Towards synergy between spin-crossover and metal-ligand bond break in molecular crystals: Structural investigations of eight seven-coordinated Fe(II) macrocyclic complexes

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Electronic Supplementary Information

Experimental Section

Synthesis and crystallization

The synthesis of the eight samples $[Fe(L)(NCX)_2]$ (X = S or Se) were performed as described by Nelson et al. for the synthesis of $[Fe(L_{222}N_3O_2)(CN)_2]$ complex [1]. All the reactions were carried out under anaerobic condition and all solvents were degassed.

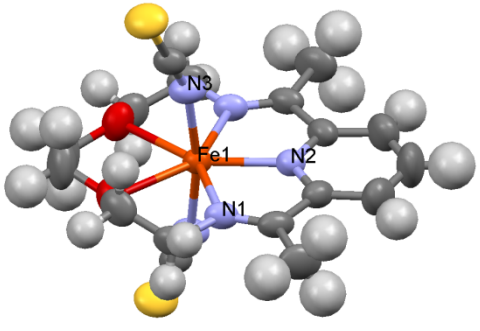
The synthesis route of $[Fe(L_{222}N_3O_2)(NCS)_2]$ is a two step procedure which involves a template reaction in the first step. The synthesis was carried out in 15 mL of methanol and 10 mL of water in which were dissolved 1.20 g (6 mmol) of iron chloride tetrahydrate, 1.0 g (6 mmol) of 2,6-diacetylpyridine, and 0.1 g of sodium dithionite (used as reducing agent to remove traces of trivalent iron ion). Then 3,6-diamine dioxaoctane-1,8-diamine (0.92mL, 6 mmol) was added dropwise. The mixture was kept under nitrogen reflux at 75 °C for 16 h approximately (formation of $[Fe(L_{222}N_3O_2)(Cl)_2]$). After filtration, 15 mL of aqueous solution containing an excess of potassium thiocyanate KNCS (2g, 0.02 mol) and 0.1 g of sodium dithionite was added. This solution was then kept stirring for ca. 6 hours at room temperature. The polycrystalline powder formed was then filtered and washed with 10 mL of degassed water and dried under vacuum. Finally 0.9 g (yield ~ 40%) of powder was collected. The synthesis of $[Fe(L_{222}N_3O_2)(NCSe)_2]$ complex was similar. The only difference was the replacement of KCN by KNCSe in the step 2.

The synthesis of $[Fe(L_{222}N_5)(NCX)_2]$, $[Fe(L_{232}N_5)(NCX)_2]$ and $[Fe(L_{223}N_5)(NCX)_2]$ (X=S or Se), are similar with the one of $[Fe(L_{222}N_3O_2)(NCX)_2]$ described above. The amine parts, are triethylenetetramine (for $L_{222}N_5$), N,N'-Bis(2-aminoethyl)-1,3-propanediamine (for $L_{232}N_5$), and N-(2-aminoethyl)- N'-(3-aminopropyl)ethylene-diamine tetrahydrochloride (for $L_{223}N_5$), respectively. In the peculiar case of the $[Fe(L_{223}N_5)(NCX)_2]$, N-(2-aminoethyl)-N'- (3-aminopropyl) ethylene-diamine tetrahydrochloride (1.84 g, 6 mmol) was dissolved in 5 mL of aqueous solution containing NaOH (0.96 g, 24 mmol) to deprotonate the amine.

Slow diffusion method in H shape tubes was used to crystallize the complexes. Precisely, after the step 1 of the synthesis, solution containing $[Fe(L)(Cl)_2]$ and aqueous solution containing KNCS or KNCSe were added to the two bottoms of the H tube separately. Water was then slowly added in the H tube for slow diffusion. After a few weeks, crystals were found at the bottom of the H tube.

Characterization and Measurements

Diffraction data on single crystal X were recorded using Bruker-Nonius diffractometer K-CCD ($\lambda = 0.7170$ Å). The crystal structures were determined by direct methods and atomic parameters were refined using SHELX[2] in the WinGX environment.[3] Magnetic susceptibility measurements were performed on a Quantum Design SQUID/VSM magnetometer, in an applied field of 1000 or 5000 G. Diamagnetic corrections for the sample holder and the material (using Pascal constants) were applied.



a) b)

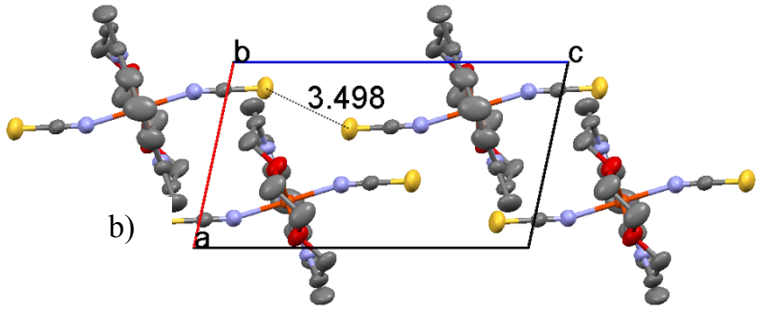


Fig. S1 a) Molecular structure and b) Crystal packing of $[Fe(L_{222}N_3O_2)(NCS)_2]$ at 293 K. Hydrogen atoms have been omitted for clarity in b.

