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Single-Ion-Magnet Behavior in a Two-Dimensional Coordination Polymer Constructed from Co^{II} Nodes and a Pyridylhydrazone Derivative

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S *Supporting Information*

ABSTRACT: A novel two-dimensional (2D) coordination polymer, $[Co(ppad)_2]_n$ (**1**), resulted from the assembly of Co^{II} ions based on a versatile ligand termed N^3-(3-pyridoyl)-3-pyridinecarboxamidrazone. Alternating/direct-current magnetic studies of compound **1** indicate that the spatially separated high-spin Co^{II} ions act as single-ion magnets (SIMs). The present work represents the first case of a 2D Co^{II}-based SIM composed of a monocomponent organic spacer.

The construction of coordination polymers (CPs) is a hot topic in crystal engineering,[1] and CPs have attracted significant attention because of their intriguing architectures and topologies.[2,3] In particular, the main interest in such CPs arises from their exciting physical and chemical properties, which can ultimately lead to applications. During the last 2 decades, we have been witnessing rapid development in the field of single-molecule magnets (SMMs).[4] SMMs demonstrate slow relaxation of magnetic moments after removal of an external magnetic field as well as allow observations of quantum tunneling of magnetization (QTM) and quantum-phase interference effects and thus have been suggested for applications in high-density information storage and quantum spintronics.[4] Therefore, CPs with slow magnetic relaxation have attracted more attention, such as single-chain-magnet (SCM)- and SMM-based CPs.[5] Apart from their structural role in sustaining solid-state architectures, the metal ions in CPs are the source of most of the useful physical properties including magnetism. The early reported examples of SMMs were multinuclear aggregates of high-spin 3d metal ions, whereas later multidimensional networks of SMMs were also developed.[6] Recently, there is particular interest in molecular systems with only one spin carrier, large magnetic anisotropy, no intermetallic interactions, and properties consistent with SMMs termed single-ion magnets (SIMs). Most of the reported SIMs contain late lanthanide ions ($4f^n$, where $n > 7$),[7] and only a few examples of SIMs containing first-row transition metals are known, i.e., cobalt(II),[8] manganese(III),[9] nickel(I),[10] iron(I),[11] iron(II),[12] and iron(III)[13] complexes. As is well-known, the slow relaxation of magnetization and high magnetic anisotropy derived from single Co^{II} ions rarely appeared in the compounds reported previously;[14−16] most of the known cases are mononuclear zero-dimensional species, much less the Co^{II}-containing CPs with sequential a two-dimensional (2D) layer or a three-dimensional framework obtained in a controlled and deliberate manner. In 2014, Andruh and co-workers first reported two 2D CPs that are assembled from Co^{II} ions using linear and angular ligands simultaneously; the well-separated Co^{II} ions behave as SIMs.[17] Coincidentally, Machura et al. used dicyanamide and 2-amino-1,3,5-triazine as a coupler and an end-capped ligand, respectively, leading to a 2D Co^{II} CP in which the independently six-coordinated Co^{II} ions feature SIM behavior.[18] Obviously, the splendid examples mentioned above were self-assembled by using the strategy of mixed ligands in order to separate the metal ions spatially but at the same time form the extended structure satisfactorily, whereas the desirable case is not subject to immediate achievement when only one kind of ligand is introduced into the system.

As the representative of multidentate connectors, acylhydrazone ligands, a class of special Schiff bases, provide variously positioned binding sites and are identified as preeminent chelators to yield monometallic compounds with ordinary low-dimensional structures in the field of magnetic materials because of the inherent advantages for secluding the spin centers and further precluding the superexchange magnetic coupling.[19] On the other hand, the neutral bis(pyridine) derivatives are the most commonly used bridges for binding discrete metal−organic units as CPs with multidimensional networks.[20] Thus, we turned our attention to integrating these two types of ligands as site-directing bonders with the aim of organizing the system in which the coexistence of outspread architecture and sufficiently isolated magnetic metal ions will probably be observed. On the basis of the above considerations, an ingenious ligand (Scheme S1), N^3-(3-pyridoyl)-3-pyridinecarboxamidrazone (ppad), was synthesized through a combination of 3-cyanopyridine and 3-pyridylcarbonyl hydrazide (Supporting Information). Then, the resulting 2D CP of the formula $[Co(ppad)_2]_n$ (**1**) with concise structural characteristics was prepared and investigated by spectroscopic techniques, X-ray diffraction (XRD), and magnetic measurements. Compound **1** was obtained by the following general procedure: reaction of a solution containing

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cobalt(II) acetate and the ppad ligand under hydrothermal conditions (Supporting Information). Details of the crystallographic investigation are given in Table S1.

