

# Anion driven modulation of magnetic intermolecular interactions and spin crossover properties in an isomorphous series of mononuclear iron(III) complexes with a hexadentate Schiff base ligand

Ivan Nemeč, \*<sup>a</sup> Radovan Herchel,<sup>a</sup> Ivan Šalitroš,<sup>b,d</sup> Zdeněk Trávníček,<sup>a</sup> Ján Moncol,<sup>b</sup> Hartmut Fuess,<sup>c</sup> Mario Ruben<sup>d</sup> and Wolfgang Linert<sup>e</sup>

<sup>a</sup> Regional Centre of Advanced Technologies and Materials, Department of Inorganic Chemistry, Faculty of Science, Palacký University, Tr. 17. Listopadu 12, CZ-77146 Olomouc, Czech Republic.

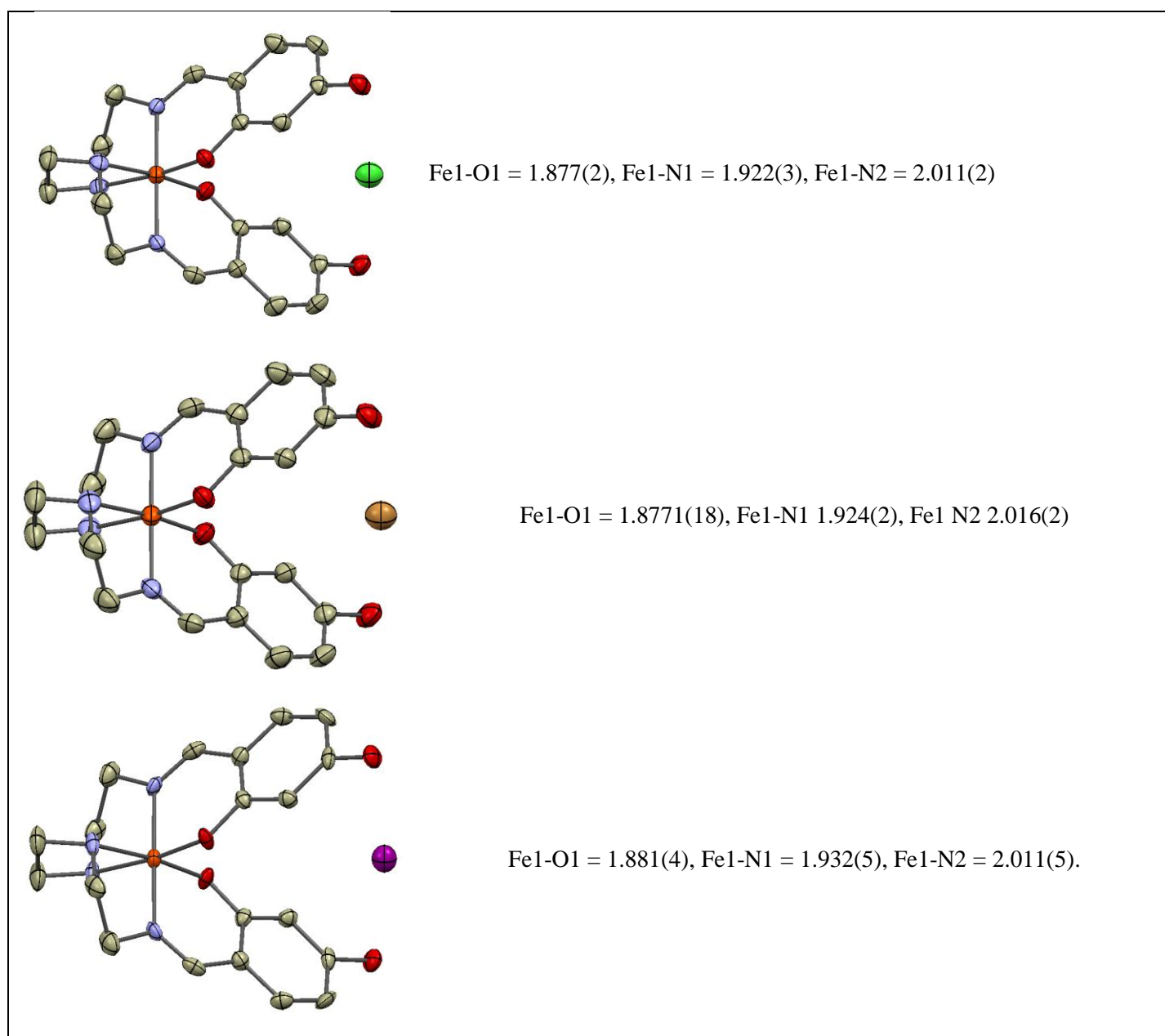
<sup>b</sup> Institute of Inorganic Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37, Bratislava, Slovakia.

