Supporting Information

Nature of cyanoargentate bridge defining spin crossover in new 2D Hofmann clathrate analogues

Valerii Y. Sirenko,[a] Olesia I. Kucheriv,[a] Sergiu Shova,[b] Sergii I. Shylin,[c] Vadim Ksenofontov,[d] Igor O. Fritsky,[a,e] Wolfgang Tremel[d] and Il'ya A. Gural'skiy*[a]

[a.] *Department of Chemistry, Taras Shevchenko National University of Kyiv, 64 Volodymyrska St., 01601 Kyiv, Ukraine. E-mail: illia.guralskyi@univ.kiev.ua*
[b.] *Department of Inorganic Polymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Gr. Ghica Voda, 700487 Iasi, Romania*
[c.] *Ångström Laboratory, Department of Chemistry, Uppsala University, 75120 Uppsala, Sweden*
[d.] *Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, 55128 Mainz, Germany*
[e.] *Innovation development center ABN, 2/37 Pirogov St., 01030 Kyiv, Ukraine*

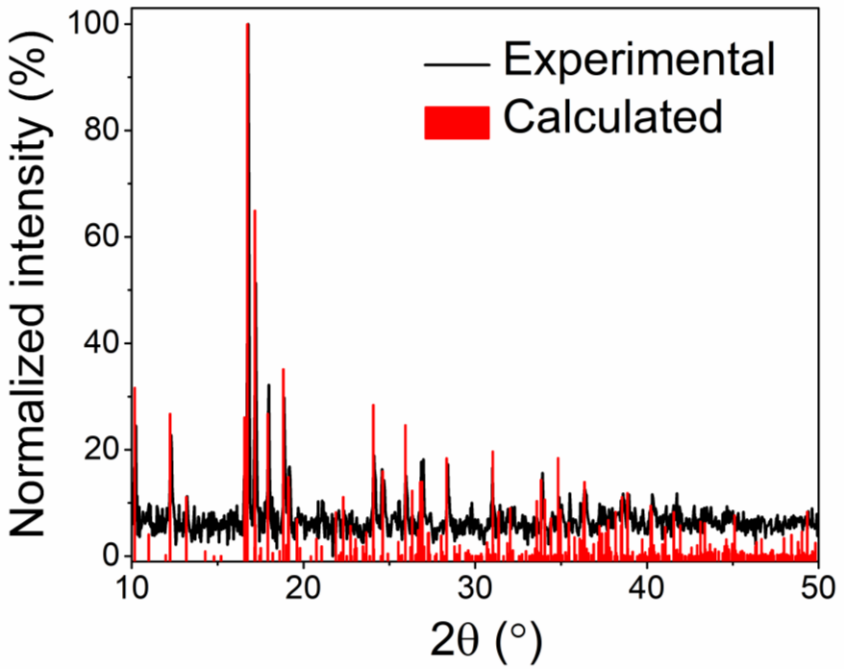

Figure S1. Experimental (black line) and calculated (red column) PXRD patterns of **1** in the HS state

