

ELECTRONIC SUPPLEMENTARY INFORMATION

Thermodynamics of spin crossover in a bis(Terpyridine) cobalt(II) complex featuring a thioether functionality

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Experimental Section.

Materials and instrumentation.

FTIR spectra on solid samples were recorded with an ATR - Shimadzu-IRaffinity1 spectrometer. Mass spectra were measured in the Laboratório de Espectrometria de Massas (LABEM-LADETEC) at the Instituto de Química – UFRJ via direct injection of a solution of **1** into a hybrid high resolution Quadrupole-Orbitrap spectrometer by Thermo QExactive (Thermo Scientific) with electrospray ionization mode. Elemental analysis (C, H, N) was performed with a Perkin Elmer 2400 series II analyser.

Electronic Spectroscopy.

Electronic spectra of an acetonitrile solution of **1** ($6.6 \cdot 10^{-5}$ M) were acquired on a Varian Cary UV spectrophotometer with a scan speed of 100 nm/min and a bandwidth of 5 nm. The spectra were normalized according to the equation:

$$\text{Normalised Absorption}(\lambda) = \frac{\text{Absorbance}(\lambda) - \text{Absorbance}(1000 \text{ nm})}{\text{Absorbance}(300 \text{ nm}) - \text{Absorbance}(1000 \text{ nm})}$$

The spectra before normalisation are reported in Figure S5.

NMR Spectroscopy.

The compound **1** (~5mg) was dissolved directly in CD₃CN and 600 μL were transferred in the NMR tube for the NMR acquisition at variable temperature (233K to 333K) on a JEOL ECZR instrument operating at 600.17 MHz and equipped with a ROYAL JEOL probe.

EPR spectroscopy

EPR spectra at X-band (ca. 9.4 GHz) were acquired by using an Elexsys E500 spectrometer (Bruker GmbH) equipped with a SHQ cavity and a ESR900 continuous flow cryostat for low temperature operation. The measured solid-state sample of **1** was the same pellet used for magnetometric measurements. The frozen solution was prepared by dissolving a small amount of **1** and transferring it to a standard EPR tube. The solution was pre-frozen in liquid nitrogen before insertion in the cavity.

Magnetometry.

Samples employed for magnetic measurements consisted of pressed microcrystalline powders of **1**, wrapped in Teflon^(TM) tape. The magnetic characterization was performed on Quantum Design MPMS (Magnetic Properties Measurement System) equipment provided with a 5 T magnet and on Quantum Design MPMS-3. The magnetization (M) dependence with the absolute temperature was investigated between 10 and 300 K using a magnetic field (B) of 5 T, and between 60 and 10 K with a field of 0.1 T to prevent magnetic saturation. After subtraction of the diamagnetic contribution of the sample holder

and the sample, evaluated with Pascal's constants, magnetic susceptibility per mole (χ_M) was evaluated as $\chi_M = M_M/B$.

X-ray diffraction studies.

Single crystal X-ray diffraction data for **1** was collected on a Bruker D8 Venture diffractometer using Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, data reduction and cell refinement were performed by using the Bruker Instrument Service v4.2.2 and SAINT V8.34A softwares.^{1,2} The structure was solved by direct methods using the SHELXS program, and refinement was performed using SHELXL based on F^2 through full-matrix least squares routine³ within WinGX package.⁴ Empirical multi-scan absorption corrections using equivalent reflections were performed with SADABS program.⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined using the riding model.⁶ The structures were drawn using Mercury⁷ and ORTEP software⁴. The Powder X-Ray Diffraction (PXRD) pattern was recorded on a Bruker New D8 Advance DAVINCI diffractometer in a θ - θ configuration equipped with a linear detector. The patterns were collected within the range 2.9 – 50° (2θ) using CuK_α radiation ($\lambda = 1.5398 \text{ \AA}$) with a step of 0.02° and an exposure time of 0.3 s/step .

