ cm$^3$ mol$^{-1}$ K and a Weiss constant $\theta = 10.76$ K (Fig. S8). The positive value of $\theta$ confirms that ferromagnetic coupling is dominant. Upon further cooling, the $\chi_M T$ value undergoes an abrupt decrease to 1.08 cm$^3$ mol$^{-1}$ K at 2.0 K suggesting overall antiferromagnetism in the low-temperature range. The Néel temperature, as deduced from the peak position of $d\chi_M T/dT$, was $T_N = 3.0$ K. Based on the crystal structure, the magnetic analysis of 2-Mn was carried out by treating the system as a square lattice of dinuclear units (layer of dimers). The expression of the magnetic susceptibility for the dimeric moiety ($\chi_{\text{dimer}}$) was deduced from an isotropic Heisenberg Hamiltonian: $H = -JS_{\text{Mn1}}S_{\text{Mn2}}$, where $J$ is the exchange coupling through the double EO-N$_3$ bridges. The dimeric units were assumed to have an effective spin associated with the follow equation.

\[
\chi_M = \frac{N\beta^2 g^2}{kT} \left[ 0.25 + 0.14995x + 0.3094x^2 \right]
\]

(1)

The expression [eqn (3)] derived by Curie for a square lattice of classical spins was then used to describe the magnetic properties of the “layer of dimers” in 2-Mn.

\[
\chi_M = \frac{N g^2 \beta^2 S(S+1)}{3kT} \left[ (1+u) - \left(1 - \frac{|J_s|}{kT} \right) \right]
\]

(3)

where $u$ is the Langevin function, $u = \text{coth}(J_s/2kT) - J_s/2kT$. The solid line represents the best fit given in the text. The inset shows the $\chi_M T$ vs T plots at the indicated field.

In addition, the $\chi_M T$ of 2-Mn becomes field-dependent at low-temperatures (Fig. 7 inset), where $\chi_M T$ abruptly increases below 3.4 K under a weak applied field, suggesting the onset of magnetic ordering due to spin-canted antiferromagnetism and a field-induced magnetic transition. Evidence for magnetic ordering of spin-canted antiferromagnetism was demonstrated by zero-field-cooled/field-cooled (ZFC/FC) magnetization. At 20 Oe, the ZFC/FC shows a divergence below 3.0 K indicating irreversible behavior arising from the formation of a magnetically ordered state (Fig. S9). The presence of magnetic ordering of spin-canted antiferromagnetism was also confirmed by measured alternating current (ac) magnetic susceptibility data, in which a sharp cusp of the in-phase ($\chi''$) signal at 3.4 K with the corresponding out-of-phase ($\chi'$) signals were obtained (Fig. S10).

The isothermal magnetizations $M(H)$ of 2-Mn were performed at 2.0 K up to 50 kOe (Fig. 8). In the low field region ($H < 10$ kOe), $M$ increases slowly and after a gradual increase, it becomes linear up to the field reaches about 40 kOe, where a second change, though a pronounced loss, happens. Such magnetization behavior suggests a spin-flop (SF) magnetic transition. In the SF transition, the antiparallel spin alignment “flops” perpendicular to the applied magnetic field. The $H_{SF}$ and $H_C$ are found at 10.5 and 26.5 kOe, respectively, by $dM/dH$ (Fig. 8).
inset). The $M$ value of 4.14 $N\beta$ at 50 kOe is lower than the expected saturation value of 5.0 $N\beta$ anticipated for a Mn$^{2+}$ ion ($S = 5/2$, $g = 2.0$). Furthermore, the magnet-like behavior of $2\cdot$Mn was established by the measurement of a magnetic hysteresis loop, which shows a small hysteresis loop at 2.0 K with a coercive field ($H_c$) of ~80 Oe and a remnant magnetization of 0.0064 $N\beta$ (Fig. 8, inset). The canting angle can be estimated to around 0.07° based on the remnant magnetization.23

