Syntheses, structures, and magnetic properties of three new chain compounds based on a pentagonal bipyramidal Co(II) building block†

Dong Shao, Le Shi, Shao-Liang Zhang, Xin-Hua Zhao, Dong-Qing Wu, Xiao-Qin Wei and Xin-Yi Wang*

Starting from the pentagonal bipyramidal single-ion magnet \([\text{Co} \text{tdmmb}] \text{[H}_2\text{O}]_2 \text{[BF}_4]_2\) and a series of linear bridging ligands of different lengths, three new cobalt(iii) one-dimensional (1D) coordination polymers, \([\text{Co} \text{tdmmb} \text{pyz}] \text{[BF}_4]_2 \text{CH}_3\text{CN-H}_2\text{O} \ (\text{1}), \ [\text{Co} \text{tdmmb} \text{apy}] \text{[BF}_4]_2 \text{2CH}_3\text{CN} \ (\text{2}), \ and \ [\text{Co} \text{tdmmb} \text{bpe}] \text{[BF}_4]_2 -3\text{CH}_3\text{CN} \ (\text{3}) \ (\text{tdmmb} = 1,3,10,12\text{-tetramethyl-1,2,11,12-tetra}-\text{aza}[3][2,6] \text{pyridino}[3][2,9] \text{110-phenanthrolinophan-2,10-diene)} \ (\text{pyz} = \text{pyrazine}) \ (\text{apy} = 4\text{-aminopyridine}) \ (\text{bpe} = 1,2\text{-di(4-pyridyl)ethane}), \ have been synthesized and characterized structurally and magnetically. Symmetric ligands \text{pyz} and \text{bpe} result in the nearly linear chains in \text{1} and \text{3}, while the asymmetric ligand \text{apy} leads to the zig-zag chain in \text{2}. As the length of the ligands increases, the intrachain Co⋯Co distance also increases, i.e. 7.56, 7.70, and 13.85 Å for \text{1}–\text{3}, respectively. Magnetic investigation revealed the gradual decrease in the magnetic interactions between the Co\(^{2+}\) ions from \text{1} to \text{3}, along with the increase in the intrachain Co⋯Co distances. Due to the existence of the weak antiferromagnetic (AF) interaction, the SIM behavior of the starting material is presupposed in compounds \text{1} and \text{2}, and they show a simple paramagnetic behavior. While for \text{3}, field-induced slow magnetic relaxation was observed at a low temperature with an energy barrier of \(U_{\text{eff}} = 19\) K. This observation suggests that the magnetic interaction between the Co\(^{2+}\) centers in \text{3} is negligible, consistent with the very long Co⋯Co distance in \text{3}. These 1D compounds are rare chain compounds composed of metal centers with a nearly \(D_{3h}\) symmetry. Notably, compound \text{3} is the second example of a 1D Co(iii) chain compound displaying a SIM behavior. These studies illustrated that the magnetic interaction between the SIMs can be used to tune slow magnetic relaxation.

Introduction

Slow magnetic relaxation in molecule nanomagnets, including single-ion magnets (SIMs), single-molecule magnets (SMMs) and single-chain magnets (SCMs), has been extensively studied in the emerging field of molecular magnetism.\(^{1-4}\) For possible applications at a practical temperature, a high magnetization reversal barrier \((U)\) is required, which is mainly governed by the magnetic anisotropy of the system. In this sense, magnetic anisotropy is of ultimate importance to the performance of the molecule nanomagnets.\(^5\) However, numerous studies have also shown that magnetic anisotropy is not the only factor determining the slow relaxation of the magnetization, especially for the 3d and 4f SIMs.\(^6-9\) For example, although some mononuclear Ni\(^{II}\) or Co\(^{III}\) complexes have very large \(D\) values, either easy-axis with a \(D \approx -200\) cm\(^{-1}\) or easy-plane with a \(D > 70\) cm\(^{-1}\), the slow magnetic relaxation is either with a very small effective energy barrier \((U_{\text{eff}} < 10\) cm\(^{-1}\))\(^6\) or one that is not observed at all.\(^7\) As for the lanthanide-SIMs, although the highest energy barrier is reported over 1000 cm\(^{-1}\),\(^8\) the highest temperature for the observation of the hysteresis loop is still lower than 20 K.\(^3\) Moreover, it has been observed frequently that in a series of compounds of similar structures, the order of effective energy barriers is sometimes independent of the order of the \(D\) parameters.\(^9\) Thus, understanding the factors that influence both the \(U_{\text{eff}}\) and the slow magnetic relaxation is of great importance for the development of better performing molecule nanomagnets.

