Supporting Information

Unprecedented hetero-bimetallic three-dimensional spin crossover coordination polymer based on the tetrahedral [Hg(SeCN)₄]²⁻ building block

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Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000-400 cm⁻¹ region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

General procedures and materials. All the reactions were carried out at room temperature under an air atmosphere and all chemicals and solvents used were reagent grade without further purification. The Hg(SCN)₂, Hg(SeCN)₂, KSCN, KSeCN and the ligand bpe were from commercial sources.

The two complexes were obtained by diffusion method in three-arm H-type vessels. One arm of the vessel contained a methanol solution (1 mL) of FeCl₂ (0.10 mmol, 12.7 mg), while the middle arm contained a water solution of K₂[HgXCN)₄] (1 mL) prepared in situ by mixing Hg(XCN)₂ (0.1 mmol) and KXCN (0.2 mmol) (X = S, Se). A methanol solution (1 mL) of bpe (0.10 mmol, 18.4 mg) was added to the other arm. After the slowly adding methanol to all the three arms, the vessels were sealed, and kept in a quiet and black place. Light orange block-like crystals of $\{Fe(bpe)[Hg(SCN)_4]\}_n$ (1) and $\{Fe(bpe)[Hg(SeCN)_4]\}_n$ (2) suitable for single crystal X-ray analysis were obtained after about two weeks with the yield about 55%. Anal. Calcd. for C₁₆H₁₂FeHgN₆S₄ (1): C, 28.55; H, 1.80; N, 12.49. Found: C, 28.48; H, 1.71; N, 12.61. Main IR bands (cm⁻¹): 2130 (s, vSCN). Anal. Calcd. for C₁₆H₁₂FeHgN₆Se₄ (2): C, 22.33; H, 1.41; N, 9.77. Found: C, 22.22; H, 1.31; N,

9.87. Main IR bands (cm⁻¹): 2130 (s, vSCN).

X-ray data collection and structure refinement. Single crystals of the two complexes for X-ray diffraction analysis with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker APEX2 CCD diffractometer with a MoK α sealed tube (λ = 0.71073 Å) at 293 K and 100 K, using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXL-2014 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the nonhydrogen atoms were refined with anisotropic displacement coefficients, assigned isotropic displacement coefficients U(H) =1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbons. CCDC 1894401-1894403 for complexes 1, 2-HS (293K) and 2-LS (100K) contain the supplementary crystallographic data for this paper. These data can be obtained free of Cambridge Crystallographic charge from the Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of the crystal parameters, data collection, and refinement are summarized in Table S1.

	1(293K)	2-HS (293K)	2-LS(100K)
Formula	$C_{16}H_{12}FeHgN_6S_4$	$C_{16}H_{12}FeHgN_6Se_4$	$C_{16}H_{12}FeHgN_6Se_4$
FW	673.00	860.60	860.60
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	Fddd	Fddd	Fddd
<i>a</i> (Å)	13.3667(7)	13.2273(5)	12.9098(9)
b (Å)	20.5131(13)	20.9742(10)	20.5604(11)
c (Å)	36.0076(14)	36.5434(10)	36.051(2)
α (Å)	90	90	90
<i>6</i> (Å)	90	90	90
γ (Å)	90	90	90
∨ (ų)	9873.0(9)	10138.3(7)	9569.1(10)
Ζ	16	16	16
$ ho_{calcd}$ (g cm ⁻³)	1.811	2.255	2.389
μ (mm ⁻¹)	7.151	12.379	13.115
F(000)	5120	6272	6272
ϑ (°)	3.25 to 25.01	3.276 to 25.01	3.35 to 25.01
Unique reflections	13417	15013	5683
Reflections (I > 2σ)	2186	2241	2116
GOF on F ²	1.078	1.001	0.971
$R_1[I > 2\sigma(I)]$	0.0334	0.0483	0.0417
wR ₂ (all data)	0.0882	0.1526	0.1064
$ ho_{ m max}/ ho_{ m min}$ (e Å ⁻³)	1.150/-0.903	1.384/-2.092	1.621/-1.547

Table S1. Crystal data and details of diffraction experiments for complexes 1 and 2.

Hg(1)-S(1) $2.5852(16)$ Hg(1)-S(2) $2.5029(12)$ Fe(1)-N(1) $2.154(5)$ Fe(1)-N(2) $2.156(5)$ Fe(1)-N(3) $2.194(4)$ S(2)-Hg(1)-S(1) $100.94(6)$ S(1)#4-Hg(1)-S(1) $99.46(7)$ S(2)-Hg(1)-S(1)#4 $119.43(7)$ S(2)#4-Hg(1)-S(2) $116.42(10)$ N(1)#1-Fe(1)-N(1) $88.9(3)$ N(1)#1-Fe(1)-N(2)#2 $88.6(3)$ N(1)-Fe(1)-N(2)#3 $88.6(2)$ N(2)#2-Fe(1)-N(2)#3 $93.9(3)$ N(1)-Fe(1)-N(3)#1 $90.31(17)$ N(2)#2-Fe(1)-N(3)#1 $87.71(16)$	5) 7)
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N(2)#2-Fe(1)-N(3)#1 87.71(16)	1
	1
N(2)#3-Fe(1)-N(3)#1 91.54(17)	1
N(1)#1-Fe(1)-N(3) 90.31(17)	1
N(1)-Fe(1)-N(3) 90.47(17)	
N(2)#2-Fe(1)-N(3) 91.54(17)	
N(2)#3-Fe(1)-N(3) 87.71(16)	

 Table S2. Selected bond lengths (Å) and angles (°) for complex 1.

