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Supplementary Information

$[Fe(abpt)_2(NCSe)_2]$ polymorph A: Structural studies into the spin crossover behaviour

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Table S1 - Crystal data and refinement results for **A** at 50 K, 75 K, 100 K, 108 K, 125 K and 150 K.

	50(2) K	**75(2) K**	**100(2) K**	**108(2) K**	**125(2) K**	**150(2) K**
Empirical formula	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$
Formula weight	742.33	742.33	742.33	742.33	742.33	742.33
Temperature / K	50(2)	75(2)	100(2)	108(2)	125(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	8.4368(5)	8.4405(5)	8.4499(6)	8.4550(6)	8.4560(3)	8.4649(4)
b / Å	9.9497(6)	9.9558(6)	9.9648(6)	9.9691(7)	9.9693(4)	9.9787(5)
c / Å	16.3497(10)	16.3563(9)	16.3673(10)	16.3559(11)	16.3570(7)	16.3697(8)
β / °	93.1257(13)	93.1270(10)	93.1342(13)	93.0618(13)	93.0825(7)	93.0951(9)
V / Å^3	1370.41(14)	1372.40(14)	1376.09(15)	1376.65(17)	1376.91(9)	1380.71(12)
Z	2	2	2	2	2	2
ρ_{calc} / (g/cm^3)	1.799	1.796	1.792	1.791	1.790	1.786
μ / mm^{-1}	3.254	3.249	3.240	3.239	3.239	3.230
F(000)	736.0	736.0	736.0	736.0	736.0	736.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo*Kα* (λ = 0.71073)	Mo*Kα* (λ = 0.71073)
2θ range for data collection / °	4.794 to 56.55	4.792 to 56.56	4.788 to 56.552	4.788 to 56.562	4.786 to 56.532	4.782 to 55.748
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 13, -21 ≤ l ≤ 19	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21	-11 ≤ h ≤ 10, -12 ≤ k ≤ 13, -21 ≤ l ≤ 19	-11 ≤ h ≤ 11, -13 ≤ k ≤ 11, -20 ≤ l ≤ 21	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -20 ≤ l ≤ 21	-11 ≤ h ≤ 11, -13 ≤ k ≤ 8, -16 ≤ l ≤ 21
Reflections collected	9150	21905	9170	11504	15248	9538
R_{int} / R_{sigma}	0.0328 / 0.0397	0.0388 / 0.0245	0.0322 / 0.0386	0.0306 / 0.0313	0.0336 / 0.0279	0.0287 / 0.0329
Data/restraints/parameters	3380/0/202	3400/0/202	3399/0/202	3424/0/202	3421/0/202	3282/0/202
Goodness-of-fit on F^2	1.070	1.091	1.047	1.075	1.093	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0742	R_1 = 0.0320, wR_2 = 0.0696	R_1 = 0.0356, wR_2 = 0.0753	R_1 = 0.0321, wR_2 = 0.0662	R_1 = 0.0311, wR_2 = 0.0655	R_1 = 0.0325, wR_2 = 0.0671
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.0769	R_1 = 0.0385, wR_2 = 0.0719	R_1 = 0.0454, wR_2 = 0.0785	R_1 = 0.0397, wR_2 = 0.0687	R_1 = 0.0384, wR_2 = 0.0679	R_1 = 0.0416, wR_2 = 0.0702
Largest diff. peak/hole / (e Å^{-3})	0.81/-0.65	0.86/-0.69	0.93/-0.61	0.72/-0.66	0.66/-0.63	0.73/-0.69

Table S1 continued - Crystal data and refinement results for **A** at 175 K, 200 K, 225 K, 250 K, 275 K and 300 K.