Among many factors that influence the slow magnetic relaxation process, the magnetic interaction is of great importance. For the multinuclear SMMs, strong intra-cluster interactions could lead to a more isolated ground state, while the inter-cluster interactions might lead to long-range magnetic
ordering other than SMM behaviour. As a matter of fact, the role of the magnetic interaction on the SMM behavior has been perfectly demonstrated in the radical bridged lanthanide SMMs \([[(M\text{e}_{2}S_{5})_{2}N]_{3}(\text{THF})L]_{\text{2}}[\mu^{-}\eta^{-}\eta^{-2}N_{2}]\] \((Ln = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er})\). Although the energy barrier is only 227.0(4) cm\(^{-1}\) for the \(\text{Tb}^{3+}\) compound, the strong magnetic interaction transmitted by the \(N_{2}\) radical leads to the observation of the hysteresis loop up to 14 K. In addition, magnetic interaction can directly increase the energy barriers of the SMMs and SCMs. For example, the anisotropic magnetic exchange can result in strong magnetic anisotropy and SMMs with high energy barriers, as demonstrated both by theoretical calculations and the experimental results reported by us. On the other hand, because the magnetic interaction in SCMs is responsible for the additional energy component known as the correlation energy, SCMs might display relaxation barriers higher than those of their counterpart SMMs.

For the SMMs, the magnetic interaction is usually believed to reduce the \(U_{\text{eff}}\) as it is responsible for the enhancement of the quantum tunnelling of magnetization (QTM) effects. Diamagnetic dilution is commonly used to suppress the dipole–dipole interaction between the mononuclear centres and better SMMs can thus be prepared. However, careful tuning of the magnetic interactions between the SMMs is scarcely reported. For this purpose, using counter ions of different sizes and organic bridging ligands of different lengths are two reasonable approaches.

For the magnetic anisotropic spin centers, the pentagonal bipyramidal metal centres, including both the transition metal centers and lanthanides, are of great value. Very recently, a field-induced SIM behaviour was observed in a series of mononuclear Co\(^{III}\) compounds of a pentagonal bipyramid geometry by our group for the first time. These compounds are constructed from pentadentate macrocyclic ligands \((L_{N_{2}O_{2}}\) and \(L_{N_{2}}\), Fig. 1) and the Co\(^{III}\) centers are of easy-plane magnetic anisotropy. As the axial ligands of these seven coordinated compounds are usually labile, these compounds are ideal starting materials for the construction of higher dimensional magnetic materials. In this work, the rigid ligand \(\text{tdmmb}\) \((\text{tdmmb} = 1,3,10,12-\text{tetramethyl}-1,2,11,12-\text{tetracyclo[2.2.2]octa[2]aza[3][2,6]pyridino[3][2,9]-1,10-pheanthrolinephane-2,10-dien})\) was used as it can maintain the same equatorial geometry of the Co\(^{III}\) centers. Easy-plane magnetic anisotropy was confirmed in a series of Co\(^{III}\) compounds where the axial donor atoms are C, N, O and S atoms. Herein, from the starting material \([\text{Co(tdmb)}(\text{H}_{2}O)_{2}]^{2+}\) and a series of organic ligands of different lengths, a family of 1D coordination polymers, \([\text{Co(tdmb)}(L)][\text{BF}_{4}]\cdot\text{Solv} (L = \text{pyz} (1), \text{apy} (2), \text{and bpe} (3), \text{pyz} = \text{pyrazine}, \text{apy} = 4\text{-aminopyridine}, \text{and bpe} = 1,2\text{-di(4-pyridyl)ethane, Fig. 1})\) were successfully constructed. Magnetic investigations showed that compounds 1 and 2 were typical paramagnetic complexes while 3 exhibited a field-induced slow magnetic relaxation behaviour. We attributed the difference in their magnetic properties to the different intrachain magnetic interactions transmitted by different bridges: weak antiferromagnetic (AF) magnetic coupling in 1 and 2 while a negligible one in 3. In addition, to the best of our knowledge, compound 3 is the second reported example of a 1D Co\((n)\) chain compound that displays a SIM behaviour.