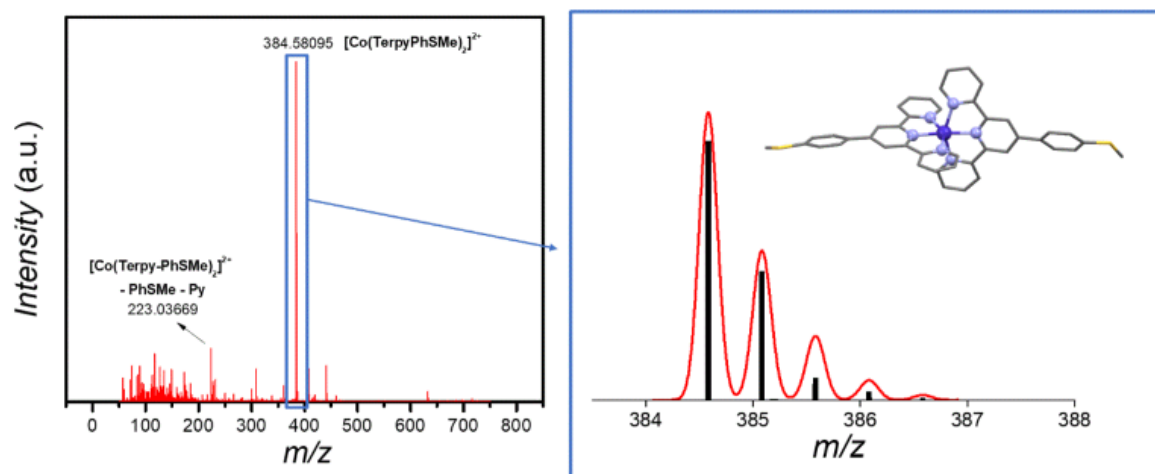


Figure S1: Mass spectrum of **1** (left). Right: comparison between the observed (black bars) and calculated (red line) isotopic distribution of the molecular peak of **1**.

Table S1: Summary of data collection and crystal structure refinement for **1**.

1	
Formula	C ₄₄ H ₃₄ CoF ₁₂ N ₆ P ₂ S ₂
Fw (g mol ⁻¹)	1059.76
T (K)	99(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	18.3621(15)
<i>b</i> (Å)	15.4938(11)
<i>c</i> (Å)	15.9852(12)
α (°)	90
β (°)	107.896(3)
γ (°)	90
Volume (Å ³)	4327.7(6)
<i>Z</i>	4
ρ calc. (Mg m ⁻³)	1.627
μ (mm ⁻¹)	0.661
F(000)	2148
θ range (Deg.)	1.980 – 28.381
	-24 \leq h \leq 24
	-20 \leq k \leq 20
	-21 \leq l \leq 21
Data collected/ Independent reflections	146720/10807
<i>R</i> _{int}	0.1220
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	10807/ 0 / 604
GOF on <i>F</i> ²	1.031
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.0449, 0.1113
<i>R</i> ₁ ; <i>wR</i> ₂ (all)	0.0620, 0.1235
$\Delta\rho$ max; $\Delta\rho$ min (e \cdot Å ⁻³)	0.434, -0.751

Table S2: Continuous Shape Measures Calculations of the coordination sphere of **1**.

Compound	OC-6	TPR-6	JPPY-6	HP-6	PPY-6
1	4.677	9.682	23.261	34.555	19.103

OC-6 Octahedron, TPR-6 Trigonal prism, JPPY-6 Johnson pentagonal pyramid J2, HP-6 Hexagon, PPY-6 Pentagonal pyramid

