Supporting Information

Spin-state Diversity in a Series of Cobalt(II) PNP Pincer Bromide Complexes

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Experimental

Synthetic Methods & Materials. The complexes described below are air- and moisturesensitive, and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21-24 °C). All solvents were sparged with argon and dried using a solvent purification system. Hydrocarbon solvents were passed through packed columns of neutral alumina and Q5 reactant. Acetonitrile, ethereal, and halogenated solvents were passed through two columns of neutral alumina. DMF and alcohol solvents were passed through columns of activated molecular sieves. The ligands P^CN^CP, P^NN^NP, and P^ON^OP were synthesized according to established procedures.³²⁻³⁴ All other materials were purchased from commercial sources and used without further purification.

Physical Methods. Elemental analyses (EA) were performed by Robertson Microlit Laboratories. Electrospray ionization mass spectrometry (ESI-MS) was performed with a JEOL JMR-600H mass spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer with a TCI cryoprobe in dry, degassed solvents. ¹H NMR spectra were referenced to TMS using the residual proteo impurities of the solvent.⁵⁹ All chemical shifts are reported in the standard δ notation in parts per million; positive chemical shifts are a higher frequency than the reference. Solution magnetic moments were determined by the Evans method using a sealed capillary containing 5% CHCl₃/CDCl₃ as internal reference.⁶⁰⁻⁶³ Perpendicularmode X-band electron paramagnetic resonance (EPR) spectra were collected in ethanol glass at 77 K using a Bruker EMX spectrometer. Electrochemical experiments were carried out with a Biologic VSP-300 potentiostat or a Pine Wavedriver 10 potentiostat. Electrochemical experiments were carried out in acetonitrile solutions with 1.0 mM analyte and 0.20 M Bu₄NPF₆ or Bu₄NBF₄. The working electrode was a glassy carbon disc with a diameter of 3 mm or 1 mm; the counter electrode was a glassy carbon rod; and the reference electrode was a silver wire in $0.20 \text{ M Bu}_4\text{NPF}_6$ or Bu₄NBF₄ in CH₃CN separated from the bulk solution by a Vycor frit. Potentials were referenced at 100 mV/s (unless otherwise noted) to the ferrocene/ferrocenium couple at 0 V using ferrocene as an internal reference.

Magnetic measurements. Solid state magnetic susceptibility measurements were performed using a Quantum Design model MPMS-XL SQUID magnetometer on crystalline samples of **1-3**, prepared under a dinitrogen atmosphere. Microcrystalline samples were loaded in polyethylene bags (1 cm × 1.5 cm) and sealed in the glovebox, inserted into a straw and transported to the SQUID magnetometer under dinitrogen. Prior to variable temperature experiments, the field dependence of magnetization was measured for each sample at 100 K in order to detect the presence of any bulk ferromagnetic impurities. The perfect linearity found in the *M* vs *H* plots at 100 K (Figure S2) for compounds 1.0.25CH₂Cl₂ and **3** are consistent with the absence of ferromagnetic impurities. In compound 2.EtOH the *M* vs *H* data below 2500 Oe show slight curvature, which might be attributed to trace ferromagnetic impurities. The temperature dependence of magnetic susceptibility was measured between 1.8 K and 300 K at a dc field of 1000 Oe for compounds 1.0.25CH₂Cl₂ and **3** (Figure 7). For compound 2.EtOH the same data were collected both at 1000 Oe and 5000 Oe (Figure S3): we found the susceptibility contribution from the trace ferromagnetic impurities is present at 1000 Oe, as indicated by the gradual increase of $\chi_M T$ at temperatures greater than 150 K, but is quenched at 5000 Oe.

Data were corrected for the magnetization of the sample holder; diamagnetic corrections of the sample were applied using Pascal's constants.⁶⁴ Magnetization measurements were collected in the temperature range 2-20 K at applied dc fields of 1, 2, 3, 4, and 5 T (Figure S4) for compound 1.0.25CH₂Cl₂. The magnetization data were fit with ANISOFIT 2.0⁵⁸ to quantify the magnetic anisotropy parameters with the help of following spin Hamiltonian:

$$H = \sum_{i=1}^{n} g\beta \,\bar{S}_i \cdot \bar{H} + \sum_{i=1}^{n} [D_i S_{z,i}^2 - 1/3D_i \,S_i (S_i + 1) + E_i (S_{x,i}^2 - S_{y,i}^2)] \quad (\text{eqn 1})$$