![Fig. 8. The isothermal magnetization of 2·Mn at 2.0 K. The insets give the derivation of M vs H and a blow-up of the hysteresis loop.](image)

To further substantiate the existence of spin-flop, the field dependence of the ac magnetic susceptibilities, $\chi_M'(H)$, at different temperatures and the temperature dependence of FC magnetizations, $\chi_M(T)$, at different fields were collected at different temperatures. As shown in Fig. S11, at 2.0 K, the $\chi_M(H)$ shows a sharp and a round peak for the transitions of the Mn1 center in $2\cdot$Mn, which were reported as originating from the weak single-ion anisotropy of the high-spin Mn$^{2+}$ ions.22,25 Therefore, we assume that the spin-canted antiferromagnetism in 2·Mn can be attributed to weak single-ion magnetic anisotropy of distorted Mn$^{2+}$ site.

![Fig. 9. Plot of $\chi_M T$ vs. $T$ of 3·Co in an applied field of 1 kOe from 2 to 300 K.](image)

![Fig. 10. Field dependence of the magnetization of 3·Co at 2.0 K. The insets give the derivation of M vs H and a blow-up of the hysteresis loop.](image)

**Compound 3·Co.** The $\chi_M T$ vs. $T$ for compound 3·Co is shown in Fig. 9. At 300 K, the $\chi_M T$ value is 3.46 cm$^3$ mol$^{-1}$ K, which is greater than the expected value for a high-spin Co$^{2+}$ ion (1.87 cm$^3$ mol$^{-1}$ K with $g = 2.0$). Upon cooling, the $\chi_M T$ first decreases smoothly, reaching a minimum value of 2.03 cm$^3$ mol$^{-1}$ K at 25 K, then rises rapidly, reaching a sharp maximum value of 5.14 cm$^3$ mol$^{-1}$ K at 18.5 K and finally drops again to 0.08 cm$^3$ mol$^{-1}$ K at 2.0 K. The data above 50 K obeys the Curie-Weiss law with a Curie constant $C = 3.01$ cm$^3$ mol$^{-1}$ K and a Weiss constant $\theta = -2.67$ K (Fig. S14). The continuous decrease in $\chi_M T$ from 300 K to 25 K can be attributed to both the spin-orbit coupling of the octahedral Co$^{2+}$ ions and the moderate antiferromagnetic coupling in 3·Co. The abrupt increase in $\chi_M T$ at temperatures below 25 K suggests spin-canted antiferromagnetism, while the final rapid drop in $\chi_M T$ at temperatures below 18.5 K may be due to interlayer antiferromagnetic ordering and/or saturation effects.

The ZFC/FC magnetizations of 3·Co performed at 100 Oe (Fig. S15) were non-bifurcated and show a sharp maximum at 18.4 K suggesting the occurrence of antiferromagnetic ordering with $T_N = 18.4$ K. The temperature dependence of the ac susceptibility of 3·Co was also measured at a zero dc field (Fig. S16), which shows a sharp frequency-independent of $\chi_M''$ signals with the absence of $\chi_M'$ signals, thus confirming the onset of antiferromagnetic ordering and implies the existence of a magnetic phase transition.

The field dependence of the magnetizations of 3·Co at 2.0 K (Fig. 10) shows a sigmoidal shape with an abrupt increase at a field above 2.8 kOe to reach a value of 0.42 $N\beta$ at 50 kOe. This
sigmoidal magnetization clearly indicates a field-induced magnetic transition of metamagnetism.\textsuperscript{21} In the metamagnetic transition, the net moments aligned antiparallel by weak antiferromagnetic interactions are overcome by an external field, resulting in the state going from AF to P. The critical field of transition, $H_C$, at 2.0 K was estimated to be about 3.6 kOe determined by $dM/dH$. The $M$ value of 0.42 $\mu_B$ at 50 kOe is far below the expected saturation value of 2–3 $\mu_B$ for an isotropic high-spin Co$^{2+}$ system, confirming the antiferromagnetic nature of 3-Co. In addition, a hysteresis loop is clearly obvious at 2.0 K, (Fig. 10, inset), indicating hard magnet behavior. The hysteresis loop shows a remnant magnetization of 0.24 $\mu_B$ at 2.0 K, the maximum of magnetic susceptibilities, investigated by the measurements of various fields of the FC magnetization curves measured under different external fields for compound 3-Co.