**Experimental section**

**Physical measurements**

Infrared spectra (IR) data were measured on KBr pellets using a Nexus 870 FT-IR spectrometer in the 4000–400 cm\(^{-1}\) range. Elemental analyses of C, H, and N were performed at an Elementar Vario MICRO analyzer. Powder X-ray diffraction data (PXRD) were recorded at 298 K on a Bruker D8 Advance diffractometer with a Cu Ka X-ray source (\(\lambda = 1.5405\) Å) operated at 40 kV and 40 mA. Magnetic susceptibility data were collected using a Quantum Design SQUID VSM magnetometer on samples of crushed crystals. Direct current (dc) magnetic susceptibility measurements were performed in the temperature range of 2–300 K under an applied field of 1000 Oe. Alternative current (ac) susceptibility measurements were performed with a 2 Oe ac oscillating field in an operating frequency range of 1–1000 Hz under a dc field of 0 or 1000 Oe. Magnetization data were collected in the 0 to 70 kOe field range at 2.0 K. Experimental susceptibilities were corrected for the diamagnetism of the sample holders and that of the compounds according to Pascal’s constants.

**Materials and synthesis**

All reagents were commercially available and used as received. The starting material \([\text{Co(tdmb)}(\text{H}_{2}O)_{2}]^{2+}\) was synthesized according to a literature procedure. The purity of the samples were confirmed by the PXRD spectra (Fig. S1, ESIF) and the elemental analysis.
[Co(tdmmb)(pyz)][BF₄]₂·CH₃CN·H₂O (1). The compound [Co(tdmmb)(H₂O)]₂[BF₄]₂ (100 mg, 0.15 mmol) was dissolved in 50 mL of boiling methanol. A ten-fold excess of pyz (120 mg, 1.5 mmol) was then added and the solution was refluxed for half an hour. Addition of a concentrated methanol solution of NaBF₄ to the hot solution gave an orange precipitate of the product, which was collected and washed with diethyl ether. Single crystals of 1 were prepared as follows. 20 mg of 1 was dissolved in 3 mL of acetonitrile and was added to a test tube. Diethyl ether was allowed to diffuse into the acetonitrile solution. Orange needle-like single crystals formed in 2 days. The crystals were filtered. Yield: ~15 mg. Elemental analysis (%) for C₂₉H₂₉B₂CoF₈N₁₀O: C, 45.40; H, 3.94; N, 18.38.

X-ray crystallography

Single-crystal X-ray diffraction analyses of 1–3 were collected on a Bruker APEX II or APEX Duo diffractometer with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å). The APEX program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT. Absorption corrections were applied with SADABS. The structures were solved by the direct method and refined by the full-matrix least-squares method on F² using the SHELXTL crystallographic software package. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms.

Results and discussion

Crystal structure descriptions

Single-crystal X-ray diffraction analyses of 1–3 revealed that 1 and 3 crystallize in the triclinic P1 space group and 2 in the orthorhombic Pnma space group (Table 1). All compounds

Table 1 Crystallographic data and structure refinement parameters for complexes 1–3

