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Electronic Supplementary Information

Competing Ferro- and Antiferromagnetic Interactions in a Hexagonal Bipyramidal Nickel Thiolate Cluster

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Instrumentation.

Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance equipped with a 1-D Lynxeye silicon strip detector and Cu radiation (1.54178 Å). The C, H, N and S analysis was performed by NuMega Resonance Labs. Magnetic measurements were carried out on a Quantum Design MPMS3.

X-ray crystallography.

X-ray diffraction data were collected using a Bruker APEX-II CCD diffractometer, with Mo Kα radiation (λ = 0.71070 Å). Multi-scan absorption corrections were applied to the intensity data. The structure was solved using the direct method (using *SHELXS-2013/4*)[1] and refined using the full-matrix least-squares method using F^2 (*SHELXL-2013/4*)[1] operated by *Olex2* software package[2] and *Yadokari-XG* software package.[3] All non-hydrogen atoms were refined using anisotropic parameters. Hydrogen atoms were included in the calculated positions and refined using a riding model. Crystallographic diagrams were obtained using the ORTEP program.[4] Crystal data are shown in

Table S1.

Magnetometry.

The magnetic sample was prepared by adding fine crystalline powder to a VSM powder sample holder from Quantum Design. The addition was carried out in small increments and after each increment the sample in the holder was firmly pressed into a pellet. This was done so as to reduce any crystallite orientation during the measurements. All magnetic measurements were performed on a Quantum Design MPMS-3 SQUID Magnetometer with a four second scan speed. The compound's magnetic susceptibility was measured from 2 to 300 K using an applied field of 1000 Oe. The variable-temperature magnetization measurements were carried out at 2.00 K, 4.00 K, and 6.00 K from 0 to 70000 Oe applied field. All data were corrected for diamagnetic contributions using Pascal's constants (χ_D = −0.00139136 emu/mol).

The best fit of the $\chi_M T$ data was obtained using the program *PHI*.[5] Isotropic exchange interactions between adjacent spin centers were considered and a total of

two exchange parameters were defined. The parameter J_{FM} represented planar-planar Ni coupling and J_{AFM} was defined for planar-capping coupling. The following parameters of best fit were found: J_{FM} = 12.9 cm^{-1}, J_{AFM} = -30.7 cm^{-1}, g = 2.1 ($R = \Sigma (\chi_M T_{Obs} - \chi_M T_{Calc})^2 / \Sigma \chi_M T_{Obs}^2 = 7.26 \times 10^{-5}$).

The best fit of the variable temperature magnetization data was obtained using MagProp, a sub-routine of the Data Analysis and Visualization Environment.[6] This data was modelled as an S = 4 giant spin using a Hamiltonian containing an average axial zero-field splitting term and a Zeeman term (Eq. 2). The following parameters of best fit were found: $|D|$ = 0.35 cm^{-1}, g = 2.2 ($R = \Sigma (M_{Obs} - M_{Calc})^2 / \Sigma M_{Obs}^2 = 1.11 \times 10^{-4}$).

Synthesis.

A CH_2Cl_2 solution (15 ml) of 2-pySH (1.639 g, 14.74 mmol) was added to a CH_3CN (15 ml) solution of $[Ni(H_2O)_6](BF_4)_2$ (509.2 mg, 1.496 mmol), and the mixture was stirred overnight. The resulted dark green-yellow solution was evacuated to dryness. The residual solid was dissolved to CH_2Cl_2 and was filtrated to

remove insoluble material. The filtrate was evacuated to dryness. The residual solid was dissolved to small amount of CH_2Cl_2 and excess amount of 2-propanol was added to the solution. The resulted precipitate was collected by filtration. The obtained crude product was purified by recrystallization. A CH_3CN solution of the crude product and excess NH_4PF_6 was placed under 2-propanol vapor for seven days, and the resulted deep brown cubic crystals were collected by filtration. The crystals were washed with water, 2-propanol and diethyl ether and were dried *in vacuo*. Yield 171.3 mg (35.0 %). Anal. found: C, 33.28; H, 2.94; N, 9.38; S, 14.73 %; calcd. for $C_{72}H_{66}F_{24}N_{18}Ni_8P_4S_{12}$: C, 33.03; H, 2.54; N, 9.63; S, 14.70 %. UV–vis (CH_3CN) λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 225sh (93700), 270sh (66500), 320 (63400).