<sup>c</sup> Materials Science, Darmstadt University of Technology, D-64287, Darmstadt, Germany. E-mail: [hfuess@tu-darmstadt.de](mailto:hfuess@tu-darmstadt.de)

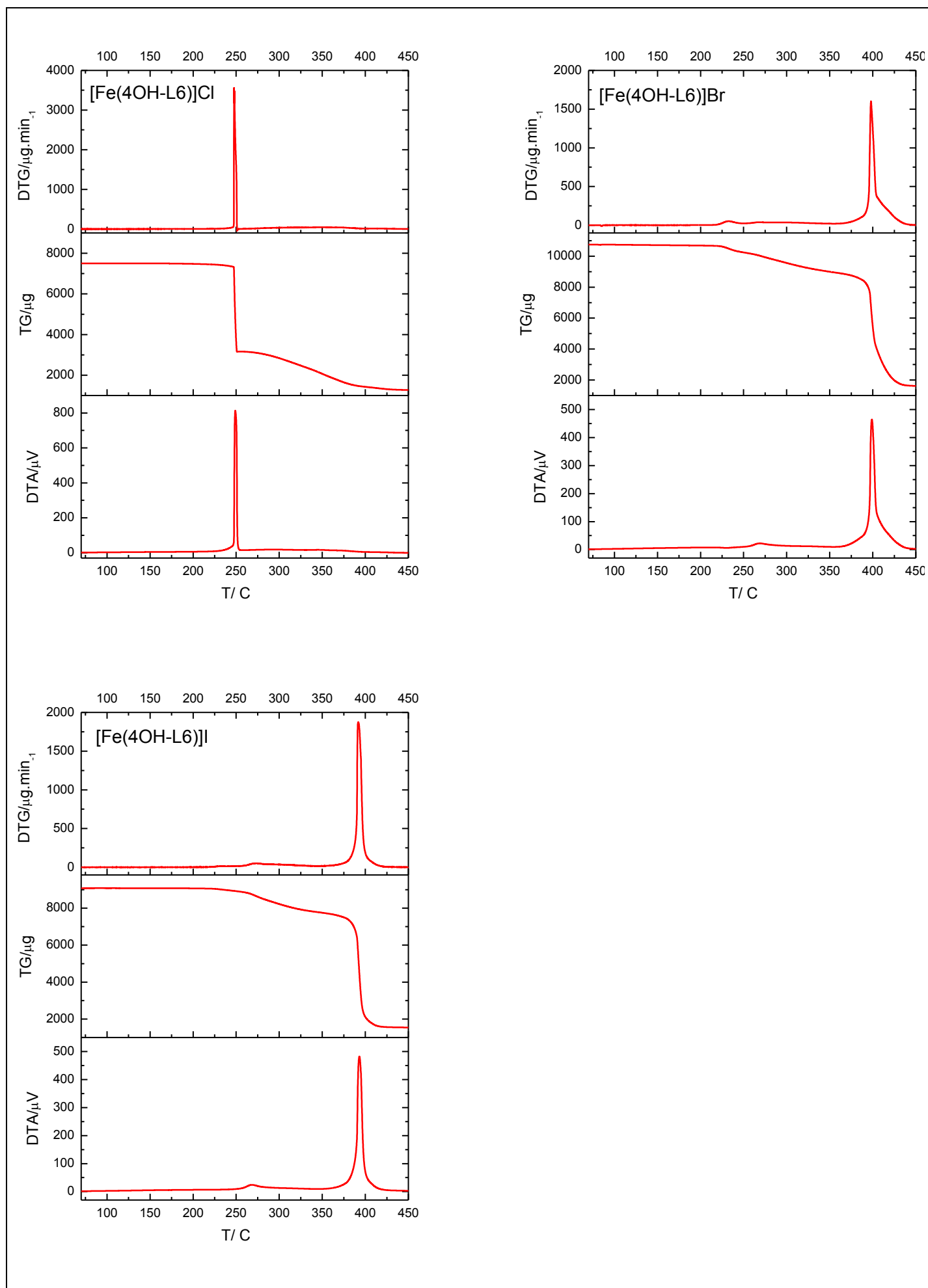
<sup>d</sup> Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany

<sup>e</sup> Institute of Applied Synthetic Chemistry, Vienna University of Technology, 1060 Vienna, Austria.

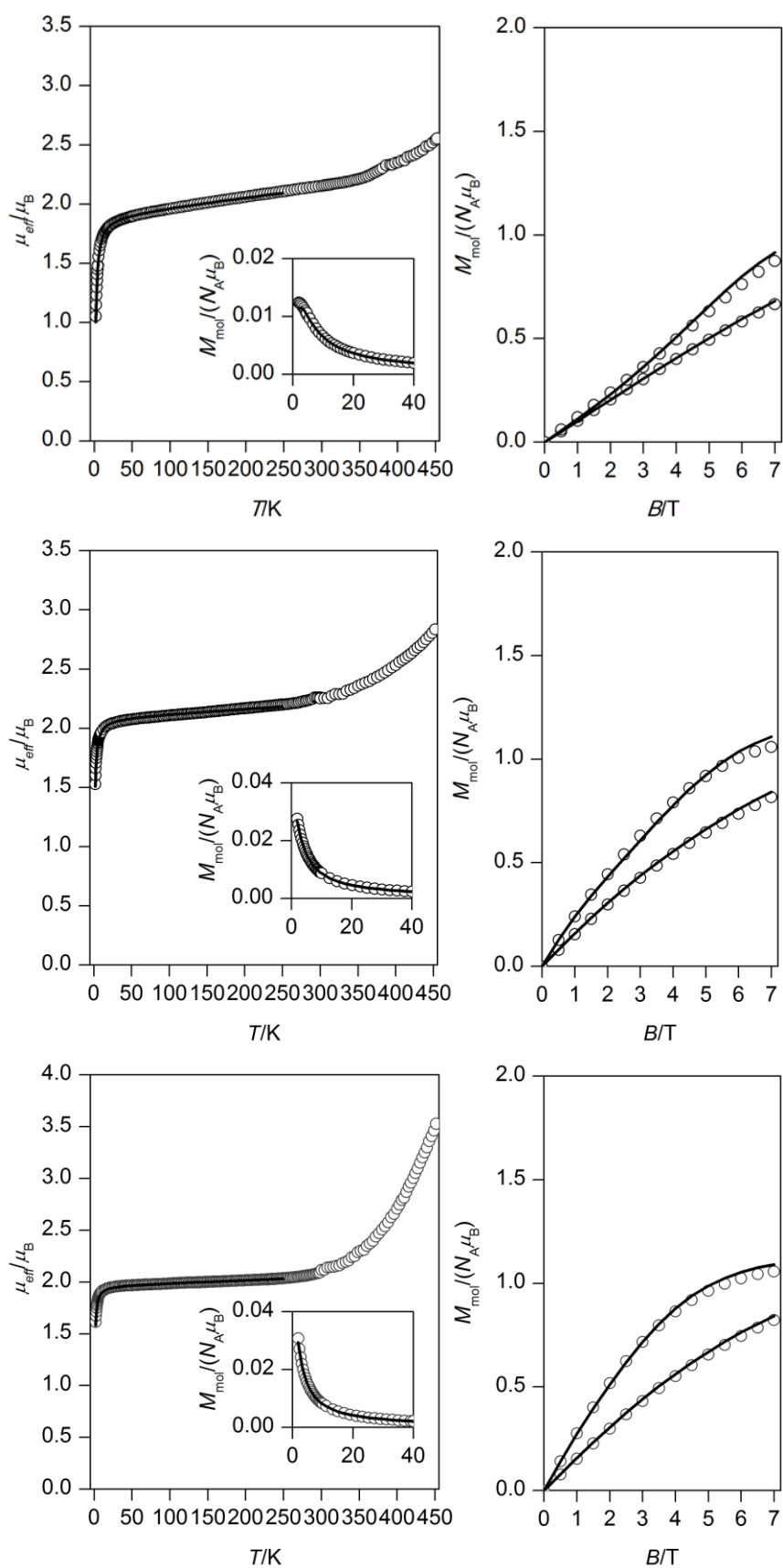
**Fig.S1** The ORTEP graphics of the title compounds: [Fe(4OH-L6)]X, X = Cl<sup>-</sup> (**1a**, on top), Br<sup>-</sup> (**1b**, in the middle row), I<sup>-</sup> (**1c**, down). Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å).



