Electronic Supplementary Information

for

Relationship between strength of hydrogen bonding and spin crossover behaviour in a series of iron(III) Schiff base complexes

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CONTENT:

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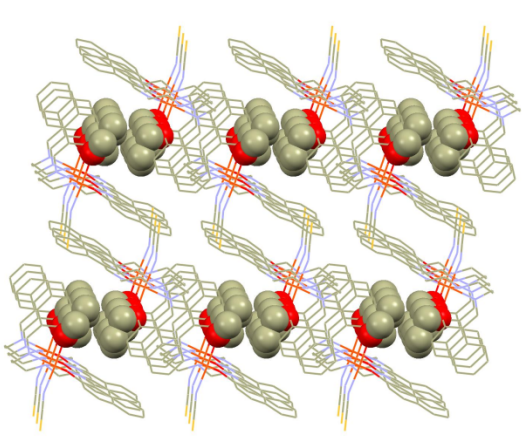
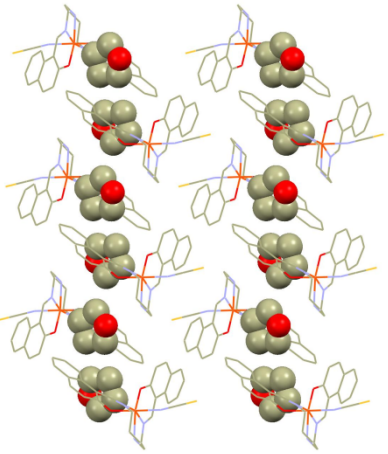
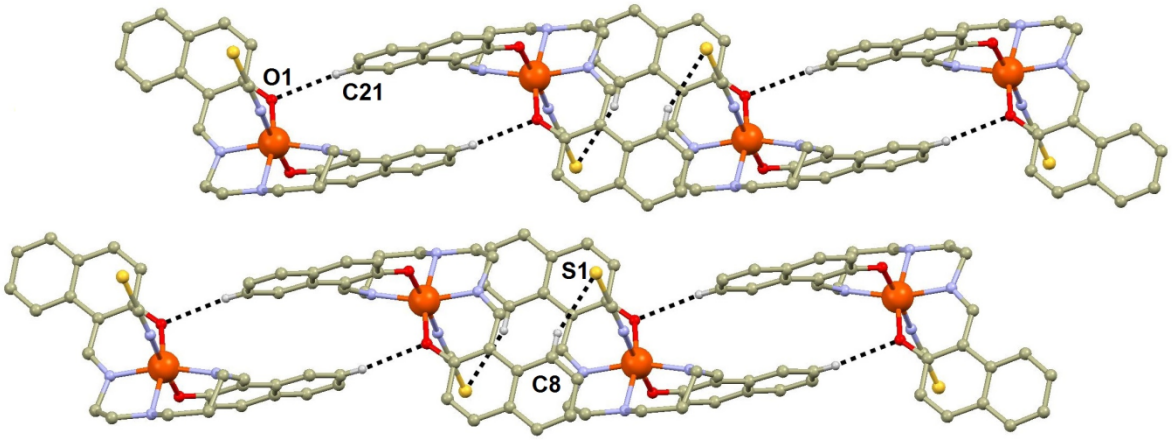
Fig. S1 Crystal packing of [Fe(L5)(NCS)]·THF, THF stands for tetrahydrofuran and it is displayed in a spacefill (70% of van der Walls radii) model (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines)



along the *a** axis

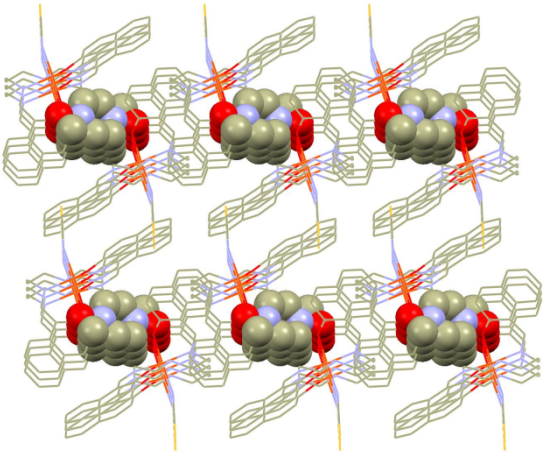


along the *b* axis



d(C21···O1) = 3.475(2) Å, *d*(C8···S1) = 3.753(2) Å

Fig. S2 Crystal packing of [Fe(L5)(NCS)]·MeOH·0.5 PYZ, PYZ stands for pyrazine and both solvates are displayed in a spacefill (70% of van der Walls radii) model (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



