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Reversible Switching of a Cobalt Complex by Thermal, Pressure, and Electrochemical Stimuli: Abrupt, Complete, Hysteretic Spin Crossover

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S Supporting Information

ABSTRACT: Triply switchable [Co^{II}(dpzca)$_2$] shows an abrupt, reversible, and hysteretic spin crossover ($T_{1/2}\downarrow$ = 168 K, $T_{1/2}\uparrow$ = 179 K, and $\Delta T_{1/2}$ = 11 K) between the high-spin (HS) and low-spin (LS) states of cobalt(II), both of which have been structurally characterized. The spin transition is also reversibly triggered by pressure changes. Moreover, in a third reversible switching mechanism for this complex, the magnetic properties can be switched between HS cobalt(II) and LS cobalt(III) by redox.

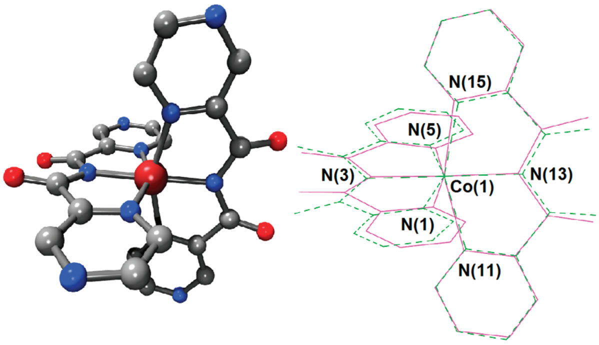

Figure 1. Crystal structure of **1** at 298 K (left) and overlaid with the structure at 90 K (right, green dashed lines); 90 K structure in pink solid lines, with the atoms used in the fit labeled.

The bistability offered by spin-crossover (SCO) complexes has resulted in sustained research interest due to potential applications in molecular electronics.[1] SCO has been observed for d^4−d^7 transition metal ions, with iron(II) complexes the most common.[2]

In contrast, cobalt(II) SCO complexes are less common[2a,3] and in general give gradual and incomplete thermally induced SCO.[2a,4] The few examples of complete and hysteretic SCO for cobalt(II) are mononuclear complexes of ligands derived from bi-/terpyridine,[5] amido-aryl ligands,[6] 4-terpyridone,[7] or 3-formylsalicylic acid[8] (Figure S1). In hysteretic SCO, $T_{1/2}$ (the temperature at which there is 1:1 high-spin (HS):low-spin (LS) ratio) depends on whether the sample is being cooled ($T_{1/2}\downarrow$) or heated ($T_{1/2}\uparrow$). Only three of these complexes are structurally characterized. Of those, the most abrupt SCO ($T_{1/2}\downarrow$ = 221 K and $T_{1/2}\uparrow$ = 229 K; $\Delta T_{1/2}$ = 8 K) involves the quasi-two-coordinate HS complex [Co^{II}(Ar)(NHAr′)] increasing coordination number due to strengthening of the Co-η^6-arene interaction on going to LS.[6] The other two systems, [Co^{II}(C14-terpy)$_2$](BF$_4$)$_2$·H$_2$O and [Co^{II}(4-terpyridone)$_2$](CF$_3$SO$_3$)$_2$·H$_2$O, undergo more complex SCO, involving two HS states. In the former, a phase change from the initial HS state to a second HS state occurs via an incomplete hysteretic spin transition ($T_{1/2}\uparrow$ = 184 K, $T_{1/2}\downarrow$ = 206 K; $\Delta T_{1/2}$ = 22 K) before a nonhysteretic, abrupt, and complete transition to the LS state occurs at $T_{1/2}$ = 50 K.[5b] In the latter, a gradual decrease in magnetic moment is observed from 300 to 217 K, followed by a hysteretic transition to a second HS state ($T_{1/2}\uparrow$ = 217 K, $T_{1/2}\downarrow$ = 225 K; $\Delta T_{1/2}$ = 10−12 K) and then a hysteretic transition to the LS state ($T_{1/2}\downarrow$ = 155.6 K, $T_{1/2}\uparrow$ = 188.5 K; $\Delta T_{1/2}$ = 32.9 K).[7]