**Fig.S2** Thermogravimetric data for compounds **1a-1c**



**Fig.S3** Magnetic data for **1a** (on top), **1b** (in the middle) and **1c** (bottom). Left: temperature dependence of the effective magnetic moment. Inset: temperature dependence of the magnetization measured at  $B = 0.1$  T. Right: field dependence of magnetization at  $T = 2.0$  and 4.6 K. Empty circles – experimental data; full lines – the best fits to the experimental data *via* 1D network model (eqn. 4). The calculated parameters are listed in Table 3.



**Table S1.** Full listing of parameters derived using Taylors' equations for X-band powder EPR spectra measured 77 K.<sup>a</sup>

	$g_x$	$g_y$	$g_z$	$a$	$b$	$c$	$\Sigma$	$V/\lambda$	$\Delta/\lambda$	$V/\Delta$
compound 1	-2.208	-2.172	1.965	-0.052	1.043	0.009	1.091	10.146	60.177	0.169
	<b>-2.208</b>	<b>2.172</b>	<b>-1.965</b>	<b>0.047</b>	<b>0.055</b>	<b>0.996</b>	<b>0.998</b>	<b>-1.728</b>	<b>-10.251</b>	<b>0.169</b>
	-2.208	2.172	1.965	0.581	0.586	0.615	1.058	-0.013	-0.078	0.169
	2.208	2.172	1.965	1.053	-0.062	-0.009	1.113	-8.405	-49.847	0.169
	-2.172	-2.208	1.965	-0.062	1.053	-0.009	1.113	8.405	-49.847	-0.169
	<b>-2.172</b>	<b>2.208</b>	<b>-1.965</b>	<b>0.055</b>	<b>0.047</b>	<b>0.996</b>	<b>0.998</b>	<b>1.728</b>	<b>-10.251</b>	<b>-0.169</b>
	-2.172	2.208	1.965	0.586	0.581	0.615	1.058	0.013	-0.078	-0.169
	2.172	2.208	1.965	1.043	-0.052	0.009	1.091	-10.146	60.177	-0.169
compound 2	-2.208	-2.173	1.964	-0.052	1.043	0.009	1.091	10.044	61.657	0.163
	<b>-2.208</b>	<b>2.173</b>	<b>-1.964</b>	<b>0.048</b>	<b>0.055</b>	<b>0.996</b>	<b>0.998</b>	<b>-1.659</b>	<b>-10.183</b>	<b>0.163</b>
	-2.208	2.173	1.964	0.581	0.586	0.615	1.058	-0.013	-0.079	0.163
	2.208	2.173	1.964	1.053	-0.062	-0.009	1.113	-8.372	-51.395	0.163
	-2.173	-2.208	1.964	-0.062	1.053	-0.009	1.113	8.372	-51.395	-0.163
	<b>-2.173</b>	<b>2.208</b>	<b>-1.964</b>	<b>0.055</b>	<b>0.048</b>	<b>0.996</b>	<b>0.998</b>	<b>1.659</b>	<b>-10.183</b>	<b>-0.163</b>
	-2.173	2.208	1.964	0.586	0.581	0.615	1.058	0.013	-0.079	-0.163
	2.173	2.208	1.964	1.043	-0.052	0.009	1.091	-10.044	61.657	-0.163
compound 3	-2.207	-2.177	1.967	-0.053	1.044	0.008	1.093	9.988	71.082	0.141
	<b>-2.207</b>	<b>2.177</b>	<b>-1.967</b>	<b>0.048</b>	<b>0.055</b>	<b>0.997</b>	<b>0.999</b>	<b>-1.439</b>	<b>-10.239</b>	<b>0.141</b>
	-2.207	2.177	1.967	0.581	0.586	0.615	1.059	-0.011	-0.078	0.141
	2.207	2.177	1.967	1.053	-0.061	-0.008	1.112	-8.538	-60.765	0.141
	-2.177	-2.207	1.967	-0.061	1.053	-0.008	1.112	8.538	-60.765	-0.141
	<b>-2.177</b>	<b>2.207</b>	<b>-1.967</b>	<b>0.055</b>	<b>0.048</b>	<b>0.997</b>	<b>0.999</b>	<b>1.439</b>	<b>-10.239</b>	<b>-0.141</b>
	-2.177	2.207	1.967	0.586	0.581	0.615	1.059	0.011	-0.078	-0.141
	2.177	2.207	1.967	1.044	-0.053	0.008	1.093	-9.988	71.082	-0.141