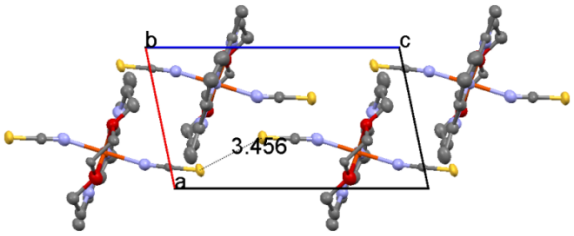


Fig. S2 Crystal packing of $[Fe(L_{222}N_3O_2)(NCS)_2]$ at 120 K. Hydrogen atoms have been omitted for clarity.

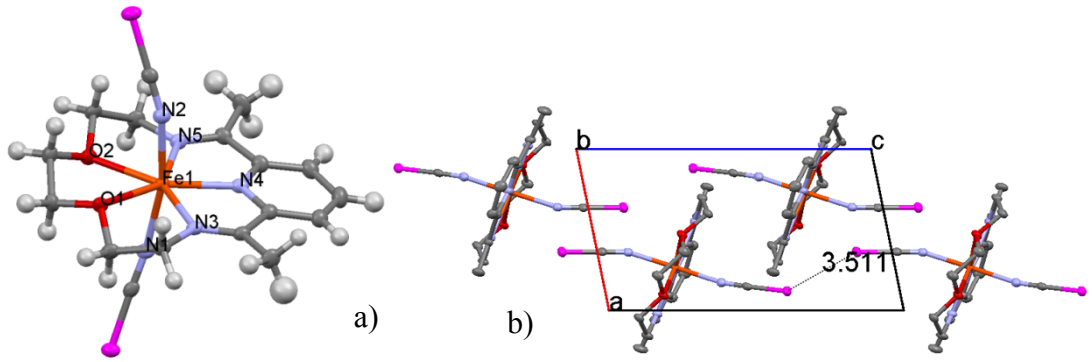


Fig. S3 a) Molecular structure and b) Crystal packing of $[Fe(L_{222}N_3O_2)(NCSe)_2]$ at 100 K. Hydrogen atoms have been omitted for clarity in b.

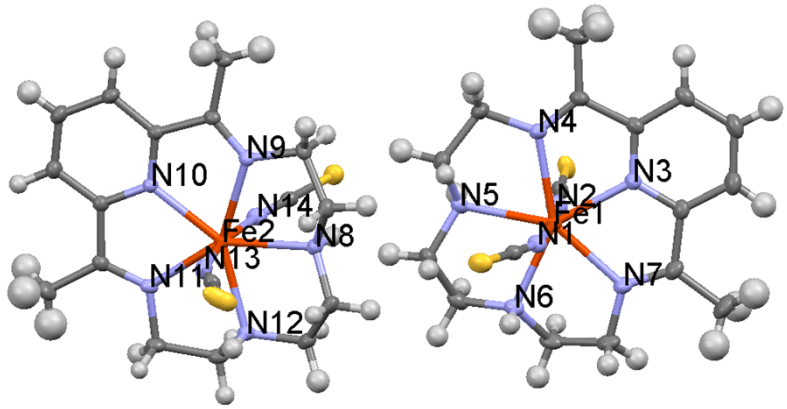


Fig. S4 Molecular structure of $[Fe(L_{222}N_5)(NCS)_2]$ at 110 K.

