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# Two-Dimensional Coordination Polymers Constructed Using, Simultaneously, Linear and Angular Spacers and Cobalt(II) Nodes. New Examples of Networks of Single-Ion Magnets

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Supporting Information

**ABSTRACT:** Two novel bidimensional coordination polymers, $[Co(azbbpy)(4,4'\text{-bipy})_{0.5}(DMF)(NCS)_2]\cdot MeOH$ (**1**) and $[Co(azbbpy)(bpe)_{0.5}(DMF)(NCS)_2]\cdot 0.25H_2O$ (**2**), resulted from the assembling of cobalt(II) ions by 1,3-bis(4-pyridyl)azulene, using either 4,4′-bipyridyl or 1,2-bis(4-pyridyl)ethylene as neutral spacers. The cobalt(II) nodes in **1** and **2** act as single-ion magnets (SIMs).

The construction of coordination polymers (CPs) is a hot topic in crystal engineering.[1] The main interest in such compounds arises from their exciting physical and chemical properties, which can ultimately lead to applications. 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 of these materials (e.g., magnetism, color, luminescence).

The node-and-spacer approach, formulated more than 20 years ago by Robson,[2] remains a widely employed strategy for the design of coordination polymers. The spacers (exodentate or divergent ligands) are generally organic molecules, either neutral or anionic. We mention here polycarboxylate ions as anionic spacers, which generate an extremely rich coordination chemistry.[3] The exobidentate ligands can be linear or angular. Among the neutral linear spacers, the most popular are the bis(4-pyridyl) derivatives: 4,4′-bipyridyl (4,4′-bipy), 1,2-bis(4-pyridy)ethylene (bpe), bis(4-pyridyl)acetylene, and 1,4-bis(4-pyridyl)benzene.[4] The number of coordination polymers incorporating both a neutral and an anionic spacer is quite large.[5] On the other hand, the synthesis of coordination networks that simultaneously use two neutral spacers is a more delicate problem because mixtures of different compounds can be formed. However, several beautiful examples of coordination polymers with mixed neutral spacers have been reported in the literature.[6]

Recently, we reported one of the first coordination polymers to be constructed using an angular neutral spacer: 1,3-bis(4-pyridyl)azulene (azbbpy), which generates zigzag chains.[7] This ligand has a lot of potential in crystal engineering, and its ability to act as a spacer deserves to be exploited. Herein, we present two 2D coordination polymers that are assembled from cobalt(II) ions using two spacers (azbbpy and either 4,4′-bipy or bpe): $[Co(azbbpy)(4,4'\text{-bipy})_{0.5}(DMF)(NCS)_2]\cdot MeOH$ (**1**) and $[Co(azbbpy)(bpe)_{0.5}(DMF)(NCS)_2]\cdot 0.25H_2O$ (**2**) (DMF = dimethylformamide). These two compounds have been obtained following the same general procedure: reacting a solution containing cobalt(II) nitrate and potassium thiocyanate with a solution of the two spacers (Supporting Information). Details of the crystallographic investigation are given in Table S1.

Because the topologies of the two sheetlike coordination polymers are similar, only the crystal structure of **1** will be described in detail (Figure 1). Each cobalt(II) ion acting as a node is six-coordinate with two nitrogen atoms from the pyridyl fragments arising from two azbbpy molecules (Co1−N3 = 2.184(6) Å, Co1−N5 = 2.168(7) Å), one nitrogen from a 4,4′-bipy bridge (Co1−N4 = 2.179(6) Å), one oxygen atom from the DMF molecule (Co1−O1 = 2.172(7) Å), and two nitrogen atoms from the thiocyanato terminal ligands in trans positions (Co1−N1 = 1.992(9) Å, Co1−N2 = 2.061(9) Å), building a slightly distorted octahedral environment. Each cobalt center is connected to three others by bridging ligands, two azbbpy and one 4,4′-bipy, resulting in distorted hexagonal meshes (Figure 1). Within a mesh, the distance between the cobalt(II) ions are 14.02 and 11.48 Å (through azbbpy and across 4,4′-bipy, respectively). The crystallographic investigation of compound **2** shows that the dimensions of the meshes can by tuned by replacing the 4,4′-bipy ligand with a longer one, such as bpe (Figure S1). The intralayer intermetallic distances are almost