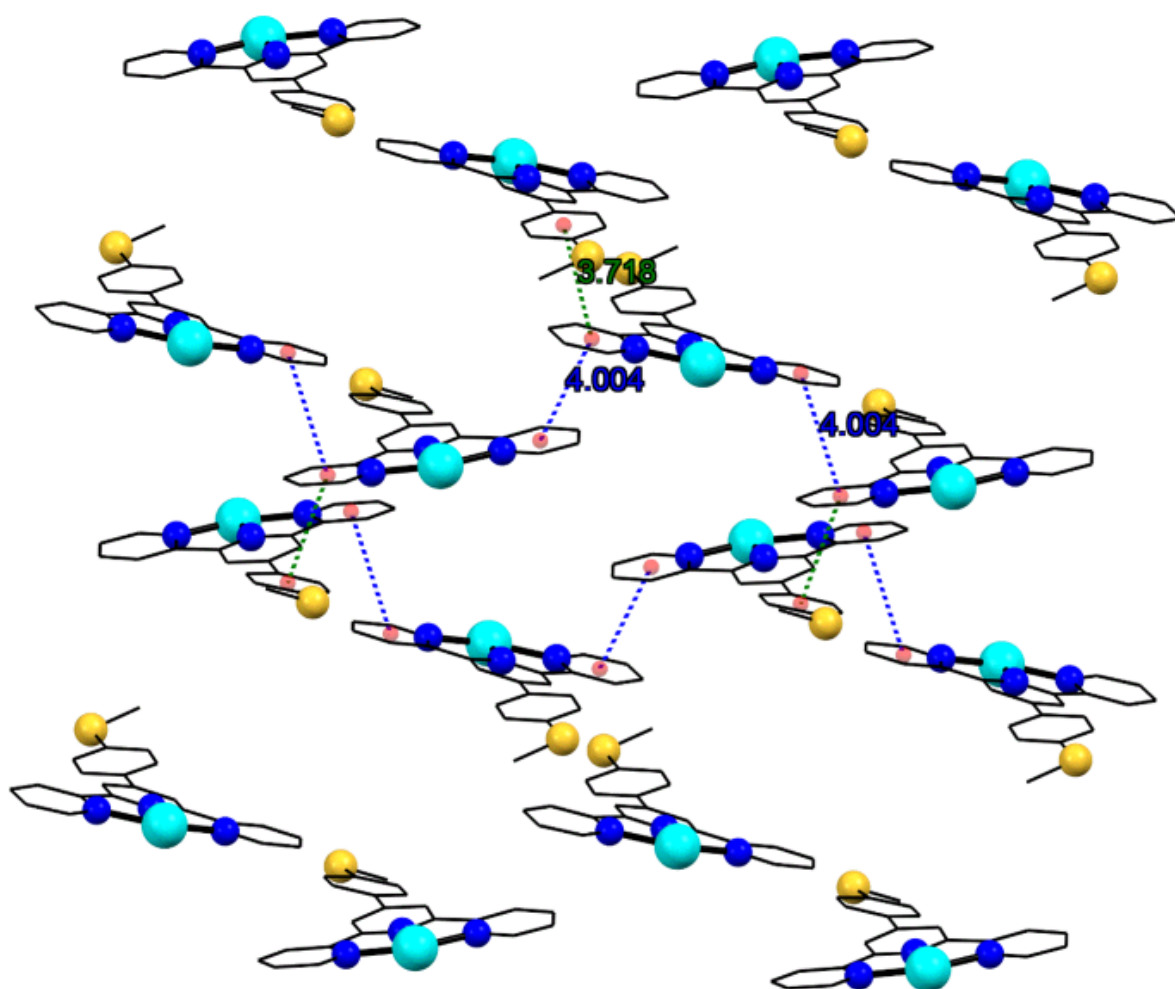


Figure S2: View of crystal packing of **1** emphasizing $\pi \cdots \pi$ stacking between adjacent units. Hydrogen atoms, PF_6^- anion and one of the **TerpyPhSMe** ligand were omitted for clarity. Colour code: cobalt(II) (cyan), carbon (black lines), nitrogen (blue), sulphur atoms (yellow). Blue and green dashed lines represent the distances between centroids. Red points represent the centroids.