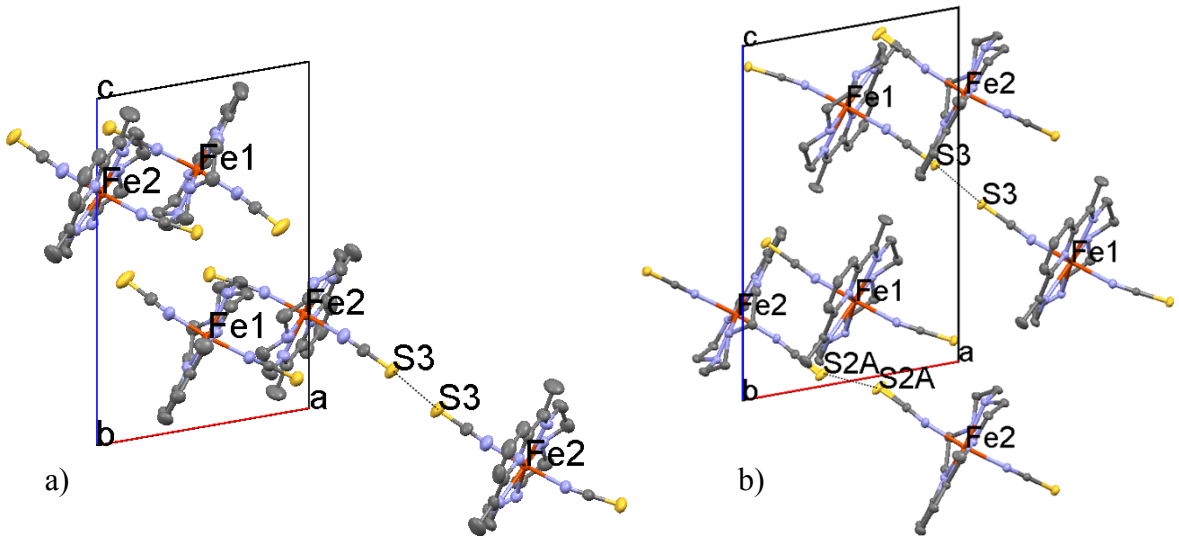


Fig. S5 Crystal packing of [Fe($L_{222}N_5$)($NCS)_2$] at a) 250 K, and b)110 K. Hydrogen atoms have been omitted for clarity.

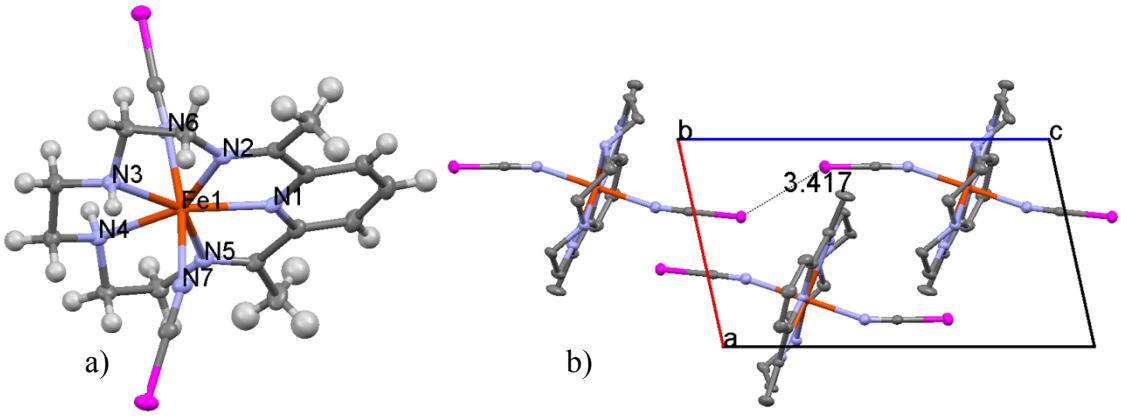


Fig. S6 a) Molecular structure and b) Crystal packing of [Fe($L_{222}N_5$)($NCSe)_2$] at 100 K. Hydrogen atoms have been omitted for clarity in b.

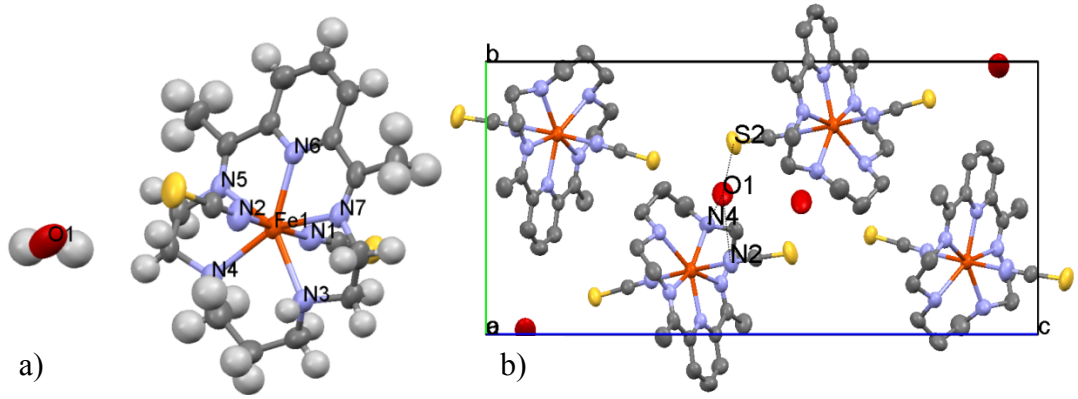


Fig. S7 a) Molecular structure and b) Crystal packing of [Fe($L_{232}N_5$)($NCS)_2$]·0.5H_2O at 300 K. Hydrogen atoms have been omitted for clarity in b.

