Solvent-Induced Structural Diversity and Magnetic Research of Two Cobalt(II) Complexes

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ABSTRACT: The solvent-induced topological and structural diversities of two Co(II) complexes, namely, [Co-(L)2(SCN)2] (Co1) and [Co2(L)2(SCN)(OAc)3] (Co2) (L = 8-methoxyquinoline), were comparatively analyzed. Certain proportions of L, Co(OAc)2·4H2O, and NaSCN were mixed and dissolved in CH3OH at 60°C to obtain complex Co1. Complex Co2, an asymmetric dinuclear compound, was obtained by simply replacing CH3OH with CH3CN as the solvent. The Co(II) ion in complex Co1 was coordinated by the N2O5 mode provided by two L ligands and two SCN anions. The two Co(II) ions in Co2 were in the N2O3 and NO3 coordination environment and were linked by two μ2-OAc bridges and one rare μ2-OAc′ bridge. Weak interaction analysis revealed that complexes Co1 and Co2 exhibited 6-connected shp and 14-connected fcu nets, respectively. Magnetic studies showed that Co1 demonstrated single-ion magnet behavior under 2000 Oe. These behaviors are indicative of clearly field-induced single-ion magnetic behavior with Ueff = 34.7(2) K and τ0 = 2.7(2) × 10−7 s under 2000 Oe dc field, respectively. By contrast, Co2 lacked frequency dependence under zero-field conditions. Electrospray ionization mass spectrometry indicated that two complexes were stable in N,N-dimethylformamide.

INTRODUCTION

The design and synthesis of complexes with desirable clusters and diverse facies have drastically progressed over the past decade. The molecular structure in the solid can be controlled to generate functional molecules with newfangled topological structures and prospective properties.1 Three main approaches for regulating the synthesis of complexes with different structures and functions exist: (1) the change of metal ions with specific functions (Scheme 1).2 For example, a monoelectron metallic ion is a prerequisite for the construction of a magnetic material. (2) The change of different organic ligands. Organic ligands play an important role in the formation of complexes. The most important parameters for consideration in ligand selection are coordinating ability, mode, flexibility/rigidity, and geometry.3 (3) The change of bridging and end-group ligands.4 Nevertheless, producing products with completely different structures through solvent-induced methods, wherein the reaction solvent is varied and different organic ligands, are held constant, is difficult and rare.

Recently, great progress has been made in 3d-based single-ion magnets (SIMs),5,6 especially mononuclear cobalt complex. The first example of field-induced Co-based SIM was published by Pardo and his co-workers.7 This advancement is an important deviation from former works on complexes with different structures through solvent-induced methods, wherein the reaction solvent is varied and other conditions, such as metal ions, ligands, and bridging ligands, are held constant, is difficult and rare.

Received: June 15, 2019
Accepted: September 12, 2019
Published: December 4, 2019
more deeply because of its strong magnetic aeolotropism. In 2014, the slow relaxation behavior was inspected with easy-plane anisotropy, and the appearance was expounded by Gómez-Coca.17,21 The aeolotropism of the metal ions that form clusters clarifies the entire magnetic behavior. Previous work has advanced from Mn12 clusters of mixed valence to mono-valent clusters containing aeolotropic 3d metals, namely, because these clusters can construct isomorphic structures with different magnetic aeolotropism.13–16 Numerous compounds based on these divalent Co(II) complexes exhibit single-molecule magnetism.17–21 Therefore, a large amount of Co(II) complex is designed and synthesized by various methods. According to the relevant principles, chemists have designed and modified ligands, metal ions, and bridging ligands in various ways to facilitate the construction of a wide range of Co(II) single-molecule magnet (SMM).22 However, there are rare examples of the construction of molecular materials in which solvents induce different magnetic behaviors.

Herein, the rare solvent-induction synthesis of two structurally different Co(II) complexes, namely, [(Co-(L)2(SCN)2)] (I) and [Co2(L)2(SCN)(OAc)3] (2), was realized through the reaction of 8-methoxyquinoline (L), NaSCN, and Co(OAc)2·4H2O at 60 °C with different solvents. Specifically, complexes Co1 and Co2 were prepared using methanol and acetonitrile as solvents, respectively. Both solvents are not involved in the products. Complexes Co1 and Co2 form 6-connected shp and 14-connected fcu nets, respectively. Magnetic studies on two complexes show that Co1 exhibited SIM behavior under 2000 Oe dc field and that Co2 lacked frequency dependence under 0 Oe. Comparing the experimentally obtained electron paramagnetic resonance (EPR) spectra with the simulated spectra revealed that the fitting of the simulated data (D > 0) is better than that of experimental data (D < 0). The results of ESI-MS indicate that complexes Co1 and Co2 are stable in N,N-dimethylformamide (DMF).

