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Abrupt spin transition in a modified-terpyridine cobalt(II) complex with a highly-distorted  $[CoN_6]$  core

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The cobalt(II) complex incorporating  $\pi$ -conjugated substituent, [Co(Naph-C2-terpy]<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**1**; Naph-C2-terpy = 4'-(2-naphthoxy(ethoxy))-2,2':6',2''-terpyridine), exhibits an abrupt spin transition (ST) behavior (cooperative factor *C* = 0.91) while its solvated product, **1**·2MeOH, shows gradual spin crossover (SCO) behavior (*C* = 0.49). Single crystal X-ray structural analyses demonstrated that the octahedral coordination core [CoN<sub>6</sub>] in **1** shows larger distortion in both high-spin and low-spin states than solvated **1**·2MeOH or another two derivatives, [Co(R-terpy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (R = 2-naphthyl (**2**), 9-anthracenyl (**3**)). The respective distortion parameters ( $\Sigma$ ) are compared with those for previously reported SCO cobalt(II) compounds. The highly-distorted [CoN<sub>6</sub>] core in **1** ( $\Sigma$  = 126 in the HS state and 101.6 in the LS state) was stabilized by strong intermolecular interactions and observed an abrupt ST behaviour.

terpyridone)<sub>2</sub>]( $CF_3SO_3$ )<sub>2</sub>· $H_2O$ ,<sup>[19]</sup>

## Introduction

Molecular compounds exhibiting spin state changes of their metal centres (termed spin crossover (SCO) or spin transition (ST) compounds) have attracted much attention because of the bistability in their magnetic, optical and structural properties. They have been widely investigated for potential application as sensors and memory devices in molecular electronics.<sup>[1-3]</sup> Up to now, numerous SCO compounds incorporating  $d^n$  (n = 4–7) transition metal ions have been reported. In particular, iron(II) SCO compounds have been well-studied because the 3d<sup>6</sup> electron state in iron(II) yields significant differences in properties between the diamagnetic low-spin (LS, S = 0) and paramagnetic high-spin (HS, S = 2) states, with both abrupt (cooperative factor  $C \approx 1$ ) and hysteretic ST behaviour (C > 1) being reported.<sup>[4-7]</sup> In contrast to iron(II) compounds, reports discussing SCO behaviour for mononuclear cobalt(II) compounds are guite limited, reflecting the difficulties in achieving suitable molecular design for cobalt(II) complexes that exhibit abrupt ST behaviour,<sup>[8]</sup> rather than gradual or incomplete SCO behaviour.<sup>[9-15]</sup> To the best of



However, the degree of distortion in the octahedral cores has rarely been discussed when investigating SCO behaviour even though intermolecular interactions producing cooperativity would be expected to influence the distortions occurring in cores.

our knowledge, mononuclear cobalt(II) compounds of only

seven ligand designs (as well as some of their derivatives) have been shown to generate complete and abrupt or hysteretic ST

behaviours.<sup>[16-22]</sup> Further, detailed investigations of magneto-

structural relationships have been performed for the following

complexes<sup>§</sup>: Ar'CoN(H)Ar<sup>#</sup>,<sup>[17]</sup> [Co(C14-terpy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>[18b]</sup> [Co(4-

 $[Co(pyterpy)_2](PF_6)_2 \cdot 2CH_3OH^{[21]}$  and  $Co(Cl_2Gm)_3(Bn-C_{16}H_{33})_2$ .<sup>[22]</sup>

For example, Brooker and co-workers reported a mononuclear

cobalt(II) complex incorporating the dpzca ligand, which

showed abrupt and hysteretic ST behaviour.<sup>[20]</sup> This neutral

compound has no uncoordinated counter anions or lattice

solvents, and shows a transformation of crystal systems by ST

between HS and LS states. Our group has reported hysteretic

and reverse ST behaviour by the cobalt(II) complex, [Co(C14-

[Co(dpzca)<sub>2</sub>],<sup>[20]</sup>

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Crystallographic data, experimental, TGA measurements and additional magnetic properties. CCDC numbers: 1589729–1589734. For ESI and crystallographic data in CIF or another electronic format, see DOI: 10.1039/x0xx00000x

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In this study, we report the thermally-induced, reversible, complete and abrupt ST behaviour of a new cobalt(II) complex,