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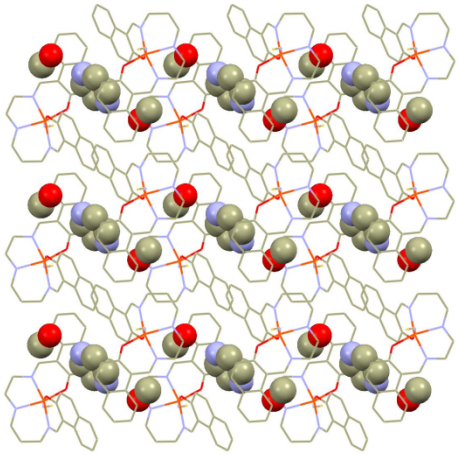
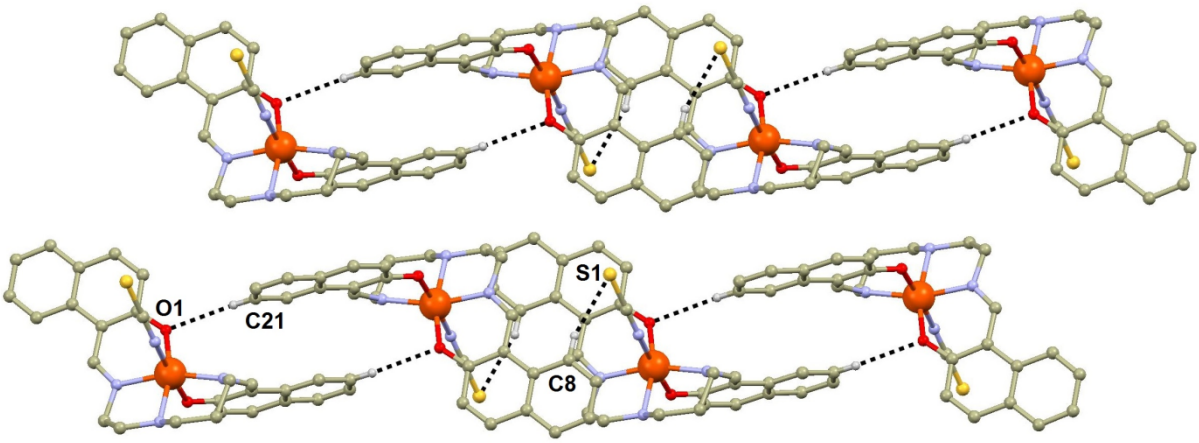
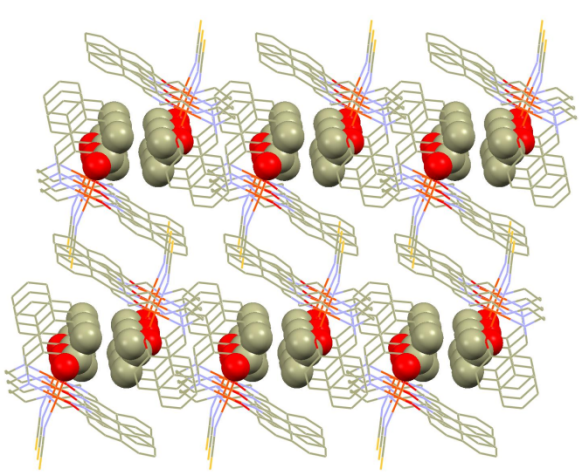