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<td>0.833→0.667</td>
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a R₁ = \sum||F₀|| - |F₁||/|\sum|F₀|. b wR₂ = \{\sum[w(F₀² - F₂)]²/\sum[w(F₀²)]²\}¹/².
1–3 have regular chain structures and their structures are depicted in Fig. 2 and 3. Although the asymmetric units of 1–3 are different from each other and contain different numbers of unique cobalt centers, namely, one, one-half, and two unique cobalt centers in 1–3 (Fig. S2, ESI†), respectively, all three compounds contain 1D regular chains where the cobalt centers are bridged by the organic ligands. In the asymmetric unit of 1, there are two half pyz ligands each lying about independent inversion centres (Fig. S2, ESI†). As for compound 2, half of the tdmmb ligand and half of the apy ligand are present in the asymmetric unit with a mirror plane passing through the whole molecule (Fig. S2, ESI†). As depicted in Fig. 2 as an example, all the cobalt ions in the three compounds are in a N\textsubscript{7} coordination environment with a slightly distorted pentagonal bipyramid geometry. The equatorial positions were occupied by five nitrogen atoms from the macrocyclic pentadentate ligand tdmmb, and the axial positions were occupied by two nitrogen atoms from the bridging ligands. The average Co–N\textsubscript{eq} lengths of 2.17(2), 2.17(1), and 2.16(6) Å in 1–3 are almost in accordance with the distance of 2.16(2) in the staring material.\textsuperscript{15c} However, the average Co–N\textsubscript{axial} bond lengths of 1–3 (2.23(9), 2.27(4), and 2.22(1) Å in 1–3, respectively) are slightly larger as compared to the axial Co–O bond length in [Co(tdmmb)(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+} (2.172 (2) Å). The N\textsubscript{axial}–Co–N\textsubscript{axial} are nearly linear with bond angles of 174.6°, 178.6°, and 176.6° for 1–3, respectively. The rigid planar structure of the tdmmb ligand results in the very similar local structures of the cobalt centers. Actually, the degree of deviation from the standard pentagonal bipyramid can be estimated from the continuous shape measures (CShMs) calculated by SHAPE 2.0.\textsuperscript{19} The CShMs of the cobalt centers were calculated to be 0.101, 0.109, and 0.167 for 1–3, which are close to zero in the ideal \(D\textsubscript{sh}\) symmetry.

Interestingly, the one-dimensional structures in compounds 1 and 3 are nearly linear chains, while the chain in compound 2 is a zig-zag chain (Fig. 3). This difference might be related to the nature of the bridging ligands. In compounds 1 and 3, ligands pyz and bpe are both symmetric bidentate linear ligands with two identical nitrogen atoms, while the apy ligand in 2 contains two different nitrogen donor atoms. Apparently, the –NH\textsubscript{2} group in the apy ligand results in the remarkably bended Co–N–C\textsubscript{pyridine} links and thus the zig-zag chain structure of 2. Due to the different lengths of the bridging ligands, the shortest intrachain Co–Co distances increase from 7.34 and 7.70 Å for 1 and 2, to 13.86 Å for 3. In the packing diagrams (Fig. S3, ESI†), those 1D chains were isolated from each other by very week hydrogen bonds and/or molecular interactions, leading to the shortest interchain Co–Co distances being 9.74(3), 12.33(4), and 10.07(9) Å for 1–3, respectively. This leads to the negligible interchain magnetic interactions.

![Fig. 2](image2.png)

**Fig. 2** A view of a fragment of the crystal structure of 1. Hydrogen atoms are omitted for clarity. Symmetry codes: #1: 2 – x, 1 – y, 1 – z; #2: 2 – x, 1 – y, –z.

**Fig. 3** The 1D chain structures of complexes 1–3. Hydrogen atoms are omitted for clarity.

Magnetic properties

Temperature-dependent magnetic susceptibilities data of 1–3 in the temperature range of 2–300 K were measured under a dc field of 1 kOe and are depicted in Fig. 4 and 5. The \(\chi_M T\) values at 300 K for 1–3 were 2.62, 3.09, and 2.60 cm\(^3\) mol\(^{-1}\) K, respectively. Those values are significantly larger than the spin-only value of 1.875 cm\(^3\) mol\(^{-1}\) K for a high-spin Co\textsuperscript{II} ion (\(S = 3/2, g = 2\)), indicating the large magnetic anisotropy of Co\textsuperscript{II} in a nearly \(D\textsubscript{sh}\) ligand field.\textsuperscript{2c} Upon cooling, the \(\chi_M T\) values of 1 and 3 decrease monotonously down to a minimum of 0.70 and 1.43 cm\(^3\) mol\(^{-1}\) K. While for 2, the \(\chi_M T\) decreases to a minimum of 2.22 cm\(^3\) mol\(^{-1}\) K at 9 K, and...
increases again up to 3.08 cm$^3$ mol$^{-1}$ K at 2 K. The decrease in the $\chi_M T$ values for all compounds is very possibly due to the intrinsic magnetic anisotropy of the Co$^{II}$ ions and/or intrachain antiferromagnetic interactions. While for compound 2, the increase in the $\chi_M T$ value indicates the presence of the canting of the antiparallel spins.