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	<b>1</b> ·2MeOH @100K	<b>1</b> ·2MeOH @273K	<b>1</b> @93K	<b>1</b> @200K	2·2CHCl <sub>3</sub> @100K	<b>3</b> ·2.5MeOH @100K
Co-N1 (Å)	2.033(2)	2.105(6)	2.001(5)	2.114(4)	2.051(4)	1.991(2)
Co-N2 (Å)	1.888(2)	1.966(4)	1.901(5)	2.019(3)	1.888(4)	1.873(2)
Co-N3 (Å)	2.037(2)	2.117(5)	2.008(5)	2.167(3)	2.062(4)	2.001(2)
Co-N4 (Å)	2.132(2)	2.103(4)	2.168(5)	2.149(4)	2.103(4)	2.133(2)
Co-N5 (Å)	1.921(2)	1.965(4)	1.962(5)	2.032(3)	1.910(4)	1.932(2)
Co-N6 (Å)	2.123(2)	2.126(5)	2.171(5)	2.160(3)	2.096(4)	2.133(2)
					0.0	

Table 1Co-N distances in 1.2MeOH, 1, 2.2CH2Cl2 and 3.2.5MeOH

 $[Co(Naph-C2-terpy)_2](BF_4)_2$  (**1**; Naph-C2-terpy = 4'-(2-naphthoxy(ethoxy))-2,2':6',2"-terpyridine), incorporating  $\pi$ -conjugated substituents. Solvated **1**, **1**-2MeOH, also showed complete but more gradual SCO behaviour than occurs for unsolvated **1**. In both cases, the crystal structures of their HS and LS states were obtained, clearly demonstrating their structural transformation on undergoing SCO. **1** incorporates a

highly-distorted coordination geometry for each  $[CoN_6]$  core, giving rise to higher cooperativity. We were able to corroborate cooperativity of the SCO behaviour and distortion

of the [CoN6] cores by preparing a further seven derivative cobalt(II) complexes of types  $[Co(R-terpy)_2](BF_4)_2$  (R = 2-naphthyl (2), 9anthracenyl (3)) and  $[Co(Naph-Cn-terpy)_2](BF_4)_2$  (n = 4 (4), 6 (5), 8 (6), 10 (7), 12 (8)) and investigating their SCO behaviour as well as also obtaining their crystal structures.

### **Results and discussion**

Crystal structures. Complex 1.2MeOH was prepared by reaction of Naph-C2-terpy with Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeOH (see experimental section in supporting information, SI) and recrystallizing the initial product from methanol-acetone (v/v = 1:3) to yield single crystals of 1.2MeOH. 1.2MeOH was characterized by elemental analysis and single crystal X-ray diffraction (SXRD) measurements. The SXRD determination for 1.2MeOH was performed at 100 K and 273 K. 1.2MeOH crystalizes in the triclinic space group P-1. Two Naph-C2terpy ligands coordinate to the cobalt(II) metal centre meridionally to yield a  $N_6$  donor set. The crystal structure of 1.2MeOH is displayed in Figure 1. At 100 K, a Jahn-Teller distortion, as expected for cobalt(II) ions, was observed to yield a tetragonally distorted coordination environment for the  $[CoN_6]$  core, with the cobalt(II) to apical pyridine donors (N4 and N6) bonds being elongated relative to those occupying the equatorial positions (Table 1). Crystal parameters and the packing structure of 1.2MeOH are given in Table S1 and Figures 2(a) and 2(b), with full structural data available from the CCDC.<sup>[28]</sup>



**Figure 1.** Molecular structure of **1**·2MeOH. Counter anions, H atoms, and solvent molecules are omitted for clarity. Colour code: Co; magenta, C; grey, N; blue, O; red.

Molecules of 1·2MeOH are assembled via  $\pi$ - $\pi$  interactions along the *a* axis. Lattice MeOH molecules are incorporated by intermolecular interactions with naphthalene substituents and terpyridine cores. These MeOH were found to be removed by heating up to 340 K, confirmed by thermogravimetric analysis (TGA) (Figure S1). 1·2MeOH showed a single-crystal to singlecrystal (SCSC) transformation on standing its crystal at 80 °C for 30 min. A single crystal of the de-solvated product 1 was used for SXRD measurements which were carried out at 93 K and 200 K. Unlike 1·2MeOH, 1 crystallizes in the monoclinic system  $P2_1/n$ . The crystal packing for 1 is shown in Figures. 2(b) and 2(c), which indicates that the complex units are assembled via intermolecular  $\pi$ - $\pi$  and CH- $\pi$  interactions.