along the *c* axis

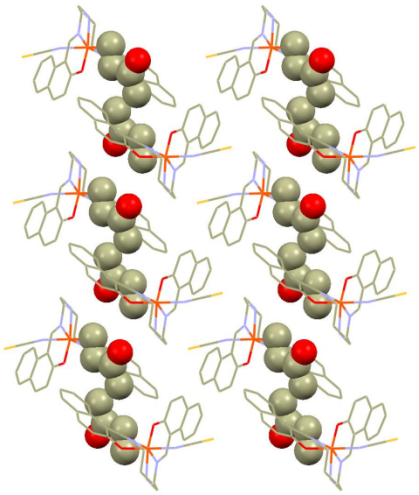


d(C21···O1) = 3.507(3) Å, *d*(C8···S1) = 3.818(2) Å

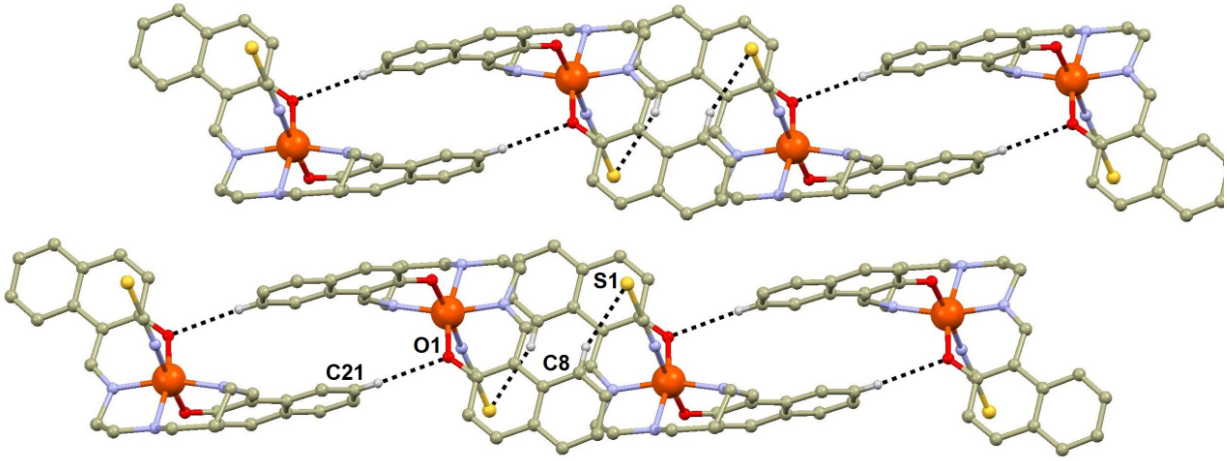
Fig. S3 Crystal packing of [Fe(L5)(NCS)]·MEK,.MEK stands for butanone and it is displayed in a spacefill (70% of van der Walls radii) mode (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



along the *a** axis

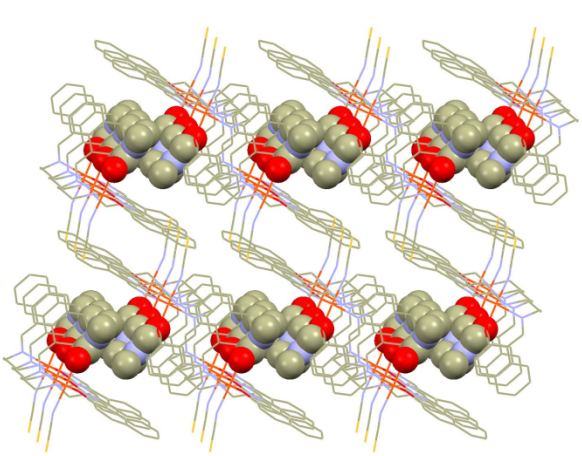


along the *b* axis



d(C21···O1) = 3.623(2) Å, *d*(C8···S1) = 3.826(2) Å

Fig. S4 Crystal packing of [Fe(L5)(NCS)]·DMF, where DMF stands for *N,N'*-dimethylformamide and it is displayed in a spacefill (70% of van der Walls radii) mode (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