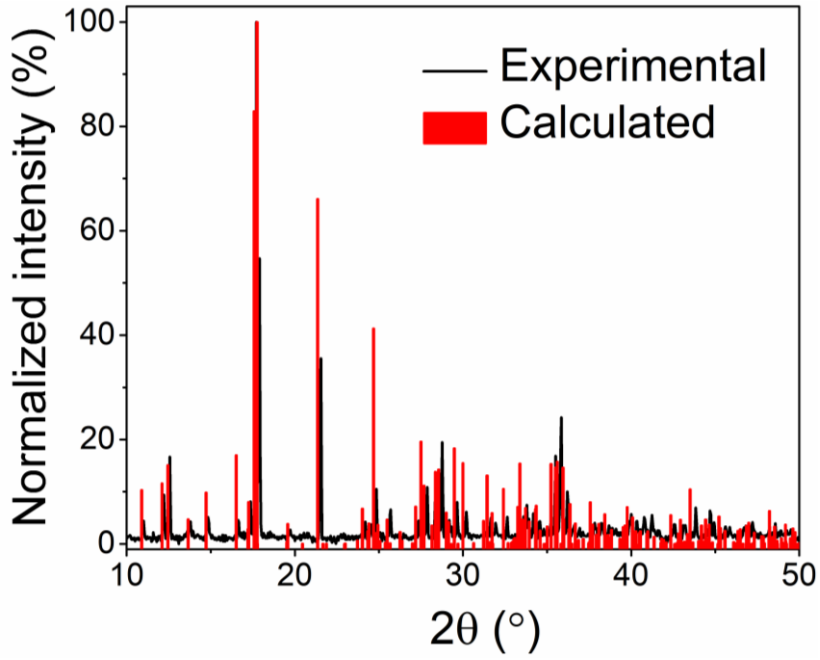

Figure S2. Experimental (black line) and calculated (red column) PXRD patterns of **2** in the HS state

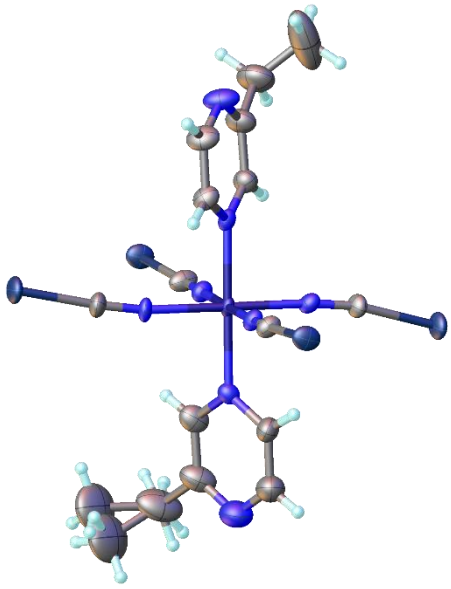

Figure S3. Illustration of Etpz disorder in **1**.

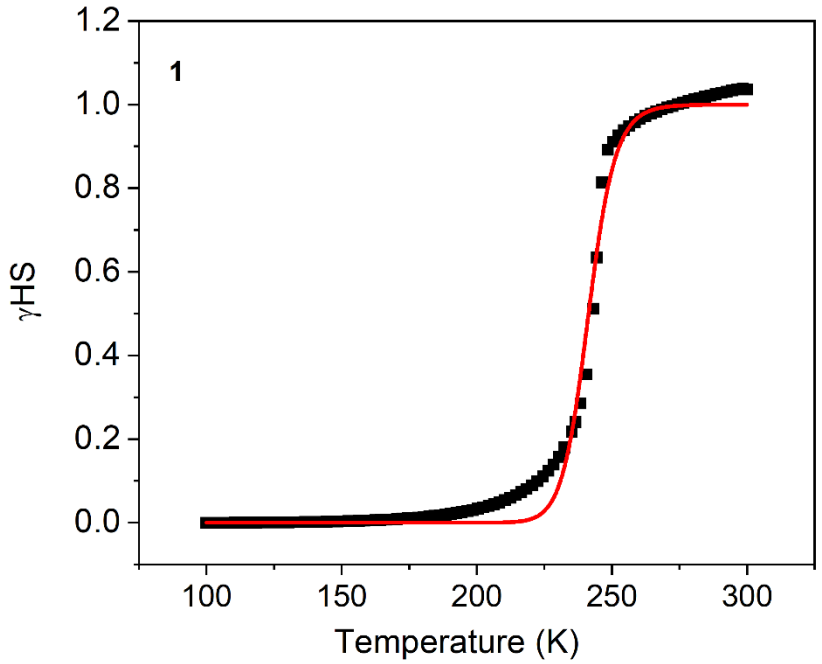

Figure S4. Heating curve of **1** obtained from a fit of magnetic susceptibility to the domain model. The calculations indicate the presence of ~10 SCO centers per domain.