## RESULTS AND DISCUSSION

**Crystal Structure.** X-ray results suggest that Co1 is a neutral uninuclear complex and crystallizes in the monoclinic space group C2/c (Table S1a), in which the six-coordinated Co(II) cores are surrounded by two N,O-chelated 8-methoxyquinolines and two N atoms from two SCN− anions (Figure 1a). The two 8-methoxyquinoline and two SCN− ligands are cis to each other. By contrast, Co2 crystallizes in the P21/c space group with the monoclinic crystal system (Table S1a), which contains two six-coordinated Co(II) ions. Both Co ions are connected by one 8-methoxyquinoline ligand and two bridging μ2-CH3COO− anions. In addition, Co1 is surrounded by one N,O-chelated 8-methoxyquinoline ligand and four O atoms from three CH3COO− anions. Co2 is surrounded by one N,O-chelated 8-methoxyquinoline ligand, one SCN−, and three O atoms from three CH3COO− anions (Figure 1b). Co–Co are bridged by three CH3COO− anions. Calculated results obtained using SHAPE suggest that the geometry of the six-coordinative Co(II) in Co1 and Co2 can be viewed as octahedral in geometry (Tables S3–S5). The distance between the Co(II) ion and ligand N atoms is approximately 2.08 Å. In Co1, the distances between the Co(II) ion and SCN− N atoms are 1.999 and 2.004 Å and those between the Co(II) ion and ligand O atoms are 2.309 and 2.371 Å. In Co2, the distances between Co and O are within the limit of 1.988–2.255 Å and those between Co and N are within the limit of 2.047–2.153 Å (Table S1b).

The supramolecular weak interaction of Co1 involves C–H···N/S and π···π. The distances of this supramolecular weak interaction are all within a reasonable range (Figure S1a,b and Table S2). Thus, Co1 come down to a 6-connected shp net (Figure 2a) with distances of 5.22–6.03 Å between the centers of Co(I). The supramolecular weak interaction of Co2 contains C–H···π and π···π with distances that are all within a reasonable range (Figure S1c,d and Table S2). Thus, Co2 forms a 14-connected fcu net (Figure 2b) with length distances of 10.68–12.25 Å between the centers of Co(II).

**Thermal Analysis.** Thermogravimetric analysis (TGA) was accomplished to inspect the thermostabilization of Co1 and Co2. The crystals were heated up to 800 °C in nitrogen gas with a heating speed of 5 °C/min. The first weight loss platform (34.1%) experienced by Co1 from the temperature extent of 30–250 °C, which accorded with the loss of the coordinating ligand (calcd 32.3%). Co2 did not have free solvents. The first weight loss platform of 17.8% experienced by Co2 from the temperature extent of 30–180 °C, which accorded to the loss of one coordinating SCN− and one coordinating CH3COO− (calcd 17.4%) (Figure S2b). The thermal behavior and formula of Co1 and Co2 are consistent.

**Magnetic Properties.** The dc magnetic susceptibilities of Co1 and Co2 were tested over the temperature extent 2–300 K under 1000 Oe (Figure S3a,c). At 300 K, χ′′T values are 2.97 cm³·K·mol⁻¹ for Co1 and 5.75 cm³·K·mol⁻¹ for Co2, which are bigger than the estimated 1.875 cm³·K·mol⁻¹ for every uncorrelated Co⁡²⁺ ion value (S = 3/2) and indicate the orbital contribution of O₃ Co(II).22 These values are likely due to the considerable magnetic aeolotropism of Co1 and Co2. At low temperature, χ′′T reduces slightly up to ca. 100 K (Co1) and 80 K (Co2) before experiencing a shallow minimal value at ca. 14 K (Co1) and 33 K (Co2), and a peak is finally observed at 7 K for Co1, then quickly decreases to approximately 2.3 (Co1) and 3.7 (Co2) cm³·K·mol⁻¹ at 2 K, respectively. The results of 1/χ′ versus T at 100–300 K

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Figure 1. Complexes Co1 (a) and Co2 (b)’s structures.