The initial values obtained for axial (*D*) and rhombic (*E*) anisotropy parameters for $1 \cdot 0.25 \text{CH}_2\text{Cl}_2$ are respectively $D = 16.16 \text{ cm}^{-1}$ and $E = 8.52 \text{ cm}^{-1}$, which gave |E/D| > 1/3 for compound $1 \cdot 0.25 \text{CH}_2\text{Cl}_2$; thus the *D* and E parameters were re-determined by the customary assignment of the principal values of D-tensor.⁶⁵ The $\chi_M T$ vs *T* data for $1 \cdot 0.25 \text{CH}_2\text{Cl}_2$ and $2 \cdot \text{EtOH}$ were fitted with the magnetic interpretation program PHI⁴⁸ using the spin Hamiltonians $\hat{H} = \mu_B g B \hat{S} + (D/3) \hat{O}_2^0$ $+ E \hat{O}_2^2$ (where \hat{O} is the Stevens operators) for $1 \cdot 0.25 \text{CH}_2\text{Cl}_2$ and $\hat{H} = \mu_B g B \hat{S}$ for $2 \cdot \text{EtOH}$; in both cases the *g*-factor is isotropic

 $(\mathbf{P}^{\mathbf{C}}\mathbf{N}^{\mathbf{C}}\mathbf{P})\mathbf{CoBr_2}$ (1). A colorless solution of $\mathbf{P}^{\mathbf{C}}\mathbf{N}^{\mathbf{C}}\mathbf{P}$ (200.5 mg, 506.9 µmol) in 5 mL of $\mathbf{CH}_2\mathbf{Cl}_2$ was added slowly to a 5 mL blue solution of \mathbf{CoBr}_2 (110.8 mg, 506.5 µmol) in $\mathbf{CH}_3\mathbf{CN}$. The solution developed a dark purple color and was stirred for 12 h. The solvent was then removed *in vacuo*. The crude purple product was redissolved in 4 mL $\mathbf{CH}_2\mathbf{Cl}_2$ and layered underneath 10 mL of pentane. After 1.5 days, the solution was decanted and the resulting dark purple crystals were washed with pentane and dried *in vacuo* (yield 298.1 mg, 96%). Anal. Calc. (Found) for

 $C_{23}H_{43}NP_2CoBr_2$ (%): C, 44.97 (44.72), H 7.06 (7.04), N 2.28 (2.15). ESI-MS (CH₃CN) *m/z*: 533.1 ([M–Br]⁺). μ_{eff} (5% CHCl₃/CDCl₃, Evans method, 298 K): 4.6. EPR (EtOH, 77 K): $g_1 = 2.29$, $g_2 = 2.01$, $A_2 = 90$ G.

[($\mathbf{P}^{N}\mathbf{N}^{N}\mathbf{P}$)CoBr]Br (2). A colorless solution of $\mathbf{P}^{N}\mathbf{N}^{N}\mathbf{P}$ (109 mg, 273 µmol) in 4 mL of CH₂Cl₂ was added slowly to a blue solution of CoBr₂ (60.0 mg, 273 µmol) in 6 mL of CH₃CN. A red precipitate developed and the reaction mixture was stirred for 12 h. To assist precipitation, 2 mL of Et₂O were added. The suspension was then filtered and the resulting red solid washed with 3 x 2 mL Et₂O and dried *in vacuo* (yield 155 mg, 92%). X-ray quality crystals were grown by cooling a saturated EtOH solution at -35 °C. Anal. Calc. (Found) for C₂₁H₄₁N₃P₂CoBr₂ (%): C 40.93 (41.12), H 6.71 (6.96), N 6.82 (6.58). ESI-MS (CH₃CN) *m/z*: 535.0 ([M–Br]⁺). EPR (EtOH, 77 K): *g*₁ = 2.31, *g*₂ = 2.01, *A*₂ = 90 G.