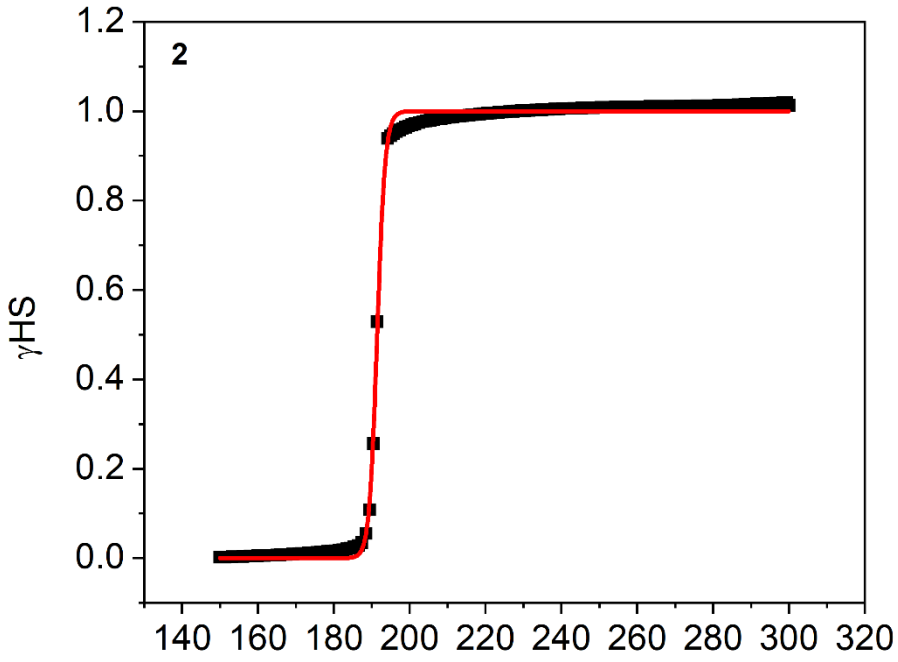

Figure S5. Heating curve of **2** obtained from a fit of magnetic susceptibility to the domain model. The performed calculations indicate the presence of ~17 SCO centers per domain.

Table S1. Bond lengths for **1**^{LS} (200 K).

	Bond length (Å)		Bond length (Å)		Bond length (Å)
Ag2–Ag1	3.0191(8)	N1–C1	1.141(8)	N6–C7	1.322(10)
Ag2–C4^{1}	2.059(6)	N2–C2	1.144(8)	N6–C6	1.329(11)
Ag2–C2^{2}	2.038(7)	N3–C3	1.141(8)	C8–C7	1.375(10)
Ag1–C1	2.070(6)	N5–C8	1.336(8)	C12–C11	1.383(9)
Ag1–C3^{3}	2.064(6)	N5–C5	1.333(8)	C12–C15	1.531(11)
Fe1–N1	1.941(5)	N4–C4	1.148(8)	C5–C6	1.400(10)
Fe1–N2	1.952(5)	N7–C14	1.329(8)	C15–C16	1.463(11)
Fe1–N3	1.934(5)	N7–C11	1.336(8)	C6–C9	1.533(12)
Fe1–N5	2.007(5)	N8–C12	1.328(9)	C9–C10B	1.528(19)
Fe1–N4	1.933(5)	N8–C13	1.328(9)	C9–C10A	1.507(16)
Fe1–N7	1.998(5)	C14–C13	1.379(9)		

$^{1}1–x, 1–y, 1–z$; $^{2}1/2–x, –1/2+y, 1/2–z$; $^{3}+x, –1+y, +z$

Table S2. Bond angles for **1**^{LS} (200 K).