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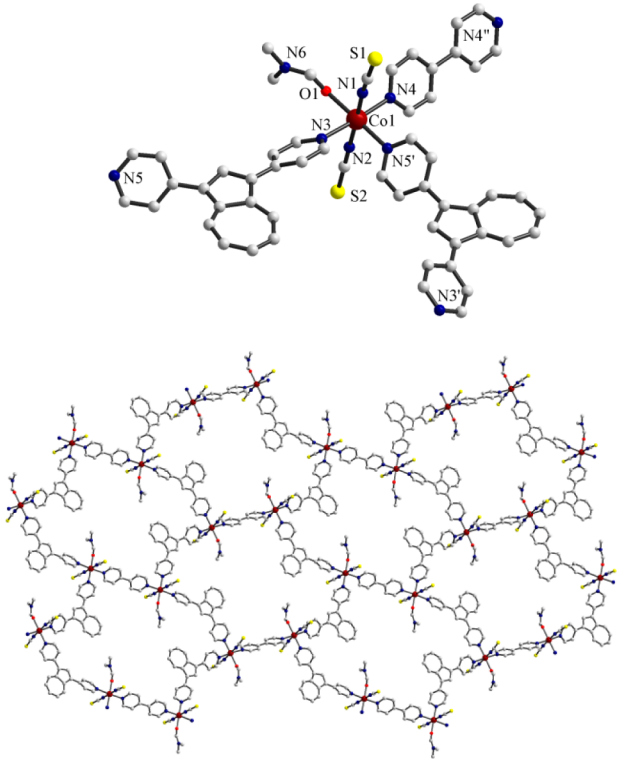


**Figure 1.** Crystal structure of $[Co(azbbpy)(4,4'\text{-bipy})_{0.5}(DMF)(NCS)_2]\cdot MeOH$ (**1**): (a) the coordination environment of the Co(II) ion and (b) a view of a fragment of the neutral layer. The solvent molecule of crystallization was omitted for clarity.

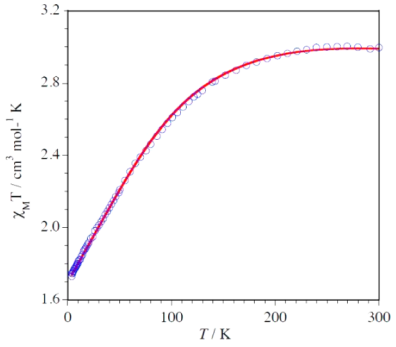


**Figure 2.** Temperature dependence of the product $\chi_M T$ for compound **1**: ○, experimental data; red trace, best-fit curve determined through eq 1.

equal for this compound (13.92 and 13.67 Å through the azbbpy and bpe spacers, respectively). Selected bond distances and angles for compounds **1** and **2** are collected in Table S2.

The possibility of any intralayer magnetic interaction between the metal ions in **1** and **2** is discarded because of the very large intermetallic distance. From this point of view, these compounds seem to be not very appealing. However, the ac magnetic measurements show that the cobalt(II) ions behave as single-ion magnets (SIMs). Let us first focus on the static magnetic properties of **1** and **2**. The $\chi_M T$ versus $T$ curve ($T$ = 2−300 K) for compound **1** is represented in Figure 2 (Figure S2 for compound **2**). The room-temperature values of the product $\chi_M T$ ($\chi_M$ being the magnetic susceptibility per one Co(II) ion) for compounds **1** and **2** are 3.0 and 2.86 $cm^3\ mol^{-1}$ K, respectively. They are higher than the spin-only value (1.875

