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### Reversible On–Off Switching of the Hysteretic Spin Crossover in a Cobalt(II) Complex via Crystal to Crystal Transformation

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S Supporting Information

ABSTRACT: Reversible controlling and switching of magnetic bistability remains relatively difficult. Here, reversible on-off switching of a hysteretic spin transition in a Co<sup>II</sup> complex via a single-crystal to single-crystal (SC-SC) transformation during dehydration and rehydration was reported. Upon dehydration, a switching from a basically low spin state to an abrupt and hysteretic spin crossover (SCO) with broad hysteresis loops was achieved. Hysteretic and anisotropic crystal lattice expansion or contraction in the spin transition temperature range was also observed in the dehydrated complex. The magneto-structural relationship in this system was established on the basis of detailed structure analyses on both the hydrated and dehydrated examples over a wide range of temperatures. The elimination of guest internal



pressure, the tuning of the supramolecular interactions, and the strong electron-lattice coupling should be responsible for the hysteretic SCO in the dehydrated complex.

#### INTRODUCTION

Bistable materials with two switchable states in a certain range of external stimuli have attracted continuous research interest for their potential applications in switches, sensors, and memory devices.<sup>1-4</sup> Among these switchable materials, molecular solids showing electric or magnetic bistabilities are particularly interesting with typical examples such as SCO materials,<sup>2</sup> single-molecule magnets (SMMs),<sup>3</sup> and organic radicals.<sup>4</sup> Toward this end, spin crossover (SCO) materials represent ideal candidates for their electronic conversion between low-spin (LS) and high-spin (HS) states in the presence of an external stimulus, such as temperature, light, and pressure.<sup>5</sup> The development of SCO systems with a 30-50 K hysteresis loop spanning the room-temperature region is greatly desired.<sup>5c</sup> For hysteretic SCO behavior, strong cooperative intermolecular interactions, such as hydrogen bonding,  $\pi \cdots \pi$  interactions, halogen bonding, and so on, are considered to be of great significance. These intermolecular interactions can be carefully designed from the concept of crystal engineering. Therefore, various chemical and physical approaches have been successfully utilized to obtain the SCO materials of hysteretic loops in various temperature regions.<sup>6,7</sup> Of particular interest among them are the dynamic molecular systems which are responsive to solvent or guest molecules through a single-crystal to single-crystal (SC-SC) transformation, especially those with reversibility.<sup>6</sup> Notably, the reversible switching of the thermal hysteresis loop via the SC-SC event reported in the Hoffman-type SCO frameworks is very attractive.<sup>6</sup> On the other hand, the switching of SCO behavior in a SC-SC fashion in an isolated system has been

mostly reported in Fe<sup>II</sup> complexes and is usually nonhysteretic.

In contrast to the overwhelming majority of Fe<sup>II/III</sup>-based SCO complexes, Co<sup>II</sup> SCO complexes are less common and usually exhibit gradual, incomplete, and nonhysteretic SCO behaviors.<sup>9</sup> This is mainly attributed to the partial occupation of the antibonding e<sub>g</sub> orbitals in the ground state, which leads to smaller structural changes arising from a spin transition. However, the smaller energy barriers between the potential surfaces of the HS and LS states of CoII induce a faster spin transition dynamics and a high sensitivity of SCO behavior to the crystalline environment or the solvents is thus anticipated.<sup>9a</sup> These characteristics offer both opportunities and challenges for designing and synthesizing high-performance cobalt(II) SCO materials. Indeed, in comparison with those for the Fe<sup>II</sup> systems, the ligands for the appropriate ligand field for the Co<sup>II</sup> SCO complexes are much fewer, among which terpyridine and its derivatives have probably been the most studied.<sup>9b</sup> In all of the Co<sup>II</sup> SCO materials, examples of a hysteretic SCO transition are relatively rare, 10-12reflecting the challenge in developing hysteretic bistable  $\mathrm{Co}^{\mathrm{II}}$ SCO materials.

With the above in mind, we recently designed and synthesized the ligand 4'-(4-bromophenyl)-2,2':6',2"-terpyridine (L; Scheme 1) to exploit the SCO properties of  $Co^{II}$ complexes. The additional phenyl ring and the bromide atom were introduced to the parent terpy ligand, with the hope of

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inducing possible halogen bonding and  $\pi - \pi$  interactions. Using a multicomponent strategy, we obtained the ion pair bicomponent system  $[Co^{II}(L)_2][Co^{II}(NCS)_4]$ ·2MeCN with the coexistence of SMM and SCO behaviors.<sup>13a</sup> Furthermore, we realized the reversible on-off switching between SCO and SMM behaviors via a SC-SC event in the mononuclear Co<sup>II</sup> complex  $[Co^{II}(L)_2](DPAS)_2 \cdot DMF \cdot 2H_2O$  (DPAS<sup>-</sup> = 4-(phenylamino)benzenesulfonate; Scheme 1).<sup>13b</sup> In this system, the weak supramolecular interactions and local coordination environment of the Co<sup>II</sup> centers were effectively and reversibly modified during dehydration-rehydration processes. These results indicate that anions and solvent molecules play significant roles in the magnetic behaviors of the Co<sup>II</sup> SCO complexes, which inspired us to further develop dynamic molecular CoII materials through the modification of the anions and guest solvent molecules.