Figure 2. Uninodal 6-connected shp net of (a) Co1 and 14-connected fcu net of (b) Co2.
and TIP = 8.5 conclusive admeasurement of the ZFS factors. As the frequency range of 60–259 GHz for Co(II) ion is for Co2

\[ \text{AF coupling for } \text{Co2} \]

intensities of magnetization curves of 2.86 and 4.30 N

\[ T \]

the instruments (235 GHz and Co polarization operator, D where according to the Curie–Weiss law obtained calculated Curie values (C) of 2.98 and 5.94 cm²·K·mol⁻¹ for Co1 and Co2, respectively. The Weiss values \( \theta \) of Co1 and Co2 are −0.75 and −8.89 K (Figure S3a,c), respectively. The C constants are regular for \( O_h \), negative \( \theta \) constants indicate intracluster AF coupling for Co2, and the contribution of orbital from Co(II) ion is for Co1 and Co2. The M–H for complexes Co1 and Co2 was measured at 5 T (Figure S3b,d). The magnetization curves of Co1 and Co2 under Leigh magnetic intensities of field suddenly increase before tardily increasing to 2.86 and 4.30 Nμ at 2 K under 5 T, which exhibits that Co1 and Co2 express sizeable magnetic aeolotropism.

In order to understand the magnetic aeolotropism, the PHI program is used to fit the magnetic anisotropy of \( \chi''_m \)T versus T and M versus H curves at different temperatures by the aid of an aeolotropic spin Hamiltonian (with \( g_\parallel = g_\perp \))

\[
\hat{H} = D(\hat{S}_{z}^2 - 1/3\hat{S}^2) + E(\hat{S}_{x}^2 - \hat{S}_{y}^2) + \mu_B \sum_{i=x,y,z} \hat{S}_i \hat{B}_i
\]

where \( D = \) axile ZFS factor, \( E = \) orthotropic ZFS factor, \( \hat{S} = \) polarization operator, \( B = \) magnetic detection, \( g = \) Landé parameter, and \( \mu_B = \) Bohr magneton. The best-fitting values are \( g_z = g_\parallel = 2.69, g_x = 2.21, D = +36.61 \text{ cm}^{-1}, E = -1.02 \text{ cm}^{-1}, \) and TIP = 8.5 × 10⁻⁴ cm³·mol⁻¹ with a residual of 2.03 × 10⁻³. In the fitting process, the symbol of the \( D \) value is found to be critical and a good fit is obtained with the positive \( D \).

**HF-EPR Studies of Co1.** A high-frequency EPR (HF-EPR) instrument is integrant, which further confirmed the magnetic aeolotropism of Co1. HF-EPR instruments were collected over the frequency range of 60–259 GHz in the interest of getting a conclusive admeasurement of the ZFS factors. As the \( D \) values (36.61 cm⁻¹) are going beyond the frequency extent in the instruments (235 GHz—10 cm⁻¹), between Kramers doublets \( m_S = \pm 1/2 \) and \( m_S = \pm 3/2 \), no transitions are inspected (Figure 3a). The HF-EPR spectrum of Co1 contains three symbols, representative for a spin \( S = 3/2 \) arrangement with huge and plus \( D \) values. All EPR spectra indicates that the intra-Kramer transitions originate in the lowest doublet \( m_S = \pm 1/2 \) multiplied by \( \Delta m_S = \pm 1 \), which confirms the frequency dependence by observing the field of the inflection point (Figure 3b). HF-EPR spectra of Co1 could be well imitated by using the \( D \) value measured by the SQUID instrument (Figure 3). The \( D \) value is affirmed to be plus. For Co1, the imitation is made using the \( D \) factor achieved by SQUID (+36.62 cm⁻¹), and the zero field splitting parameter \( E \) and the intrinsic \( g \) value are adjusted at the same time, which provides an axial \( g \)-tensor \( [g_z = g_\parallel = 2.50(2), g_x = 2.18(2)] \) and \( |E| / |D| \approx 0.145 \). If the sign of the \( D \) value is set to a minus value, a reasonable analog spectrum cannot be obtained (Figure 3a). It is worth noting that because of the large \( D \) value and the limitations of the technique, the transition between Kramers doublets \( m_S = \pm 1/2 \) and \( m_S = \pm 3/2 \) has not been observed, as shown by several single nuclear Co(II) complexes. The obtained Hamilton parameters are not extremely accurate, but the forward symbol of the \( D \) value has been clearly confirmed, which further indicates existing plane magnetic aeolotropism of Co1.

