Electronic Supplementary Information (ESI)

Hydrate of neutral iron(III) complex based on pyruvic acid thiosemicarbazone ligand with abrupt spin-crossover with $T_{1/2}$=340 K and wide hysteresis loop of 45 K

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Author Contributions

The synthesis and characterizations of compounds, M.B., N.S., and A.L.; X-ray analysis and crystal structure description, L.Z. and S.S.; *dc* magnetic measurements, K.Z., A.V.; EPR measurements, A.A.; measured and contributed to analyses of [57]Fe Mössbauer spectral data and the DFT calculations, M.B.; writing the original draft, M.B., N.S.. All authors discussed the results and contributed to the final manuscript.

Contents

Instrumental techniques

Elemental analysis and Electron-priobe X-ray microanalysis. The purity of the complexes and their solvation state was verified by determining the carbon, hydrogen, nitrogen, and sulfur content at the Vario Micro Cube (Elementar) CHNOS elemental analyzer.

EPMA was performed with a Zeiss Supra-25 analytical field emission electron microscope equipped with a Gemini electron optical column at magnification varying from 600 to 6200 depending on the sample and the electron beam energy of 9.7-20 keV. The depth of beam penetration into the sample was 1-3 μm.

Thermogravimetric Analysis. The TGA was performed using a NETZSCH STA 449F3 thermal analyzer. Approximately 14.07 mg of sample were placed into an Al_2O_3 crucible with a prehole on the lid and then heated from 25 to 400 °C. The thermogravimetric analysis was performed in a high-purity argon atmosphere with a gas flow rate of 12 ml·min⁻¹, at the heating rate of 10 °C·min⁻¹.

FT-IR Spectroscopy. Infrared spectra were recorded at room temperature in the range of 4000–50 cm⁻¹ (50 averaged scans, the apparent resolution is 4 cm⁻¹) on a FT-IR Bruker Vertex 70V spectrometer in the attenuated total reflectance (ATR) mode with a Platinum-ATR (Bruker) accessory equipped with a pure diamond crystal (diamond ATR polarization accessory with 1 reflection top-plate and pressure arm).

Powder X-ray diffraction. PXRD was measured using a Rigaku SmartLab SE powder diffractometer with a 1D strip detector at room temperature (CuK_α radiation, step = 0.02°, single crystal cuvette). The PXRD pattern is used as a fingerprint for identifying the crystalline phase presented in a material.

Single crystal X-ray diffraction. Crystal data for **1**: $C_8H_{13}FeN_6O_5S_2$, F.w. 393.21, black prism, 0.25×0.35×0.53 mm³, monoclinic, $P2_1/n$. $T = 150(1)$ K: $a = 11.1829(3)$, $b = 10.4546(3)$, $c = 12.7936(3)$ Å, $\beta = 102.816(3)$, $V = 1458.47(7)$ Å³, $Z = 4$, $d_{calcd} = 1.791$ g/cm³, $\mu = 13.53$ cm⁻¹, $2\theta_{max} = 66.2°$; 33763 reflections collected, 5244 independent, $R_{int} = 0.0233$; $R_1 = 0.0256$ for 4680 observed data $[I > 2\sigma(I)]$ with 11 restraints and 220 parameters; $wR_2 = 0.0636$ (all data); final G.o.F. = 1.002. $T = 350(1)$ K: $a = 11.2865(2)$, $b = 10.4627(2)$, $c = 12.9417(2)$ Å, $\beta = 102.964(2)$, $V = 1489.30(5)$ Å³, $Z = 4$, $d_{calcd} = 1.754$ g/cm³, $\mu = 13.25$ cm⁻¹, $2\theta_{max} = 66.0°$; 34128 reflections collected, 5271 independent, $R_{int} = 0.0245$; $R_1 = 0.0341$ for 4229 observed data $[I > 2\sigma(I)]$ with 11 restraints and 220 parameters; $wR_2 = 0.0848$ (all data); final G.o.F. = 1.003.