<sup>a</sup> In general, there are 48 possibilities for assigning three g-values with the different signs to  $g_x$ ,  $g_y$  and  $g_z$ . According to Taylor's deduction, only combinations that meet the condition of  $g_z + g_y - g_x > 0$  are acceptable. Only solutions marked with the red colour, in which the values of  $\Delta/\lambda$  were physically acceptable, were considered as meaningful.

**Table S2.** Full listing of parameters derived using Taylors' equations for X-band frozen MeOH solution EPR spectra measured at 77 K.<sup>a</sup>

	$g_x$	$g_y$	$g_z$	$a$	$b$	$c$	$\Sigma$	$V/\lambda$	$\Delta/\lambda$	$V/\Delta$
compound 1	-2.245	-2.212	1.946	-0.067	1.053	0.008	1.114	7.912	63.454	0.125
	<b>-2.245</b>	<b>2.212</b>	<b>-1.946</b>	<b>0.059</b>	<b>0.067</b>	<b>0.994</b>	<b>0.997</b>	<b>-1.042</b>	<b>-8.356</b>	<b>0.125</b>
	-2.245	2.212	1.946	0.581	0.586	0.623	1.068	-0.012	-0.097	0.125
	2.245	2.212	1.946	1.063	-0.076	-0.008	1.136	-6.858	-55.001	0.125
	-2.212	-2.245	1.946	-0.076	1.063	-0.008	1.136	6.858	-55.001	-0.125
	<b>-2.212</b>	<b>2.245</b>	<b>-1.946</b>	<b>0.067</b>	<b>0.059</b>	<b>0.994</b>	<b>0.997</b>	<b>1.042</b>	<b>-8.356</b>	<b>-0.125</b>
	-2.212	2.245	1.946	0.586	0.581	0.623	1.068	0.012	-0.097	-0.125
	2.212	2.245	1.946	1.053	-0.067	0.008	1.114	-7.912	63.454	-0.125
compound 2	-2.245	-2.210	1.944	-0.067	1.053	0.009	1.113	7.912	60.027	0.132
	<b>-2.245</b>	<b>2.210</b>	<b>-1.944</b>	<b>0.059</b>	<b>0.067</b>	<b>0.994</b>	<b>0.996</b>	<b>-1.098</b>	<b>-8.327</b>	<b>0.132</b>
	-2.245	2.210	1.944	0.581	0.585	0.623	1.068	-0.013	-0.098	0.132
	2.245	2.210	1.944	1.063	-0.077	-0.009	1.136	-6.802	-51.602	0.132
	-2.210	-2.245	1.944	-0.077	1.063	-0.009	1.136	6.802	-51.602	-0.132
	<b>-2.210</b>	<b>2.245</b>	<b>-1.944</b>	<b>0.067</b>	<b>0.059</b>	<b>0.994</b>	<b>0.996</b>	<b>1.098</b>	<b>-8.327</b>	<b>-0.132</b>
	-2.210	2.245	1.944	0.585	0.581	0.623	1.068	0.013	-0.098	-0.132
	2.210	2.245	1.944	1.053	-0.067	0.009	1.113	-7.912	60.027	-0.132
compound 3	-2.244	-2.216	1.946	-0.068	1.054	0.007	1.116	7.782	73.92	0.105
	<b>-2.244</b>	<b>2.216</b>	<b>-1.946</b>	<b>0.060</b>	<b>0.066</b>	<b>0.995</b>	<b>0.997</b>	<b>-0.875</b>	<b>-8.310</b>	<b>0.105</b>
	-2.244	2.216	1.946	0.581	0.585	0.623	1.069	-0.010	-0.098	0.105
	2.244	2.216	1.946	1.063	-0.076	-0.007	1.135	-6.897	-65.512	0.105
	-2.216	-2.244	1.946	-0.076	1.063	-0.007	1.135	6.897	-65.512	-0.105
	<b>-2.216</b>	<b>2.244</b>	<b>-1.946</b>	<b>0.066</b>	<b>0.060</b>	<b>0.995</b>	<b>0.997</b>	<b>0.875</b>	<b>-8.310</b>	<b>-0.105</b>
	-2.216	2.244	1.946	0.585	0.581	0.623	1.069	0.010	-0.098	-0.105
	2.216	2.244	1.946	1.054	-0.068	0.007	1.116	-7.782	73.92	-0.105