The dynamical magnetic characterizations of Co1 and Co2 were tested by instruments of ac magnetic susceptibilities. Complex Co1 does not exhibit frequency dependence of \( \chi'' \) at zero dc-field from the 9 to 997 Hz frequencies range (Figure 4a). This discovery shows that moments are not blocked above 2 K. Under the 2000 Oe static magnetic field, nevertheless, Co1 exhibits the strong temperature and frequency dependence, that is, nonzero \( \chi'' \). From 2 to 6 K, the \( \chi'' \) peaks can be observed, indicating the presence of SMM behavior of Co1 (Figure 4b). By contrast, Co2 (Figure 4c) does not exhibit any
χ″ symbol in the zero dc-field at the frequencies of 1, 10, and 997 Hz above 2 K. No virtual components were obtained.

The Cole–Cole data (Figure 5a–c) were modeled by using a universal Debye model, and the fitted factors τ and α are listed in Table S6. For Co1, factor α is within the limit of 0.05–0.15, which encompasses representative CoII-based SMMs and reveals a single magnetic relaxation. Temperature-dependent relaxation time was obtained under the assumption of the Orbach process in accordance with the Arrhenius law (τ = τ0 exp[Ueff/kBT]). The energy hill and attempt time are Ueff = 34.7(2) K and τ0 = 2.7(2) × 10−7 s under 2000 Oe dc field (Figure 5d), respectively.

The monometallic contorted O3Co in complex Co1 can be ascribed to the huge axial zero-field splitting (D = 36.61 cm−1 procured by magnetic data fitting), and ac susceptibility instruments announce an aeolotropism fill of Ud = 23.9 K. Complex Co2 also shows contorted O6 coordinative configuration about the Co centers, Co1···Co2 are bridged by three CH3COO− anions with the distance of 3.413 Å, the different coordinative configuration, the structural distorted degree, and the ligand field strength affect the anisotropy of CoII ions, and significant easy-plane zero-field splitting prohibits any SMM behavior.

ESI-MS Analyses of Co1 and Co2. The stability of Co1 and Co2 in solution was analyzed through ESI-MS. A small amount of the complexes was dissolved in DMF, and the solution was diluted with acetonitrile (Figures 6 and S6). In the positive mode, the highest intensity peaks in Co1 and Co2 correspond to [CoL2]+ and [Co2L2], respectively. This correspondence suggests that the core structures of Co1 and Co2 remain intact in solution. The peaks at m/z = 422.08 and 349.03 are ascribed to [CoL(SCN)(C6H5NO)]+ (b, calculated 422.08) and [CoL(SCN)(C6H5NO)]+ (a, calculated 349.03), respectively, which both contain the CoL core structure of Co1 (Table S7 and Figure S4). By contrast, the main peak for Co2 is at m/z = 613.04 and is assigned to [Co2L2(CH3COO)3]+ (c, calculated 613.04). This peak is derived from the dissociation of the terminal group of SCN−, and some peaks are similar to the main peak, like m/z = 539.03 and 585.05; they are assigned to [Co2L2(CN)(CH3COO)(OH)]+ (f, calculated 539.03) and [Co2L2(CH3COO)2(CH3O)]+ (e, calculated 585.05). A strong peak with the relative intensity of 0.955 at m/z = 527.03 attributed to [Co2L2(CH3COO)3(C6H5NO)]+ (d, calculated 527.03) from the dissociation of one L and one SCN− (Table S7 and Figure S5) is also present, and there are also some peaks that dissociate one ligand, m/z = 453.97 and 499.03; they are assigned to [Co2L(CH3COO)3]+ (h, calculated 453.97) and [Co2L(CH3COO)2(CH3O)(C6H5NO)]+ (g, calculated 499.03). In the negative mode, only the metal salt fragment [Co(SCN)3]− (m/z, 232.86, calculated 232.86) is present regardless of the ion source voltage (Figures S6–S8 and Table S8).
CONCLUSIONS

In summary, complexes Co1 and Co2 are obtained through solvent-induced reaction. These complexes are structurally different. For example, a rare μ2-OAc− bridge is present in Co2. Magnetic studies on complexes Co1 and Co2 indicate that Co1 exhibits no frequency dependence at 0 Oe dc-field conditions and exhibits SIM behavior at 2000 Oe. Given these characteristics, Co1 is an interesting addition to Co SIM families. Complex Co2 lacks frequency dependence under zero dc-field conditions. This research provides an actual example of the construction of structurally different complexes through the simple alteration of the reaction solvent. It also illustrates that the solvent-induced method has considerable potential for producing complexes with unique structures and properties. This facile method provides a new avenue for the synthesis of multifunctional molecules.