(P^oN^oP)CoBr₂ (3). To a blue solution of CoBr₂ (47.5 mg, 217 µmol) in 8 mL of THF was added solid P^oN^oP (90.6 mg, 227 µmol), immediately producing a dark purple solution. After stirring for 2 h, the solvent was removed *in vacuo* and the solid was washed with diethyl ether, filtered, and dried *in vacuo* (yield 98.2 mg, 73%). Recrystallization by layering dichloromethane solutions of **3** with pentane produced high quality crystals in up to 31% yield; attempts at higheryielding crystallizations resulted in the formation of an uncharacterized orange byproduct. Anal. Calc. (Found) for C₂₁H₃₉NO₂P₂CoBr₂ (%): C 40.80 (40.79), H 6.36 (6.29), N 2.27 (2.24). ESI-MS (CH₃CN) *m/z*: 537.0 ([M–Br]⁺). µ_{eff} (5% CHCl₃/CDCl₃, Evans method, 298 K): 3.9. EPR (EtOH, 77 K): $g_1 = 2.28$, $g_2 = 2.01$, $A_2 = 85$ G.

	$(P^{c}N^{c}P)CoBr_{2}$	[(P ^R N ^R P)CoBr]Br	$(\mathbf{D}^{0}\mathbf{N}^{0}\mathbf{D})\mathbf{C}_{0}\mathbf{D}_{\mathbf{r}}$	
	$0.25(CH_2Cl_2)(1)$	•0.5(EtOH) (2)	$(\mathbf{r} \ \mathbf{N} \ \mathbf{r}) COBI2(3)$	
Empirical formula	$C_{46.5}H_{87}Br_4ClCo_2N_2P_4$	$C_{44}H_{88}Br_4Co_2N_6P_4O$	$C_{42}H_{78}Br_4Co_2N_2O_4P_4$	
Formula weight	1271.05	1278.61	1236.44	
Crystal system	Triclinic	Monoclinic	Triclinic	
Space group	ΡĪ	P2 ₁ /n	ΡĪ	
<i>a</i> / Å	12.0654(3)	22.5471(16)	10.8010(13)	
<i>b</i> / Å	15.2061(5)	7.7900(6)	15.6582(19)	
<i>c</i> / Å	15.6909(5)	34.827(2)	16.0040(17)	
α / deg	94.7370(10)	90	98.515(3)	
β / deg	91.7490(10)	102.912(4)	97.341(3)	
γ / deg	99.8640(10)	90	98.331(3)	
$V/\text{\AA}^3$	2823.60(15)	5962.4(7)	2617.6(5)	
Ζ	4	8	2	
Refl. Collected	38277	65369	46533	
Indep. Refl.	11491	12271	10647	
R1 $(I > 2\sigma)^a$	0.0296	0.0303	0.0297	
wR2	0.0750	0.0719	0.0660	
(all data) ^{b}	0.0730	0.0718	0.0000	
		6 EtOH.		
SQUEEZE		Calc:132e/uc,		
		found: 124e/uc		
${}^{a}\mathbf{R}1 = \sum F_{o} - F_{c} / \sum F_{o} . {}^{b}\mathbf{w}\mathbf{R}2 = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]\}^{1/2}.$				

 Table S1. X-ray Diffraction Data Collection and Refinement Parameters.

 (DCNCD)C+D+



Figure S1. ORTEP of molecule B in the asymmetric unit of $(P^ON^OP)CoBr_2$ (3). Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.



Figure S2. ¹H NMR spectra from Evans Method magnetic moment determinations^{1, 2} for $(P^{C}N^{C}P)CoBr_{2}$ (1, 13.3 mM) and $(P^{O}N^{O}P)CoBr_{2}$ (3, 13.2 mM) in CDCl₃ solution.

Compound	E _{pa} (ox1)	E _{pa} (ox2)	E _{pa} (ox3)	E _{pa} (ox4)
1	0.35	0.58	0.75	1.29
2	0.34	-	0.71	1.20
3	0.33	-	0.70	1.07

Table S2. Oxidation potentials vs $Fe(Cp)_2^{+/0}$ (V) for (P^EN^EP)CoBr₂ complexes, (E = C, 1; N, 2; O, 3).



Figure S3. The *M* vs *H* plots of **1-3**, obtained at 100 K. For $1 \cdot 0.25$ CH₂Cl₂ and **3** the linear fit of the experimental data indicates the absence of ferromagnetic impurities in all those compounds. For **2**·EtOH the data below 3000 Oe is slightly deviated from linearity, indicative of possible presence of trace amount of ferromagnetic impurities.