	Angle (°)		Angle (°)		Angle (°)
C4^{1}–Ag2–Ag1	83.84(18)	N4–Fe1–N5	88.7(2)	N8–C12–C11	120.5(6)
C2^{2}–Ag2–Ag1	99.58(19)	N4–Fe1–N7	90.9(2)	N8–C12–C15	118.9(7)
C2^{2}–Ag2–C4^{1}	175.4(3)	N7–Fe1–N5	179.1(2)	C11–C12–C15	120.6(7)
C1–Ag1–Ag2	79.62(18)	C1–N1–Fe1	178.2(5)	N8–C13–C14	123.0(6)
C3^{3}–Ag1–Ag2	93.94(18)	C2–N2–Fe1	172.0(5)	N7–C11–C12	122.5(6)
C3^{3}–Ag1–C1	170.4(2)	N1–C1–Ag1	173.9(6)	N5–C5–C6	122.6(7)
N1–Fe1–N2	90.0(2)	C3–N3–Fe1	174.9(5)	N6–C7–C8	123.4(8)
N1–Fe1–N5	91.0(2)	C8–N5–Fe1	122.1(4)	C16–C15–C12	110.3(8)
N1–Fe1–N7	89.80(19)	C5–N5–Fe1	122.8(5)	N6–C6–C5	121.6(8)
N2–Fe1–N5	91.7(2)	C5–N5–C8	114.9(6)	N6–C6–C9	117.3(8)
N2–Fe1–N7	88.7(2)	C4–N4–Fe1	173.8(5)	C5–C6–C9	121.1(8)
N3–Fe1–N1	178.6(2)	C14–N7–Fe1	121.1(4)	C10B–C9–C6	109(2)
N3–Fe1–N2	89.5(2)	C14–N7–C11	116.6(6)	C10A–C9–C6	112.6(13)
N3–Fe1–N5	90.3(2)	C11–N7–Fe1	122.3(4)	N4–C4–Ag2^{1}	169.2(6)
N3–Fe1–N7	88.9(2)	C12–N8–C13	116.7(6)	N2–C2–Ag2^{4}	175.7(6)
N4–Fe1–N1	89.9(2)	N7–C14–C13	120.6(6)	N3–C3–Ag1^{5}	172.6(6)
N4–Fe1–N2	179.6(2)	C7–N6–C6	115.5(7)		
N4–Fe1–N3	90.6(2)	N5–C8–C7	122.1(7)		

$^{1}1–x, 1–y, 1–z$; $^{2}1/2–x, –1/2+y, 1/2–z$; $^{3}+x, –1+y, +z$; $^{4}1/2–x, 1/2+y, 1/2–z$; $^{5}+x, 1+y, +z$

Table S3. Bond lengths for **1**^{HS} (304 K).

	Bond length (Å)		Bond length (Å)		Bond length (Å)
Ag1–Ag2	3.0724(9)	N1–C1	1.139(8)	N6–C6	1.313(12)
Ag1–C3^{1}	2.055(7)	N7–C11	1.315(9)	N4–C4	1.122(8)
Ag1–C1	2.061(7)	N7–C14	1.321(8)	C14–C13	1.368(11)
Fe1–N1	2.121(5)	C3–N3	1.137(8)	C12–C15	1.570(11)
Fe1–N7	2.231(5)	N8–C13	1.320(10)	C5–C6	1.397(12)
Fe1–N3	2.122(5)	N8–C12	1.323(10)	C6–C9	1.557(11)
Fe1–N5	2.226(6)	N5–C8	1.324(9)	N2–C2	1.125(8)
Fe1–N4	2.133(6)	N5–C5	1.325(9)	C15–C16	1.441(11)
Fe1–N2	2.128(6)	C8–C7	1.360(11)	C9–C10B	1.51(2)
Ag2–C4^{2}	2.063(7)	C11–C12	1.369(10)	C9–C10A	1.509(18)
Ag2–C2^{3}	2.050(7)	N6–C7	1.304(11)		

^{1}+*x*, –1+*y*, +*z*; ^{2}1–*x*, 1–*y*, 1–*z*; ^{3}3/2–*x*, –1/2+*y*, 3/2–*z*

Table S4. Bond angles for **1**^{HS} (304 K).