The magnetic phase transition for compound 3-Co was further investigated by the measurements of various fields of the FC magnetic susceptibilities, $\chi_M(T)$, and the field dependence of the magnetizations, $M(H)$, at different temperatures. As shown in Fig. 11, the maximum of $\chi_M(T)$ shifts to lower temperature with increasing applied field, until the $\chi_{M}(T)$ reaches a plateau at a field larger than 2000 Oe, indicating that the weak interlayer antiferromagnetic interaction is overcome by the external field. As shown in Fig. S17, at 2.0 K, the step-wise $M(H)$ curve clearly indicates field-induced magnetic transition from AF to P. This step-wise magnetization becomes less pronounced with increasing temperature, and the differentials of these curves show peaks that shift to lower fields with increasing temperature (Fig. S18) indicating the phase transitions of metamagnetism. Combining $M(H)$, FCM and the frequency-independent $\chi_{M}^{\prime}$ data, the magnetic phase ($T$, $H$) diagram was plotted in Fig. S19. The $H_C$ decreases with increasing temperature and finally disappears at about 18.4 K. The solid line of $H_{C}(T)$ in Fig. S19, on an analysis of the $M$–$H$ curves, signifies a typical magnetic transition from AF to P corresponding to metamagnetic materials.

Taking into account the structural features of compound 3-Co, although the adjacent spin Co$^{2+}$ ions are related to a crystallographic inversion center, all of the [Co$_2$(EO-N$_2$)$_3$] moieties are connected by 2$_1$ helices with opposite chirality. The different orientations of opposite chirality may induce the occurrence of antisymmetric exchange, thus resulting in spin canting. Moreover, the highly distorted octahedral Co$^{2+}$ site might exhibit considerable anisotropy, which also provides a contribution to the spin canting in 3-Co. Similar results have been observed in several compounds with same space group.\textsuperscript{26}

The structural and magnetic properties of compounds 1-Cu–3-Co are comparable to those of known compounds with similar structures and dimensionalities. For compound 1-Cu, the Cu$^{2+}$ ions are linked by single EO-N$_3$ to form a 1D chain and the overall AF exchange interactions are observed with no long-range ordering above 2.0 K, which is consist with the results for 1D Cu$^{2+}$ compound with single EO-N$_3$ bridging.\textsuperscript{27} The 2D layered structure of 2-Mn and 3-Co is similar to those of reported 2D compound composing a [M$_4$(EO-N$_3$)$_3$] building unit.\textsuperscript{23} Compound 2-Mn crystallizes in centrosymmetric space group Pnca, which forbid the occurrence of centrosymmetric space group due to the presence of inversion centers between the Mn$^{2+}$ sites. Thus, the spin canting in 2-Mn can be attracted by single-ion magnetic anisotropy. In contrast, although the adjacent spin Co$^{2+}$ ions in compound 3-Co are related to a crystallographic inversion center, all of the [Co$_2$(EO-N$_2$)$_3$] units are linked by 2$_1$ helices with opposite chirality. Thus, the spin canting 3-Co was attracted by both of antisymmetric interaction and single-ion magnetic anisotropy.