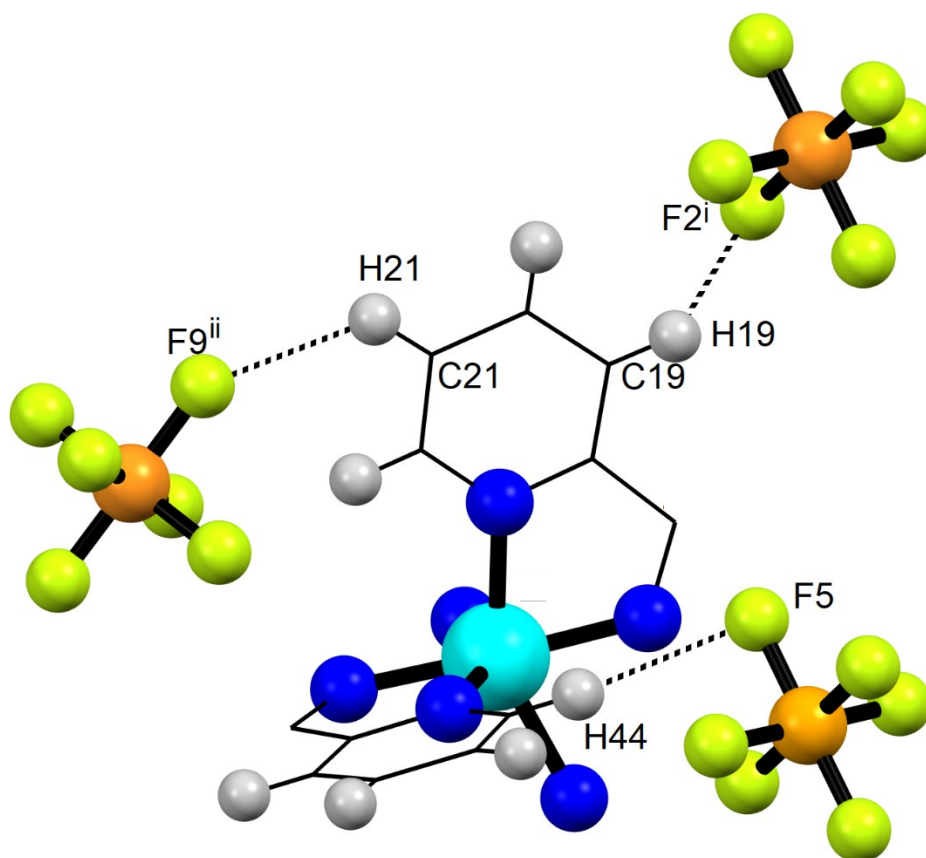


Figure S3: View of crystal packing of **1** emphasizing C-H...F short contacts. Hydrogen atoms, PF₆⁻ anions and part of the **TerpyPhSMe** ligands were partially omitted for clarity.

Colour code: cobalt(II) (cyan), carbon (black lines), nitrogen (blue), sulphur (yellow), phosphorous (orange) and fluorine atoms (light green). Black dashed lines represent the atoms involved in the intermolecular interaction. Symmetry operations used to generate equivalent atoms: $i = 2-x, 1-y, 1-z$; $ii = 1-x, 0.5+y, 0.5-z$.

Table S3: Parameters for the intermolecular non classic C-H...F hydrogen bonds.

H...D	H...A (Å)	D...A (Å)	D-H...A (°)
C44-H44...F5	2.44	3.089	125
C19-H19...F2 ⁱ	2.38	3.044	127
C21-H21...F9 ⁱⁱ	2.44	3.080	125

D = donor, A = acceptor, H= hydrogen atom. Symmetry operations used to generate equivalent atoms: i = 2-x, 1-y, 1-z; ii= 1-x, 0.5+y, 0.5-z.