<sup>a</sup> In general, there are 48 possibilities for assigning three g-values with the different signs to  $g_x$ ,  $g_y$  and  $g_z$ . According to Taylor's deduction, only combinations that meet the condition of  $g_z + g_y - g_x > 0$  are acceptable. Only solutions marked with the red colour, in which the values of  $\Delta/\lambda$  were physically acceptable, were considered as meaningful.

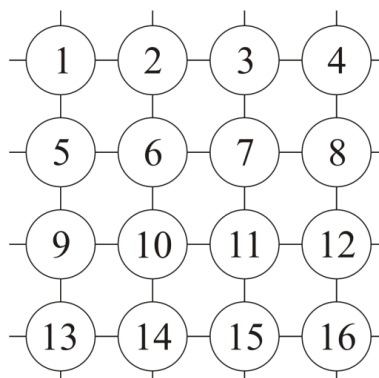
**Table S3.** Classification of spin states according to the spin Hamiltonian (eq.2) in zero magnetic field according to the  $C_2$  point symmetry group.

S	A	B	Total zero-field states	Total magnetic states
1/2	8398	8398	16796	33592
3/2	12618	12576	25194	100776
5/2	11628	11628	23256	139536
7/2	7776	7728	15504	124032
9/2	3876	3876	7752	77520
11/2	1467	144	2907	34884
13/2	399	399	798	11172
15/2	80	72	152	2432
17/2	9	9	18	324
19/2	1	0	1	20

**Table S4** The average bond length parameters, octahedral angular distortion parameter for purely LS or HS [Fe(X-L6)].A derivatives.

