Intermolecular interactions in $1 \cdot (CIO_4)_2$.

The hydrogen-bonded chains are linked through intermolecular interactions that involve C atoms from a pyrazole group and oxygen atoms from a carboxylic acid group of neighboring molecules (dO1…C8 = 3.192 Å at 400 K) (Figure S1) giving rise to layers of complexes on the bc plane separated by layers of perchlorate anions (Figure S2). In the structure at 120 K the number of contacts increases as a result of the significant shortening of *a* and *b* axis on lowering the temperature. Thus, neighbouring [Fe(bppCOOH)₂]²⁺ complexes belonging to the *bc* planes present two types of contacts involving C atoms from a pyrazole group and oxygen atoms from a carboxylic acid group (dO3…C1 = 3.185 Å and dO1…C7 = 3.056 Å) (Figure S1). On the other hand, [Fe(bppCOOH)₂]²⁺ complexes of neighboring layers present short contacts at 120 K, which involve CH groups of the pyrazole rings (dC2…C2 = 3.709 Å) (Figure S3). These short contacts do not appear in the structure at 400 K.





•

(b)

Fig. S1 View of a layer of $[Fe(bppCOOH)_2]^{2+}$ complexes with the intermolecular interactions between complexes belonging to different hydrogen-bonded chains as dashed lines in the structure of $[Fe(bppCOOH)_2](CIO_4)_2$ (**1(CIO_4)_2**) at 400 K (a) and 120 K (b).



(a)



Fig. S2 Projection of the structure of $[Fe(bppCOOH)_2](CIO_4)_2$ (**1CIO**₄) at 400 K (a) and 120 K (b) in the *ac* plane with the $[Fe(bppCOOH)_2]^{2^+}$ belonging to the same hydrogen-bonded chain coloured in red or blue.



Fig. S3 View of two layers of $[Fe(bppCOOH)_2]^{2^+}$ complexes with the intermolecular interactions between complexes belonging to different layers as dashed lines in the structure of $[Fe(bppCOOH)_2](CIO_4)_2$ (**1(CIO_4)**₂) at 120 K. $[Fe(bppCOOH)_2]^{2^+}$ complexes belonging to the same hydrogen-bonded chain are coloured in red or blue.



Fig. S4 Thermal dependence of the unit cell parameters of [Fe(bppCOOH)₂](ClO₄)₂ (1(ClO₄)₂).



Fig. S5 Thermal dependence of the unit cell parameters of [Fe(bppCOOH)₂](BF₄)₂ (1(BF₄)₂).



Fig. S6 Experimental powder X-ray diffraction patterns (top) at 298 K (blue line) and 400 K (red line) and simulated one (bottom) at 120 K (purple line) and 400 K (red line) of $[Fe(bppCOOH)_2](CIO_4)_2$ (**1(CIO_4)**₂).







Fig. S7 Thermal dependence of the experimental powder X-ray diffraction pattern of $[Fe(bppCOOH)_2](CIO_4)_2$ (1(CIO₄)₂).



Fig. S8 Experimental powder X-ray diffraction pattern at 298 K (blue) and simulated one from the structure solved at 120 K (red) of $[Fe(bppCOOH)_2](BF_4)_2$ (**1(BF_4)_2**).



Fig. S9 Projection in the *bc* plane of the structure of $1(CF_3SO_3)_2.Me_2CO$ at 120 K (C(black), N(blue), O(red), Fe(brown), S(yellow), F(green)).



Fig. S10 Experimental PXRD pattern (red), simulated one from the structure solved at 300 K (blue), experimental PXRD pattern of the desolvated sample (yellow) and experimental PXRD pattern of the resolvated sample (green) of **1(CF₃SO₃)₂.yMe₂CO**.



(a)



(b)





Fig. S11 Thermogravimetric analysis of $1(CF_3SO_3)_2.yMe_2CO$ (a), $1(AsF_6)_2.yMe_2CO$ (b) and $1(SbF_6)_2.yMe_2CO$ (c).







(b)



Fig. S12 Projection in the *ab* plane of the structures of $1(AsF_6)_2.yMe_2CO$ at 120 K (a) and 300 K (b) and $1(SbF_6)_2.yMe_2CO$ at 120 K (c) and 300 K (d). (C(black), N(blue), O(red), Fe(brown), As(grey), Sb(grey) and F(green)).