Herein, we present a Co<sup>II</sup> complex where the hysteretic SCO can be reversibly switched on and off. Through a reversible dehydration/rehydration process between  $[Co^{II}(L)_2][BDS]$ .  $2H_2O(1\cdot 2H_2O)$  and  $[Co^{II}(L)_2][BDS](1, H_2BDS = benzene-$ 1,3-disulfonic acid; Scheme 1) occurring in a SC-SC fashion, the magnetic behavior transfers from basically LS in 1.2H<sub>2</sub>O to a cooperative SCO with a hysteresis loop in 1. Moreover, hysteretic and anisotropic lattice expansion or contraction in the SCO temperature range was observed in 1. Detailed singlecrystal structure analyses over a wide range of temperatures revealed that the elimination of guest internal pressure, the significant modification of the intermolecular interactions, and the strong electron-lattice coupling are responsible for the observed spin bistability in the dehydrated form. Notably, the electron-lattice coupling herein refers to the correlation and synergetic changes of the spin state of the metal center and the crystal lattice.

#### RESULTS AND DISCUSSION

**Syntheses and Structures.** Dark red single crystals of 1· 2H<sub>2</sub>O were prepared by a slow evaporation method from  $[Co(L)_2](ClO_4)_2$ ·3DMF (see details in the Experimental Section). Thermal gravimetric analysis (TGA) of 1·2H<sub>2</sub>O revealed a one-step dehydration process with ca. 3.30% weight loss at 20–150 °C under a dry N<sub>2</sub> flow, corresponding to the release of two lattice H<sub>2</sub>O molecules (calculated weight loss 3.25%, Figure 1). After loss of the two lattice water molecules, the TGA curve of 1·2H<sub>2</sub>O exhibits a negligible mass loss up to ca. 400 °C, suggesting the high thermal stability of the dehydrated form of 1. On the basis of this TGA result, the



Figure 1. TGA curves for compounds 1·2H<sub>2</sub>O (blue), 1 (red), and 1·2H<sub>2</sub>O-re (green).

dehydrated form of 1 can be prepared by heating the sample of 1.2H<sub>2</sub>O at 400 K, in the X-ray diffractometer (for single-crystal and powder XRD measurements), in the SQUID machine (for the magnetic measurement), or under a dynamic vacuum (for other measurements, see details in the Experimental Section). Furthermore, 1 resorbs water and returns to the rehydrated form (1·2H<sub>2</sub>O-re) upon exposure to air for several hours. TGA was also performed on the dehydrated form 1 and the rehydrated form 1.2H2O-re. For 1, the experimental weight loss is ca. 0.03%, which indicates the completeness of the dehydration of 1·2H<sub>2</sub>O to 1. For 1·2H<sub>2</sub>O-re, the TGA curve is almost identical with that of 1.2H2O with a 3.36% weight loss, suggesting the reversibility of the dehydration and rehydration processes. This reversible process was also confirmed by singlecrystal X-ray diffraction (SCXRD), powder XRD (Figure S1), elemental analyses, and magnetic measurements (vide infra).

Interestingly, the dehydration can occur in a SC-SC fashion by heating a single crystal of 1.2H<sub>2</sub>O in the X-ray diffractometer at 400 K for 1/2 h. SCXRD analyses were conducted on both 1.2H2O and the in situ generated single crystal of 1 at various temperatures  $(300 \rightarrow 120 \rightarrow 350 \text{ K for})$  $1.2H_2O$  and  $400 \rightarrow 120 \rightarrow 350$  K for 1). In addition, the SCXRD was also performed on a rehydrated single crystal of 1. 2H<sub>2</sub>O-re at 300 K to confirm the complete reversibility of the dehvdration and rehydration even in a SC-SC fashion. The data collection and structure refinement parameters for 1. 2H<sub>2</sub>O, 1, and 1·2H<sub>2</sub>O-re are given in Tables S1-S4 in the Supporting Information, and the selected bond lengths and bond angles at several specific temperatures are given in Tables 1 and 2 and Tables S5 and S6. Given in Tables 1 and 2 are also some more specific structural parameters, including the averaged Co-N bonds, the continuous shape measure values (CShMs, calculated using SHAPE<sup>14</sup>), and so on (vide infra). Both  $1.2H_2O$  and 1 crystallize in the triclinic space group  $P\overline{1}$  at all studied temperatures. For both forms, the asymmetric units contain one  $Co^{2+}$  ion, two unique L ligands, and one BDS<sup>2-</sup> anion (Figure 2). The Co<sup>II</sup> ion is coordinated by six N atoms from two L ligands in a bis-meridional fashion, forming an axially compressed  $CoN_6$  octahedron where the  $Co-N_{equatorial}$ bonds are longer than the  $Co-N_{axial}$  bonds. The CShM values relative to an ideal octahedron increase slightly from 2.413 at 200 K to 2.546 at 300 K for 1.2H2O and decrease remarkably from 3.747 at 300 K to 2.422 at 200 K for 1 (Tables 1 and 2). These values are consistent with a large distortion from the ideal octahedron of the local Co<sup>II</sup> geometry for all structures. For the bond angles, the axial N<sub>2</sub>-Co-N<sub>5</sub> angle in 1·2H<sub>2</sub>O is