**Conclusions**

The introduction of a bifunctional ligand, Htzbp, in combination with tetrazolyl and 2,2'-bipyridyl groups, permitted three new azide-based coordination polymers to be synthesized. With tzbp ligands functioning as a chelating coordination polymer, compound 1-Cu adopts a single end-on N$_3$ (EO-N$_3$) bridged 1D zigzag structure, while 2-Mn and 3-Co adopts 2D layered structures comprised of double EO-N$_3$ bridged dinuclear motifs, [M$_2$(EO-N$_3$)$_3$], interlinked by chelating/bridging of tzbp ligands. Magnetic studies reveal the existence of intrachain antiferromagnetic interactions that are dominant in compound 1-Cu. Compounds 2-Mn and 3-Co exhibit spin-canted antiferromagnetism with $T_K$ = 3.0 and 18.4 K, respectively. In addition, below $T_K$, the field-induced magnetic transitions of spin-flop and metamagnetism for 2-Mn and 3-Co, respectively, were also observed. The studies show that the use of bifunctional tetrazolate/2,2'-bipyridine ligand is particularly promising for use in the construction of extended networks containing a highly distorted metal site that can give rise to versatile bulk magnetic behavior.

**Experimental Section**

**Synthesis**

All solvents and reagents where used as received, no purification was necessary. All reactions were performed under aerobic conditions. \textit{Caution!} Azido compounds are potentially explosive; such compounds should be synthesized and used in small quantities and treated with the utmost care at all times. The precursor of 6-caino-2,2'-bipyridine was prepared as previously reported.\textsuperscript{29} [Cu(N$_3$)$_2$(tzbp)$_n$] (1-Cu). A mixture of Cu(ClO$_4$)$_2$	extperiodcentered 6H$_2$O (23 mg, 0.062 mmol), 6,6'-dicaino-2,2'-bipyridine (bpCN, 23 mg, 0.125 mmol), Na$_3$N$_3$ (17 mg, 0.25 mmol), DMF (6ml) and H$_2$O (1 ml) was placed in a Teflon reactor (25 ml) and heated at 100 °C for two days. After the mixture was gradually cooled to room
temperature at a rate of 1 °C h⁻¹, dark-green crystals of 1·Cu
suitable for X-ray study were obtained. The solid product was
washed with water, isolated by suction filtration and dried in air.
Yield: 43% (based on bpCN). A powder X-ray diffraction pattern
of the bulk sample compared well with the pattern simulated from
the single-crystal data (vide infra). Anal. Calcld (found) for
C₁₀H₉CuN₆O: C, 40.45; H, 2.02; N, 38.27. Found: C, 40.14; H,
2.13; N, 38.32. IR data (KBr disk, cm⁻¹): 2072(s), 2051(vs), 1615
(m), 1602 (m), 1498 (m), 1458 (s), 1442 (s), 1378 (w),
1332 (w), 1257 (w), 1177 (m), 1147 (m), 1037 (w), 1012 (m), 827
(w), 799 (s), 787 (s), 762 (m), 730 (m), 696 (m), 662 (m), 603
(w).

[Mn₂(N₃)₂(tzbp)]_2 (2·Mn). A mixture of Mn(ClO₄)₂·6H₂O
(90.1 mg, 0.25 mmol), 6-cyano-2,2'-bipyridine (bpCN, 46 mg,
10.25 mmol), and NaN₃ (50 mg, 0.75 mmol) in H₂O (6 mL) was
placed in a Teflon reactor (25 mL). The mixture was heated
according to the following temperature program: increasing the
temperature to 160 °C at 18.3 °C/h, holding at 160 °C for 72 h,
and then cooling to 30 °C at a rate of 2.3 °C/h. The yellow block
of crystals of 2·Mn suitable for single-crystal X-ray diffraction
analysis were obtained. The crystals were rinsed a few times with
H₂O and dried in air. Yield: 47% (based on bpCN). A powder X-
ray diffraction pattern of the bulk sample compared well with the
pattern simulated from the single-crystal data (vide infra). Anal.
Calcld for C₁₀H₉Mn₂N₆O: C, 41.56; H, 2.41; N, 38.98. Found: C,
41.26; H, 2.19; N, 39.39. IR data (KBr disk, cm⁻¹): 2055 (vs),
1610 (s), 1594 (s), 1574 (s), 1479 (w), 1433 (s), 1373 (m), 1323
(s), 1276 (w), 1016 (w), 1005 (w), 1153 (m), 790 (s), 759 (s), 741
(s), 691 (s), 651 (m), 607 (w).