We have also synthesized cobalt(II) complexes incorporating  $\pi$ conjugated naphthyl and anthracenyl substituents rather than alkyl chains.  $[Co(R-terpy)_2](BF_4)_2$  (R = 2-naphthyl (2), 9anthracenyl (3)) were prepared by reacting the corresponding R-terpy ligand with Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeOH–CHCl<sub>3</sub>, resulting in microcrystalline precipitates. Single crystals of 2.2CHCl3 and 3.2.5MeOH were obtained by recrystallization of the initial products from dichloromethane and methanol, respectively (see Experimental section in SI). These complexes were characterized by elemental analyses and SXRD measurements. The X-ray structures and corresponding molecular assemblies are displayed in Figures. S2 and S3. The crystal parameters for the compounds are given in Table S2. 2.2CHCl<sub>3</sub> assembles through CH- $\pi$  interactions and  $\pi$ - $\pi$  interactions resulting in 3-D assembly networks. 3.2.5MeOH forms 2-D assembly networks via  $\pi - \pi$  interactions.

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**Figure 2.** Molecular assembly of  $1 \cdot 2$ MeOH: (a) view along the *ac* plane. Counter anions are omitted for clarity. (b) Intermolecular interactions involving lattice MeOH molecules. Molecular assembly of **1**: (c) view along the *ac* plane. (d) Intermolecular interaction networks. Counter anions are omitted for clarity. Color code: Co; magenta, C; grey, N; blue, O; red. Blue-dashed lines indicate intermolecular interactions.

**Magnetic behaviours.** The SCO behaviours of single crystals of **1**, **1**·2MeOH, **2**·2CHCl<sub>3</sub> and **3**·2.5MeOH were investigated employing a Superconducting Quantum Interference Device (SQUID) using sweep mode and scan rate of 5 K min<sup>-1</sup> (Figure 3). Magnetic susceptibilities are displayed by  $\chi_m T$  versus Tcurves, where  $\chi_m$  is the molar magnetic susceptibility and T is the temperature. The  $\chi_m T$  value of **1** at 5 K, 0.46 cm<sup>3</sup> K mol<sup>-1</sup> is consistent with the presence of LS cobalt(II) in an octahedral coordination environment.<sup>[18a]</sup> Upon heating, an abrupt ST occurred at  $T_{1/2} = 124$  K. The  $\chi_m T$  value increased to 2.26 cm<sup>3</sup> K mol<sup>-1</sup> at 400 K which is in accord with the expected HS state for cobalt(II) ion. We confirmed no scan rate dependency on the View Article Online DOI: 10.1039/C8DT02367K ARTICLE

ST behaviour by measuring several cycles of the  $\chi_m T$  versus T plot with scan rates of 2 K min<sup>-1</sup>, 1 K min<sup>-1</sup> and 0.5 K min<sup>-1</sup>, where each  $\chi_m T$  plot versus T traced the result obtained for the 5 K min<sup>-1</sup> measurement (Figure S4). The cooperative factor C for **1** was estimated to be 0.91 using the fitting of the regular solution model to the experimental  $\chi_m T$  plots (See experimental section).<sup>[29]</sup> This value is high enough to produce abrupt ST behaviour. In comparison, **1**-2MeOH exhibited more gradual SCO behaviour than **1** which is in accord with the C value of 0.49.



**Figure 3.** Magnetic behaviours of (a) 1.2MeOH (triangle plots) and 1 (circle plots), (b) 2.2CHCl<sub>3</sub>, and (c) 3.2.5MeOH for the heating (red) and cooling (blue) processes.

This abrupt ST behaviour observed for **1** was further investigated by a differential scanning calorimetry (DSC) measurement by thermal treated sample of **1** at 400 K for 1 h to remove lattice solvent molecules. The DSC curve was obtained for 100 K to 293 K with a scan rate of 5 K min<sup>-1</sup>. During the heating process (Figure 4), an endothermic peak was observed at around 116 K, which agrees with the  $T_{1/2}$  for the ST. During the cooling process, an exothermic peak was observed around 130 K, confirming that the phase transition in **1** occurs reversibly.



Figure 4. DSC curves for 1. Red and blue lines correspond to heating and cooling processes, respectively.