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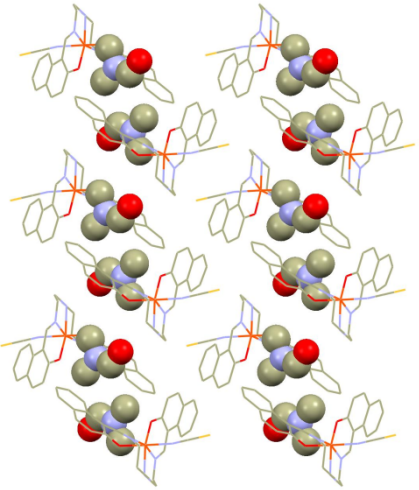
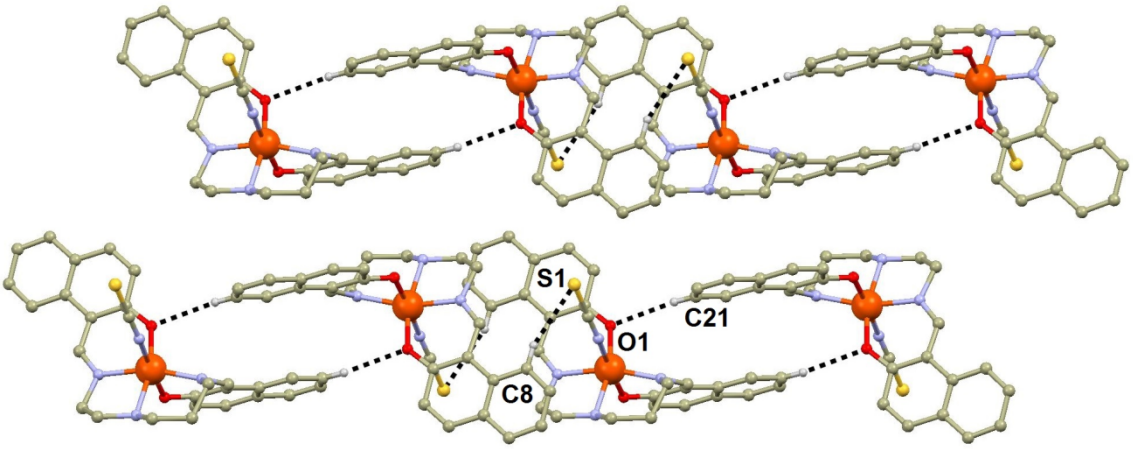
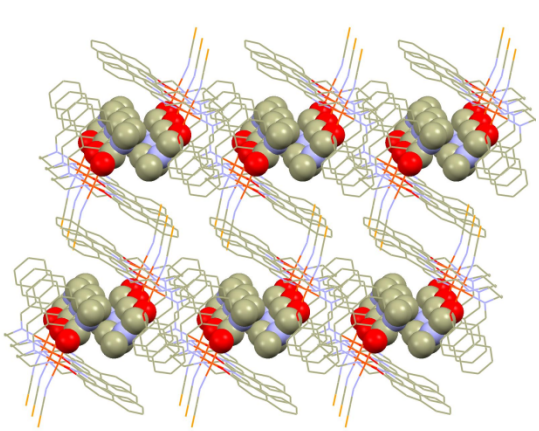


along the *b* axis

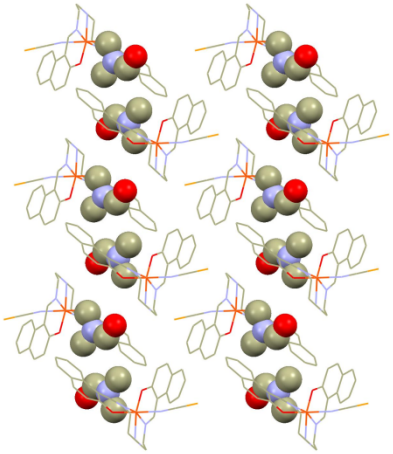


150 K *d*(C21···O1) = 3.456(2) Å, *d*(C8···S1) = 3.819(2) Å
298 K *d*(C21···O1) = 3.546(5) Å, *d*(C8···S1) = 3.816(4) Å

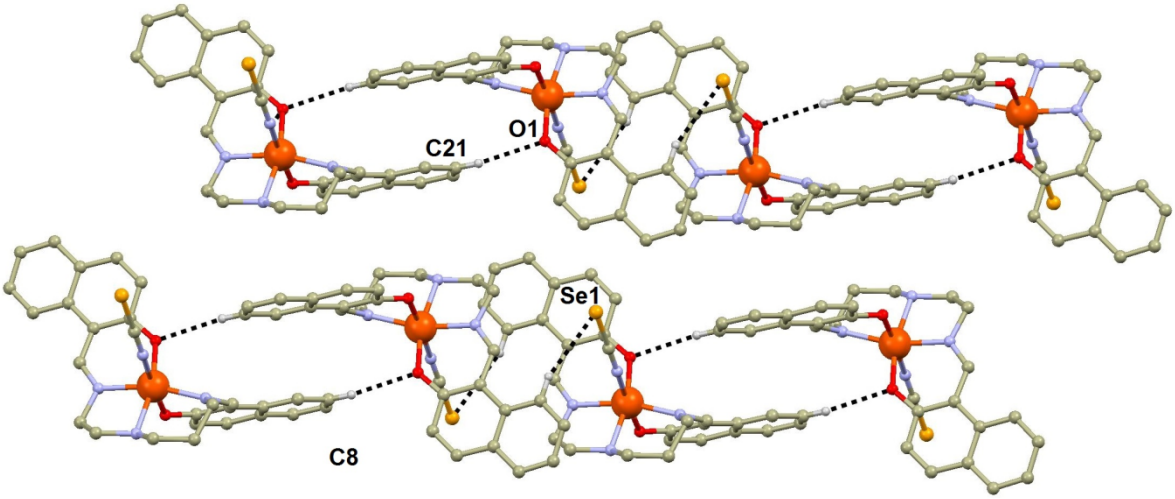
Fig. S5 Crystal packing of [Fe(L5)(NCSe)]·DMF, where DMF stands for *N,N'*-dimethylformamide and it is displayed in a spacefill (70% of van der Walls radii) model (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