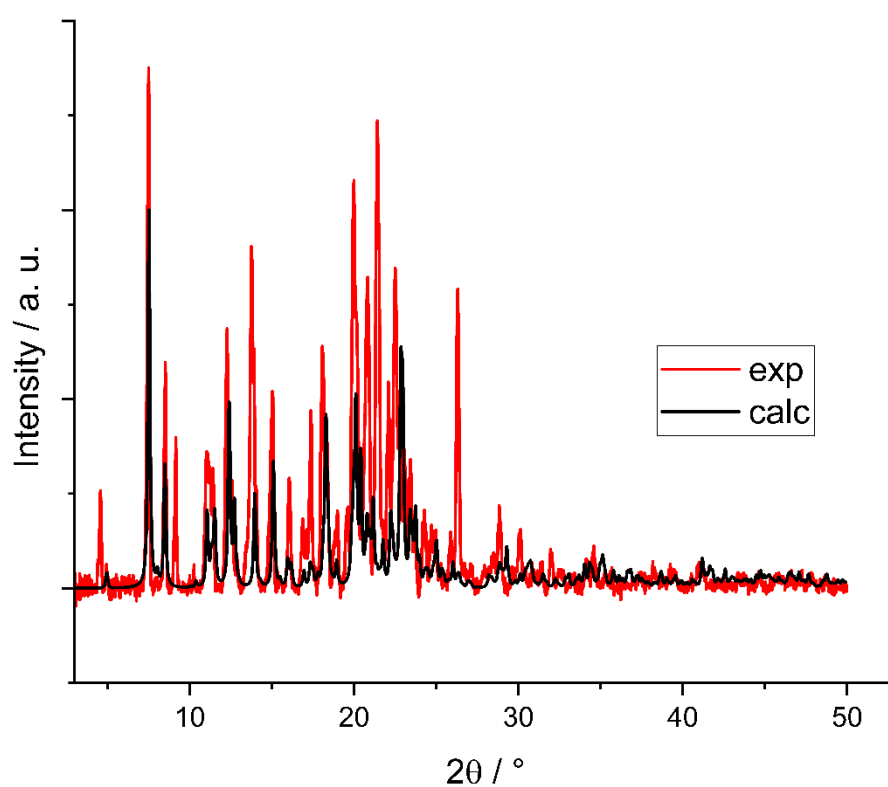


Figure S4: Powder X-Ray diffractogram of **1** (red line) measured at room temperature and the calculated one from the structure determined by single crystal X diffraction (black line).