## Table 1. Selected Bond Lengths (Å) and Structural Parameters for $1.2H_2O$

	<i>T</i> (K)					
	300	260	230	200		
	$cooling \rightarrow$					
Co(1) - N(1)	2.027(4)	2.020(3)	2.012(3)	2.003(3)		
Co(1) - N(3)	2.039(4)	2.028(3)	2.021(3)	2.018(3)		
Co(1) - N(4)	2.132(4)	2.140(2)	2.143(3)	2.147(3)		
Co(1) - N(6)	2.120(4)	2.127(2)	2.129(3)	2.129(3)		
Co-N <sub>equatorial</sub>	2.079	2.079	2.076	2.0745		
Co(1) - N(2)	1.887(4)	1.883(2)	1.874(2)	1.874(3)		
Co(1) - N(5)	1.915(4)	1.917(2)	1.915(2)	1.915(3)		
Co-N <sub>axial</sub>	1.901	1.900	1.894	1.894		
Co-N <sub>av</sub>	2.020	2.019	2015	2.014		
CShMs <sup>a</sup>	2.546	2.460	2.435	2.413		
dihedral angle (deg) <sup>b</sup>	88.039	88.114	88.237	88.551		
$\sum^{c}$	90.57	88.3	87.51	86.76		
		<i>T</i> (K)				
	200	230	260	300		
	heating $\rightarrow$					
Co(1)-N(1)	2.009(2)	2.014(2)	2.023(3)	2.030(3)		
Co(1) - N(3)	2.015(2)	2.018(2)	2.028(3)	2.043(3)		
Co(1) - N(4)	2.141(2)	2.141(2)	2.140(3)	2.133(3)		
Co(1) - N(6)	2.130(2)	2.126(2)	2.125(2)	2.122(3)		
Co-N <sub>equatorial</sub>	2.073	2.074	2.079	2.082		
Co(1) - N(2)	1.870(6)	1.874(6)	1.880(2)	1.896(2)		
Co(1) - N(5)	1.915(0)	1.915(4)	1.917(2)	1.926(3)		
Co-N <sub>axial</sub>	1.892	1.895	1.898	1.911		
Co-N <sub>av</sub>	2.013	2.014	2.019	2.025		
CShMs <sup>a</sup>	2.436	2.436	2.473	2.560		
dihedral angle (deg) <sup>b</sup>	88.367	88.285	88.098	88.193		
$\sum^{c}$	87.45	87.54	88.87	91.32		

<sup>*a*</sup>CShMs: continuous shape measure values. <sup>*b*</sup>Value of the dihedral angle between the least-squares planes defined by the coordinated pyridyl rings of the two Brphterpy ligands. <sup>*c*</sup> $\Sigma$  is the sum of the deviation from 90° of the 12 cis angles of the CoN<sub>6</sub> octahedron.

close to 175° and is almost temperature independent from 120 to 350 K, while it is temperature dependent in 1, ranging between 175.0 and 169.1° from 120 to 400 K (Tables S5 and S6 in the Supporting Information). In addition, the average Co–N bond length (Co–N<sub>av</sub>) increases slowly from 2.013 Å at 200 K to 2.025 Å at 300 K in 1·2H<sub>2</sub>O ( $\Delta$  = 0.012 Å), while it increases abruptly from 2.009 Å at 200 K to 2.085 Å at 300 K in 1 ( $\Delta$  = 0.076 Å) (Tables 1 and 2). These bond lengths are in accordance with the reported values for terpy-based Co<sup>II</sup> SCO complexes.<sup>10,15,16</sup>

To further estimate the structural distortions, the distortion parameters  $\sum$  (the sum of the deviation from 90° of the 12 cis N–Co–N angles) were calculated for both 1·2H<sub>2</sub>O and 1 (Tables 1 and 2). The  $\sum$  values for 1·2H<sub>2</sub>O vary in the range of 86.76–91.32 with  $|\Delta \sum| = 3.81$  (upon cooling from 300 to 200 K) and 3.87 (upon heating from 200 to 300 K). These values are very close to those for the LS Co<sup>II</sup> complexes and suggest a basically LS state of 1·2H<sub>2</sub>O.<sup>10,11</sup> For 1, the  $\sum$  values at 200 and 230 K are around 87, indicating a LS state. Upon an increase in temperature, the  $\sum$  values become obviously larger with  $|\Delta \sum| = 23.53$  (cooling from 300 to 200 K) and 30.09 (heating from 300 to 200 K), reflecting a large structural distortion during the spin transition. The relatively large  $|\Delta \sum|$ values are comparable with those of reported hysteretic Co<sup>II</sup> SCO complexes.<sup>10,15</sup> For example, Hayami and co-workers