Figure S4. The $\chi_M T$ vs *T* data collected for compound **2**·EtOH between 1.8 and 300 K, measured at 1000 Oe and 5000 Oe. At 1000 Oe, the trace amount of ferromagnetic impurities contributes to the gradual increase of $\chi_M T$ data above 150 K; the ferromagnetic susceptibility contribution is quenched at 5000 Oe to give a linear $\chi_M T$ vs *T* consistent with paramagnetic behavior.



Figure S5. Field dependence of magnetization for compounds **1-3** (solvated), collected at 2 K in dc fields between 0 T and 5 T.

Magnetic Modeling for Complex 3

The thermodynamic parameters of spin crossover behavior for compound **3** were estimated by fits of the variable temperature $\chi_M T$ data to equations based on the ideal solution model.^{3, 4} In the most complete model, the two Co(II) complexes would have independently optimized g and temperature-independent magnetic susceptibility (*TIP*) values, which could be different in the lowand high-spin states (LS and HS, respectively). In addition, axial and rhombic magnetic anisotropy terms (*D* and *E*, respectively) should be available for Co(II) ions in the HS state. Assuming that one Co(II) ion, Co(1), undergoes spin crossover, and the other, Co(2), is HS at all temperatures, we identify ten variables that could be fit: $g_{HS(Co2)}$, $g_{HS(Co1)}$, $f_{IP_{HS(Co2)}}$, $f_{IP_{HS(Co1)}}$, $TIP_{LS(Co1)}$, ΔH , T_C , $D_{(Co2)}$ and $E_{(Co2)}$. Since a model that contained all these variables would be overparameterized, we attempted several different approximations of the g and TIP values to estimate the thermodynamic parameters associated with spin crossover, as summarized below.

(1) Did not fit the low T downturn in $\chi_M T$ to avoid effects of magnetic anisotropy (8 variables): no $D_{(Co2)}$ and $E_{(Co2)}$

(2) Same as (1), with the additional assumption that HS forms of the complexes have the same g and *TIP* values (6 variables): no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = g_{HS(Co1)}$ and $TIP_{HS(Co2)} = TIP_{HS(Co1)}$

(3) Same as (1) but all *TIP* values fixed at 0 (5 variables).

(4) Same as (2), with the additional assumption that TIP = 0 based on magnetic behavior of compounds 1 and 2 (4 variables). This might not be reasonable because 3 is showing spincrossover, and the other compounds do not, and thus magnetic excited states should be energetically closer to the ground state: no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = g_{HS(Co1)}$ and all TIP = 0. (5) Fix HS *g* value at 2.44 based on numerical evaluation of the susceptibility data (four variables). Considering both Co(1) and Co(2) are high spin at 300 K, the average *g* value (= g_{hs}) is calculated at 2.44. At 30 K we assume that Co(1) is LS and Co(2) is HS, and the $\chi_M T$ value is not significantly affected by the magnetic anisotropy of high-spin Co(2) and weak antiferromagnetic coupling. In that case, the corresponding $\chi_M T$ value of 1.65 cm³Kmol⁻¹ is the sum of the susceptibility contributions of a 50:50 mixture of high- and low-spin Co(II) ions. Subtracting the susceptibility contribution of high-spin Co(2) (0.5 mole fraction of **3**, 1.39 cm³Kmol⁻¹ for $g_{av} = g_{hs} = 2.44$) we obtain the susceptibility contribution of the low-spin Co(1) center as 0.26 cm³Kmol⁻¹ (remaining 0.5 mole fraction of **3**). This value extracts $g_{ls} = 2.36$ for the low-spin Co(1) center, which is reasonable for an $S = \frac{1}{2}$ Co(II) ion in a pentacoordinate geometry.⁵⁻⁷ Implicit in this estimation are several requirements: first, that HS *TIP* values are zero, otherwise *g* values can't be extracted simply from $\chi_M T$; second, that the spin crossover event is complete at the highest temperature measured. Parameters changed: no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = g_{HS(Co1)} = 2.44$ and all *TIP*_{HS} = 0.

(6) Fix HS g value at 2.44 based on room temperature χT value (three variables). Implicit in this estimation are several requirements TIP = 0 based on magnetic behavior of compounds 1 and 2, that the spin crossover event is complete at the highest temperature measured: no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = g_{HS(Co1)} = 2.44$ and all TIP = 0.