EXPERIMENTAL SECTION

Materials and Measurements. Commercial general solvents and reagents were used without further purification. The Fourier transform infrared spectra were collected with KBr pellets in the extent of 400–4000 cm−1 on a pycoerythrin spectrum spectrometer. Elemental analyses (C, H, N, and S) were tested on a vario MICRO cube 2400. The thermal analysis was performed on LABSYS thermogravimetry–differential thermal analysis at a heating speed of 5 °C/min in N2. The diffraction data for complexes 1 and 2 were gathered in Φ and ω scan modes on a Bruker SMART CCD diffractometer (λ = 0.71073 Å, Mo Kα radiation). The compound structures were worked by the immediate means, which succeeded by the difference Fourier synthesis method, and then the whole-matrix least square technique on the F2 was refined by the SHELXL.27 The hydrogen atom is placed in the calculative position, and the equidirectional refinement is performed using a horse-riding model. Table S1 provides an overview of the X-ray crystallography data and refinement details of these complexes. The CCDCC numbers are 1784410 (Co1) and 1874411 (Co2). Temperature- and magnetic field-related magnetic susceptibility measurement by using QD MPMS SQUID-XL-5 magnetometer has been implemented. The tested polarization rate is checked to the diamagnetism of the constituent atoms. In the sample, for preventing the free movement of the grains, the silicone grease is used for embedding in samples that prevent free movement of particles.28 ESI-MS data were tested at 275 °C with Thermo Exactive. The injection speed is 0.3 mL/h in the range of 200–2000 m/z.

Synthesis. Complex Co1. A mixture of 29 mg Co(OAc)2⋅4H2O, 42 mg 8-methoxyquinoline, 8.1 mg NaSCN, and 6 mL CH3OH was stirred for 1 h at room temperature and then sealed in a 20 mL glass bottle and heated at 60 °C for 3 days. It was then cooled to room temperature over a day. Red crystals of complex Co2 were obtained. Yield, 29% (based on Co(OAc)2⋅4H2O). IR data for Co2 (KBr, cm−1): 3719 (m), 2834 (m), 2087 (s), 1715 (s), 1517 (s), 1384 (m), 1257 (w), 1109 (m), 979 (w), 836 (m), 781 (w). Elemental analyses calcd (%) for C22H18CoN4O2S2: C, 53.55; H, 3.68; N, 12.63; S, 13.00. Found: C, 53.16; H, 3.85; N, 11.16; S, 12.65.

Complex Co2. A mixture of 29 mg Co(OAc)2⋅4H2O, 42 mg 8-methoxyquinoline, 8.1 mg NaSCN, and 6 mL CH3CN was stirred for 1 h at room temperature and then sealed in a 20 mL glass bottle and heated at 60 °C for 3 days. It was then cooled to room temperature over a day. Red crystals of complex Co2 were obtained. Yield, 29% (based on Co(OAc)2⋅4H2O). IR data for Co2 (KBr, cm−1): 3719 (m), 2834 (m), 2087 (s), 1715 (s), 1517 (s), 1384 (m), 1257 (w), 1109 (m), 979 (w), 836 (m), 781 (w). Elemental analyses calcd (%) for C22H18CoN4O2S2: C, 53.55; H, 3.68; N, 12.63; S, 13.00. Found: C, 53.16; H, 3.85; N, 11.16; S, 12.65.

ASSOCIATED CONTENT

Supporting Information

Crystal structure and data, powder X-ray diffraction, TGA, HRESI-MS, and magnetic characterizations (PDF)

Crystallographic information of Co1 and Co2 (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSFC (21771043, 51572050 and 21601308), Guangxi Natural Science Foundation (2016GXNSFAA38008S and 2015GXNSFDA139007).

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