## Table 2. Selected Bond Lengths (Å) and Structural Parameters for 1 $\,$

	T (K)				
	300	260	230	200	
	cooling $\rightarrow$				
Co(1)-N(1)	2.098(5)	2.093(5)	2.004(5)	2.000(3)	
Co(1) - N(3)	2.132(5)	2.127(5)	2.012(6)	2.012(3)	
Co(1) - N(4)	2.134(5)	2.113(5)	2.125(5)	2.143(3)	
Co(1) - N(6)	2.134(4)	2.130(5)	2.136(5)	2.140(3)	
Co-N <sub>equatorial</sub>	2.124	2.120	2.069	2.068	
Co(1) - N(2)	1.987(4)	1.957(5)	1.858(5)	1.871(3)	
Co(1) - N(5)	1.981(5)	1.950(5)	1.907(5)	1.925(3)	
Co-N <sub>axial</sub>	1.984	1.954	1.883	1.898	
Co-N <sub>av</sub>	2.078	2.055	2.006	2.015	
CShMs <sup>a</sup>	3.747	3.394	2.404	2.422	
dihedral angle (deg) <sup>b</sup>	84.686	85.018	89.491	89.526	
$\sum^{c}$	110.4	107.8	88.03	86.87	
	<i>T</i> (K)				
	200	230	260	300	
	heating $\rightarrow$				
Co(1)-N(1)	2.004(4)	2.004(5)	2.060(3)	2.115(4)	
Co(1) - N(3)	2.007(5)	2.016(5)	2.010(3)	2.152(4)	
Co(1) - N(4)	2.131(4)	2.124(5)	2.100(2)	2.132(4)	
Co(1) - N(6)	2.139(4)	2.138(5)	2.100(2)	2.135(3)	
Co-N <sub>equatorial</sub>	2.070	2.071	2.070	2.133	
Co(1) - N(2)	1.857(4)	1.856(5)	1.870(2)	1.995(4)	
Co(1) - N(5)	1.915(4)	1.907(5)	1.880(2)	1.980(4)	
Co-N <sub>axial</sub>	1.886	1.882	1.870	1.987	
Co-N <sub>av</sub>	2.009	2.008	2.05	2.085	
CShMs <sup>a</sup>	2.451	2.452	2.586	3.984	
dihedral angle (deg) <sup>b</sup>	89.570	89.496	88.7125	82.339	
$\sum^{c}$	87.45	87.41	93.4	117.54	

<sup>*a*</sup>CShMs: continuous shape measure values. <sup>*b*</sup>Value of the dihedral angle between the least-squares planes defined by the coordinated pyridyl rings of the two Brphterpy ligands. <sup>*c*</sup> $\Sigma$  is the sum of the deviation from 90° of the 12 cis angles of the CoN<sub>6</sub> octahedron.



**Figure 2.** Asymmetric units of  $1\cdot 2H_2O$  (left) and 1 (right). The red and blue arrows represent the dehydration and rehydration process, respectively. The dotted lines indicate the O-H…O and C-H…O hydrogen bonds, which disappear in the dehydrated form. The H atoms have been omitted for the sake of clarity.

recently reported a complex,  $[Co(C14\text{-terpy})_2](BF_4)_2$ ·MeOH, in which the  $\Sigma$  values were 91.6 (LS) and 117.8 (HS) with the

 $|\Delta \Sigma|$  value being 26.2.<sup>10b</sup> In addition, the  $\Sigma(LS)$ ,  $\Sigma(HS)$ , and  $|\Delta \Sigma|$  values were 76.1, 110.8, and 34.7, respectively, in a nonterpy-based Co<sup>II</sup> SCO complex,  $[Co(dpzca)_2]$ , reported by Brooker et al.<sup>11a</sup> All of these above structural parameters clearly indicate that 1 undergoes a hysteretic spin transition, while 1·2H<sub>2</sub>O is a basically LS complex.

Differential Scanning Calorimetry Measurements. To probe the expected SCO transition in  $1\cdot 2H_2O$  and 1, differential scanning calorimetry (DSC) experiments were performed on the ground crystal samples of  $1\cdot 2H_2O$  and 1. For  $1\cdot 2H_2O$ , the DSC curve shows no peaks below 300 K, consistent with the basically LS state of  $1\cdot 2H_2O$  (Figure S2 in the Supporting Information). A broad endothermic peak observed at 375 K is consistent with the loss of water molecules. For 1 (Figure 3), in the first cycle, sharp exothermic



Figure 3. Differential scanning calorimetry (DSC) results of 1, recorded in three cooling and warming cycles with different scan rates of 2 (blue curve), 5 (red curve) and 10 K min<sup>-1</sup> (green curve).

and endothermic peaks were observed at 240 K upon cooling and 271 K upon heating, respectively, at a scan rate of 2 K  $min^{-1}$ . In the second and third cycles with faster scan rates (5 and 10 K min<sup>-1</sup>), the peaks did not change positions in the heating mode but appeared at a slightly higher temperature (246 K) in the cooling mode, generating a stable hysteretic effect of about 25 K. The sharp peaks and the presence of a thermal hysteretic effect indicate the occurrence of a first-order phase transition in 1. The integrated enthalpy and entropy values are  $\Delta H = -8.52$ , -7.79, and -10.16 kJ mol<sup>-1</sup> and  $\Delta S =$ -35.50, -31.66, and -41.30 J mol<sup>-1</sup> K<sup>-1</sup> for the three cycles for the HS to LS transition (cooling). On the other hand for the LS to HS transition,  $\Delta H = 12.79$ , 12.05, and 13.96 kJ  $mol^{-1}$  and  $\Delta S = 47.19$ , 44.46, and 51.51 J  $mol^{-1}$  K<sup>-1</sup> for the three cycles. The values are similar to those obtained for other Co<sup>II</sup> SCO complexes with an abrupt spin transition.<sup>10a</sup> It was noted that the enthalpy changes in the heating mode are larger than those in the cooling mode. This observation might reflect a larger structural change during the SCO in the same temperature range, which is consistent with the larger  $\Delta \Sigma$ value during heating from 200 to 300 K (30.09) in comparison with that (23.53) during cooling. Furthermore, the large entropy change (compared with the  $\Delta S = R \ln[(2S + 1)_{HS}/(2S$  $(+ 1)_{LS}$  = 5.8 J mol<sup>-1</sup> K<sup>-1</sup> for a pure SCO transition from S = 1/2 to 3/2 for a Co<sup>II</sup> center) clearly reveals a considerable contribution from the structure transformation and lattice vibration during the phase transition, which is consistent with the structure analyses.