along the *a** axis

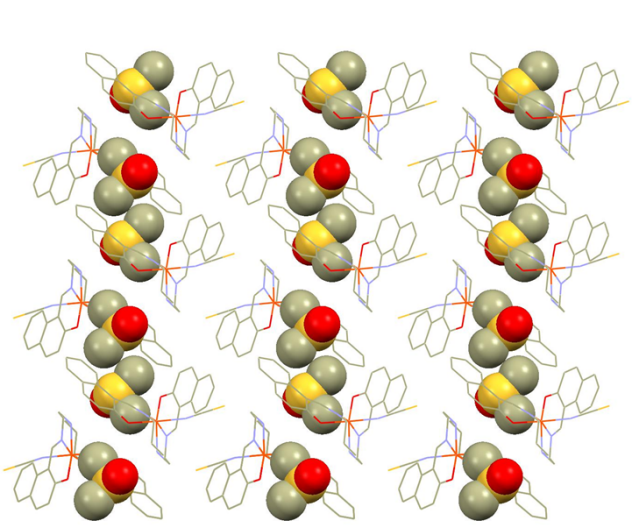


along the *b* axis



150 K *d*(C21···O1) = 3.468(6) Å, *d*(C8···Se1) = 3.882(5) Å
308 K *d*(C21···O1) = 3.552(5) Å, *d*(C8···Se1) = 3.914(4) Å

Fig. S6 Crystal packing of [Fe(L5)(NCS)]·DMSO, DMSO stands for dimethyl sulfoxide and it is displayed in a spacefill (70% of van der Walls radii) model (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



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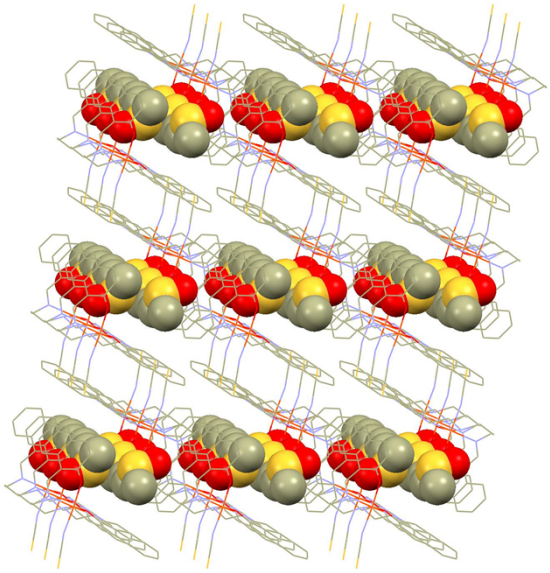
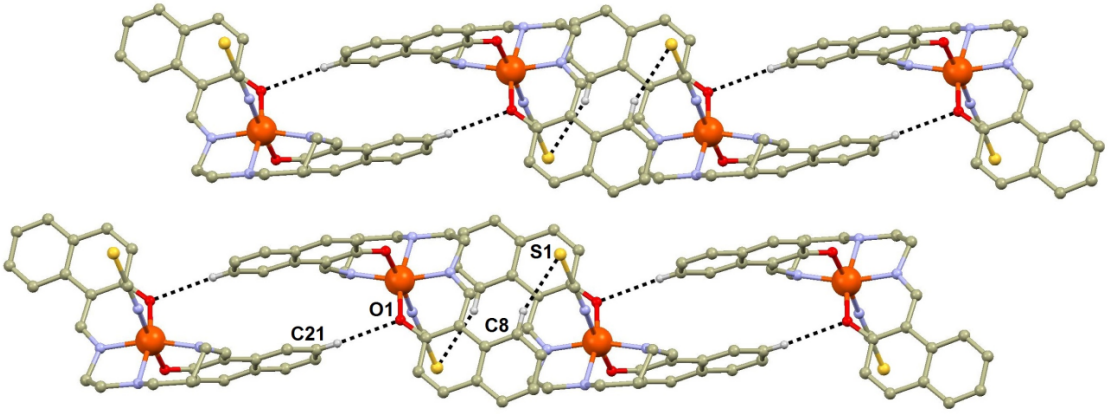
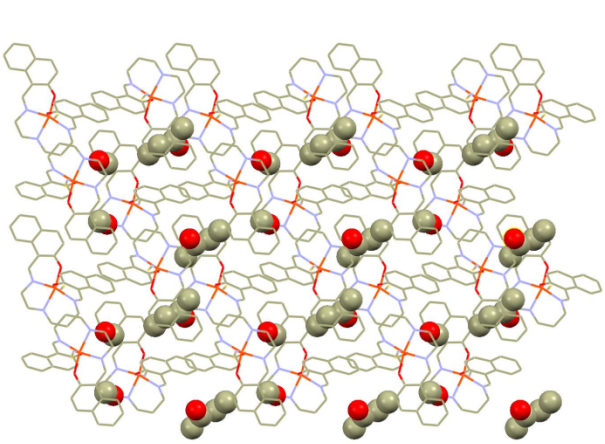