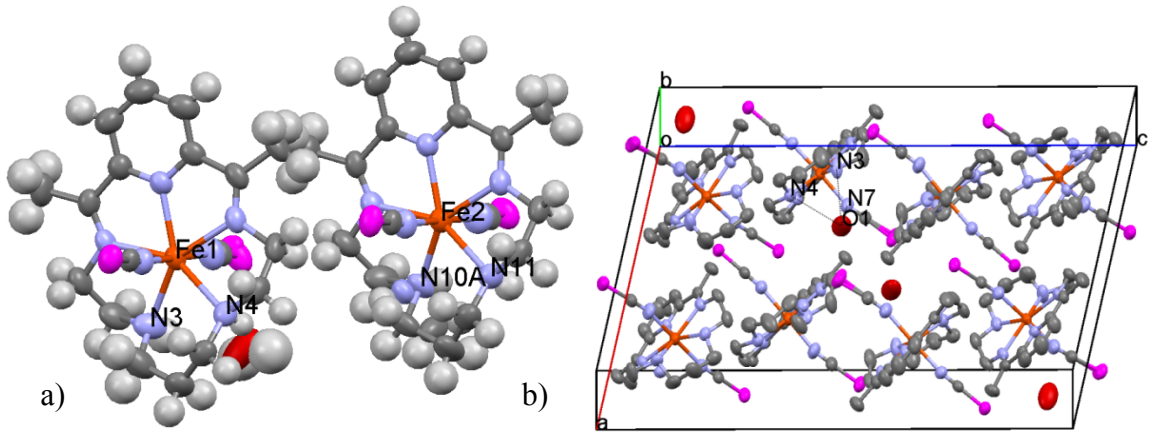


Fig. S8 a) Molecular structure and b) Crystal packing of $[Fe(L_{232}N_5)(NCSe)_2]\cdot 0.25H_2O$ at 293 K. Hydrogen atoms have been omitted for clarity in b.

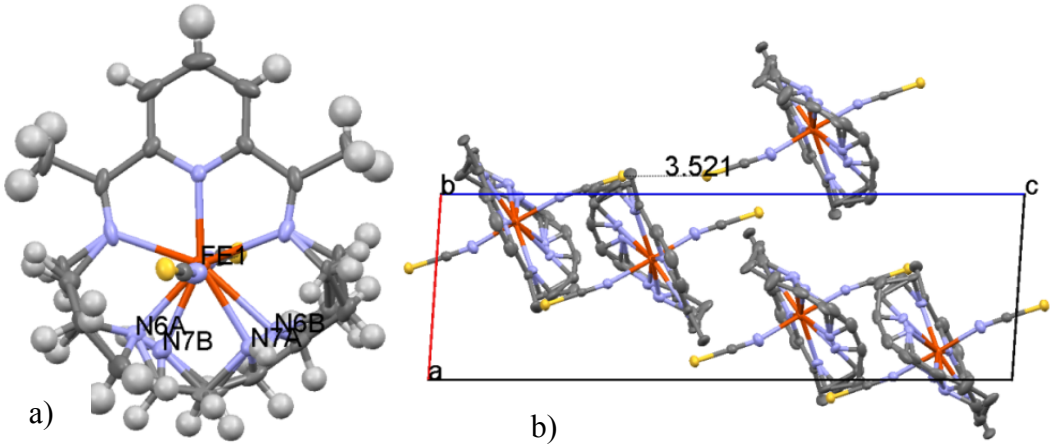


Fig. S9 a) Molecular structure and b) Crystal packing of $[Fe(L_{223}N_5)(NCS)_2]$ at 110 K. Hydrogen atoms have been omitted for clarity in b.

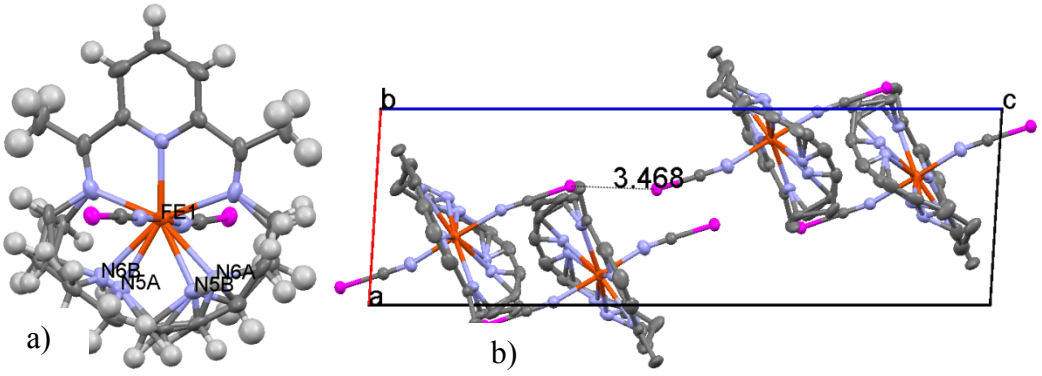


Fig. S10 a) Molecular structure and b) Crystal packing of $[Fe(L_{223}N_5)(NCSe)_2]$ at 110 K. Hydrogen atoms have been omitted for clarity in b.