In contrast to iron(II),[9] there are few reports of pressure-induced SCO for cobalt(II).[2a] Infrared studies on five-coordinate complexes of diphenylphosphinoamine-based ligands show gradual, incomplete SCO above 1 GPa.[10] Near-edge X-ray absorption studies of octahedral complexes of 3-formylsalicylic acid[11] or tris(pyrazolyl)borate[12] based ligands under pressure revealed SCO that was gradual but more complete than when thermally induced. High pressures (6.5−9.0 GPa) induced SCO in HS complexes that did not undergo thermal SCO.[11]

Here we report the neutral, mononuclear complex [Co^{II}(dpzca)$_2$] (**1**, Figure 1) that, unlike the pyrazine−pyridine imide analogue [Co^{II}(pypzca)$_2$] which remains HS to 4 K,[13] displays thermally induced reversible, complete, abrupt, and hysteretic SCO. We also show that applying pressure reversibly induces SCO at 298 K. Complex **1** also displays a reversible oxidation to diamagnetic cobalt(III), thus offering a third method of reversibly altering the magnetic susceptibility, in this case between three unpaired electrons in HS cobalt(II) and none in LS cobalt(III).

[Co^{II}(dpzca)$_2$] (**1**) is readily prepared (Supporting Information (SI)). It is insoluble, or poorly soluble, in all common solvents (Table S1), which is ideal for producing a stable and robust material in good yield. Other key advantages of **1** over most SCO materials are that it has no uncoordinated anions and is solvent-free. Like HS [Co^{II}(pypzca)$_2$],[13] **1** crystallizes in the tetragonal space group $I4_1/a$ at 298 K (Table S2), and the asymmetric unit contains just a quarter of **1**. The two terdentate dpzca$^-$ ligand strands are each coordinated to the cobalt(II)

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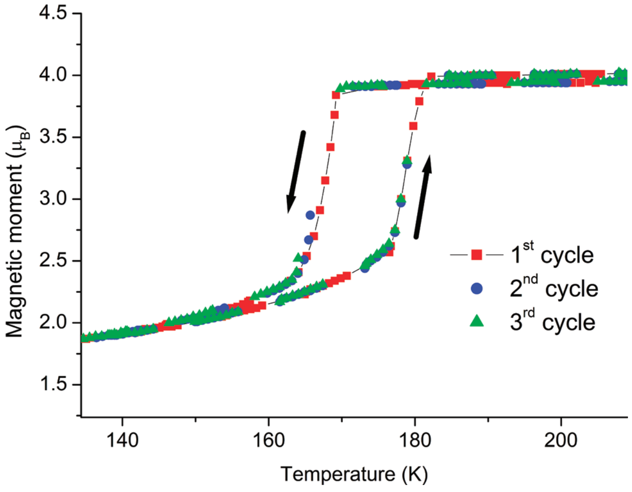

Figure 2. Temperature dependence (at a sweep rate of 5 K min^{-1}) of the magnetic moment of a powder sample of **1** over three consecutive cycles reveals the reversibility of the hysteresis loop. Note that the solid lines simply join the data points.