	175(2) K	**200(2) K**	**225(2) K**	**250(2) K**	**275(2) K**	**300(2) K**
Empirical formula	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$
Formula weight	742.33	742.33	742.33	742.33	742.33	742.33
Temperature / K	175(2)	200(2)	225(2)	250(2)	275(2)	300(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	8.4815(4)	8.4971(3)	8.5401(5)	8.5815(4)	8.6022(3)	8.6181(4)
b / Å	9.9987(5)	10.0240(4)	10.0947(5)	10.1622(5)	10.1941(4)	10.2163(4)
c / Å	16.3984(9)	16.4110(6)	16.4597(9)	16.5208(9)	16.5527(6)	16.5785(7)
β / °	93.1310(10)	93.1650(7)	93.2083(10)	93.2926(10)	93.3872(7)	93.4701(9)
V / Å^3	1388.57(12)	1395.67(9)	1416.76(13)	1438.35(13)	1449.00(9)	1456.98(11)
Z	2	2	2	2	2	2
ρ_{calc} / (g/cm^3)	1.775	1.766	1.740	1.714	1.701	1.692
μ / mm^{-1}	3.211	3.195	3.147	3.100	3.077	3.061
F(000)	736.0	736.0	736.0	736.0	736.0	736.0
Radiation	Mo*Kα* (λ = 0.71073)	MoKα (λ = 0.71073)	Mo*Kα* (λ = 0.71073)	MoKα (λ = 0.71073)	Mo*Kα* (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection / °	4.774 to 56.556	4.764 to 52.736	4.736 to 56.546	4.708 to 52.734	4.694 to 52.744	4.686 to 52.728
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 8, -21 ≤ l ≤ 16	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20	-11 ≤ h ≤ 11, -13 ≤ k ≤ 8, -16 ≤ l ≤ 21	-10 ≤ h ≤ 10, -12 ≤ k ≤ 8, -16 ≤ l ≤ 20	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -19 ≤ l ≤ 20
Reflections collected	9355	15588	10118	8953	16262	11766
R_{int} / R_{sigma}	0.0303 / 0.0364	0.0329 / 0.0223	0.0330 / 0.0390	0.0314 / 0.0343	0.0373 / 0.0255	0.0347 / 0.0314
Data/restraints/parameters	3444/1/202	2861/0/202	3517/0/202	2938/0/202	2963/0/202	2977/0/202
Goodness-of-fit on F^2	1.050	1.101	1.050	1.070	1.091	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, wR_2 = 0.0697	R_1 = 0.0295, wR_2 = 0.0633	R_1 = 0.0391, wR_2 = 0.0760	R_1 = 0.0373, wR_2 = 0.0815	R_1 = 0.0358, wR_2 = 0.0812	R_1 = 0.0377, wR_2 = 0.0849
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.0739	R_1 = 0.0351, wR_2 = 0.0649	R_1 = 0.0585, wR_2 = 0.0821	R_1 = 0.0514, wR_2 = 0.0870	R_1 = 0.0475, wR_2 = 0.0855	R_1 = 0.0577, wR_2 = 0.0930
Largest diff. peak/hole / (e Å^{-3})	0.75/-0.64	0.64/-0.51	0.79/-0.63	0.72/-0.56	0.76/-0.58	0.90/-0.60

Table S1 continued - Crystal data and refinement results for **A** at 325 K and 350 K.

	325(2) K	**350(2) K**
Empirical formula	$C_{26}H_{20}FeN_{14}Se_2$	$C_{26}H_{20}FeN_{14}Se_2$
Formula weight	742.33	742.33
Temperature / K	325(2)	350(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / Å	8.6327(5)	8.6423(4)
b / Å	10.2367(6)	10.2507(4)
c / Å	16.6049(10)	16.6132(7)
β / °	93.4981(11)	93.5248(9)
V / Å^3	1464.65(15)	1468.97(11)
Z	2	2
ρ_{calc} / (g/cm^3)	1.683	1.678
μ / mm^{-1}	3.045	3.036
F(000)	736.0	736.0
Radiation	Mo*Kα* (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection / °	4.676 to 52.734	4.672 to 52.746
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 8$, $-20 \le l \le 16$	$-10 \le h \le 10$, $-12 \le k \le 12$, $-19 \le l \le 20$
Reflections collected	8669	14266
R_{int} / R_{sigma}	0.0338 / 0.0394	0.0379 / 0.0306
Data/restraints/parameters	2992/0/202	3004/0/202
Goodness-of-fit on F^2	1.045	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.0894	R_1 = 0.0408, wR_2 = 0.0900
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1041	R_1 = 0.0657, wR_2 = 0.1013
Largest diff. peak/hole / (e Å^{-3})	0.87/-0.61	0.93/-0.64

Table S2 - Unit cell and structural parameters for $[Fe(abpt)_2(NCSe)_2]$ polymorph **A** collected at 225 K ($\sim T_{1/2}$) during cooling (↓) and warming (↑) cycles.