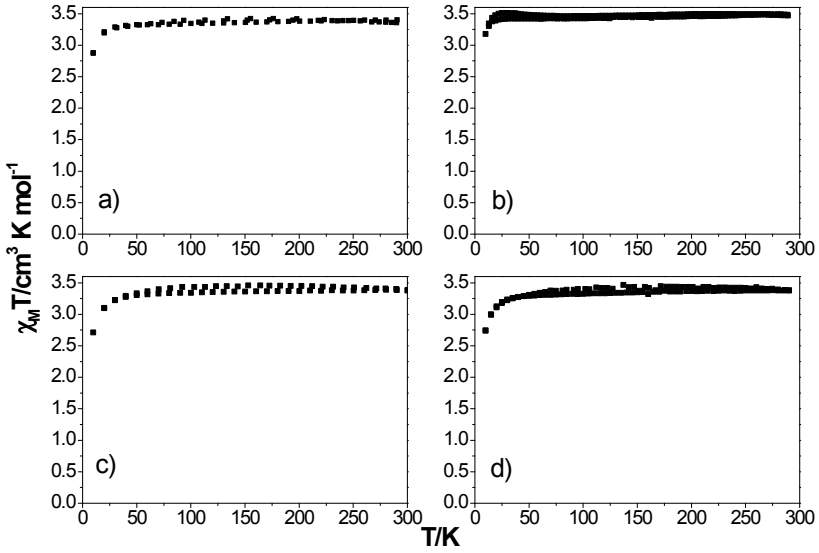


Fig. S11 Temperature dependence of χ_MT for thiocyanate coordinated complexes. a) [Fe($L_{222}N_3O_2$)(NCS)$_2$], b) [Fe($L_{222}N_5$)(NCS)$_2$], c) [Fe($L_{232}N_5$)(NCS)$_2$]·H_2O and d) [Fe($L_{223}N_5$)(NCS)$_2$]·H_2O

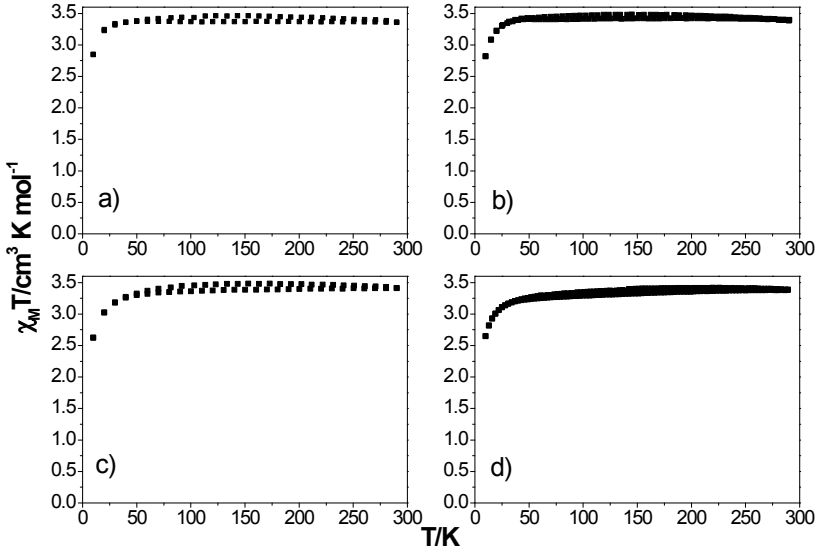


Fig. S12 Temperature dependence of χ_MT for selenocyanate coordinated complexes. a) [Fe($L_{222}N_3O_2$)(NCSe)$_2$], b) [Fe($L_{222}N_5$)(NCSe)$_2$], c) [Fe($L_{232}N_5$)(NCSe)$_2$]·H_2O and d) [Fe($L_{223}N_5$)(NCSe)$_2$]·$2H_2O$

Figures S11 and S12 show the magnetic properties as a function of temperature, expressed as the χ_{MT} vs T plot, with χ_M being the molar magnetic susceptibility and T the temperature. From 5 to 300 K, the studied complexes are totally paramagnetic with a χ_{MT} product higher than 3.25 cm^3 K mol^{-1} over the temperature range 20 -300 K. The χ_{MT} product firstly increases upon warming from 5 K due to zero-field splitting of the high spin Fe(II) centres in nonperferct octahedral surroundings, reaching a plateau of ca. 3.5 cm^3 K mol^{-1} near 20 K. For all the compounds, the χ_{MT} values remain constant indicating that no spin crossover occur. This confirms that all samples are HS in the temperature range 5 to 300 K.