[Co₂(N₃)₂(tzbp)]_2 (3·Co). A solution of Co(ClO₄)₂·6H₂O (91.1
mg, 0.25 mmol), 6-cyano-2,2'-bipyridine (bpCN, 45 mg, 0.25
mmol), and NaN₃ (50 mg, 0.75 mmol) in H₂O (6 mL) was placed
in a Teflon reactor (25 mL). The mixture was heated according to
the following temperature program: increasing the temperature to
140 °C at 18.3 °C/h, holding at 140 °C for 72 h, and then cooling
to 30 °C at a rate of 2.3 °C/h. The orange block crystals suitable
for single-crystal X-ray diffraction analysis were obtained. The
crystals were rinsed a few times with H₂O and dried in air. Yield:
52% (based on bpCN). A powder X-ray diffraction pattern of the
bulk sample compared well with the pattern simulated from the
single-crystal data (vide infra). Anal. Calcld for C₁₀H₉Co₂N₆O:
C, 40.72; H, 2.16; N, 38.87. Found: C, 41.17; H, 2.55; N, 38.95. IR
data (KBr disk, cm⁻¹): 2066 (vs), 1600 (s), 1574 (m), 1532 (s), 1515 (w),
1482 (w), 1467 (s), 1463 (m), 1440 (s), 1402 (w), 1369 (w), 1178 (m),
1153 (m), 1023 (w), 1009 (w), 829 (w), 785 (s), 762 (s), 737 (s), 690 (s),
655 (m), 634 (m), 602 (w).

Crystallographic Measurements

The single crystals of compounds 1·Cu, 2·Mn and 3·Co
were mounted on the tip of a glass fiber with dimensions of 0.19 × 0.14
× 0.05 mm, 0.26 × 0.20 × 0.11 mm, and 0.19 × 0.18 × 0.15 mm,
respectively. Intensity data were collected at 150 (2) K within the
limits of 2.43° < θ < 30.01° for 1·Cu, 2.75° < θ < 30.48° for
2·Mn, and 2.62° < θ < 28.28° for 3·Co using a Brucker-Nomius
APEXII CCD diffractometers with graphite-monochromated Mo
Kα radiation (λ = 0.7107 Å). The structures were solved by
conventional methods and refined by full-matrix least-squares on
all F2 data using SHELX2014 in conjunction with the Olex2
graphical user interface. All non-hydrogen atoms were refined
anisotropically, whereas the hydrogen atoms were placed in ideal,
calculated positions, with isotropic thermal parameters riding on
their respective carbon atoms. Experimental details for X-ray data
collection and the refinements of compounds 1·Cu, 2·Mn and
3·Co are presented in Table 1.

Magnetic measurement

Variable temperature dc magnetic susceptibility measurements
and ac magnetic susceptibility measurements were collected on
microcrystalline samples, restrained in eicosane to prevent
toriing, on a Quantum Design MPMS-7 SQUID and a PPMS
magnetometer equipped with 7.0 T and 9.0 T magnets,
respectively, operated in the range of 2.0–300.0 K. Diamagnetic
corrections were estimated from Pascal’s constants³⁶ and
subtracted from the experimental susceptibility data to obtain the
molar paramagnetic susceptibility of the compounds.

Other Studies

Infrared spectra were recorded for the solid state (KBr pellets) on
a Nicolet Magna 550 FTIR spectrometer in the range of 4000-400
cm⁻¹. Elemental analyses were carried out using an Elementar
Vario EL III analyzer. Thermogravimetric analysis was
performed on a Seiko Instrumental, Inc., EXSTAR6000 TG/DTA
detector with a heating rate of 5 °C/min under a nitrogen
atmosphere. Powder diffraction data were recorded on a
SHIMADZU XRD-6000 X-ray diffractometer at 30 kV and 30
mA with Cu-Kα radiation (α = 1.5406 Å), with a step size of 0.028
in θ and a scan speed of 1 s per step.