**Powder XRD Experiments.** Variable-temperature PXRD experiments were further performed to monitor the structural

phase transition (Figure 4. The PXRD patterns of  $1.2H_2O$  were recorded from 300 to 350 K. Then, the sample was



Figure 4. Experimental variable-temperature powder X-ray diffraction patterns (PXRD) from  $1.2H_2O$  to 1, together with the simulated PXRD patterns calculated from the single-crystal structures measured at 300 K. The diffraction data were recorded on a powder sample of  $1.2H_2O$  following the sequential heating–cooling–heating processes (300  $\rightarrow$  400  $\rightarrow$  200  $\rightarrow$  350 K).

further heated to 400 K to generate 1 in situ. As we can see, the PXRD patterns at 300 and 350 K of 1·2H<sub>2</sub>O closely matched the simulated pattern from the single-crystal data, indicating its phase purity. At 400 K, the PXRD pattern differs significantly from those at 300 and 350 K and closely matches the calculated pattern for the dehydrated sample 1, confirming the occurrence of a structural transformation due to dehydration. After that, the PXRD patterns of 1 were then collected on subsequent cooling and heating cycles from 350 to 200 and back to 350 K. Upon cooling from 350 to 250 K, no obvious change in the positions of the peaks was detected. At these HS phases of 1, the powder patterns showed four strong reflections at  $2\theta = 7.4$ , 9.7, 12.8°, and 17°. Upon cooling to 230 K, the spin transition took place and thus a new LS phase of 1 appeared. While the peak at 12.8° splits into two peaks at 13.1 and 13.5°, the other three strong reflections exhibit considerable shifts. These variations reflect a remarkable moving of the crystal lattice. Upon further cooling to 200 K and subsequent heating to 250 K, the powder patterns were almost the same as that at 200 K, suggesting the LS state in this temperature region. Moreover, the pattern of the HS phase was recovered when the complex was warmed to 300 K, confirming the full reversibility of the structural transformation of 1.

**Thermal- and Guest-Induced Spin Transition.** Variable-temperature magnetic susceptibilities were first recorded on a collection of small crystals of  $1\cdot 2H_2O$  under 1 kOe up to 350 K (Figure 5a). For  $1\cdot 2H_2O$ , the  $\chi_M T$  values remain almost constant at 0.45 cm<sup>3</sup> mol<sup>-1</sup> K from 2 to 240 K, which is in accordance with literature values for LS terpy-based Co<sup>2+</sup> complexes.<sup>16</sup> Upon further heating, the  $\chi_M T$  value gradually increases to 1.1 cm<sup>3</sup> mol<sup>-1</sup> K at 350 K, reflecting the basically LS state of  $1\cdot 2H_2O$ . Further heating to 400 K leads to an abrupt increase to 2.4 cm<sup>3</sup> mol<sup>-1</sup> K at 400 K (Figure S3 in the Supporting Information). According to the TGA and DSC data, this final increase should be caused by the dehydration of the sample under dynamic vacuum during the magnetic measurement. Then, the sample was further kept at 400 K for 1 h to obtain the entirely dehydrated phase of 1 and the



Figure 5. (a-c) Variable-temperature magnetic susceptibility data of  $1\cdot 2H_2O$  and 1 measured on the microcrystals (a), powders from the wellground single crystals (b), and a single crystal (c). The red and green data points were obtained by using a settle mode, while the blue and violet data points were recorded by using sweep modes at 2 and 5 K min<sup>-1</sup> scan rates, respectively. (d) Reversible variation of the unit cell volume during the dehydration–rehydration processes and SCO transitions.



Figure 6. Temperature dependence of the crystal lattice parameters of  $1\cdot 2H_2O$  (circles) and 1 (squares): (a) *a* axis; (b) *b* axis; (c) *c* axis; (d) unit cell volume.

magnetic data were recorded further during heating and cooling processes for four cycles with both settle (cycles 1 and 2) and sweep modes (cycles 3 and 4 at 2 and 5 K min<sup>-1</sup> scan rates, respectively).

After dehydration, a singular SCO behavior with a wide thermal hysteresis loop was observed for 1 (Figure 5a). At 300 K, the  $\chi_{\rm M}T$  value of 1 is 2.2 cm<sup>3</sup> mol<sup>-1</sup> K and decreases slowly to 2.0 cm<sup>3</sup> mol<sup>-1</sup> K at 250 K. Below this temperature,  $\chi_{\rm M}T$ shows an abrupt and complete SCO transition centered at  $T_{1/2}\downarrow = 235$  K in the first cooling mode. Upon warming in the heating mode,  $\chi_{\rm M}T$  increases steeply with  $T_{1/2}\uparrow = 267$  K, giving a 35 K apparent thermal hysteresis loop. Notably, this abrupt SCO with a significant hysteresis loop is close to room temperature. To check the stability of the hysteresis, the cooling—heating cycles were repeated three more times using settle and sweep modes with different scan rates (Figure 5a). In the following cycles, the SCO takes place at  $T_{1/2}\downarrow = 250$  K, 15 K higher than that observed in the first cycle, while the  $T_{1/2}\uparrow$  values stay almost the same for all cycles. This observed shrinking of the loop is not uncommon in SCO systems and could be attributed to the change in the size of the crystalline sample during the initial abrupt transition.<sup>12</sup> After the first cycle, the characteristics of the loops were independent of the scan rates, giving a stable hysteresis loop of 20 K width.