center meridionally, through one imide (Co−N3 = 2.049(3) Å) and two pyrazine (Co−N1 = 2.145(3) Å) nitrogen donors, at a bite angle of 77.51(7)° (Figure 1, Figure S3, Table S4). At 90 K, the space group is monoclinic $P2_1/c$, with the entire complex in the asymmetric unit (Figure 1, Figure S4, Table S3). As expected for a cobalt(II) center in the LS state, it is Jahn−Teller distorted: the four equatorial bonds are considerably shorter ($\mathrm{Co{-}N_{imide}}$: N3 = 1.91(1), N13 = 1.94(1) Å; $\mathrm{Co{-}N_{pyrazine}}$: N1 = 1.99(1), N5 = 1.97(1) Å) than the apical positions ($\mathrm{Co{-}N_{pyrazine}}$: N11 = 2.19(1), N15 = 2.20(1) Å), and the average bite angles for the N1 and N11 ligands, 82.6 and 79.7° respectively, are closer to 90° (Figure S4, Table S5). This Jahn−Teller axial elongation confirms that the observed magnetic behavior is due to SCO rather than valence tautomerism (cobalt(II)-ligand ↔ cobalt(III)-radical anion ligand).[14]

In contrast to the symmetrical contraction usually seen in iron(II) SCO systems, SCO in **1** induces a Jahn−Teller-influenced change from compressed (T = 1.05 at 298 K) to elongated (T = 0.89 at 90 K) octahedral coordination[15] of cobalt(II), accompanied by an 11% decrease in the volume of the coordination sphere (Table S6). In other words, on cooling the Jahn−Teller effect causes contraction in one plane and a slight elongation perpendicular to this. This results in significant changes to the intermolecular packing interactions (these are detailed in the SI, including Figures S5−S16 and Tables S7 and S8) and a crystallographic phase change.

The observed and calculated powder X-ray diffraction patterns at 298 K match well (Figure S17), confirming that the powder has the same structure as the single crystals. Variable-temperature magnetic susceptibility measurements were performed on **1** (Figures 2 and S18).

At 300 K, the χT product of 2.0 $\mathrm{cm^3\ K\ mol^{-1}}$ (4.0 μ_B) is consistent with HS cobalt(II) in an octahedral environment.[16] Upon cooling, an abrupt spin transition with $T_{1/2}{\downarrow}$ = 168 K is observed. At 50 K the χT is 0.35 $\mathrm{cm^3\ K\ mol^{-1}}$ (1.7 μ_B), in good agreement with the spin-only value of 0.38 $\mathrm{cm^3\ K\ mol^{-1}}$ (1.7 μ_B) expected for a LS cobalt(II) center (S = 1/2). This value remains relatively constant down to 2 K. Upon heating again, $T_{1/2}{\uparrow}$ = 179 K, giving a hysteresis loop of $\Delta T_{1/2}$ = 11 K (Figures 2 and S18). Three consecutive thermal cycles were performed: these show that the magnetic behavior, including the hysteresis loop, is reproducible and hence fully reversible (Figures 2 and S18).