Fig. S13 Hydrogen-bonds (blue-dashed lines) between the $[Fe(bppCOOH)_2]^{2+}$ complexes and acetone molecules in the structure of $1(AsF_6)_2$.yMe₂CO at 120 K.



Fig. S14 CH… π contacts between [Fe(bppCOOH)₂]²⁺ complexes in the structures of $1(AsF_6)_2.yMe_2CO$ (top) and $1(SbF_6)_2.yMe_2CO$ (bottom) at 120 K.

These chains are connected through short contacts involving C=O groups from carboxylic acid groups and two CH from pyrazole and pyridine rings from a $[Fe(bppCOOH)_2]^{2+}$ complex belonging to a different chain with the following distances (3.355 Å C1-C9, 3.265 Å C2-C9 and 2.871 Å C10-H1 for **1(AsF_6)_2.yMe_2CO** and 3.289 Å C3-C9 and 2.896 Å C2-H11 for **1(AsF_6)_2.yMe_2CO**). In contrast to this, CH···· π contacts are not observed in the structures solved at 300 K. Finally, AsF₆⁻ or SbF₆⁻ anions inserted between the chains present numerous short contacts with neighboring $[Fe(bppCOOH)_2]^{2+}$ complexes.



Fig. S15 Simulated PXRD pattern from single crystal X-ray diffraction structure at 300 K (blue) and experimental one of the compound (red), after desolvation (yellow) and after resolvation (green) at 300 K powder X-ray diffraction patterns of **1(AsF₆)₂.yMe₂CO** (top) and **1(SbF₆)₂.yMe₂CO** (bottom).



Fig. S16 Projection in the *bc* plane of the structure of **2(CIO₄)₂·yMe₂CO** at 300 K.



Fig. S17 Powder X-ray diffraction pattern at 300 K (red), simulated one from the single crystal X-ray diffraction structure at 300 K (blue) and of desolvated crystals after heating to 400 K (green) of $2(CIO_4)_2$ ·yMe₂CO.



Fig. S18 Thermal dependence of magnetic susceptibility times temperature (χ_M T) of **1(AsF₆)₂·yMe₂CO** (top) and **1(SbF₆)₂·yMe₂CO** (bottom).



Fig. S19 Kinetics for 1(CIO₄)₂.

The kinetics has been fitted using a so-called sigmoidal law. This law describes a self-accelerated process, often associated with cooperative systems. This cooperativity arises from the large difference in metal-ligand bond lengths, resulting in elastic intercations caused by change in internal pressure as the spin transition proceeds.^[1] In this model, the relaxation rate $k_{HL}(T,n_{HS})$ depends both on the temperature T and the HS fraction n_{HS} as follows:

 $\begin{aligned} &dn_{HS}/dT = -n_{HS} \ k_{HL}(T,n_{HS}) \\ & \text{with} \ k_{HL}(T,n_{HS}) = k_{HL}(T) exp[\alpha(T)(1-n_{HS})] \end{aligned}$

and $k_{HL}(T) = k_{\infty} exp(-E_A/k_BT)$

 $\alpha(T)$ is a self-accelerated factor, E_A the activation energy of the process and k_{∞} the frequency factor. For each temperature, the fitting procedure gives a value of $k_{HL}(T)$ and $\alpha(T)$. Both values are summarized in the table 1.

T/K	k _{HL} / s⁻¹	α(T)
50	1.67017E-5	3.01231
52	3.14302E-5	3.1485
54	4.62833E-5	3.544
56	1.05163E-4	3.417
58	1.58461E-4	3.3
60	3.35463E-4	3.189

Table S1: $k_{HL}(T)$ and $\alpha(T)$ for compound [Fe(bppCOOH)₂](CIO₄)₂

An Arrhenius plot allows the determination of the frequency factor and activation energy for the compound: $E_A = 614 \text{ cm}^{-1} \text{ et } k_{\infty} = 723 \text{ s}^{-1}$.

Magnetization under irradiation of $[Fe(bppCOOH)_2](ClO_4)_2$ as a function of the temperature has been recorded. More precisely, the temperature was decreased continuously from 100 K to 10 K under continuous irradiation (532 nm). The temperature was then re-increased up to 100 K, still under irradiation (Fig. S20).