(7) Fix HS g value at 2.44 for Co(2) based on room temperature χT value (six variables). Implicit in this estimation are several requirements: first, that HS *TIP* of Co(2) values are zero, second that the spin crossover event is complete at the highest temperature measured: no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = 2.44$ and all $TIP_{HS(Co2)} = 0$ (8) Same as (7), add: assume that TIP = 0 based on magnetic behavior of compounds 1 and 2 (4 variables). Fix HS *g* value at 2.44 for Co(2) based on room temperature χT value (four variables). Assume that the spin crossover event is complete at the highest temperature measured: no $D_{(Co2)}$ and $E_{(Co2)}$; $g_{HS(Co2)} = 2.44$ and all TIP = 0.

(9) Same as (1), but considered all *TIP* values are same (6 variables).

Model 1. In this model we considered the Co(2) stays HS and Co(1) undergoes SCO. The variable temperature $\chi_{\rm M}T$ data of **3** are fitted with the expression:

$$\begin{split} \chi_{M}T &= \left[\frac{g_{HS(Co2)}^{2}}{8}C_{HS} + \frac{TIP_{HS(Co2)}}{2}*T\right] + \frac{\left[\frac{g_{HS(Co1)}^{2}}{8}C_{HS} + \frac{TIP_{HS(Co1)}}{2}*T\right] - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2}*T\right]}{1 + exp\left[\frac{\Delta H}{R}*\left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} \\ &+ \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2}*T\right] \end{split}$$

The best fit of the data between 25 and 300 K (R = 0.99999) gives: $g_{\text{HS}(\text{Co2})} = 2.17$, $TIP_{\text{HS}(\text{Co2})} = 0.00049 \text{ cm}^3 \text{ mol}^{-1}$, $g_{\text{HS}(\text{Co1})} = 2.22$, $g_{\text{LS}(\text{Co1})} = 3.17$, $TIP_{\text{HS}(\text{Co1})} = 0.00137 \text{ cm}^3 \text{ mol}^{-1}$, $TIP_{\text{LS}(\text{Co1})} = 0.00196(4) \text{ cm}^3 \text{ mol}^{-1}$, $\Delta H = 7.79(1) \text{ KJ mol}^{-1}$, $T_{\text{C}} = 166(1) \text{ K}$. The entropy term ΔS is calculated as 46.93(3) J K⁻¹ mol}^{-1} from the expression $\Delta S = \Delta H/T_{\text{C}}$.



Figure S6. Fit of the temperature dependence of magnetic susceptibility according to model 1.

Model 2. We attempt to fit the variable temperature $\chi_M T$ data of **3** both Co(1) and Co(2) are high spin at 300 K, but only 50% of cobalt center is doing spin crossover, therefore at $T_C = T_{1/2}$ only ¹/₄ cobalt is low spin.

$$\chi_{M}T = \frac{\left[\frac{g_{HS}^{2}}{4}C_{HS} + \frac{TIP_{HS}}{2}*T\right] - \left[\frac{g_{LS}^{2}}{8}C_{LS} + \frac{TIP_{LS}}{2}*T\right]}{1 + exp\left[\frac{\Delta H}{R}*\left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} + \left[\frac{g_{LS}^{2}}{8}C_{LS} + \frac{TIP_{LS}}{2}*T\right]$$

where *g*, *C* and *TIP* are the Landé factor, Curie constant and temperature-independent paramagnetism terms of the S = 3/2 (HS), and S = 1/2 (LS) states, respectively; *R* is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50). The best fit of the data between 25 and 300 K (R = 0.99999) extracts: $g_{\text{HS}} = 2.200(1)$, g_{LS} = 2.90(5), *TIP*_{HS} = 0.0018(4) cm³ mol⁻¹, *TIP*_{LS} = 0.0024(2) cm³ mol⁻¹, $\Delta H = 7.708(2)$ KJ mol⁻¹ and $T_C = 166(1)$ K. The entropy term ΔS is calculated as 46.4 J K⁻¹ mol⁻¹ from the expression $\Delta S =$ $\Delta H/T_C$.



Figure S7. Fit of the temperature dependence of magnetic susceptibility according to model 2.