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University.

Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed
experimental procedures, TGA plots, PXRD patterns, additional
crystallographic diagrams and other magnetic diagram.
CCDC 1439545-1439547. For ESI and crystallographic data in
ccif or other electronic format. See DOI: 10.1039/b000000x/

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Table 1. Crystallographic Data for 1·Cu, 2·Mn and 3·Co

<table>
<thead>
<tr>
<th></th>
<th>1·Cu</th>
<th>2·Mn</th>
<th>3·Co</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C_{11}H_{7}CuN_{9}</td>
<td>C_{11}H_{7}MnN_{9}</td>
<td>C_{11}H_{7}CoN_{9}</td>
</tr>
<tr>
<td>fw</td>
<td>328.81</td>
<td>320.20</td>
<td>973.62</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
<td>Pbca</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>a / Å</td>
<td>6.7773(5)</td>
<td>8.9867(7)</td>
<td>10.7778(8)</td>
</tr>
<tr>
<td>b / Å</td>
<td>20.7006(16)</td>
<td>14.7912(11)</td>
<td>12.1999(9)</td>
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<tr>
<td>c / Å</td>
<td>8.3965(7)</td>
<td>17.9613(13)</td>
<td>9.5936(7)</td>
</tr>
<tr>
<td>α / °</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β / °</td>
<td>91.2110(10)</td>
<td>90</td>
<td>106.3912(16)</td>
</tr>
<tr>
<td>γ / °</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V / Å³</td>
<td>1177.72(16)</td>
<td>2387.5(3)</td>
<td>1181.84(15)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>T / K</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>D, / g cm⁻³</td>
<td>1.854</td>
<td>1.782</td>
<td>1.822</td>
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<td>µ / mm⁻¹</td>
<td>1.864</td>
<td>1.115</td>
<td>1.461</td>
</tr>
<tr>
<td>(Δρ)max, min / e Å⁻³</td>
<td>0.750, -0.859</td>
<td>0.420, -0.331</td>
<td>0.425, -0.330</td>
</tr>
<tr>
<td>Measured/independent (Rint) reflections</td>
<td>7088/2155(0.0163)</td>
<td>16277/2741(0.0200)</td>
<td>9074/2945(0.0179)</td>
</tr>
<tr>
<td>Observed reflections [I &gt; 2σ(I)]</td>
<td>1997</td>
<td>2616</td>
<td>2670</td>
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<tr>
<td>Goodness-of-fits on F²</td>
<td>1.109</td>
<td>1.251</td>
<td>1.055</td>
</tr>
<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)]</td>
<td>0.0406, 0.1213</td>
<td>0.0370, 0.0845</td>
<td>0.0238, 0.0596</td>
</tr>
</tbody>
</table>

*R₁ = (∑|F₀| - |Fₐ|) / ∑|F₀|, wR₂ = [∑w( (F₀² - Fₐ²)² )]¹/² * [∑w(F₀²)]"
Three new azide-bridged coordination polymers, \([\text{M} \text{N}_3 \text{tzbp}]_n\) (\(\text{M} = \text{Cu}, \text{1-Cu}; \text{Mn}, \text{2-Mn}; \text{Co}, \text{3-Co}\)), were successfully prepared by introducing a bifunctional tetrazolate/2,2′-bipyridine ligand, \(6^{+}(1\text{H-tetrazol}-5\text{-yl})\)-2,2′-bipyridine (Hztbp), from the \textit{in situ} \([2+3]\) cycloaddition of 6-cyano-2,2′-bipyridine in the presence of an excess of sodium azide under hydrothermal conditions.