293 K		120 K	
Fe1 — O1	2.302(2)	Fe1 — O1a	2.27(1)
		Fe1 — O1b	2.30(1)
Fe1 — N1	2.200(1)	Fe1 — N1a	2.176(9)
		Fe1 — N1b	2.203(9)
Fe1 — N2	2.119(2)	Fe1 — N2	2.15(1)
Fe1 — N3	2.103(2)	Fe1 — N3a	2.070(9)
		Fe1 — N3b	2.086(9)

Table S1 Selected geometric parameters (Å) for $[Fe(L_{222}N_3O_2)(NCS)_2]$ at 293 K and 120 K.

Fe1 — O1	2.309(3)	Fe1 — N1	2.107(4)
Fe1 — O2	2.286(2)	Fe1 — N2	2.112(4)
Fe1 — N4	2.119(4)	Fe1 — N3	2.214(3)
		Fe1 — N5	2.219(3)

Table S2 Selected geometric parameters (Å) for $[Fe(L_{222}N_3O_2)(NCSe)_2]$ at 100 K

250 K		*110 K*	
Fe1 — N1	2.168(2)	Fe1 — N1	2.1429(9)
Fe1 — N2	2.136(2)	Fe1 — N2	2.1238(9)
Fe1 — N3	2.183(2)	Fe1 — N3	2.1797(9)
Fe1 — N4	2.249(2)	Fe1 — N4	2.2847(9)
Fe1 — N5	2.119(2)	Fe1 — N5	2.313(1)
Fe1 — N6	2.103(2)	Fe1 — N6	2.2739(8)
Fe1 — N7	2.256(2)	Fe1 — N7	2.251(1)
Fe2 — N8	2.299(3)	Fe2 — N8	2.320(1)
Fe2 — N9	2.284(2)	Fe2 — N9	2.2572(8)
Fe2 — N10	2.179(2)	Fe2 — N10	2.179(1)
Fe2 — N11	2.250(3)	Fe2 — N11	2.2580(9)
Fe2 — N12	2.270(2)	Fe2 — N12	2.2863(9)
Fe2 — N13	2.154(2)	Fe2 — N13	2.1366(9)
Fe2 — N14	2.130(2)	Fe2 — N14	2.1624(8)

Table S3 Selected geometric parameters (Å) for $[Fe(L_{222}N_5)(NCS)_2]$ at 250 K and 110 K

293 K		100 K	
Fe1 — N1	2.182(2)	Fe1 — N1	2.180(2)
Fe1 — N2	2.255(2)	Fe1 — N2	2.265(2)
Fe1 — N3	2.300(2)	Fe1 — N3	2.306(2)
Fe1 — N4	2.303(2)	Fe1 — N4	2.297(2)
Fe1 — N5	2.260(2)	Fe1 — N5	2.259(2)
Fe1 — N6	2.146(3)	Fe1 — N6	2.141(2)
Fe1 — N7	2.146(3)	Fe1 — N7	2.135(2)

Table S5 Selected geometric parameters (Å) for $[Fe(L_{222}N_5)(NCSe)_2]$ at 293 K and 100 K

300 K		100 K	
Fe1 — N1	2.147(3)	Fe1 — N1	2.226(1)
Fe1 — N2	2.165(3)	Fe1 — N2	2.257(1)
Fe1 — N3	2.366(2)	Fe1 — N3	2.370(1)
Fe1 — N4	2.300(2)	Fe1 — N4A	2.491(6)
Fe1 — N5	2.270(2)	Fe1 — N4B	2.302(2)
Fe1 — N6	2.227(2)	Fe1 — N5	2.273(1)
Fe1 — N7	2.254(2)	Fe1 — N6	2.141(1)
		Fe1 — N7A	2.19(1)
		Fe1 — N7B	2.12(1)

Table S6 Selected geometric parameters (Å) for $[Fe(L_{232}N_5)(NCS)_2]\cdot 0.5H_2O$ at 300 K and 100 K

293 K		110 K	
Fe1 — N1	2.231(2)	Fe1 — N1	2.233(2)
Fe1 — N2	2.271(3)	Fe1 — N2	2.274(2)
Fe1 — N3	2.311(4)	Fe1 — N3A	2.297(3)
		Fe1 — N3B	2.500(9)
Fe1 — N4	2.364(3)	Fe1 — N4	2.364(2)
Fe1 — N5	2.247(3)	Fe1 — N5	2.255(2)
Fe1 — N6	2.155(3)	Fe1 — N6	2.146(2)
Fe1 — N7	2.163(3)	Fe1 — N7	2.146(2)
Fe2 — N8	2.232(2)	Fe2 — N8	2.227(2)
Fe2 — N9	2.279(3)	Fe2 — N9	2.280(2)
Fe2 — N10A	2.26(1)	Fe2 — N10A	2.277(5)
Fe2 — N10B	2.47(1)	Fe2 — N10B	2.466(5)
Fe2 — N11	2.370(3)	Fe2 — N11	2.370(2)
Fe2 — N12	2.262(3)	Fe2 — N12	2.261(2)
Fe2 — N13	2.150(3)	Fe2 — N13	2.135(2)
Fe2 — N14	2.142(3)	Fe2 — N14	2.145(2)