along the *b* axis

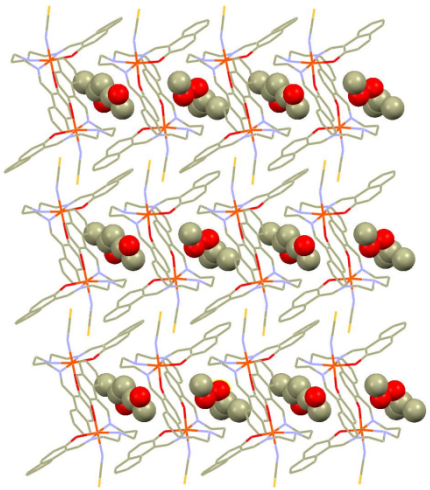


d(C21···O1) = 3.448(3) Å, *d*(C8···S1) = 3.801(3) Å

Fig. S7 Crystal packing of [Fe(L5)(NCS)]·0.5 MEK·0.5 MeOH, MEK stands for butanone and both solvates are displayed in a spacefill (70% of van der Walls radii) model (top left and top right); the weak non-covalent contacts of the complex molecules framework (down, solvent molecules are not displayed, hydrogen atoms are omitted for clarity, except for the atoms responsible for the formation of the C–H···O/S contacts -black dashed lines.