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Figure 5. Views illustrating the terpyridine-cobalt molecule of

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Σ@LS	<i>Σ@</i> HS	ΔΣ	φ@LS	φ@HS	$\Delta \varphi$	Magnetic behaviour	$Tc^{\uparrow}$	Reference	
101.6	126.0	24.4	174.4	170.5	3.9	Abrupt No hysteresis	100 K	This work (1)	
89.2	105.7	16.5	175.2	174.7	0.5	Gradual	116 K	This work (1·2MeOH)	
87.6	-	-	175.7	-	-	Gradual	180 K	0 K This work ( <b>2</b> ·2CHCl <sub>3</sub> )	
86.6	-	-	177.2	-	-	Gradual	250 K	This work ( <b>3</b> ·2.5MeOH)	
90	117	27	178.3	178.2	0.1	Gradual	150 K	[Co(terpy) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> <sup>[14]</sup>	
91.6	117.8	26.2	175.8	173.3	2.5	Abrupt Hysteresis	50 K	[Co(C14terpy) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ·MeOH <sup>[20b]</sup>	
92.8	119.4	26.6	179.2	175.9	3.3	Abrupt Hysteresis	175 K	$[Co(terpyridone)_2](CF_3SO_3)_2 \cdot H_2O^{[21]}$	
76.1	110.8	34.7	178.1	180	1.9	Abrupt Hysteresis	170 K	[Co(dpzca) <sub>2</sub> ] <sup>[22]</sup>	
91.7	116.1	24.4	178.6	180	1.4	Abrupt Hysteresis	190 K	$[Co(pyterpy)_2](PF_6)_2 \cdot 2MeOH^{[23]}$	
The ym	T versus 7	plots for	r 2.2CHCl	and 3.2.5	MeOH a	re shown (a) <b>1</b> ·2MeO	H and (b)	1 in the LS (blue) and the HS (red) state	

The  $\chi m T$  versus T plots for 2·2CHCl<sub>3</sub> and 3·2.5MeOH are shown in Figures 3(b) and 3(c). 2·2CHCl<sub>3</sub> is in the LS state at 100 K with a  $\chi_m T$  value of 0.39.  $\chi_m T$  then gradually increases to 1.73 cm<sup>3</sup> K mol<sup>-1</sup> at 400 K; this is an expected value for a HS cobalt(II) ion. 3·2.5MeOH was also found to be in the LS state at 100 K, but even at 400 K the value was only 0.74 cm<sup>3</sup> K mol<sup>-1</sup>, with this compound showing incomplete gradual SCO behaviour. The  $\chi_m T$  plots for the cooling process followed the same trace as found for the heating process, indicating no effect of lattice solvents on SCO behaviour. The cooperative factors for these derivatives estimated from the gradual SCO behaviours are 0.37 for 2·2CHCl<sub>3</sub> and 0.24 for 3·2.5MeOH, which are smaller than the value for **1**.

In order to investigate the influence of the length of the appended alkyl chain on the magnetic properties of complexes of the present type, the series of complexes given by  $[Co(Naph-Cn-terpy)_2](BF_4)_2$  (n = 4 (4), 6 (5), 8 (6), 10 (7), 12 (8)) were synthesized, and the corresponding susceptibility measurements were performed for the powder samples. Complexes 4 - 8 each show no cooperative effect but display gradual SCO behaviour over the temperature range 5 – 400 K (Figure. S5).

**Discussions.** We further investigated the resultant ST behaviour in terms of the distortions occurring in the octahedral environment of the cobalt(II) centres in the LS and HS states. A terpyridine-cobalt molecule of **1** shows larger structural changes associated with the spin state changes than **1**·2MeOH (Figure 5, Figure S6).