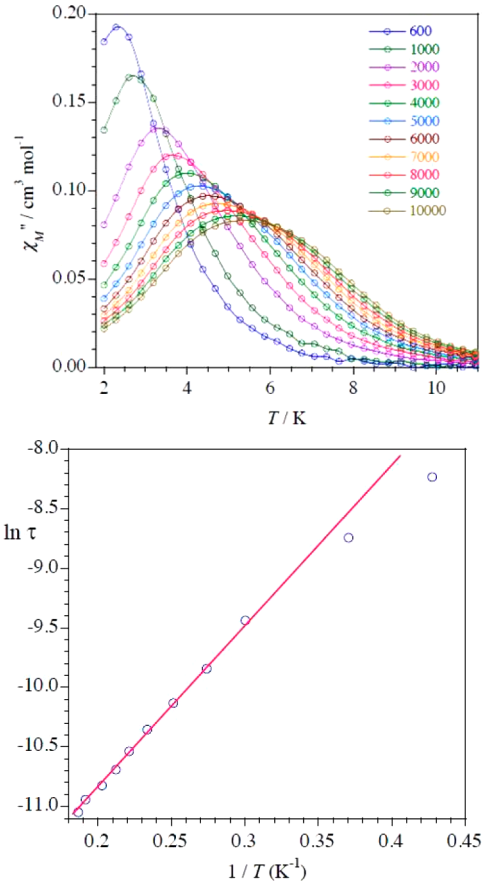


**Figure 3.** Top: Frequency dependence of the out-of-phase ac susceptibilities from 1.8 to 12.0 K under a 1000 Oe dc field for **1**. Bottom: The relaxation time of the magnetization ln $\tau$ versus $T^{-1}$ plot for **1**. The solid line represents the Arrhenius fit.

$cm^3\ mol^{-1}$ K), indicating a significant orbital contribution to the magnetic moment. Upon cooling, the value of $\chi_M T$ decreases slowly until $T$ = 200 K and then further decreases sharply to reach 1.73 and 1.65 $cm^3\ mol^{-1}$ K for **1** and **2**, respectively. The magnetic data were fitted through a methodology developed by us that is based on the following Hamiltonian[8]

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

where $\lambda$ is the spin−orbit coupling and $\alpha$ is an orbital reduction factor defined as $\alpha = A\kappa$. The parameter $\kappa$ considers the reduction of the orbital momentum caused by the delocalization of the unpaired electrons, and the $A$ parameter contains the admixture of the upper $^4T_{1g}(^4P)$ state into the $^4T_{1g}(^4F)$ ground state ($A$ = 1.5 and 1 in the weak and strong crystal-field limits, respectively). As a result of the distortion from the ideal $O_h$ symmetry of the Co(II) chromophore, the triplet orbital $^4T_{1g}$ ground state splits into singlet and doublet levels ($^4A_2$ and $^4E$, respectively) with an energy gap of $\Delta$. The best-fit parameters using the experimental data from the whole temperature range are $\alpha$ = 1.26(1), $\lambda$ = −153(1) $cm^{-1}$, and $\Delta$ = −350(2) $cm^{-1}$ for **1** and $\alpha$ = 1.20(1), $\lambda$ = −162(1) $cm^{-1}$, and $\Delta$ = −630(5) $cm^{-1}$ for **2**.


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The alternating current (AC) magnetic susceptibility measurements for compounds **1** and **2** under a 0 G static field show no out-of-phase signals (Figure S3, **1** and Figure S4, **2**), suggesting a fast quantum tunneling of the magnetization (QTM). Application of a direct current field of 1000 G suppresses the QTM and the frequency dependence of the out-of-phase ac susceptibilities is clearly observed (tops of Figures 3 and S5 for **1** and **2**, respectively). The relaxation times obtained from the out-of-phase susceptibility peaks were fitted to an Arrhenius law (bottoms of Figures 3 and S5 for **1** and **2**, respectively), giving values for the energy barrier ($E_a$) and pre-exponential factor ($\tau_0$) of 9.7 $cm^{-1}$ and 1.2 × $10^{-6}$ s, respectively, for **1** and 5.8 $cm^{-1}$ and 1.7 × $10^{-6}$ s, respectively, for **2**.

The two compounds presented herein enlarge the family of Co(II) SIMs, which is not very large so far. It is interesting that the slow relaxation of the magnetization for single cobalt(II) ions was observed with various stereochemistries: tetrahedral,[9] square-pyramidal,[10] and octahedral.[11] Most of these compounds are mononuclear species. As far as we are aware, there are only few examples of coordination polymers in which the cobalt(II) ions display a SIM behavior.[12] Further work on magnetic polymers constructed using 1,3-bis(4-pyridyl)azulene as a spacer is in progress in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and crystallographic information for **1** and **2** (Tables S1−S2), crystal structure of **2** (Figure S1), temperature dependence of the product $\chi_M T$ for compound **2** (Figure S2), and magnetic plots for **1** (Figure S3) and **2** (Figures S4 and S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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