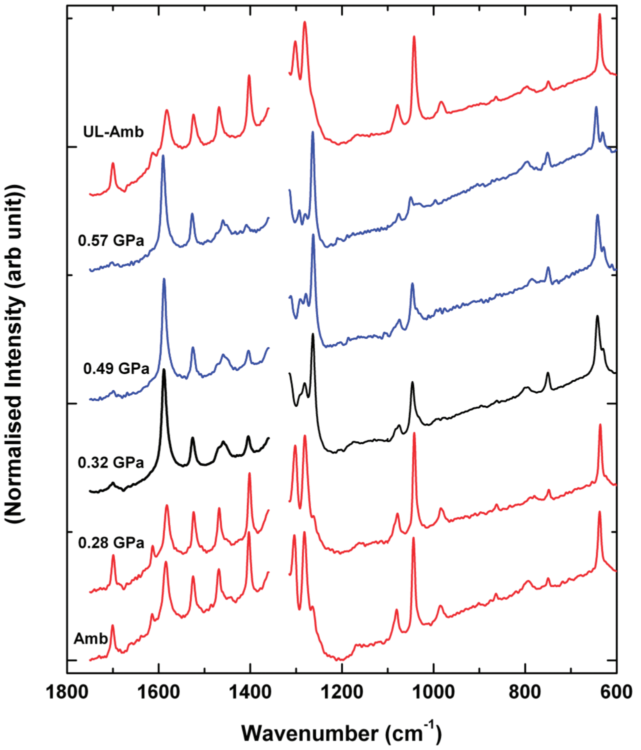

Figure 3. Effect of pressure on Raman spectra of **1** at 298 K. Bottom to top: pressure loading spectra, from ambient (red line = HS state) to 0.28, 0.32 (black line = mixture of HS and LS states), 0.49, and 0.57 GPa (blue line = LS state), then pressure unloaded spectrum at ambient pressure.

SCO usually becomes more gradual and incomplete when the sample either is precipitated as a powder or is a physically ground crystalline complex.[17] Powder samples of **1** undergo abrupt, complete, and hysteretic SCO. Presumably the crystallographic phase change, along with the associated changes in intermolecular interactions, is responsible for the hysteresis.[5b,18]

The observed shortening of the equatorial Co−N bond lengths on SCO from HS to LS indicates that the $T_{1/2}$ of ca. 175 K at ambient pressure will be shifted to higher temperatures by application of pressure.[2a] We studied the Raman response at high pressure using a diamond anvil cell (see SI for details) and find that SCO can be induced at 298 K, reversibly (Figure 3, Figure S19, Table S9).

Electrochemical oxidation of an acetonitrile suspension of **1** to soluble $[\mathrm{Co^{III}(dpzca)_2}]^+$ at 0 V (1.04 $\mathrm{e^-}$ per **1** are transferred, Figure S20) facilitated our cyclic voltammetry studies. These reveal three *reversible* one-electron reductions of $[\mathrm{Co^{III}(dpzca)_2}]^+$ (Figure 4, Table S10): one metal based (E_m = −0.22 V) and two ligand based (E_m = −1.46, −1.84 V). This electrochemical switching provides a *third* reversible method of altering the magnetic moment of **1**, in this case from ca. 4 to 0 μ_B by oxidation to LS cobalt(III).

To our knowledge, **1** is the first cobalt complex to display *abrupt hysteretic SCO as well as reversible redox* behavior (although such behavior has been reported for iron(II) complexes[20]). In addition, **1** is shown to be highly pressure sensitive, with thermally induced SCO occurring at 175 K and pressure-induced

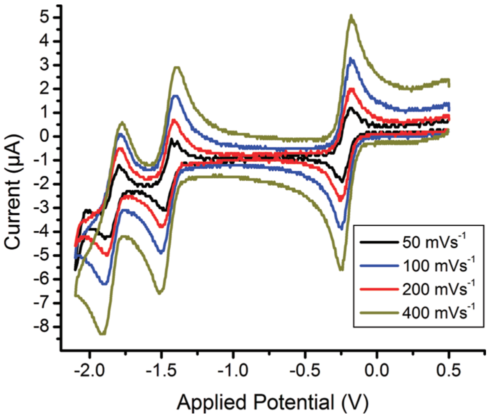

Figure 4. CV study of an acetonitrile solution of $[\mathrm{Co^{III}(dpzca)_2}]^+$ vs 0.01 mol L^{-1} Ag/AgNO$_3$. $[\mathrm{Co^{III}(dpzca)_2}]^+$ is more easily reduced than complexes of related imide ligands (Table S8).[19]

SCO readily occurring at 298 K. Importantly, **1** is solvent- and counteranion-free, and it has been structurally characterized in both the HS and LS states. The absence of complicating factors has, for the first time, allowed a detailed structural analysis of packing interactions for hysteretic cobalt(II) SCO. We anticipate that systematic derivatization and analysis of families of related complexes will greatly assist in deepening understanding in this field; such studies are now being pursued in this group.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedure for complex **1**; X-ray data and detailed analysis of the crystal packing; XRPD studies, VT-magnetic susceptibility, and electrochemistry details of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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