Table S7 Selected geometric parameters (Å) for $[Fe(L_{232}N_5)(NCSe)_2]\cdot 0.25H_2O$ at 293 K and 110 K

Compound	$[Fe(L_{222}N_3O_2)(NCS)_2]$	
Formula	$C_{17}H_{21}FeN_5O_2S_2$	$C_{17}H_{21}FeN_5O_2S_2$
M_r (g.mol^{-1})	447.38	447.38
Colour	black	black
Crystal size (mm^3)	0.75 × 0.75 × 0.38	0.75 × 0.75 × 0.38
Crystal morphology	plate	plate
Temperature (K)	293(2)	120(2)
Crystal system	monoclinic	triclinic
Space group	P 2/n	P -1
a (Å)	7.0540(2)	7.0081(14)
b (Å)	11.7587(6)	11.651(4)
c (Å)	12.4200(6)	12.321(3)
α (°)	90	88.883(14)

β (°)	102.097(3)	78.274(15)
γ (°)	90	87.09(2)
V (Å^3)	1007.31(8)	983.7(5)
Z	2	2
Density (g.cm^{-3})	1.475	1.510
μ (mm^{-1})	0.978	1.001
No. of total reflections	1957	798
R_{obs}	0.0387	0.0699
$wR2_{obs}$	0.1078	0.1633
S	1.021	1.072

Table S8 Crystal data of $[Fe(L_{222}N_3O_2)(NCS)_2]$

Compound	$[Fe(L_{222}N_3O_2)(NCSe)_2]$	
Formula	$C_{17}H_{21}FeN_5O_2Se_2$	$C_{17}H_{21}FeN_5O_2Se_2$
M_r (g.mol^{-1})	541.16	541.16
Colour	black	black
Crystal size (mm^3)	0.25 × 0.05 × 0.03	0.25 × 0.2 × 0.2
Crystal morphology	rectangular	rectangular
Temperature (K)	293(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	7.1138(5)	7.0655(3)
b (Å)	11.8204(8)	11.6012(5)
c (Å)	12.7513(8)	12.5957(5)
α (°)	88.872(5)	87.073(3)
β (°)	77.488(5)	78.284(3)
γ (°)	87.918(5)	83.751(3)
V (Å^3)	1046.00(12)	1004.49(7)
Z	2	2
Density (g.cm^{-3})	1.718	1.789
μ (mm^{-1})	4.222	4.397
No. of total reflections	4698	4503
R_{obs}	0.1501	0.0386
$wR2_{obs}$	0.4288	0.1073
S	1.652	1.158

Table S9 Crystal data of $[Fe(L_{222}N_3O_2)(NCSe)_2]$

Compound	$[Fe(L_{222}N_5)(NCS)_2]$	
Formula	$C_{17}H_{23}FeN_7S_2$	$C_{17}H_{23}FeN_7S_2$
λ (Å)	0.71073	0.71073
M_r (g.mol^{-1})	445.41	445.41
Colour	black	black
Crystal size (mm^3)	0.1 × 0.05 × 0.03	0.38 × 0.25 × 0.25
Crystal morphology	prism	prism
Temperature (K)	250(2)	110(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	10.0780(2)	10.02920(10)
b (Å)	12.7955(4)	12.64680(10)
c (Å)	16.6985(5)	16.6405(2)

α (°)	76.0790(10)	76.6240(10)
β (°)	80.178(2)	79.8490(10)
γ (°)	89.127(2)	88.9120(10)
V (Å^3)	2058.69(10)	2020.72(4)
Z	4	4
Density (g.cm^{-3})	1.437	1.464
μ (mm^{-1})	0.952	0.970
No. of total reflections	9357	17674
R_{obs}	0.0431	0.0314
$wR2_{obs}$	0.0838	0.0768
S	1.002	1.019

Table S10 Crystal data of $[Fe(L_{222}N_5)(NCS)_2]$ complex

Compound	$[Fe(L_{222}N_5)(NCSe)_2]$	
Formula	$C_{17}H_{23}FeN_7Se_2$	$C_{17}H_{23}FeN_7Se_2$
M_r (g.mol^{-1})	539.19	539.19
Colour	black	black
Crystal size (mm^3)	0.50 × 0.50 × 0.20	0.50 × 0.50 × 0.20
Crystal morphology	plate	plate
Temperature (K)	293(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	7.275(2)	7.2421(2)
b (Å)	11.692(4)	11.5317(4)
c (Å)	12.760(4)	12.6415(3)
α (°)	85.868(2)	84.884(2)
β (°)	76.764(2)	77.206(2)
γ (°)	85.302(2)	83.702(2)
V (Å^3)	1051.4(6)	1021.02(5)
Z	2	2
Density (g.cm^{-3})	1.703	1.754
μ (mm^{-1})	4.196	4.321
No. of total reflections	4224	4595
R_{obs}	0.0344	0.0378
$wR2_{obs}$	0.0859	0.1035
S	1.03	1.036