In addition, the well-ground sample and one large single crystal (8.90 mg) of 1·2H<sub>2</sub>O were also measured using the same procedure. For the well-ground sample (Figure 5b),  $T_{1/2}\downarrow$  shifts to higher temperatures ( $T_{1/2}\downarrow$  = 249, 251, and 251 K for the three cycles), while  $T_{1/2}\uparrow$  decreases slightly to a lower temperature of 263 K, giving a smaller hysteresis of only 12 K width. For the large single crystal (Figure 5c), an apparent 53 K loop with  $T_{1/2}\downarrow = 207$  and  $T_{1/2}\uparrow = 260$  K was observed in the first cycle, while the stable loop has a width of 34 K ( $T_{1/2}\downarrow$ = 226 and  $T_{1/2}$  = 260 K). The widths of these loops are very large and unusual for the Co<sup>II</sup> SCO complexes with clear structures.<sup>10,17</sup> Moreover, the on-off switching of the hysteretic SCO bistability is fully reversible, as proved by the magnetic measurements on the rehydrated sample (Figure S4 in the Supporting Information). Clearly, the  $\chi_{\rm M}T$  vs T curve of this rehydrated sample is almost the same as that of the original  $1.2H_2O$ . Two successive cooling and warming cycles give two hysteresis loops with different widths of 39 and 19 K.

In addition to this reversible magnetic bistability, the endurance of the reversibility of this compound was further confirmed by the single-crystal X-ray data. Comparing their structures, we noticed that the dehydration triggers a structural transformation from  $1.2H_2O$  to 1 with a ~32 Å<sup>3</sup> decrease in the unit cell volume, while the SCO transition in 1 induces a phase transition with a further larger decrease in the unit cell volume of ca. 53 Å<sup>3</sup>. These distinct changes in the unit cell volume allow us to monitor the dynamic structural transformation via SCXRD (Figure 5d). The reversibility of the structural transformation and SCO transition can be repeatedly detected for at least four times in a single crystal with no apparent loss in crystal integrity. It is noteworthy that other examples showing guest-dependent multicycle reversibility of the spin state have also been reported, <sup>6f,8b,c,17a,18</sup> such as the guest-dependent SCO in a Fe<sup>II</sup>-based metal-organic framework reported by Kepert and co-workers,<sup>18a</sup> and the reversible quantitative guest sensing in a nonporous  $Fe^{II}$  complex reported by Brooker et al.<sup>18d</sup>

Furthermore, the lattice parameters of  $1.2H_2O$  and 1 determined from variable-temperature SCXRD experiments on cooling and heating are plotted in Figure 6 (see details in Tables S7 and S8). For both complexes, the *a* and *c* axes have a positive thermal expansion, while the *b* axes have a negative thermal expansion. From 200 to 300 K, the *a* (*c*) axis expands ~2% (2%) for  $1.2H_2O$  and ~6% (3%) for 1, while the *b* axis shrinks ~3% for  $1.2H_2O$  and ~6% for 1. In addition to the anisotropy of the thermal expansion, the most remarkable difference in the lattice expansion between  $1.2H_2O$  and 1 is the appearance of the thermal hysteresis loops for the lattice parameters of 1. The width of the hysteresis loops for all three axes are ca. 30 K with  $T_{1/2}\downarrow = 250$  K and  $T_{1/2}\uparrow = 280$  K (Figure 6). These anisotropic lattice changes of both  $1.2H_2O$ 

and 1 are in good agreement with their SCO behaviors, indicating the strong coupling of the SCO transition and lattice expansion or contraction.

**Magneto–Structural Correlation.** Careful examination of the intermolecular interactions in both  $1.2H_2O$  and 1revealed the structure–function relationship of the observed properties and the switching of the SCO properties upon dehydration. As depicted in Figures 2 and 7a, the two water



**Figure 7.** (a, b) Change in the hydrogen-bonding interactions between two  $BDS^{2-}$  anions and four water molecules in  $1\cdot 2H_2O$ , which can be broken (b) and reconstructed (a) by dehydration and rehydration. (c, d) Intermolecular  $\pi \cdots \pi$  interactions between pyridines (type A, green; type B, red) and benzene rings (type C, blue) in 1 $\cdot 2H_2O$  and 1, which can be reversibly modified during dehydration–rehydration.

molecules of  $1\cdot 2H_2O$  have rich hydrogen bonds (HBs) between themselves (O7...O8 = 2.862 Å, O7...O8' = 2.993 Å) and their neighbors, including the O atoms of BDS<sup>2-</sup> (O6... O7 = 2.826 Å, O4...O8' = 2.951 Å) and the CH groups of the *L* ligand (O7...H30 = 2.762 Å, O7...H33 = 2.629 Å, O7...H39 = 2.579 Å). Connected by the OH...O HBs, two BDS<sup>2-</sup> anions are linked together by four H<sub>2</sub>O molecules in  $1\cdot 2H_2O$  (Figure 7a). These strong HBs in  $1\cdot 2H_2O$  form a rigid environment of the complex cations and generate the possible internal pressure, which could prevent the expansion of the Co<sup>II</sup> coordination sphere, lock the spin state of  $1\cdot 2H_2O$  in the LS state, and hinder its spin state switching. Removal of the lattice water unlocked these strong HB interactions in 1 (Figure 7b), which leads to a decrease in the internal pressure and stabilizes the HS state. In fact, lattice water molecules are usually able to stabilize the LS state in some Fe<sup>II/III</sup>-based SCO complexes.<sup>5b</sup> For example, lattice water molecules stabilize the LS states via HB to the ligands in the  $[Fe(3-bpp)_2]^{2+}$  hydrates<sup>19</sup> and  $[Fe(H_2bip)_3]^{2+}$  hydrates.<sup>20</sup> Dehydration of these complexes leads to the stabilization of the HS states and SCO behavior.<sup>19,20</sup> Furthermore, other small molecules (i.e., MeCN, acetone, and so on) can also stabilize the LS forms, and HS or hysteretic SCO can be observed after desolvation via SC-SC transformation.<sup>8c,21</sup>