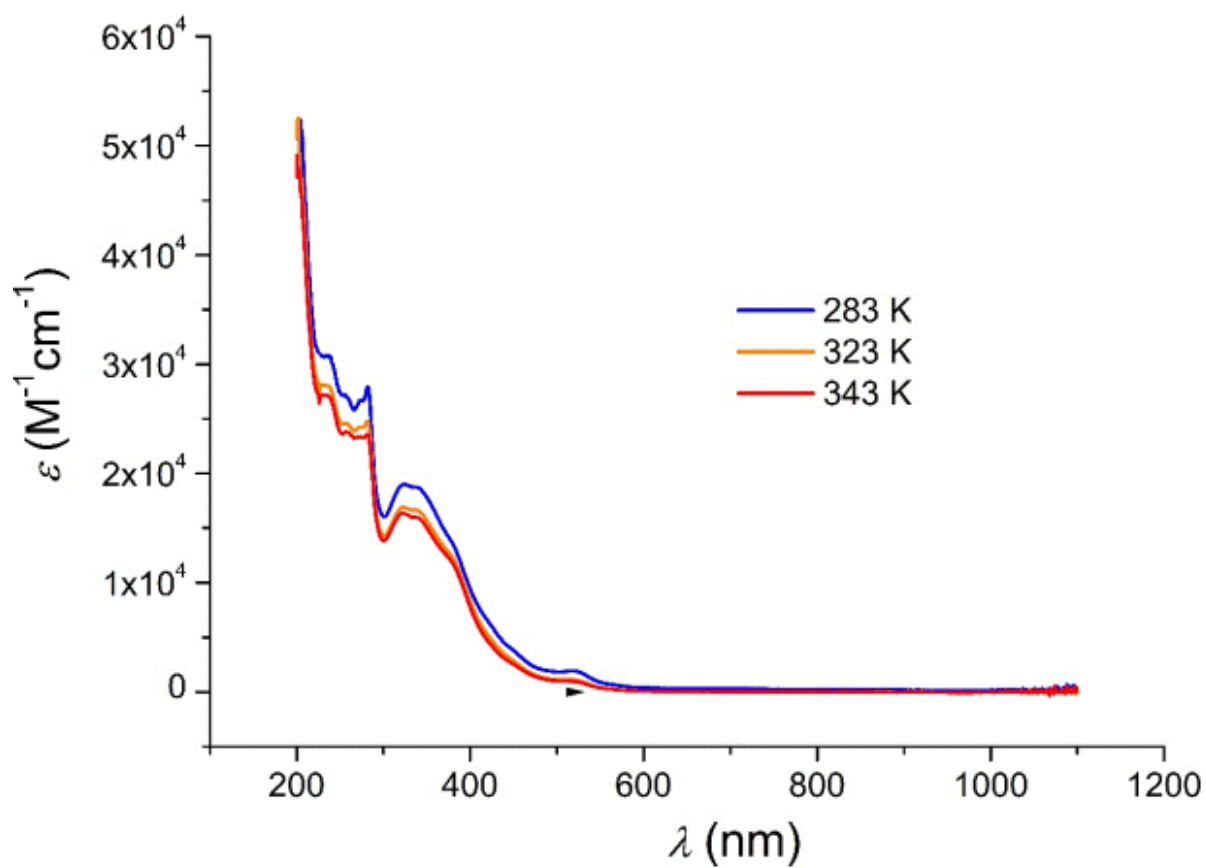


Figure S5: Temperature dependence of the electronic spectrum of a $6.6 \cdot 10^{-5} \text{ M}$ acetonitrile solution of **1**, reported as molar absorption coefficient.