Table S11 Crystal data of $[Fe(L_{222}N_5)(NCSe)_2]$ complex

Compound	$[Fe(L_{232}N_5)(NCS)_2]\cdot 0.5H_2O$	
Formula	$C_{36}H_{52}Fe_2N_{14}OS_4$	$C_{36}H_{52}Fe_2N_{14}OS_4$
M_r (g.mol^{-1})	936.90	936.90
Colour	dark blue	dark blue
Crystal size (mm^3)	0.85 × 0.38 × 0.25	0.38 × 0.15 × 0.15
Crystal morphology	rectangular	prism
Temperature (K)	300(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.7530(3)	7.66640(10)
b (Å)	11.7757(5)	11.6061(2)
c (Å)	24.0225(10)	23.8228(4)

β (°)	96.556(2)	96.2370(10)
V (Å^3)	2178.84(15)	2107.13(6)
Z	2	2
Density (g.cm^{-3})	1.428	1.477
μ (mm^{-1})	0.905	0.936
No. of total reflections	4923	8312
R_{obs}	0.0482	0.0376
$wR2_{obs}$	0.1333	0.1012
S	1.067	1.043

Table S12 Crystal data of $[Fe(L_{232}N_5)(NCS)_2]\cdot 0.5H_2O$ complex

Compound	$[Fe(L_{232}N_5)(NCSe)_2]\cdot 0.25H_2O$	
Formula	$C_{72}H_{102}Fe_4N_{28}OSe_8$	$C_{72}H_{102}Fe_4N_{28}OSe_8$
M_r (g.mol^{-1})	2230.90	2230.90
Colour	dark blue	dark blue
Crystal size (mm^3)	0.6 × 0.35 × 0.15	0.6 × 0.35 × 0.15
Crystal morphology	prism	prism
Temperature (K)	293(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	15.5939(3)	15.4575(2)
b (Å)	11.7657(2)	11.6172(2)
c (Å)	24.7536(5)	24.5781(2)
β (°)	102.3730(10)	102.4380(10)
V (Å^3)	4436.13(14)	4309.97(10)
Z	2	2
Density (g.cm^{-3})	1.670	1.719
μ (mm^{-1})	3.982	4.098
No. of total reflections	10146	14994
R_{obs}	0.042	0.0392
$wR2_{obs}$	0.1063	0.092
S	1.029	1.020

Table S13 Crystal data of $[Fe(L_{232}N_5)(NCSe)_2]\cdot 0.25H_2O$ complex

Compound	$[Fe(L_{223}N_5)(NCS)_2]$	
Formula	$C_{18}H_{25}FeN_7S_2$	$C_{18}H_{25}FeN_7S_2$
M_r (g.mol^{-1})	459.44	459.44
Colour	dark blue	dark blue
Crystal size (mm^3)	0.6 × 0.35 × 0.15	0.38 × 0.13 × 0.08
Crystal morphology	prism	prism
Temperature (K)	293(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.6865(2)	7.61060(10)
b (Å)	11.5038(4)	11.3658(2)

c (Å)	24.0051(7)	23.8383(5)
β (°)	85.856(2)	93.8260(10)
V (Å^3)	2117.08(11)	2057.43(6)
Z	4	4
Density (g.cm^{-3})	1.441	1.483
μ (mm^{-1})	0.928	0.955
No. of total reflections	6165	6008
R_{obs}	0.0585	0.0421
$wR2_{obs}$	0.1557	0.0836
S	1.076	1.161

Table S14 Crystal data of $[Fe(L_{223}N_5)(NCS)_2]$ complex

Compound	$[Fe(L_{223}N_5)(NCSe)_2]$	
Formula	$C_{18}H_{25}FeN_7Se_2$	$C_{18}H_{25}FeN_7Se_2$
M_r (g.mol^{-1})	553.22	553.22
Colour	dark blue	dark blue
Crystal size (mm^3)	0.13 × 0.13 × 0.05	0.25 × 0.13 × 0.13
Crystal morphology	prism	prism
Temperature (K)	293(2)	110(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	7.7266(3)	7.6680(2)
b (Å)	11.5898(5)	11.4447(2)
c (Å)	24.3459(9)	24.1613(5)
β (°)	93.458(2)	93.4600(10)
V (Å^3)	2176.20(15)	2116.48(8)
Z	4	4
Density (g.cm^{-3})	1.689	1.736
μ (mm^{-1})	4.057	4.171
No. of total reflections	4001	6153
R_{obs}	0.0461	0.0358
$wR2_{obs}$	0.0956	0.0772
S	0.958	1.037

Table S15 Crystal data of $[Fe(L_{223}N_5)(NCSe)_2]$ complex

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