In addition, abundant  $\pi \cdots \pi$  interactions (offset face to face mode) between the complex cations were found in both 1. 2H<sub>2</sub>O and 1 (Figure 7c,d and Tables S9 and S10). The dehydration leads to significant shortening of the  $\pi \cdots \pi$ distances (Figure 7d), which could be favorable for a cooperative spin transition. At 300 K, the crystal packing structure of 1·2H<sub>2</sub>O shows that the neighboring  $[Co(L)_2]^{2+}$ units form rather weak intermolecular  $\pi \cdots \pi$  interactions with parallel-displaced distances of 3.459 Å (type A), 3.521 Å (type B), and 3.771 Å (type C) (Figure 7c and Table S9). Decreasing the temperature to 200 K does not change these weak intermolecular interactions significantly with a change in the  $\pi \cdots \pi$  distances of around 0.03 Å (Table S9). However, upon dehydration, these distances in 1 at 300 K decrease significantly to 3.438, 3.269, and 3.651 Å, respectively (Figure 7d and Table S10). These more effective  $\pi \cdots \pi$  interactions should favor the cooperative spin transition in 1. In addition, these distances increase upon cooling (Table \$10), reaching 3.398 Å (type A), 3.395 Å (type B), and 3.585 Å (type C) at 200 K. In comparison with the 0.03 Å in 1·2H<sub>2</sub>O, the change in  $\pi \cdots \pi$  distances in 1 between 200 and 300 K is quite large (0.08 Å), reflecting the larger structural modification of the structure of 1 due to the hysteretic spin transition.

The observation of the hysteresis loops of both the SCO and lattice parameters in the same temperature region reflects the strong electron-lattice cooperativity and deserves more discussion. Recently, the changes in the lattice parameters and even the shape of macro crystals have been of significant interest. The rotation of the molecular component of the complexes is one of the driving forces. For examples, Sato et al. has demonstrated that the singular anisotropic shape change of the mononuclear Ni<sup>II</sup> and Co<sup>II</sup> complexes can be induced by the rotation of the oxalate molecules and *n*-butyl group, respectivety.<sup>22</sup> By inspecting the crystal structure studies, we attempted to rationalize the possible underlying mechanism of the anisotropic lattice expansion and contraction in 1. Usually, the increases in the molecular volume and bond length of the metal centers are isotropic during a SCO transition. Thus, the anisotropic thermal expansion of the lattice should have some specific reason. As depicted in Figure 8a, we noticed that the N1-Co--N5 bond angle experiences a pronounced decrease from 112.05 to 100.63° during the spin transition from HS to LS in 1, causing the rotation and bending of one of the ligands (Figure 8). Consequently, this SCO-driven ligand rotation and bending leads to the anisotropic expansion and contraction along the b and c axes, as schematically shown in Figure 8b. However, for  $1.2H_2O_1$ , the decrease in the N<sub>1</sub>-Co-N<sub>5</sub> bond angle is very small (101.97 to 100.69° from 300 to 120 K, Table S5), which leads to the quite small variations of its lattice parameters.



Figure 8. (a) Change in the N–Co–N bond angles and the rotation and bending of the ligands during the SCO transition of 1. (b) Schematic drawing of the SCO-driven rotation and bending of the ligands, which leads to the anisotropic thermal expansion.

#### CONCLUSION

In summary, we have presented a reversible on-off switching of the hysteretic spin transition in a mononuclear Co<sup>II</sup> complex through crystal to crystal transformation during dehydration– rehydration. Detailed experiments revealed that the switching of the spin bistability with broad thermal hysteresis loops is realized by a collaborative effect of the elimination of guest internal pressure, the modification of supramolecular interactions, and the strong electron–lattice coupling. This result highlights the significant role of the guest molecules on the turning or switching of the spin bistability.

#### EXPERIMENTAL SECTION

**Materials and Synthesis.** All reagents were commercially available and were used as received without further purification.

*Caution*! Although our samples never exploded during handling, perchlorate metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with great care.

**Synthesis of the Ligand L.** The powder of the starting material 4'-(4-bromophenyl)-2,2':6',2"-terpyridine (L) was synthesized by the reaction of 4-bromobenzaldehyde (0.01 mol, 1.85 g), 2-acetylpyridine (0.02 mol, 2.42 g), KOH (0.055 mol, 3.08 g), and ammonia (60 mL, 25%) in ethanol (100 mL) under reflux for 1 day. The crude white product has poor solubility in common organic solvents and was purified by Soxhlet extraction into chloroform (200 mL). Yield: 1.7 g, ca. 45%. Anal. Calcd for C<sub>21</sub>H<sub>14</sub>BrN<sub>3</sub>: C, 64.96; H, 3.63; N, 10.82. Found: C, 64.91, H, 3.71; N, 10.78. <sup>1</sup>H NMR spectra: Figure S5 in the Supporting Information.