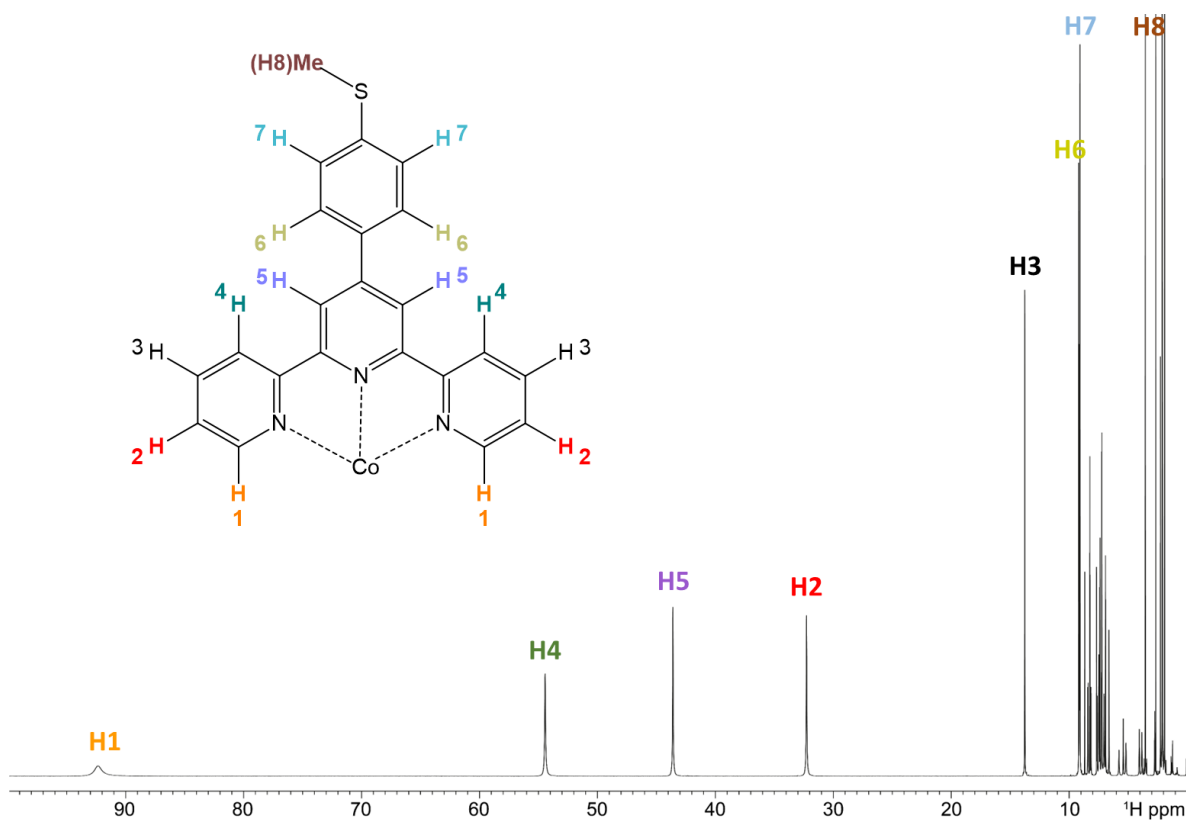


Figure S6: $^1\text{H-NMR}$ spectrum of an acetonitrile- d_3 solution of **1** at room temperature. Residual peaks are due to solvent impurities.

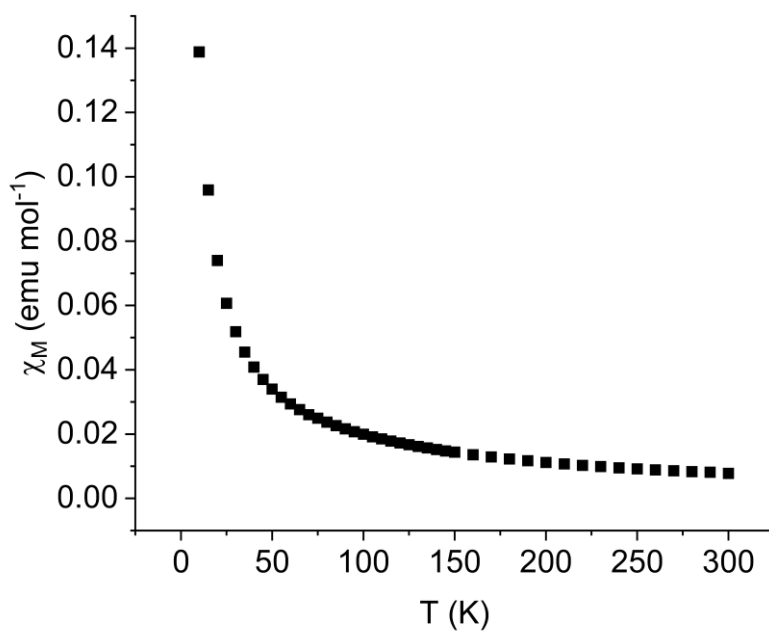


Figure S7 Plot of the temperature dependence of the molar magnetic susceptibility of the solid sample of **1**.

Table S4: Best fitting parameters employed for the temperature dependence of the chemical shifts of **1**, using Equation 3, reported in the manuscript.

	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈
C _{LS} (·10 ³)	17.1(3)	6.5(1)	2.35(6)	8.8(4)	0.8(4)	2.69(2)	1.24(5)	1.61(4)
C _{HS} (·10 ³)	44(2)	14.7(5)	6.9(3)	28(1)	32(2)	2.82(4)	5.0(2)	4.5(2)

References

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