For the detailed assessment of spin state-dependent structural distortions of [CoN6] cores, the distortion parameters  $\Sigma$  and  $\varphi$ were calculated; where  $\Sigma$  is the sum of  $|90-\alpha|$  for the twelve angles of *cis*-N-Co-N and  $\varphi$  is the inter-ligand angles for *trans*-N-Co-N.  $^{[25,26]}$  A perfectly octahedral structure gives  $\varSigma$  = 0 and  $\varphi$ = 180. The  $\Sigma$  and  $\varphi$  values for **1**·2MeOH – **3**·2.5MeOH together with the values for previously reported compounds are listed in Table 2 and Figure 6. The solvated compound 1.2MeOH gave the distortion parameters  $\Sigma$  = 89.2 (LS) and 105.8 (HS), which are both close to the values of the other the SCO cobalt(II) complexes listed. The distortion parameters  $\Sigma$  at 100 K are 87.6 and 86.6 for  $2 \cdot 2$ CHCl<sub>3</sub> and  $3 \cdot 2.5$ MeOH, respectively. These values are also close to the usual  $\Sigma$  values for the LS state of SCO compounds. On the other hand, the desolvated compound 1 was found to be more distorted both in the HS and LS states, with a  $\Sigma$  value for **1** in the HS state of 126 and 101.6 in the LS state, which are both significantly higher than those of the other SCO compounds. It is noteworthy that the  $\Delta\Sigma$  value for **1** is 24.4 and is a typical  $\Delta\Sigma$  value observed for SCO cobalt(II) compounds. The  $\varphi$  for **1** in the HS state is 170.5, which is smaller than the values for the other compounds listed. Nevertheless, this value corresponds to a substantial distortion of the  $[\text{CoN}_6]$  core in 1.  $[\text{Co}(dpzca)_2]$  reported by Brooker and co-workers  $^{[20]}$  shows a smaller  $\varSigma$  value (76.1) in the LS state likely reflecting that the dpzca ligand contains no complicating substituents and is more flexible than the terpy ligand. Further, this compound does not contain counter anions which might also affect its core structure.

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**Figure 6.** Relationship between the distortion parameters,  $\Sigma$  and  $\varphi$ , for **1**·2MeOH and **3**·2.5MeOH, as well as for the previously reported compounds listed in their LS (blue) and the HS (red) states.

These results indicate that the removal of the lattice methanol solvents from  $1\cdot 2$ MeOH leads to an increase in the structural distortion of the [CoN<sub>6</sub>] cores and, at the same time, increasing the cooperativity for SCO behaviour. On removing the lattice methanol molecules, the Co–Co centres become closer by about ~0.9 Å (from 8.923 Å to 8.045 Å), in accord with stronger intermolecular interaction being present in 1 than in  $1\cdot 2$ MeOH. Stronger intermolecular interaction might be expected to help stabilize the highly-distorted [CoN<sub>6</sub>] cores as well as to increase the cooperativity to produce the resultant observed abrupt ST behaviour.

## Conclusions

The present results are in keeping with the highly distorted core of  $[CoN_6]$  in  $[Co(Naph-C2-terpy)_2](BF_4)_2$  (1) resulting in enhanced intermolecular interaction leading to abrupt ST behaviour. We have demonstrated that a single-crystal-tosingle-crystal transformation occurs on removal of the lattice solvent from 1.2MeOH to form the above de-solvated product 1. The crystal structures of 1 and 1.2MeOH were determined in both their HS and LS states and showed that he presence of the lattice solvents in 1.2MeOH results in a reduction of the distortion of the [CoN<sub>6</sub>] core. This influences the observed SCO behaviour due to the presence of lower cooperativity and, in turn, is reflected by 1.2MeOH displaying gradual SCO behaviour - contrasting with the abrupt SCO found for 1. Overall, the present study gives new insights for the better understanding of the magneto-structural correlations in SCO compounds.

## **Conflicts of interest**

There are no conflicts to declare.

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## Notes and references

 $\begin{bmatrix} Co(pyterpy)_2 \end{bmatrix} (PF_6)_2 \cdot 2CH_3OH \quad (pyterpy) = 4'-(4'''-pyridyl) \\ 2,2':6',2''-terpyridine \end{bmatrix}^{[21]} \text{ and } Co(Cl_2Gm)_3(Bn-C_{16}H_{33})_2 \quad (Cl_2Gm = dichloro-glyoxime dianion, Bn-C_{16}H_{33} = n-hexadecyl boron). \\ \begin{bmatrix} 122 \\ 2 \end{bmatrix} \\ & \text{Abbreviations: } [Co(terpy)_2](BF_4)_2 \quad (terpy = 2,2':6',2''-terpyridine), \\ \begin{bmatrix} 122 \\ 122 \end{bmatrix} [Co(terpyR8)_2](ClO_4)_2 \quad (terpyR8 = 4''-Octoxy-2,2': 6',2''-terpyridine). \\ \end{bmatrix}$ 

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**Dalton Transactions Accepted Manuscript** 



The cobalt(II) complex  $[Co(Naph-C2-terpy)_2](BF_2)_2 \cdot 2MeOH$  (1·2MeOH) showed single crystal to single crystal transition, resulted in its desolvated product of 1. Complex 1 incorporating a highly distorted [CoN6] core was found to exhibit abrupt spin transition behavior, unlike 1·2MeOH, which showed gradual spin crossover behavior.