Fig. S20 LITH and static points for 1(CIO₄)₂.

A clear LITH hysteresis is observed bellow 70 K, that is to say that the $\chi_M T$ product is strongly different when recorded decreasing or increasing the temperature. The size and shape of LITH curve is known to be strongly dependent on the temperature sweep rate. In order to search for the possible existence of a static LITH, two kinetics under irradiation have been recorded at 50 K (Fig. S21). One kinetic has been recorded first irradiating the sample at 100 K, then decreasing rapidly the temperature to 50 K and starting the kinetic as soon as the temperature is stable at 50 K. The second kinetic has been recorded the same way but first irradiating the compound at 10 K. The two kinetics are also reported as a function of temperature (Fig. S20).



Fig. S21 Kinetics of the static points for 1(CIO₄)₂.

The two kinetics at 50 K can be reasonably well fitted by simple exponential functions (red lines of figure S21). It can be extrapolated that at infinite time the two curves are separated by about $1.0 \text{ cm}^3 \text{ K mol}^{-1}$.

Table S2. Crystallographic data

Compound	1(BF ₄) ₂	1(BF ₄) ₂	1(CF₃SO₃)₂·Me₂CO	1(CF₃SO₃)₂·0.5Me₂CO
Empirical formula	$C_{24}H_{18}B_2F_8FeN_{10}O_4$	$C_{24}H_{18}B_2F_8FeN_{10}O_4$	$C_{29}H_{24}F_6FeN_{10}O_{11}S_2$	C ₅₅ H ₄₂ F ₁₂ Fe ₂ N ₂₀ O ₂₁ S ₄
Formula weight	739.95	739.95	922.55	1787.02
Crystal color	Orange	Orange	Orange	Orange
Temperature (K)	120	350	120	300
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, Z	Monoclinic, 4	Monoclinic, 4	Orthorhombic, 8	Orthorhombic, 4
Space group	C2/c	C2/c	Pcab	Pcab
a (Å)	17.1725(4)	17.3370(10	14.8997(4)	15.1365(3)
b (Å)	16.0377(4)	16.5488(8)	21.7329(5)	21.8413(4)
c (Å)	10.6830(3)	10.692(5)	22.2566(4)	22.3085(4)
β(²)	106.691(3)	104.976(5)	90	90
V (Å ³)	2818.22(12)	2963.3(14)	7207.0(3)	7375.2(2)
ρcalc (Mg/m³)	1.744	1.659	1.700	1.609
μ(Mo _{κ-}) (mm ⁻¹)	0.643	0.611	0.640	0.621
θrange (°)	2.92 to 27.53	2.85 to 27.53	3.258 to 27.471	3.342 to 27.497
Refins collected	36207	33269	30229	25242
Independent refins, (R _{int})	3248 (0.0905)	3412 (0.0998)	7672 (0.0714)	7655 (0.0290)
L. S. parameters/ restraints	225/0	261/0	532/0	532/0
R1(F), ^[a] I>2 <i>σ</i> (I)]	0.0347	0.0553	0.0513	0.0501
wR2(F ²), ^[b] all data	0.0891	0.1839	0.1032	0.1654
$S(F^2)$, ^[c] all data	1.050	0.806	1.029	1.069

 $[a] R1(F) = \sum (|F_0| - |F_c|) / \sum |F_0|; [b] wR2(F^2) = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4]^{\frac{1}{2}}; [c] S(F^2) = [\sum w(F_0^2 - F_c^2)^2 / (n-p)]^{\frac{1}{2}}.$