	Angle (°)		Angle (°)		Angle (°)
C3^{1}–Ag1–Ag2	94.2(2)	C4^{2}–Ag2–Ag1	87.0(2)	C4–N4–Fe1	162.7(6)
C3^{1}–Ag1–C1	170.3(3)	C2^{3}–Ag2–Ag1	96.4(2)	N7–C14–C13	121.4(7)
C1–Ag1–Ag2	80.4(2)	C2^{3}–Ag2–C4^{2}	176.4(3)	N8–C13–C14	123.6(8)
N1–Fe1–N7	88.9(2)	C1–N1–Fe1	176.9(6)	N8–C12–C11	121.5(7)
N1–Fe1–N3	177.6(2)	C11–N7–Fe1	122.6(4)	N8–C12–C15	118.7(8)
N1–Fe1–N5	91.6(2)	C11–N7–C14	115.1(6)	C11–C12–C15	119.7(9)
N1–Fe1–N4	90.4(2)	C14–N7–Fe1	122.1(5)	N5–C5–C6	121.2(8)
N1–Fe1–N2	90.0(2)	N3–C3–Ag1^{4}	174.8(7)	N4–C4–Ag22	173.4(7)
N3–Fe1–N7	88.7(2)	C3–N3–Fe1	172.4(6)	N6–C6–C5	122.2(8)
N3–Fe1–N5	90.9(2)	N1–C1–Ag1	176.9(6)	N6–C6–C9	118.4(10)
N3–Fe1–N4	89.6(2)	C13–N8–C12	114.7(7)	C5–C6–C9	119.4(10)
N3–Fe1–N2	89.9(2)	C8–N5–Fe1	121.9(5)	C2–N2–Fe1	166.4(7)
N5–Fe1–N7	179.52(19)	C8–N5–C5	115.7(7)	N2–C2–Ag2^{5}	175.8(7)
N4–Fe1–N7	91.0(2)	C5–N5–Fe1	122.4(5)	C16–C15–C12	109.7(9)
N4–Fe1–N5	88.9(2)	N5–C8–C7	121.8(8)	C10B–C9–C6	105(3)
N2–Fe1–N7	87.2(2)	N7–C11–C12	123.5(7)	C10A–C9–C6	115.1(17)
N2–Fe1–N5	92.9(2)	C7–N6–C6	115.3(8)		
N2–Fe1–N4	178.2(2)	N6–C7–C8	123.8(9)		

^{1}+*x*, –1+*y*, +*z*; ^{2}1–*x*, 1–*y*, 1–*z*; ^{3}3/2–*x*, –1/2+*y*, 3/2–*z*; ^{4}+*x*, 1+*y*, +*z*; ^{5}3/2–*x*, 1/2+*y*, 3/2–*z*

Table S5. Bond lengths for **2**^{LS} (173 K).

	Bond length (Å)		Bond length (Å)		Bond length (Å)
Ag2–C2	2.072(3)	Fe1–N4	1.989(3)	C3–C3^{3}	1.142(7)
Ag2–C3	2.098(3)	Fe1–N4^{2}	1.989(3)	C5–C4	1.400(5)
Ag2–N3	2.098(3)	N1–C1	1.142(4)	C5–C8	1.512(4)
Ag2–Ag1^{1}	3.2185(4)	N2–C2	1.145(5)	C7–C6	1.384(5)
Fe1–N1	1.954(3)	N4–C7	1.353(5)	C1–Ag1	2.077(3)
Fe1–N1^{2}	1.954(3)	N4–C4	1.348(4)	C8–C9	1.526(5)
Fe1–N2	1.949(3)	N5–C5	1.332(5)		
Fe1–N2^{2}	1.949(3)	N5–C6	1.319(4)		

^{1}+*x*, 1+*y*, +*z*; ^{2}1–*x*, –1–*y*, –*z*; ^{3}–*x*, –*y*, –1–*z*

Table S6. Bond angles for **2**^{LS} (173 K).

	Angle (°)		Angle (°)		Angle (°)
C2–Ag2–C3	178.44(14)	N2–Fe1–N2^{2}	180.00(13)	N5–C5–C4	120.6(3)
C2–Ag2–N3	178.44(14)	N2^{2}–Fe1–N4^{2}	89.43(12)	N5–C5–C8	117.5(3)
C2–Ag2–Ag1^{1}	80.26(10)	N2^{2}–Fe1–N4	90.57(12)	C4–C5–C8	121.9(3)
C3–Ag2–Ag1^{1}	101.29(10)	N2–Fe1–N4	89.43(12)	N4–C7–C6	121.2(3)
N3–Ag2–Ag1^{1}	101.29(10)	N2–Fe1–N4^{2}	90.57(12)	N4–C4–C5	121.9(3)
N1–Fe1–N1^{2}	180	N4^{2}–Fe1–N4	180	N1–C1–Ag1	172.1(3)
N1–Fe1–N4	87.74(11)	C1–N1–Fe1	170.5(3)	N5–C6–C7	122.4(3)
N1^{2}–Fe1–N4	92.26(11)	C2–N2–Fe1	175.0(3)	C5–C8–C9	112.0(3)
N1^{2}–Fe1–N4^{2}	87.74(11)	C7–N4–Fe1	120.3(2)	Ag2^{4}–Ag1–Ag2^{5}	180
N1–Fe1–N4^{2}	92.26(11)	C4–N4–Fe1	123.5(3)	C1–Ag1–Ag2^{5}	104.56(10)
N2–Fe1–N1^{2}	88.41(11)	C4–N4–C7	116.0(3)	C1^{6}–Ag1–Ag2^{4}	104.56(10)
N2–Fe1–N1	91.59(11)	N2–C2–Ag2	165.2(3)	C1–Ag1–Ag2^{4}	75.44(10)
N2^{2}–Fe1–N1	88.41(11)	C6–N5–C5	117.9(3)	C1^{6}–Ag1–Ag2^{5}	75.44(10)
N2^{2}–Fe1–N1^{2}	91.59(11)	C3^{3}–C3–Ag2	174.1(5)	C1–Ag1–C1^{6}	180