Because the intrachain Co–Co distances for compounds 1 and 2 are not very long and it was widely reported that the pyrazine ligand can transmit weak magnetic interactions, their susceptibility data at a high temperature can be roughly modeled by the Fisher’s chain model$^{20}$ ($S = 3/2$) with the following Hamiltonian and expressions:

\[
H = -J \sum_{i=1}^{n} S_i S_{i+1}
\]

\[
\chi_{\text{chain}} T = \frac{N g^2 g B^2 S (S+1) + u}{3k} \left[ 1 - \frac{u}{k T} \coth \left( \frac{JS(S+1)}{kT} \right) \right] \frac{k T}{JS(S+1)}
\]

where $J$ represents the intrachain Co–Co interaction and the other symbols have the usual meanings. The best fit of the data in the temperature of 18 to 300 K gives $J = -1.23(7)$ cm$^{-1}$, $g = 2.11(6)$ and $J = -1.16(1)$ cm$^{-1}$, $g = 2.15(2)$ for 1 and 2, respectively ($R = \sum [(\chi T)_{\text{obsd}} - (\chi T)_{\text{calcd}}]^2/(\chi T)_{\text{obsd}}] = 1.0 \times 10^{-3}$). The two small negative $J$ values suggest the weak AF exchange interaction between the Co$^{II}$ centres through the pyz ligand in 1 and the apy ligand in 2. We can see that the $|J|$ value for 1 is slightly larger than that for 2, which should be due to the fact that pyz is more conjugated than apy and can transmit stronger magnetic coupling. Of course, we have to note that the magnetic fitting of the 1D Co$^{II}$ compound is not an easy job and the current analysis can only be treated as a rough estimation.

Due to the easy plane magnetic anisotropy of the cobalt centers in the pentagonal bipyramid geometry and the existence of magnetic coupling, ac susceptibility measurements were further performed to check the dynamic magnetic behavior of 1 and 2 at low temperatures. No slow magnetic relaxation was observed and both compounds exhibited a normal paramagnetic behavior without any out-of-phase ac signals under zero or 1000 Oe dc field (Fig. S4, ESI†). The lack of the field-induced slow magnetic relaxation in 1 and 2 should originate from the AF Co–Co interactions, which might modify the ground state and the relaxation pathways of the spin system.

The field dependence of magnetization of compounds 1 and 2 were measured at 2 K with a magnetic field up to 70 kOe (Fig. S5, ESI†). These curves show a typical paramagnetic behavior with the magnetization values at 70 kOe being 2.08 and 2.40 $\mu_B$ for 1 and 2, respectively. The lack of saturation for the compounds suggests the presence of appreciable magnetic anisotropy in these compounds.

As for compound 3, with the longest Co–Co distance of 13.86 Å, the intrachain Co–Co interaction can be safely neglected. This is also further suggested by the observation of the field-induced SIM behavior of 3 (vide post). The magnetic susceptibility data over the whole temperature range and also the magnetization data at 2 K were simultaneously...
fitted using the PHI program with the following spin Hamiltonian:

$$H = D(S_x^2 - S_y^2) + E(S_x^2 - S_y^2) + \mu_B g \cdot S \cdot B$$

(2)

where the $D$, $E$, $S$, $g$, $B$ represent the axial and rhombic ZFS parameters, the spin operator, and magnetic field vectors, respectively, and the $\mu_B$ is the Bohr magneton. The best fit values are $D = 21.7(7)$ cm$^{-1}$, $E = -0.4(3)$ cm$^{-1}$, $g = 2.121(1)$. The positive $D$ value confirmed the easy-plane magnetic anisotropy for a Co$^{II}$ center in the pentagonal bipyramid geometry.\(^2\)

To further probe the magnetic anisotropy of the ground state, reduced magnetization of $3$ was also measured (Fig. 6). Significant separation between the isofield curves was observed, implying the presence of large magnetic anisotropy. Best fit of the data through Anisofit 2.0 (ref. 23) yields $D = 23.6$ cm$^{-1}$, $E = -0.1$ cm$^{-1}$, and $g = 2.230$, which agree well with the previous results and the reported values for other well-isolated pentagonal bipyramidal Co$^{II}$ complexes.