Model 3. In this model we considered the Co(2) stays HS and Co(1) undergoes SCO, and there is no *TIP*. The variable temperature $\chi_M T$ data of **3** are fitted with the expression:

$$\chi_{M}T = \left[\frac{g_{HS(Co2)}^{2}}{8}C_{HS}\right] + \frac{\left[\frac{g_{HS(Co1)}^{2}}{8}C_{HS}\right] - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS}\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} + \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS}\right]$$

The best fit of the data between 25 and 300 K (R = 0.99896) gives: $g_{\text{HS}(\text{Co2})} = 2.36$, $g_{\text{HS}(\text{Co1})} = 3.02$, $g_{\text{LS}(\text{Co1})} = 2.87$, $\Delta H = 3.70(2)$ KJ mol⁻¹, $T_{\text{C}} = 224(13)$ K. The entropy term ΔS is calculated as 16.5(2) J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_{\text{C}}$. The errors in the *g* values are extremely large such that the fit values are meaningless.



Figure S8. Fit of the temperature dependence of magnetic susceptibility according to model 3.

Model 4. In this model we considered the Co(2) stays HS and Co(1) undergoes SCO, the g_{HS} of both Co(1) and Co(2) are same and there is no *TIP*. The variable temperature $\chi_{\text{M}}T$ data of **3** are fitted with the expression:

$$\chi_M T = \frac{\left[\frac{g_{HS}^2}{4}C_{HS}\right] - \left[\frac{g_{LS}^2}{8}C_{LS}\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_c}\right)\right]} + \left[\frac{g_{LS}^2}{8}C_{LS}\right]$$

The best fit of the data between 25 and 300 K (R = 0.99896) gives: $g_{\text{HS}} = 2.71(1)$, $g_{\text{LS}} = 3.00(5)$, $\Delta H = 3.70(2)$ KJ mol⁻¹, $T_{\text{C}} = 224(13)$ K. The entropy term ΔS is calculated as 16.5(2) J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_{\text{C}}$.



Figure S9. Fit of the temperature dependence of magnetic susceptibility according to model 4.

Model 5. This data fit is done based on the assumption where at 300 K for Co(1) and Co(2) the $g_{\text{HS}} = 2.44$, but considered the high spin Co(2) has *TIP* contribution. The fixed *g* value is based on the following considerations:

The variable temperature $\chi_M T$ data of **3** are fitted with the expression:

$$\chi_{M}T = 1.39 + \frac{1.39 - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2} * T\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} + \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2} * T\right]$$

where *g*, *C* and *TIP* are the Landé factor, Curie constant and temperature-independent paramagnetism of S = 1/2 (LS) states of Co(1), respectively; *R* is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50 for Co(1)). The best fit of the data between 25 and 300 K (R = 0.99935) gives for the SCO Co(1): $g_{LS(Co1)} = 1.92(4)$, $TIP_{LS(Co1)} = 0.0028(1)$ cm³ mol⁻¹, $\Delta H = 7.99(2)$ KJ mol⁻¹, $T_C = 190(1)$ K. The entropy term ΔS is calculated as 42.05 J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_C$.



Figure S10. Fit of the temperature dependence of magnetic susceptibility according to model 5.

Model 6. This data fit is done based on the assumption in the text where at 300 K for Co(1) and Co(2) the $g_{\text{HS}} = 2.44$, and there is no *TIP* for any of the cobalt. The variable temperature $\chi_{\text{M}}T$ data of **3** are fitted with the expression:

$$\chi_{M}T = 1.39 + \frac{1.39 - \left[\frac{g_{LS(co1)}^{2}}{8}C_{LS}\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} + \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS}\right]$$

where g and C are the Landé factor and Curie constant of S = 1/2 (LS) states of Co(1), respectively; R is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50 for Co(1)). The best fit of the data between 25 and 300 K (R = 0.99537) gives for the SCO Co(1): $g_{LS(Co1)} = 2.64(4)$, $\Delta H = 6.44(4)$ KJ mol⁻¹, $T_C = 160(1)$ K. The entropy term ΔS is calculated as 40.26 J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_C$.



Figure S11. Fit of the temperature dependence of magnetic susceptibility according to model 6.