CCD code	Fe-N <sub>am</sub>	Fe-N <sub>im</sub>	Fe-O	$\Sigma$
FEXXUC, Fe2 molecule	2.023	1.949	1.885	46.3
HPZDFE	2.006	1.93	1.884	43.4
FISTUW	2.000	1.931	1.879	45.1
SALTFN	1.999	1.932	1.882	46.9
EXAWUV	2.004	1.938	1.871	45.6
WOBXAN	2.022	1.939	1.9	43.5
PUWZIR	1.992	1.934	1.890	55.6
XUCLEN	2.008	1.932	1.876	50.2
<b>LS avg</b>	<b>2.007</b>	<b>1.936</b>	<b>1.883</b>	<b>47.1</b>
KUPCEE	2.171	2.114	1.915	95.7
FISVEI	2.212	2.132	1.925	100.0
JOBYEE	2.215	2.137	1.924	94.1
WOBXER	2.212	2.144	1.929	95.5
FEXXUC, Fe1 molecule	2.205	2.109	1.913	96
EXAWOP	2.209	2.105	1.902	85.5
WUBMOA, Fe1	2.218	2.124	1.932	93.9
WUBMOA, Fe2	2.246	2.133	1.932	118.8
FEPFAI04	2.187	2.105	1.900	91.4
WOBWUG	2.170	2.117	1.920	109.4
<b>HS avg</b>	<b>2.205</b>	<b>2.117</b>	<b>1.920</b>	<b>98.2</b>

**Scheme S1.** The topological scheme of 4x4 grid corresponding to the spin Hamiltonian in eq. 4.



**The calculation details for the Ising-like model and fit of the temperature dependence of the molar susceptibility for 1a-c.**

The spin Hamiltonian for the Ising-like model

$$\hat{H} = \frac{\Delta_0}{2} \hat{\sigma} - \gamma \langle \sigma \rangle \hat{\sigma}$$

where  $\sigma$  is fictitious spin with eigenvalues  $\sigma = -1$  for LS and  $\sigma = +1$  for HS states,  $\Delta_0$  is the energy difference between HS and LS states,  $\gamma$  stands for the cooperativeness of the system ( $\gamma > 0$ ) and  $\langle \sigma \rangle$  is the thermal average of the fictitious spin for which can be derived the implicit equation

$$\langle \sigma \rangle = \frac{-1 + r_{\text{eff}} \exp\left[-(\Delta_0 - 2\gamma \langle \sigma \rangle) / kT\right]}{+1 + r_{\text{eff}} \exp\left[-(\Delta_0 - 2\gamma \langle \sigma \rangle) / kT\right]}$$

where

$$x_{\text{HS}} = \frac{1}{2}(1 + \langle \sigma \rangle)$$

and  $r_{\text{eff}}$  means the effective degeneracy ratio of HS (high-spin) vs. LS (low-spin) states. The free parameters of the model are:  $\Delta_0$ ,  $\gamma$  and  $r_{\text{eff}}$ . The microscopic quantities are related to the thermodynamic quantities as

$$\Delta H = N_A \Delta_0$$

$$\Delta S = R \ln r_{\text{eff}}$$

$$T_c = \frac{\Delta H}{\Delta S}$$

The molar susceptibilities of **1a-c** were fitted as follows:

1/ the Ising-like model parameters of  $\Delta_0$ ,  $\gamma$  and  $r_{\text{eff}}$  were used to calculate the  $x_{\text{HS}}$  molar fraction vs. temperature

2/ the molar susceptibilities for the LS and HS states were calculated using simple Curie law as

$$\chi_{\text{mol}}^{\text{LS}} = \frac{N_A \mu_0 \mu_B^2 S_{\text{LS}} (S_{\text{LS}} + 1)}{3k} \frac{g_{\text{LS}}^2}{T} + \chi_{\text{TIP}}$$

with  $S_{\text{LS}} = 1/2$ , and  $g_{\text{LS}} \chi_{\text{TIP}}$  values were identical as in analyses of the low-temperature data (Table 3)

$$\chi_{\text{mol}}^{\text{HS}} = \frac{N_{\text{A}} \mu_{\text{0}} \mu_{\text{B}}^2 S_{\text{HS}} (S_{\text{HS}} + 1) g_{\text{HS}}^2}{3k T}$$

with  $S_{\text{HS}} = 5/2$ , and  $g_{\text{HS}} = 2.0$  (fixed)

3/ the overall susceptibility was calculated as

$$\chi_{\text{mol}} = x_{\text{HS}} \chi_{\text{HS}} + (1 - x_{\text{HS}}) \chi_{\text{LS}}$$