X-ray structural analysis reveals that compound **1** crystallizes in the orthorhombic space group *Pbca*. The asymmetric unit is crystallographically independent with half a Co^{II} ion and one ligand. Each Co^{II} ion acting as a node is six-coordinated with two N atoms from two pyridyl fragments arising from two ligands [Co1−N1b = 2.259(18) Å] and two N atoms and two O atoms from two other different ligands [Co1−N3 = 2.163(18) Å and Co1−O1 = 2.000(15) Å], building a deformed octahedral environment (Figure 1a). The adjacent Co^{II} centers are connected with each other by the ligands in two different directions, leading to a 2D layer parallel to the crystallographic *ab* plane (Figure 1b). All ligands adopt a unique coordination mode in which N3 and O1 atoms take a bidentate chelating mode and one pyridine N1 atom uses a monodentate bridging mode, which link each Co^{II} ion to four other neighboring Co^{II} centers, resulting in the layerlike structure. Within a $[Co^{II}]_4$ mesh, the distances between the adjacent Co^{II} ions are equal to 8.302 Å (through the ligand), as illustrated in the simplified figure of metal centers (Figure S1). The shortest interlayer Co···Co separation is 10.278 Å. Selected bond distances and angles for compound **1** are collected in Table S2.

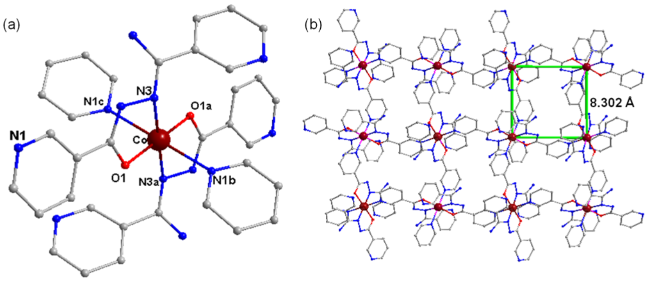

Figure 1. (a) Coordination environment of a Co ion in **1**. (b) 2D layerlike structure for **1** (H atoms are omitted for clarity).

Magnetic measurements were performed on polycrystalline samples of compound **1**, and the phase purity of the bulk materials was confirmed by powder XRD (Figure S2). As shown in Figure S3, the room-temperature $\chi_M T$ value of **1** is about 3.56 cm^3 K mol^{-1}, higher than the spin-only value (1.875 cm^3 K mol^{-1}) for a magnetically isolated Co^{II} cation, indicating a significant orbital contribution to the magnetic moment. Also, the value falls in the range of those observed for six-coordinated high-spin cobalt(II) compounds with an unquenched angular momentum.[21] Upon cooling, the $\chi_M T$ value decreases smoothly until T = 100 K and then further reduces sharply to reach a value of 1.60 cm^3 K mol^{-1} at 1.8 K. No peak value of the magnetic susceptibility is discovered in the χ_M versus T curve. The decrease of the $\chi_M T$ value for **1** would be due to antiferromagnetic coupling between the Co^{II} centers or thermal depopulation of the higher-energy Kramers doublets of the Co^{II} ions.

As far as we know, the reported magnetostructural results concerning the 2D cobalt(II) compounds (Table S3) with large intralayer (greater than 8.0 Å) and interlayer (greater than 8.6 Å) Co^{II}−Co^{II} distances, the magnetic exchange between the local spin carriers, if any, is considered to be very weak. Therefore, the magnetic data can be simulated based on the following Hamiltonian:[22]

$$\hat{H} = -\alpha\lambda(\hat{L}_{Co}\cdot\hat{S}_{Co}) + \Delta\left[\hat{L}_{z,Co}{}^{2} - \frac{1}{3}L(L+1)\right] + \mu_B B(-\alpha\hat{L}_{Co} + g_e\hat{S}_{Co}) \qquad (1)$$

where λ is the spin−orbit coupling and α is an orbital reduction factor defined as $\alpha = A\kappa$. The parameter κ considers the reduction of the orbital momentum due to delocalization of the unpaired electrons, and the A parameter includes the admixture of the upper ${}^4T_{1g}({}^4P)$ state into the ${}^4T_{1g}({}^4F)$ ground state (the value of A depends on the strength of the crystal field and varies between 1.5 and 1 for the weak and strong crystal fields, respectively). Δ is the energy gap between the singlet ${}^4A_2$ and doublet ${}^4E$ levels arising from the splitting of the triplet orbital ${}^4T_{1g}$ ground state under an axial distortion of the ideal O_h symmetry of the Co^{II} ion. As shown in Figure S3, the best-fit parameters using the experimental results in the whole temperature range are α = 1.48(1), λ = −147(1) cm^{-1}, and Δ = −482(5) cm^{-1}.