Synthesis of  $[Co(L)_2](CIO_4)_2$ ·3DMF. The *L* ligand (380 mg, 1 mmol) was dissolved in 30 mL of DMF and heated to boiling. A 10 mL portion of a water solution of  $Co(CIO_4)_2$ ·6H<sub>2</sub>O (180 mg, 0.5 mmol) was added to the above boiling solution. After heating for 10

min, the mixed dark red solution was filtered into a 50 mL beaker and kept in the dark. Dark red single crystals were obtained after slow evaporation for 2 weeks. Anal. Calcd for  $C_{51}H_{49}Br_2Cl_2CoN_9O_{11}$ : C, 48.86; H, 3.94; N, 10.05. Found: C, 48.81, H, 3.41; N, 10.08.

**Synthesis of [Co(L)<sub>2</sub>][BDS]·2H<sub>2</sub>O (1·2H<sub>2</sub>O).** A solution of  $[Co(L)_2](ClO_4)_2$ ·3DMF (200 mg) in 60 mL of MeCN was mixed with a 20 mL water solution of Na<sub>2</sub>BDS (2 mmol, 564 mg, H<sub>2</sub>BDS = benzene-1,3-disulfonic acid). After heating for 5 min, the dark red solution was cooled to room temperature and filtered. Dark red single crystals of 1·2H<sub>2</sub>O were obtained after slow evaporation for 4 days. Yield: 150 mg (ca. 65%). Anal. Calcd for C<sub>48</sub>H<sub>36</sub>Br<sub>2</sub>CoN<sub>6</sub>O<sub>8</sub>S<sub>2</sub>: C, 52.04; H, 3.27; N, 7.58. Found: C, 51.96, H, 3.48; N, 7.68.

**Synthesis of** [Co(L)<sub>2</sub>][BDS] (1). For single-crystal X-ray diffraction measurements, a single crystal of 1 was obtained by heating a single crystal of  $1\cdot 2H_2O$  in the diffractometer under a dry N<sub>2</sub> flow from 300 to 400 K at a heating rate of 3 K min<sup>-1</sup> and further annealing at 400 K for 1 h. For magnetic measurement, the well-ground crystals of  $1\cdot 2H_2O$  were heated at 400 K in the dynamic vacuum chamber of a SQUID VSM instrument for 2 h. For other physical measurements, a fresh sample of 1 was prepared by heating the sample of  $1\cdot 2H_2O$  at 400 K under a dynamic vacuum for 2 h. Anal. Calcd for C<sub>48</sub>H<sub>32</sub>Br<sub>2</sub>CoN<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: C, 53.79; H, 3.01; N, 7.84. Found: C, 53.61, H, 3.18; N, 7.74.

Synthesis of the Rehydrated  $[Co(L)_2][BDS]\cdot 2H_2O$  (1·2H<sub>2</sub>O-re). The samples of 1 were exposed at room temperature to air atmosphere for 1 day. Anal. Calcd for  $C_{48}H_{36}Br_2CoN_6O_8S_2$ : C, 52.04; H, 3.27; N, 7.58. Found: C, 51.91, H, 3.34; N, 7.62.

**Physical Measurements.** Elemental analyses for C, H, and N were measured on an Elementar Vario MICRO analyzer. PXRD measurements were recorded at various temperatures on a Bruker D8 Advance diffractometer with Cu K $\alpha$  X-ray source ( $\lambda = 1.54056$  Å) operated at 40 kV and 40 mA. TGA was measured in Al<sub>2</sub>O<sub>3</sub> crucibles using a PerkinElmer Thermal Gravimetric Analysis instrument in the temperature range of 20–700 °C under N<sub>2</sub> flow at a heating rate of 20 °C/min. DSC was performed using a Mettler Toledo DSC1 differential scanning calorimeter. Magnetic measurements were measured under a dc field of 1 kOe with a Quantum Design VSM magnetometer. The experimental data were corrected for the diamagnetic contribution to the magnetic susceptibility by means of Pascal's constants.

X-ray Crystallography. SCXRD data were collected on a Bruker D8 Venture diffractometer with a CCD area detector (Mo K $\alpha$ radiation,  $\lambda = 0.71073$  Å) at various temperatures. The APEX<sup>II</sup> 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.<sup>23</sup> Absorption corrections were applied with SADABS.<sup>24</sup> The structures were solved by direct methods and refined by full-matrix least-squares methoda on  $F^2$  using the SHELXTL crystallographic software package.<sup>25</sup> All of the nonhydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding nonhydrogen atoms. Additional details of the data collections and structural refinement parameters are provided in Tables S1-S4. CCDC 1889167-1889174, 1889176-1889181, 1889184, 1889186-1889188, and 1910380-1910383 are the supplementary variabletemperature crystallographic data for 1.2H2O and 1, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01436.

Crystallographic data and additional figures and tables X-ray crystallographic data for **1·2H<sub>2</sub>O** at 300, 260, 230, 200, and 120 K in cooling order, X-ray crystallographic

data for  $1.2H_2O$  at 200, 230, 260, 300, 320, and 350 K in heating order, X-ray crystallographic data for 1 at 400, 350, 300, 260, 230, 200, aand 120 K in cooling order, and X-ray crystallographic data for 1 at 200, 230, 260, 300, and 350 K in heating order (PDF)

#### Accession Codes

CCDC 1889167–1889174, 1889176–1889181, 1889184, 1889186–1889188, and 1910380–1910383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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