Table S2. Crystallographic data

Compound	1(AsF ₆) ₂ ·Me ₂ CO	1(SbF ₆)₂·Me₂CO	1(AsF ₆) ₂ ·2Me ₂ CO	1(SbF ₆)₂·2Me₂CO
Empirical formula	$C_{27}H_{24}As_2F_{12}FeN_{10}O_5$	$C_{27}H_{24}F_{12}FeN_{10}O_5Sb_2$	$C_{30}H_{30}As_2F_{12}FeN_{10}O_6$	C ₃₀ H ₃₀ F ₁₂ FeN ₁₀ O ₆ Sb ₂
Formula weight	1002.25	1095.93	1060.33	1153.99
Crystal color	Orange	Orange	Orange	Orange
Temperature (K)	300	300	120	120
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, Z	Tetragonal, 8	Tetragonal, 8	Tetragonal, 8	Tetragonal, 8
Space group	141cd	141cd	141cd	I41cd
a (Å)	23.4197(9)	23.6034(15)	23.3533(3)	23.4653(2)
c (Å)	14.6422(8)	14.9526(17)	14.3811(3)	14.6485(3)
β(²)	90	90	90	90
V (Å ³)	8031.0(8)	8330.4(14)	7843.1(3)	8065.8(2)
$ ho$ calc (Mg/m 3)	1.658	1.748	1.796	1.901
μ(Mo _{κ-}) (mm ⁻¹)	2.115	1.732	2.173	1.796
θrange (°)	3.282 to 27.540	3.226 to 27.604	3.227 to 27.489	3.279 to 27.530
Refins collected	21855	19539	15144	65363
Independent reflns, (R _{int})	4345 (0.0905)	4802 (0.1398)	4151 (0.0480)	4631 (0.0745)
L. S. parameters/ restraints	330/1	276/1	276/1	276/1
R1(F), ^[a] I>2 <i>σ</i> (I)]	0.0609	0.0679	0.0391	0.0315
wR2(F ²), ^[b] all data	0.1845	0.1825	0.0854	0.0773
S(F ²), ^[c] all data	0.962	0.957	1.046	1.114

 $[a] R1(F) = \sum (|F_0| - |F_c|) / \sum |F_0|; [b] wR2(F^2) = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4]^{\frac{1}{2}}; [c] S(F^2) = [\sum w(F_0^2 - F_c^2)^2 / (n-p)]^{\frac{1}{2}}.$

Table S2. Crystallographic data

Compound	1(ClO ₄) ₂	2(ClO ₄) ₂ ·1.5Me ₂ CO	2(ClO ₄) ₂ ·0.5Me ₂ CO		
Empirical formula	C ₂₄ H ₁₈ Cl ₂ FeN ₁₀ O ₁₂	C ₆₅ H ₇₀ Cl ₄ Fe ₂ N ₂₀ O ₂₇	C ₁₂₁ H ₁₂₆ Cl ₈ Fe ₄ N ₄₀ O ₅₁		
Formula weight	765.23	1816.91	3463.61		
Crystal color	Red	Red	Red		
Temperature (K)	400	120	300		
Wavelength (Å)	0.71073	0.71073	0.71073		
Crystal system, Z	Monoclinic, 4	Triclinic, 2	Triclinic, 2		
Space group	C2/c	P-1	P-1		
a (Å)	17.574(3)	8.4649(3)	8.5561(4)		
b (Å)	16.554(2)	21.2806(5)	21.3922(9)		
c (Å)	10.8254(15)	23.1689(8)	23.5484(11)		
α (º)	90	110.978(3)	69.009(4)		
β(²)	104.686(15)	95.650(3)	83.330(4)		
γ (²)	90	91.629(3)	89.892(4)		
V (Å ³)	3046.4(8)	3868.9(2)	3993.2(3)		
hocalc (Mg/m ³)	1.668	1.560	1.440		
μ(Mo _κ .) (mm ⁻¹)	0.751	0.608	0.583		
θrange (°)	2.940 to 27.664	3.525 to 25.246	3.364 to 22.634		
Reflns collected	23217	59794	60459		
Independent reflns, (R _{int})	1589 (0.178)	16847 (0.0849)	17045 (0.0848)		
L. S. parameters/ restraints	261/0	1108/0	1099/32		
R1(F), ^[a] I>2σ(I)]	0.0702	0.0682	0.1136		
wR2(F ²), ^[b] all data	0.2628	0.1555	0.4051		
S(F ²), ^[c] all data	0.846	1.036	1.062		
$[a] R1(F) = \sum (F_0 - F_c) / \sum F_0 ; [b] wR2(F^2) = [\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^4]^{\frac{1}{2}}; [c] S(F^2) = [\sum w(F_0^2 - F_c^2)^2 / (n-p)]^{\frac{1}{2}}.$					

^{1 (}a) A. Hauser, P. Gütlich and H. Spiering, *Inorg. Chem.*, 1986, **25**, 4245; (b) A. Hauser, *Top. Curr. Chem.*, 2004, **234**, 155.