The field-dependent magnetizations are measured at 2 K and the fields up to 5 T for **1** (Figure S3, inset). The value of the magnetization tends to a quasi-saturation value of 2.08 μ_B, a value that is as expected, and $S_{eff} = {}^1/_2$ with g_{av} of ca. 4.2. The M versus B/T plots at different temperatures are not superimposed on a single master curve (Figure S4), clearly indicating the presence of significant magnetic anisotropy in compound **1**. An appropriate spin Hamiltonian of eq 2 is utilized to describe the magnetic anisotropy qualitatively:

$$\hat{H} = D[\hat{S}_z{}^{2} - \hat{S}(\hat{S}+1)/3] + E(\hat{S}_x{}^{2} - \hat{S}_y{}^{2}) + g\mu_B\hat{S}\cdot B \qquad (2)$$

where μ_B is the Bohr magneton and D and E represent axial and rhombic magnetic anisotropies, respectively. The best fits of the reduced magnetization data using the *Anisofit 2.0* program[23] give D = +76 cm^{-1}, E = +6.5 cm^{-1}, and g = 2.46 (solid line in Figure S4). The positive sign of the D value for **1** illustrates strong easy-plane magnetic anisotropy, which is consistent with those previously reported of the very few other cobalt(II) SIMs.[16]

Under an oscillating field of 3.5 Oe, the temperature-dependent alternating-current (ac) magnetic susceptibility experiments with a 0 Oe static field were determined in the range of 1.8−17 K, and no out-of-phase (χ''_M) signals were observed until the temperature drops to 1.8 K (Figure S5), suggesting a fast QTM through the spin-reversal barrier. In order to find a suitable applied magnetic field to repress the QTM, depending on the χ''_M signal of compound **1** on the applied direct-current (dc) field strength at 1.8 K, 1000 Hz was performed. A χ''_M signal with a significant sharp peak at around 2000 Oe dc field indicates field-induced slow magnetic relaxation operating in the compound. Thus, 2000 Oe could be used as a suitable applied field for **1**, and in-phase and out-of-phase ac susceptibilities are clearly observed (Figures S6 and S7). The peak temperatures (T_p) in χ''_M shift from 2.4 to 5.9 K with increasing frequency from 333 to 5000 Hz. The parameter $\Phi = (\Delta T_p/T_p)/\Delta(\log f)$ = 0.3 reveals the slow magnetic relaxation and falls into the typical range ($0.1 \le \Phi \le 0.3$) of the superparamagnetic materials.[24] The relaxation time obtained from the peak values of χ''_M was fitted (Figure S8), yielding values for the energy barrier (E_a) and preexponential factor (τ_0) of 11.37 cm^{-1} and 5.03×10^{-6} s, respectively. Although the preexponential factor of 5.03×10^{-6} s deviates slightly from the range typical of SIMs (1×10^{-7}−1×10^{-11} s), the value is comparable with those of the Co^{II} SIMs reported previously, such as 1.2×10^{-6} s for $[Co(azbbpy)(4,4'\text{-bipy})_{0.5}(DMF)$-

$(NCS)_2]\cdot MeOH$,[17] 1.7×10^{-6} s for $[Co(azbbpy)(bpe)_{0.5}(DMF)(NCS)_2]\cdot 0.25H_2O$,[17] and 1.7×10^{-6} s for $[Co(atz)_2(dca)_2]_n$.[18] It should be noted that the size of the effective energy barrier of 11.37 cm^{-1} is not comparable with the $2D$ value expected for an Orbach process, whereas the relaxation process is probably attributed to a direct process or a Raman process. Such a Raman or Raman-like mechanism has been proven to occur in the dynamic magnetic relaxation of known SIMs with the easy-plane magnetic anisotropy involving six-coordinated Co^{II} SIM $[Co(acac)_2(H_2O)_2]$,[16b] a Y-Co^{II} SIM,[8] and two seven-coordinated Co^{II} SIMs.[16c]

Frequency-dependent ac susceptibilities of **1** were measured in the temperature range of 1.8−6 K. As expected, upon application of a 2000 Oe dc field, the compound displays out-of-phase ac susceptibility (χ''_M) signals typically observed for field-induced 3d SIM species (Figure S9). Furthermore, the Cole−Cole plots below 5.5 K were generated from the frequency-dependent ac susceptibility data. A generalized Debye model[25a] was used to extract the values and distribution of the relaxation time (τ). The α values are found within the range 0.28−0.44 for **1**, supporting a wide distribution of relaxation times.[25b] As shown in Figure S10, the fitted values of χ_T, χ_S, τ, and α are 0.343, 0.017, 0.00041, and 0.31 at 5.3 K and 0.432, 0.031, 0.00062, and 0.40 at 4.0 K.

In summary, a dramatic 2D CP with the Co^{II} ions combined with a versatile bridged chelate ligand was constructed. Combined dc and ac variable-temperature magnetic determinations reveal the SIM behavior of the magnetically isolated high-spin Co^{II} ions with distorted octahedral geometry. As far as we know, there are only a few instances of CPs in which the Co^{II} ions display a SIM behavior.[16,26] As a result, the exceptional example of a 2D Co^{II}-based SIM with a uniform organic linker described herein highlights the family of SIMs, and further work will be undertaken to increase the number of cobalt(II) compounds behaving as SIMs by using the present synthetic route aimed at acquiring deeper insight into these fascinating magnetic systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01651.

Synthetic process, Scheme S1, Figures S1−S10, and Tables S1−S3 (PDF)

Crystal data (CCDC 1003588) in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

After this paper was published ASAP September 8, 2015, several references were deleted, and four figures and one scheme were moved to the Supporting Information. The corrected version was reposted September 9, 2015.