The symmetry code used to generate the equivalent atoms: #1 -x+1/4, y, -z+1/4; #2 x+1/4, -y+1, z+1/4; #3 -x,-y+1,-z; #4 -x-1/4, -y+3/4, z.

	2		2*
Hg(1)-Se(1)	2.6795(15)	Hg(1)-Se(1)	2.6854(11)
Hg(1)-Se(2)	2.5983(13)	Hg(1)-Se(2)	2.6174(10)
Fe(1)-N(1)	2.129(8)	Fe(1)-N(1)	1.973(8)
Fe(1)-N(2)	2.147(8)	Fe(1)-N(2)#3	1.990(8)
Fe(1)-N(3)	2.193(7)	Fe(1)-N(3)	2.052(7)
Se(2)-Hg(1)-Se(1)	99.61(4)	Se(2)#1-Hg(1)-Se(1)	99.76(3)
S(1)#4-Hg(1)-S(1)	101.08(6)	Se(2)-Hg(1)-Se(2)#1	111.98(5)
S(2)-Hg(1)-S(1)#4	120.45(5)	Se(2)-Hg(1)-Se(1)	123.54(3)
S(2)#4-Hg(1)-S(2)	115.98(7)	Se(1)-Hg(1)-Se(1)#1	99.59(5)
N(1)#1-Fe(1)-N(1)	87.6(5)	N(1)#2-Fe(1)-N(1)	88.6(4)
N(1)#1-Fe(1)-N(2)#2	89.9(3)	N(1)-Fe(1)-N(2)#3	89.9(3)
N(1)-Fe(1)-N(2)#3	89.9(3)	N(1)#2-Fe(1)-N(2)#4	89.9(3)
N(2)#2-Fe(1)-N(2)#3	92.6(5)	N(2)#3-Fe(1)-N(2)#4	91.7(4)
N(1)#1-Fe(1)-N(3)#1	90.0(3)	N(1)#2-Fe(1)-N(3)	90.2(3)
N(1)-Fe(1)-N(3)#1	90.0(3)	N(1)-Fe(1)-N(3)	89.8(3)
N(2)#2-Fe(1)-N(3)#1	92.1(3)	N(2)#3-Fe(1)-N(3)	88.2(3)
N(2)#3-Fe(1)-N(3)#1	87.9(3)	N(2)#4-Fe(1)-N(3)	91.8(3)
N(1)#1-Fe(1)-N(3)	90.0(3)	N(1)#2-Fe(1)-N(3)#2	89.8(3)
N(1)-Fe(1)-N(3)	90.0(3)	N(1)-Fe(1)-N(3)#2	90.2(3)
N(2)#2-Fe(1)-N(3)	87.9(3)	N(2)#3-Fe(1)-N(3)#2	91.8(3)
N(2)#3-Fe(1)-N(3)	92.1(3)	N(2)#4-Fe(1)-N(3)#2	88.2(3)

 Table S3. Selected bond lengths (Å) and angles (°) for complex 2.

The symmetry code used to generate the equivalent atoms: #1 - x + 5/4, y, -z + 1/4; #2 - x + 1, -y + 1, -z + 3; x + 1/4, -y + 1, z + 1/4; #4 - x + 3/4, -y + 3/4, z (**2**) #1 - x + 1/4, -y + 5/4, z; #2 - x + 3/4, y, -z + 3/4; #3 x + 1/4, y - 1/4, -z + 1/2; #4 - x + 1/2, y - 1/4, z + 1/4.

Figure S1. (Top) View of the unit cell of compounds **1** and **2**, along [100] direction, showing the two arrays of chains, marked in red and blue, and connected through the tetrahedral $[Hg(XCN)_4]^{2-}$ units. (Bottom) Two consecutive arrays of layers viewed along [001] direction. Note as the chains run perpendicularly to each other.





Figure S2. Two orthogonal views of the same structural motive showing four fragments of chains belonging to two consecutive arrays displaying the π - π stacking. White-red connectors correspond to intermolecular C···C contacts shorter than the sum of the Van der Waals distance.





Table S3. Intermolecular π - π contacts (Å) smaller than the sum of the Van der Waals radius of C (c.a. 3.7 Å) for compound **2** in the LS and HS states.

	2 (LS)	2(HS)
C7…C4	3.41547	3.516
C8…C5	3.44301	3.455
C3…C2	3.52413	3.516
C4…C8	3.60208	
C7…C7 ⁱ	3.61958	
C1…C6	3.63153	
C4…C4 ⁱⁱ	3.64897	3.689
C1…C3	3.65171	
C3…C7	3.68167	

Figure S3. Temperature dependence of $\chi_{\rm M}$ T for compound **1**. The red line was generated using axial zero-field splitting (ZFS) for the S = 2 ground state of Fe^{II} expressed by the hamiltonian $H = g\beta HS + D[S_z^2 - S(S+1)/3]$. Assuming that $g_{\parallel} = g_{\perp}$, the best simulation of the



experimental $\chi_M T$ versus T plot affords the parameters g = 2.12, D = 13.0 cm⁻¹.

Figure S4. Temperature dependence of $\chi_M T$ for compound **2**. The red line was generated using the regular solutions thermodynamic model.



Figure S5. The calculated and measured pattern of PXRD for the complex **1**.



Figure S6. The calculated and measured pattern of PXRD for complex **2**.



Figure S7. IR spectra for the complexes **1** and **2**.