Model 7. We attempt to fit the variable temperature $\chi_M T$ data of **3** get the thermodynamic parameters of spin crossover behavior of Co(1) where the Co(2) centers remains high spin all over the temperature range. Considering both Co(1) and Co(2) are high spin at 300 K, we assume that $\chi_M T = 1.39$ cm³ K mol⁻¹ for the HS Co(2) center remains constant for the temperature range between 25 and 300 K: the assumption of no temperature-independent paramagnetism is based on the behavior of compounds **1** and **2**. The data below 25 K is ignored in the fitting to avoid the possible contribution from the intermolecular interactions and magnetic anisotropy of HS Co(2). Therefore, the variable temperature $\chi_M T$ data of **3** between 25 and 300 K are fitted using the following relation:

$$\chi_{M}T = 1.39 + \frac{\left[\frac{g_{HS(Co1)}^{2}}{8}C_{HS} + \frac{TIP_{HS(Co1)}}{2}*T\right] - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2}*T\right]}{1 + exp\left[\frac{\Delta H}{R}*\left(\frac{1}{T} - \frac{1}{T_{c}}\right)\right]} + \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP_{LS(Co1)}}{2}*T\right]$$

where *g*, *C* and *TIP* are the Landé factor, Curie constant and temperature-independent paramagnetism terms of the S = 3/2 (HS), and S = 1/2 (LS) states of Co(1), respectively; *R* is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50 for Co(1)). The best fit of the data between 25 and 300 K (R = 0.99999) gives for the SCO Co(1): $g_{\text{HS}(\text{Co1})} = 1.93(7)$, $g_{\text{LS}(\text{Co1})} = 2.03(6)$, $TIP_{\text{HS}(\text{Co1})} = 0.0018(4)$ cm³ mol⁻¹, $TIP_{\text{LS}(\text{Co1})} = 0.0024(2)$ cm³ mol⁻¹, $\Delta H = 7.71(9)$ KJ mol⁻¹, $T_C = 166(1)$ K. The entropy term ΔS is calculated as 46.4(5) J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_C$.



Figure S12. Fit of the temperature dependence of magnetic susceptibility according to model 7.

Model 8. This is very similar fit like model 7 except we did not consider the *TIP*s. The variable temperature $\chi_{M}T$ data of **3** are fitted with the expression:

$$\chi_{M}T = 1.39 + \frac{\left[\frac{g_{HS(Co1)}^{2}}{8}C_{HS}\right] - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS}\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_{C}}\right)\right]} + \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS}\right]$$

where g and C are the Landé factor and Curie constant of the S = 3/2 (HS), and S = 1/2 (LS) states of Co(1), respectively; R is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50 for Co(1)). The best fit of the data between 25 and 300 K (R = 0.99905) gives for the SCO Co(1): $g_{\text{HS}(\text{Col})} = 2.93(8)$, $g_{\text{LS}(\text{Col})} = 2.56(1)$, $\Delta H = 3.77(1)$ KJ mol⁻¹, T_C = 220(11) K. The entropy term ΔS is calculated as 17.14 J K⁻¹ mol⁻¹ from the expression $\Delta S =$ $\Delta H/T_C$.



Figure S13. Fit of the temperature dependence of magnetic susceptibility according to model 8.

Model 9. This is very similar to model 1 except we considered the *TIP* values are the same for all Co centers. The variable temperature $\chi_M T$ data of **3** are fitted with the expression:

$$\begin{split} \chi_{M}T &= \left[\frac{g_{HS(Co2)}^{2}}{8}C_{HS} + \frac{TIP}{2} * T\right] + \frac{\left[\frac{g_{HS(Co1)}^{2}}{8}C_{HS} + \frac{TIP}{2} * T\right] - \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP}{2} * T\right]}{1 + exp\left[\frac{\Delta H}{R} * \left(\frac{1}{T} - \frac{1}{T_{c}}\right)\right]} \\ &+ \left[\frac{g_{LS(Co1)}^{2}}{8}C_{LS} + \frac{TIP}{2} * T\right] \end{split}$$

where g and C are the Landé factor and Curie constant of the S = 3/2 (HS), and S = 1/2 (LS) states of Co(1), respectively; R is the gas constant; ΔH is the enthalpy term; and T_C is the spin-transition temperature (where HS:LS = 50:50 for Co(1)). The best fit of the data between 25 and 300 K (R = 0.99905) gives: $g_{\text{HS}(\text{Co2})} = 2.14$, $g_{\text{HS}(\text{Co1})} = 2.09$, $g_{\text{LS}(\text{Co1})} = 3.29$, $\Delta H = 8.38(5)$ KJ mol⁻¹, $T_C = 157(1)$ K. The entropy term ΔS is calculated as 53.3(8) J K⁻¹ mol⁻¹ from the expression $\Delta S = \Delta H/T_C$.