Temperature		225(2) K (↓)	225(2) K (↑)
Empirical formula		$FeC_{26}H_{20}N_{14}Se_2$	$FeC_{26}H_{20}N_{14}Se_2$
Crystal system		Monoclinic	Monoclinic
Space group		$P\,2_1/n$	$P\,2_1/n$
Unit cell dimensions	***a*, *b*, *c* / Å**	8.5401(5), 10.0947(5), 16.4597(9)	8.5410(5), 10.0946(5), 16.4604(9)
	α, β, γ / °	90, 93.2083(10), 90	90, 93.2069(11), 90
	V / Å^3	1416.76(13)	1416.96(13)
Z, Z'		2, 0.5	2, 0.5
Bond length / Å	**Fe1-N7**	2.032(3)	2.030(3)
	Fe1-N1	2.096(2)	2.094(3)
	Fe1-N2	2.027(2)	2.029(3)
V_{poly} / Å^3		11.234(8)	11.224(9)
Σ / °		59.0(6)	58.8(7)
Θ / °		229.4(11)	228.6(12)

Table S3 - Fe-N bond lengths for all structures, along with the distortion parameter, Σ, and the volume of the Fe octahedron, V_p.

	50(2) K	75(2) K	100(2) K	108(2) K	200(2) K	250(2) K	300(2) K	350(2) K
Fe1-N1 / Å	1.949(2)	1.951(2)	1.950(2)	1.952(2)	1.973(2)	2.098(3)	2.133(3)	2.142(4)
Fe1-N2 / Å	2.014(2)	2.016(2)	2.014(2)	2.015(2)	2.032(2)	2.168(3)	2.207(3)	2.213(3)
Fe1-N3 / Å	1.957(2)	1.957(2)	1.955(2)	1.957(2)	1.974(2)	2.086(3)	2.119(3)	2.124(3)
Σ[a] / º	49.6(6)	49.8(6)	49.9(6)	49.6(5)	52.3(5)	65.5(7)	69.4(7)	70.0(8)
V_p[b] / Å^3	10.075(7)	10.090(7)	10.067(7)	10.090(6)	10.358(7)	12.259(10)	12.839(10)	12.946(12)

[a] Σ, the angle distortion parameter, is the sum of the absolute value of the deviation of all 12 *cis* N-Fe-N angles from 90°. [b] V_p is the volume of the Fe octahedron calculated in Olex2.

Table S4 - Summary of the hydrogen bonding parameters in **A** as a function of temperature.