along the *a* axis



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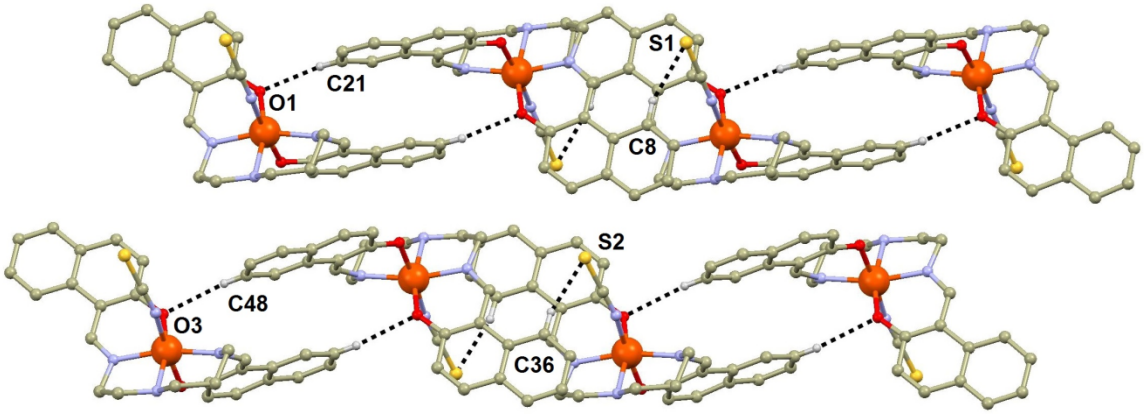
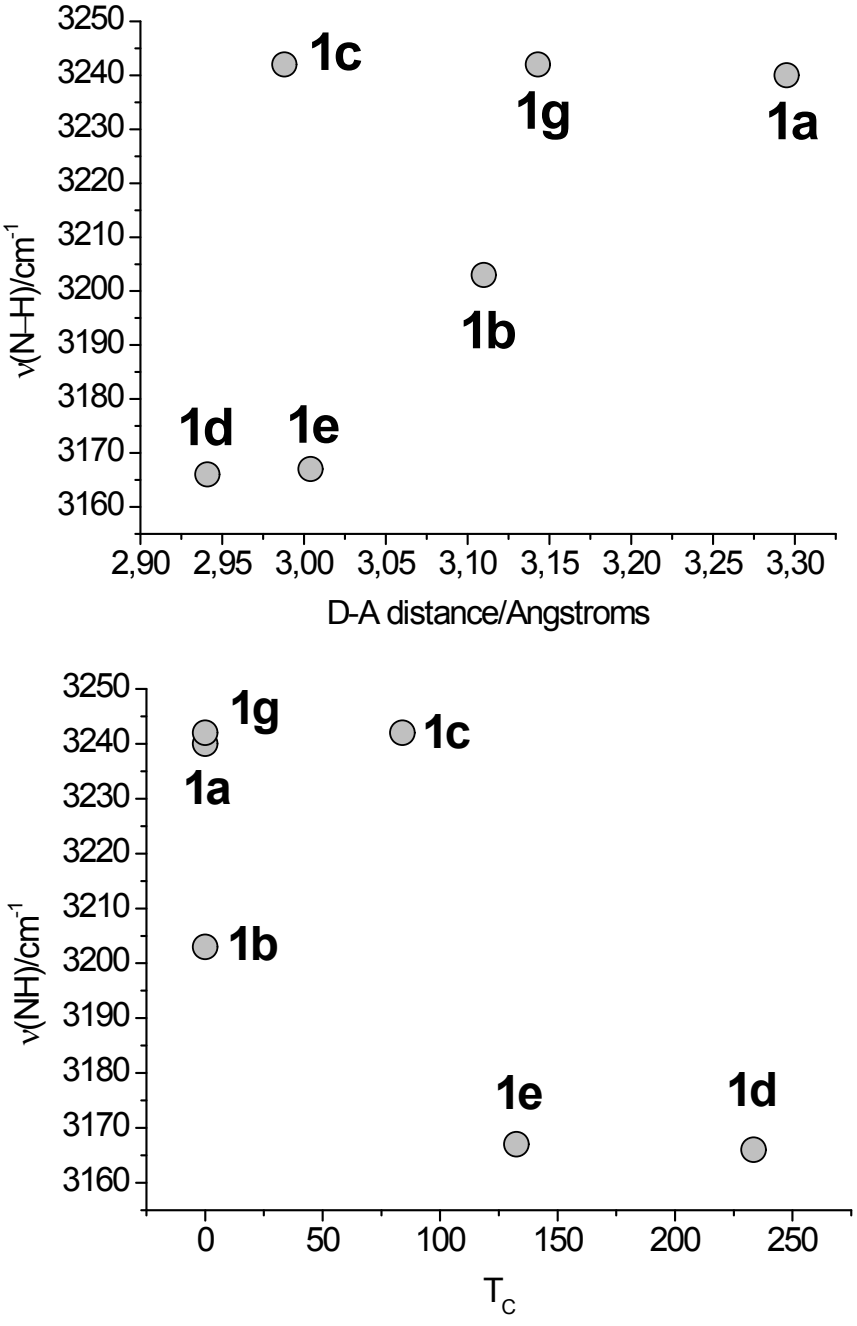


d(C21···O1) = 3.475(2) Å, *d*(C8···S1) = 3.754(2) Å, *d*(C48…O3) = 3.519(3), *d*(C8…S1) = 3.796(3)

Fig. S8 Infrared spectroscopy. **The N-H vibration frequencies as a function of donor-acceptor distance of N–H···O hydrogen bonding (above) or as a function of critical temperature of spin-crossover (bottom)**



Magnetic data interpretation

Spin Hamiltonian used to interpret high-spin iron(III) complexes:

$$\hat{H} = D(\hat{S}_z^2 - \hat{S}^2/3) - zj\langle S_a \rangle \hat{S}_a + \mu_B B g_i \hat{S}_{i,a} \qquad (1)$$

where $a = x$ and z. The first term stands for the zero-field splitting (D – an axial single-ion ZFS parameter), zj is the molecular field parameter, which was included in order to take into account also presumably weak intermolecular interactions and the last expression is Zeeman term.

With the aim to unambiguously determine the proposed parameters, the both temperature and field dependent experimental data were fitted simultaneously and moreover also the final magnetization was calculated as an integral average in order to simulate properly the powder sample signal following the procedure outlined in the paper Herchel et al.[i]