Figure S14. Fit of the temperature dependence of magnetic susceptibility according to model 9.

	(1)	(2)	(3)	(4)	(5)
GOF (R)	0.99999	0.99999	0.99896	0.99896	0.99935
# parameters	8	6	5	4	4
$g_{\text{LS Co}(1)}$	3.17 ^b	2.90(5)	2.87 ^b	3.00(5)	1.92(4)
$TIP_{LS Co(1)}$	0.0019 ^b	0.0024(2)	0 °	0 °	0.0028(1)
$g_{ m HS Co(1)}$	2.21 ^b	2.20(1)	3.02 ^b	2.71(1)	2.44 ^c
TIP _{HS Co(1)}	0.0013 ^b	0.0018(5)	0 °	0 °	0 °
$g_{ m HS \ Co(2)}$	2.18 ^b	2.20(1)	2.36 ^b	2.71(1)	2.44 ^c
TIP _{HS Co(2)}	0.00049^{b}	0.0018(5)	0 ^c	0 ^c	0 °
<i>TIP</i> _{sum} ^e	_	-	_	_	_
ΔH	7.79(1)	7.71(2)	3.70(2)	3.70(2)	7.99(2)
$T_c (= T_{1/2})$	166(1)	166(1)	224(13)	224(13)	190(2)
ΔS	46.9(3)	46.4(4)	16.52(3)	16.52(3)	42.1(2)

Table S3. Fit parameters according to above-mentioned models.^a

	(6)	(7)	(8)	(9)
GOF (R)	0.99537	0.99999	0.99905	0.99995
# parameters	3	6	4	6
$g_{\text{LS Co}(1)}$	2.64(4)	2.03(6)	2.56(1)	3.29 ^b
$TIP_{LS Co(1)}$	0 °	0.0024(2)	0 °	_ e
$g_{ m HS \ Co(1)}$	2.44 °	1.93(7)	2.93(8)	2.09 ^b
$TIP_{\rm HS Co(1)}$	0 °	0.0018(2)	0 °	_ e
$g_{ m HS Co(2)}$	2.44 °	_ c,d	_ c,d	2.14 ^b
TIP _{HS Co(2)}	0 °	0 ^{c,d}	0 ^{c,d}	_ e
<i>TIP</i> _{sum} ^e	_	_	-	0.00239(5)
ΔH	6.44(4)	7.71(9)	3.77(1)	8.38(5)
$T_c (= T_{1/2})$	160(1)	166(1)	220(11)	157(1)
ΔS	40.3(4)	46.4(5)	17.14(4)	53.3(8)

^a Units: *TIP* in cm³ mol⁻¹, ΔH in kJ mol⁻¹, $T_{\rm C}$ in K and ΔS in J K⁻¹ mol⁻¹

^b Errors are unreasonably large – see tables associated with each model's fit figure

^c Fixed value

 $^{d}\chi_{M}T$ fixed at 1.39 cm³ K mol⁻¹ for the HS Co(2) center between 25 and 300 K

^e All three *TIP* terms collected together into one parameter

Magnetic Model Summary. Generally, the parameters derived from the above models give reasonable values of *g*, *TIP* and thermodynamic parameters. Some of the models (1, 2, 7 and 9) show good visual agreement with the data. However, some of the models (1, 3 and 9) give unrealistically large errors for the *g* values and *TIP* values. Models that incorporate one or more adjustable *TIP* parameters (1, 2 and 7) provide comparably better fits than the others. We note that the *TIP* values are very large: fits of Co(II) complex susceptibility data often feature large *TIP* values due to the presence of low-lying excited states concomitant with a *T* ground state term for the free ion. Models 2 and 7 provide the best comprehensive fits to the data, but model 7 has one *g* value less than 2.0, which is not consistent with a d^7 electron configuration as found in Co(II) complexes. Therefore, we conclude that the parameters associated with *model 2* provide the best description of the data.

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