Temperature	D-H···A	D-H / Å	H···A / Å	D···A / Å	<D-H···A /°
375(2) K	N6-H6B···N7	0.87(5)	2.16(5)	2.860(5)	137(4)
	C2-H2···N4^{i}	0.93	2.80	3.580(6)	143
	N6-H6A···Se1^{ii}	0.98(5)	2.76(5)	3.563(4)	140(4)
350(2) K	N6-H6B···N7	0.86(5)	2.17(5)	2.856(5)	137(4)
	C2-H2···N4^{i}	0.93	2.79	3.575(5)	142
	N6-H6A···Se1^{ii}	1.00(5)	2.75(4)	3.554(4)	137(3)
325(2) K	N6-H6B···N7	0.89(5)	2.13(5)	2.856(5)	139(4)
	C2-H2···N4^{i}	0.93	2.79	3.571(5)	142
	N6-H6A···Se1^{ii}	0.97(5)	2.75(5)	3.547(4)	139(3)
300(2) K	N6-H6B···N7	0.84(4)	2.18(4)	2.860(4)	138(4)
	C2-H2···N4^{i}	0.93	2.78	3.559(5)	142
	N6-H6A···Se1^{ii}	1.00(4)	2.68(4)	3.541(4)	144(3)
275(2) K	N6-H6B···N7	0.86(4)	2.15(4)	2.855(4)	140(3)
	C2-H2···N4^{i}	0.93	2.75	3.530(4)	142
	N6-H6A···Se1^{ii}	0.99(4)	2.71(4)	3.535(3)	141(3)
250(2) K	N6-H6B···N7	0.85(4)	2.15(4)	2.860(4)	140(3)
	C2-H2···N4^{i}	0.94	2.69	3.477(4)	142
	N6-H6A···Se1^{ii}	1.05(4)	2.65(4)	3.519(3)	141(3)
225(2) K	N6-H6B···N7	0.86(4)	2.16(4)	2.858(4)	137(3)
	C2-H2···N4^{i}	0.93	2.54	3.313(4)	141
	N6-H6A···Se1^{ii}	0.97(4)	2.72(4)	3.502(3)	138(3)
200(2) K	N6-H6B···N7	0.90(3)	2.12(3)	2.852(3)	137(3)
	C2-H2···N4^{i}	0.95	2.39	3.181(3)	140
	N6-H6A···Se1^{ii}	1.00(3)	2.66(3)	3.490(3)	141(2)
175(2) K	N6-H6B···N7	0.90(3)	2.14(3)	2.856(3)	136(3)
	C2-H2···N4^{i}	0.95	2.36	3.145(3)	140
	N6-H6A···Se1^{ii}	0.97(2)	2.66(2)	3.484(3)	143(2)
150(2) K	N6-H6B···N7	0.92(3)	2.11(3)	2.850(3)	137(3)
	C2-H2···N4^{i}	0.95	2.35	3.136(3)	140
	N6-H6A···Se1^{ii}	0.99(3)	2.65(3)	3.479(3)	142(2)
125(2) K	N6-H6B···N7	0.94(3)	2.09(3)	2.853(3)	138(2)
	C2-H2···N4^{i}	0.95	2.35	3.132(3)	140
	N6-H6A···Se1^{ii}	0.96(5)	2.65(5)	3.476(2)	145(2)
108(2) K	N6-H6B···N7	0.90(3)	2.12(3)	2.855(3)	139(3)
	C2-H2···N4^{i}	0.95	2.35	3.134(3)	140
	N6-H6A···Se1^{ii}	0.95(3)	2.69(3)	3.476(2)	141(2)
100(2) K	N6-H6B···N7	0.92(4)	2.10(3)	2.852(4)	139(3)
	C2-H2···N4^{i}	0.95	2.34	3.135(4)	140
	N6-H6A···Se1^{ii}	0.94(3)	2.68(3)	3.470(3)	142(3)
75(2) K	N6-H6B···N7	0.93(3)	2.11(3)	2.851(3)	136(3)
	C2-H2···N4^{i}	0.95	2.34	3.132(3)	140
	N6-H6A···Se1^{ii}	0.97(3)	2.67(3)	3.469(2)	140(2)
50(2) K	N6-H6B···N7	0.92(4)	2.10(3)	2.853(3)	137(3)
	C2-H2···N4^{i}	0.95	2.35	3.134(3)	140
	N6-H6A···Se1^{ii}	0.96(3)	2.66(3)	3.465(3)	141(3)
30(2) K	N6-H6B···N7	0.91(4)	2.14(3)	2.855(4)	135(3)
	C2-H2···N4^{i}	0.95	2.35	3.133(4)	140
	N6-H6A···Se1^{ii}	0.95(4)	2.65(4)	3.467(3)	144(3)
30(2) K LIESST HS*	N6-H6B···N7	0.91(5)	2.13(4)	2.853(4)	136(4)
	C2-H2···N4^{i}	0.93	2.73	3.506(5)	142
	N6-H6A···Se1^{ii}	0.98(5)	2.69(5)	3.503(3)	140(3)

(i) 1-*x*, 1-*y*, 1-*z*; (ii) 1/2+*x*, 3/2-*y*, 1/2+*z*.

Table S5 - Summary of the π-π contacts in **A**.

Temperature	Plane 1	Plane 2	Centroid-centroid distance / Å	Offset / Å
375(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.725(2)	1.366(7)
350(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.710(2)	1.354(7)
325(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.698(2)	1.344(7)
300(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.688(2)	1.338(6)
275(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.679(2)	1.338(5)
250(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.678(2)	1.354(6)
225(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.693(2)	1.403(5)
200(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.707(2)	1.449(4)
175(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.703(2)	1.448(4)
150(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.692(1)	1.443(4)
125(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.684(1)	1.432(4)
108(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.682(1)	1.434(4)
100(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.678(2)	1.432(4)
75(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.670(2)	1.423(4)
50(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.664(2)	1.415(4)
30(2) K	(N2, C2-C6)	(N7, C9-C13)^{i}	3.663(2)	1.417(4)
30(2) K LIESST HS*	(N2, C2-C6)	(N7, C9-C13)^{i}	3.591(2)	1.263(5)

(i) 1-*x*, 2-*y*, 1-*z*;