Table S1 Crystal Data

Formula	$C_{72}H_{66}N_{18}Ni_8S_{12}P_4F_{24}$
Formula Weight	2617.6
Crystal System	monoclinic
Space group	$P2_1/n$ (No. 14)
a/Å	13.9583(3)
b/Å	22.5215(5)
c/Å	15.3686(4)
α/°	90
β/°	92.3771(13)
γ/°	90
V/Å^3	4827.1(2)
Z	2
D_{calc}/g•cm^{-3}	1.801
μ(MoKα)/mm^{-1}	1.949
F(000)	2632
Crystal Size/mm^3	0.05 × 0.05 × 0.10
Data Collection	
Temperature/K	100
Radiation [Angstrom]	Mo Kα, 0.71073
Theta Min, Max/°	1.7, 25.3
Dataset	-16: 15 ; -26: 27 ; -15: 18
Tot., Uniq. Data, R(int)	39258, 8804, 0.021
Observed Data [I > 0.0 sigma(I)]	7789
Refinement	
N_{ref}, N_{par}	8804, 625
R, wR_2, S	0.0366, 0.1040, 1.05
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens./e•Å^{-3}	-0.86, 0.83

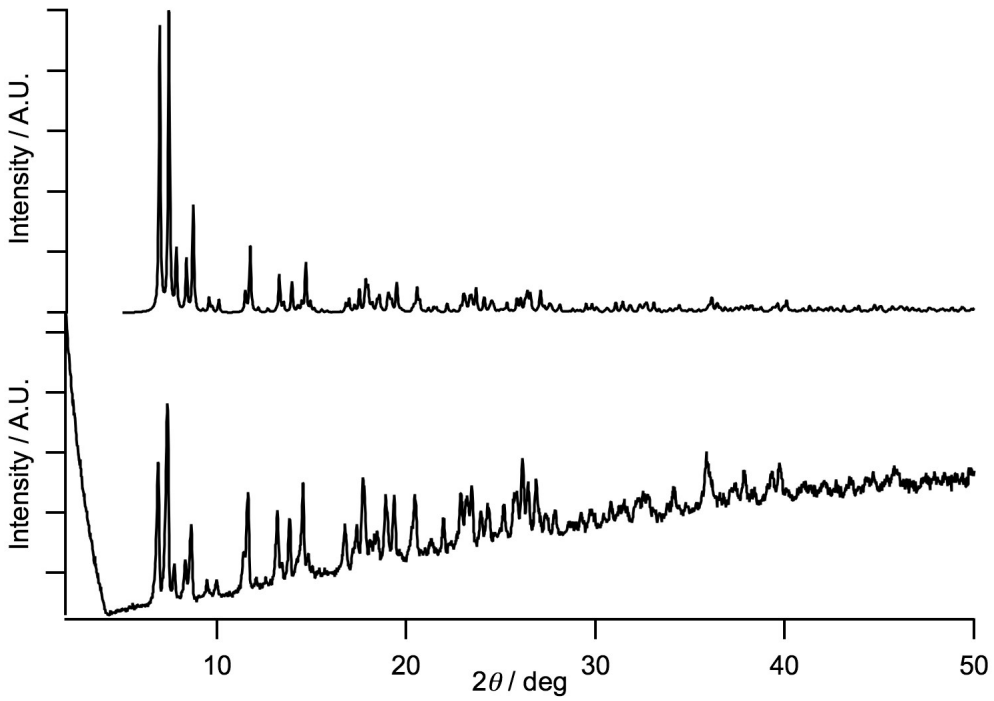

Figure S1. X-ray powder diffraction pattern of complex **1** (top: simulated pattern, bottom : observed data)

Reference

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