Magnetic data for 1f

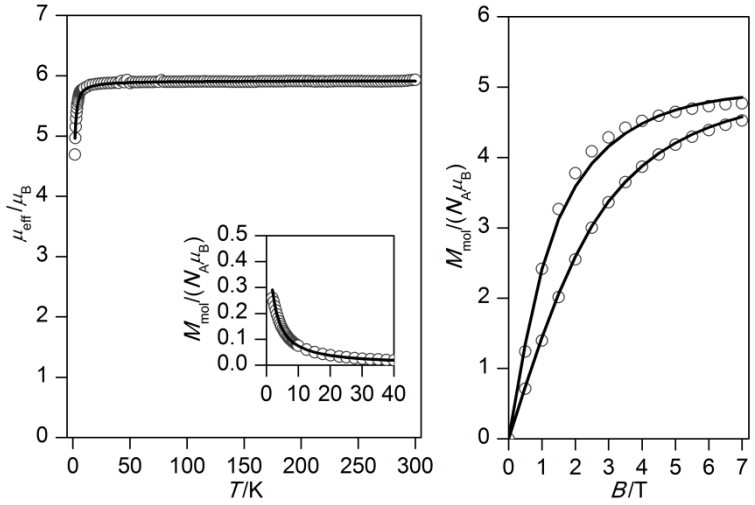


Figure S9. Magnetic data for 1f. *Left*: temperature dependence of the effective magnetic moment (calculated from the temperature dependence of magnetization at B = 0.1 T; inset). *Right*: the isothermal magnetizations measured at T = 2.0 and 4.6 K. Full lines - the best fit calculated using the equation (1), and with g = 2.00, D = −0.82 cm^{-1} and zj = −0.11 cm^{-1}.

Magnetic data for 1a

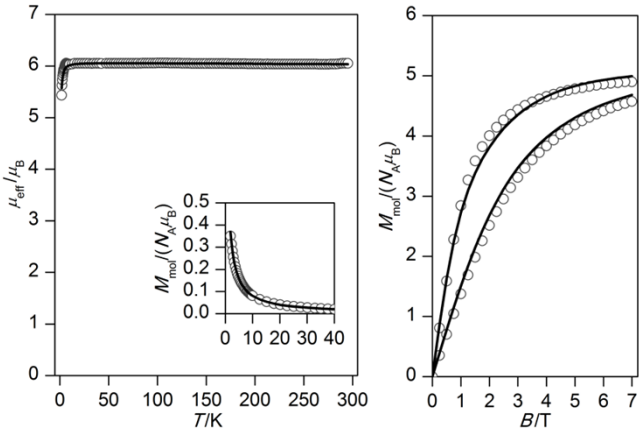


Figure S10. Magnetic data for 1a. *Left*: temperature dependence of the effective magnetic moment (calculated from the temperature dependence of magnetization at B = 0.1 T; inset). *Right*: the isothermal magnetizations measured at T = 2.0 and 5 K. Full lines - the best fit calculated using the equation 1 and with g = 2.05, D = −0.84 cm^{-1} and zj = −0.025 cm^{-1}.

Magnetic data for 1b

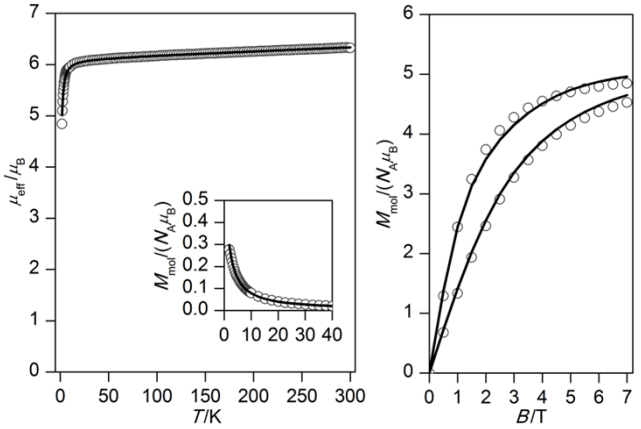


Figure S11. Magnetic data for 1b. *Left*: temperature dependence of the effective magnetic moment (calculated from the temperature dependence of magnetization at B = 0.1 T; inset). *Right*: the isothermal magnetizations measured at T = 2.0 and 5 K. Full lines - the best fit calculated using the equation 1 and with g = 2.06, D = −1.0 cm^{-1}, zj = −0.12 cm^{-1} and χ_{TIP} = 15.2 m^{3}mol^{-1}.

Table S1 The summary of the magnetic parameters for purely high-spin compounds

compound	g	D/cm^{-1}	zj/cm^{-1}	reference
1a	2.05	-0.84	-0.025	this work
1b	2.06	-1.00	-0.12	this work
1f	2.00	-0.82	-0.11	this work
1g	2.03	-0.92	-0.15	this work

[i] R. Herchel, R. Boča, J. Krzystek, A. Ozarowski, M. Dura, J. van Slageren, *J. Am. Chem. Soc.* **2007**, 129, 10306–10307.