^{1}+*x*, 1+*y*, +*z*; ^{2}1–*x*, –1–*y*, –*z*; ^{3}–*x*, –*y*, –1–*z*; ^{4}+*x*, –1+*y*, +*z*; ^{5}–*x*, –1–*y*, –*z*; ^{6}–*x*, –2–*y*, –*z*

Table S7. Bond lengths for **2**^{HS} (296 K).

	Bond length (Å)		Bond length (Å)		Bond length (Å)
Ag2–C2	2.078(3)	Fe1–N4^{2}	2.241(2)	C5–C4	1.400(4)
Ag2–C3	2.104(3)	Fe1–N1	2.172(2)	C5–N5	1.343(4)
Ag2–N3	2.104(3)	Fe1–N1^{2}	2.172(2)	C5–C8	1.511(4)
Ag1–C1^{1}	2.079(3)	C2–N2	1.135(4)	C7–C6	1.389(4)
Ag1–C1	2.079(3)	C3–C3^{3}	1.132(6)	C6–N5	1.337(4)
Fe1–N2	2.165(2)	N4–C4	1.341(3)	C8–C9	1.525(5)
Fe1–N2^{2}	2.166(2)	N4–C7	1.342(4)		
Fe1–N4	2.241(2)	N1–C1	1.141(4)		

^{1}–*x*, –*y*, 2–*z*; ^{2}1–*x*, 1–*y*, 2–*z*; ^{3}–*x*, 2–*y*, 1–*z*

Table S8. Bond angles for **2**^{HS} (296 K).

	Angle (°)		Angle (°)		Angle (°)
C2–Ag2–C3	179.12(13)	N4–Fe1–N4^{2}	180	C1–N1–Fe1	164.6(2)
C2–Ag2–N3	179.12(13)	N1^{2}–Fe1–N4^{2}	87.19(9)	N1–C1–Ag1	175.3(3)
C1–Ag1–C1^{1}	180	N1^{2}–Fe1–N4	92.81(9)	C4–C5–C8	122.5(2)
N2–Fe1–N2^{2}	180.00(10)	N1–Fe1–N4	87.19(9)	N5–C5–C4	120.2(2)
N2^{2}–Fe1–N4	91.13(9)	N1–Fe1–N4^{2}	92.81(9)	N5–C5–C8	117.2(2)
N2–Fe1–N4	88.87(9)	N1–Fe1–N1^{2}	180	N4–C4–C5	122.3(2)
N2^{2}–Fe1–N4^{2}	88.87(9)	N2–C2–Ag2	168.1(2)	N4–C7–C6	120.5(3)
N2–Fe1–N4^{2}	91.13(9)	C3^{3}–C3–Ag2	174.0(4)	N5–C6–C7	122.7(3)
N2–Fe1–N1^{2}	90.02(10)	C2–N2–Fe1	168.1(2)	C6–N5–C5	117.1(2)
N2^{2}–Fe1–N1	90.02(10)	C4–N4–Fe1	124.25(18)	C5–C8–C9	112.3(2)
N2^{2}–Fe1–N1^{2}	89.98(10)	C4–N4–C7	117.0(2)		
N2–Fe1–N1	89.98(10)	C7–N4–Fe1	118.56(17)		

^{1}–*x*, –*y*, 2–*z*; ^{2}1–*x*, 1–*y*, 2–*z*; ^{3}–*x*, 2–*y*, 1–*z*