To investigate the magnetic dynamics of $3$, ac magnetic susceptibility data were measured under a 0 or 1 kOe dc field (Fig. 7 and S6, ESI†). No out-of-phase signal was observed under a zero dc field, suggesting a fast quantum tunnelling of magnetization. However, upon application of a 1 kOe dc field, obvious temperature- and frequency-dependent ac signals were observed (Fig. 7a and S7, ESI†), indicating the field-induced SIM behaviour of $3$. Semicircle Cole–Cole plots below 4.3 K (Fig. 7b) were constructed and the values and distribution of the relaxation time $\tau$ was extracted by fitting of the Cole–Cole plots by the generalized Debye model.\(^2\) The resulting $\alpha$ values vary in the range of 0.12–0.15 (Table S2, ESI†), suggesting the narrow distribution of the relaxation time.\(^2\) Fitting of the relaxation time at a high temperature according to $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ gives the effective energy barrier $U_{\text{eff}} = 19.0$ K with a pre-exponential factor of $\tau_0 = 7.5 \times 10^{-6}$ s (Fig. 7c, Table S2, ESI†).

Due to their potential applications of the molecular nanomagnets, numerous efforts to rationally manipulate their slow magnetic relaxation have intensified during the last few years. For the SIMs, one of the important strategies is to...
reduce the QTM as it is well-known to reduce the energy barrier and significantly lower the efficient energy barrier of the relaxation. Generally, a weak magnetic interaction between the mononuclear spin centers is known to lead to considerable QTM effects and is usually undesirable for the construction of better SIMs or SMMs. On the other hand, with a strong magnetic interaction, SCMs can be constructed by connecting the SIMs or SMMs by suitable bridging ligands. For example, by connecting the Fe$^{3+}$-based pentagonal bipyramidal starting materials of easy-axial magnetic anisotropy, a series of cyano-bridged SCMs were constructed in our group.\textsuperscript{26} For the current three 3d compounds, 1–3, we can see the effect of the magnetic interaction on the magnetic dynamics. The spin centers are very similar with a nearly identical $\text{N}_5$ coordination environment. Thus, the difference of the magnetic properties of 1–3 can be safely attributed to the magnetic coupling between the spin centers. The weak magnetic interaction in compounds 1 and 2 suppresses the slow magnetic relaxation, while compound 3 remains a field-induced SIM due to the negligible magnetic coupling.

Conclusions

In summary, we reported the syntheses, crystal structures, and magnetic behavior of three homospin compounds of chain structures, where the pentagonal bipyramidal Co$^{II}$ units are bridged by organic ligands of different lengths. Due to the nature of the ligands, nearly linear chain structures were found for compounds of symmetric ligands, while a zigzag chain was observed for the complex formed by an asymmetric bridging ligand. Magnetic studies suggest the presence of a weak antiferromagnetic interaction in compounds 1 and 2, which can be neglected in compound 3. A field-induced SIM behavior was observed only in compound 3, while the slow magnetic relaxation was efficiently suppressed by the magnetic interactions, albeit their weakness, in 1 and 2. These 1D chain compounds demonstrate the importance of the magnetic interaction to the slow magnetic relaxation. Furthermore, our work illustrates that the starting materials of a pentagonal bipyramidal geometry constructed by macrocyclic pentadentate ligands are of great value for the preparation of higher dimensional coordination polymers with large magnetic anisotropy. Efforts along this way are now in progress in our lab.

Acknowledgements

We thank the Major State Basic Research Development Program (2013CB922102), NSFC (21522103, and 21471077) and NSF of Jiangsu province (BK20150017). This work was also supported by a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and the Fundamental Research Funds for the Central Universities (020514380006).

Notes and references