X-ray single crystal diffraction data were collected at 150 and 350 K on an Oxford Diffraction Gemini-R CCD diffractometer equipped with an Oxford cryostream cooler $[\lambda(MoK_\alpha) = 0.71073$ Å, graphite monochromator, ω-scans]. Data reduction with empirical absorption correction of experimental intensities (Scale3AbsPack program) was made with the CrysAlisPro software.[1]

The structures were solved by a direct method and refined on F^2 by a full-matrix least squares method using SHELX-2016 program package.[2] All non-hydrogen atoms were refined anisotropically. The positions of H atoms in water molecules were found from the

difference Fourier map. All N-H and O-H bond lengths were refined with additional restraints (SADI). Deposition numbers CCDC 2389231 (150 K) and 2389232 (350 K) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Magnetic Measurements and X-band EPR spectroscopy. The magnetic properties of complex [Fe^{III}(Hthpy)(thpy)]·H_2O (**1**) were investigated using the VSM option of the "Quantum Design" Physical Properties Measurements System PPMS–9T on the fine powder sample with a mass of about 10 mg placed into the plastic capsule. The temperature dependence of the direct current (*dc*) magnetic susceptibility (χ) of the title compound has been taken at warming and cooling modes (temperature range of 2 – 363 K) in a magnetic field B = 0.1 T at the temperature change rate 2 K/min. Magnetic moment of the samples was corrected considering sample holder contribution. Magnetic susceptibility of **1** complex was corrected for diamagnetic contribution of Pascal constants.

Continuous-wave EPR spectra were measured at X-band (9.446778 GHz) using a Bruker ELEXSYS II E500 spectrometer. Powder sample of **1** was placed in a 3 mm diameter quartz tube and filled with argon gas. Continuous flow cryostat refrigerated with liquid nitrogen was used for cooling and heating in the temperature range 100 – 368 K, with a temperature change rate of approximately 5 K/min during both heating and cooling cycles, and a 5-minute pause at each temperature to record the spectrum. The microwave power (0.6325 mW) and modulation amplitude (1 G at 100 kHz) were low enough to avoid saturation effects and line broadening.

[57]Fe Mössbauer spectroscopy. [57]Fe Mössbauer absorption spectra of **1** complex were recorded on WissEl (Germany) spectrometer operating in a constant acceleration mode. [57]Co in the Rh matrix was used as the source of γ-quants. Spectra at low temperatures were measured using a continuous flow helium cryostat CF-506 (Oxford Instruments) with a controllable temperature. In the temperature range of 300−365 K, the Mössbauer resistive furnace MRF-750 K was utilized. Isomer shift values were taken with respect to α-Fe. The γ-quantum source and the standard absorber were at room temperature. Least-squares-fitted parameters are given with their standard deviation of statistical origin (in parentheses). The spectra were fit in an assumption of different widths and equal intensities of doublet resonance lines. The polycrystalline absorber **1** contained 50 mg of material per cm^2 (~0.31 mg cm^2 of [57]Fe).

Computational details. All density functional theory (DFT) calculations were carried out using the Gaussian 09 (Revision B.01) computational package[3] on the servers and workstations of the FRC PCP MC RAS, Chernogolovka. Calculations of the neutral complex [Fe^{III}(Hthpy)(thpy)] were performed with an unrestricted wave function. Geometry optimizations were done without any symmetry constraints. The X-ray structure of neutral complex Fe^{III}(Hthpy)(thpy)]·H_2O at 150 K was used as the starting structure for structural optimization. For the [Fe^{III}(Hthpy)(thpy)] complexes, the

molecular geometries and harmonic vibrational frequencies were calculated using the 6-311+G(d,p) basis set. Final electronic energies (E_{el}) for the DFT functionals were obtained by means of single point calculations (SP) using the 6-311+G(2df,2p) basis set. The total electronic energies E_0 ($E_0 = E_{el} + E_{ZPV}$) were calculated by combining the electronic energies computed by means of SP calculations with the zero point vibration energies (E_{ZPV}) evaluated at the geometry optimization level of theory. The TPSSh[4] functional was employed in this study. The exchange interaction parameter was evaluated within the broken symmetry approximation by Ginsberg, Noodleman, Yamaguchi, and others.[5-7]

Reference to the instrumental techniques:

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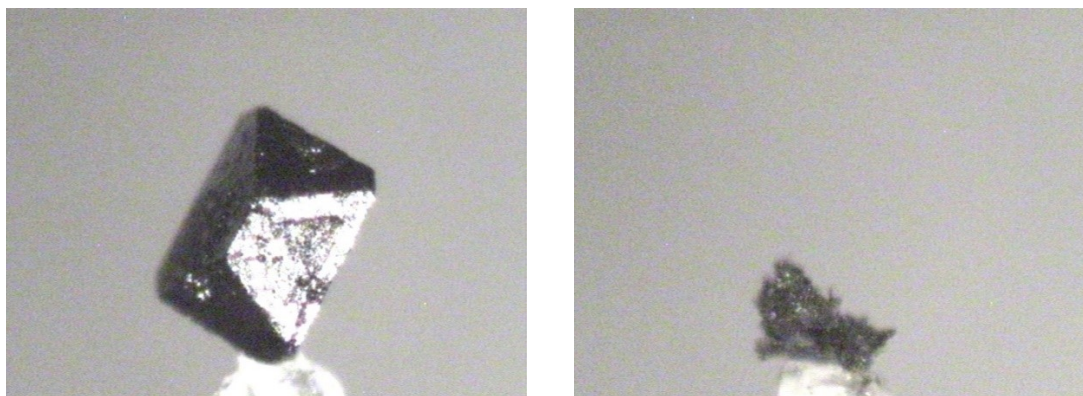
Figure S1. Photo of the crystal of $[Fe^{III}(Hthpy)(thpy)]·H_2O$ (**1**) during X-ray measurements in heating at 150 K (left) and at 364 K (right).
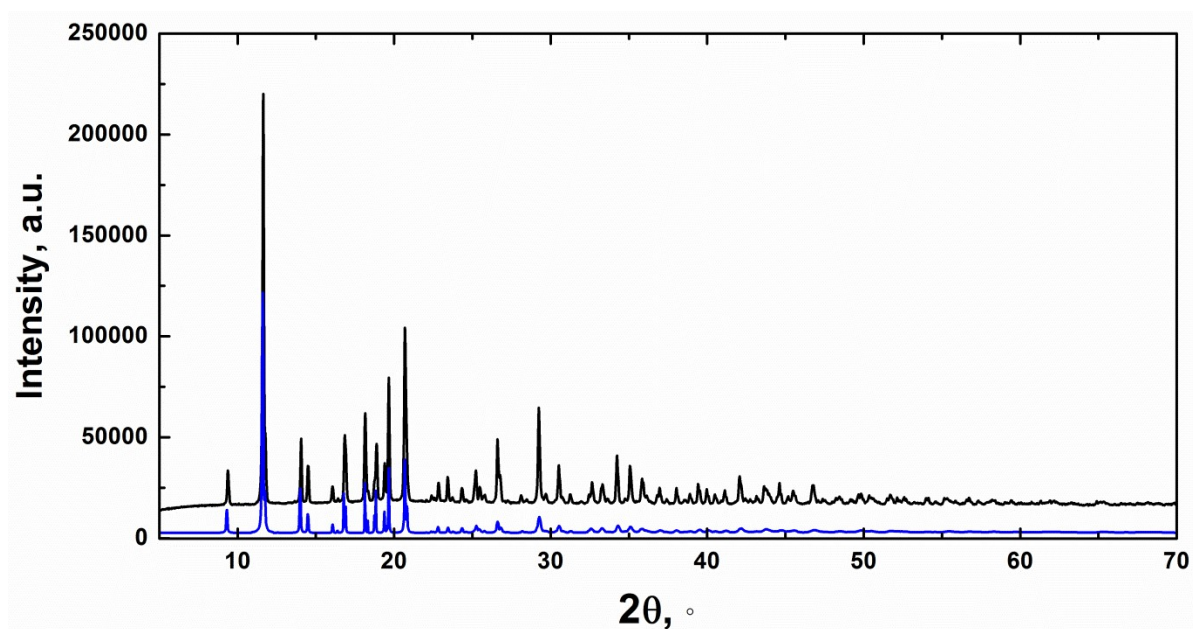
Figure S2. PXRD pattern in the 2θ range from 5° to 70° for $[Fe^{III}(Hthpy)(thpy)]·H_2O$ at 296 K (black line) with simulations based on 150 K single crystal structure (blue line).
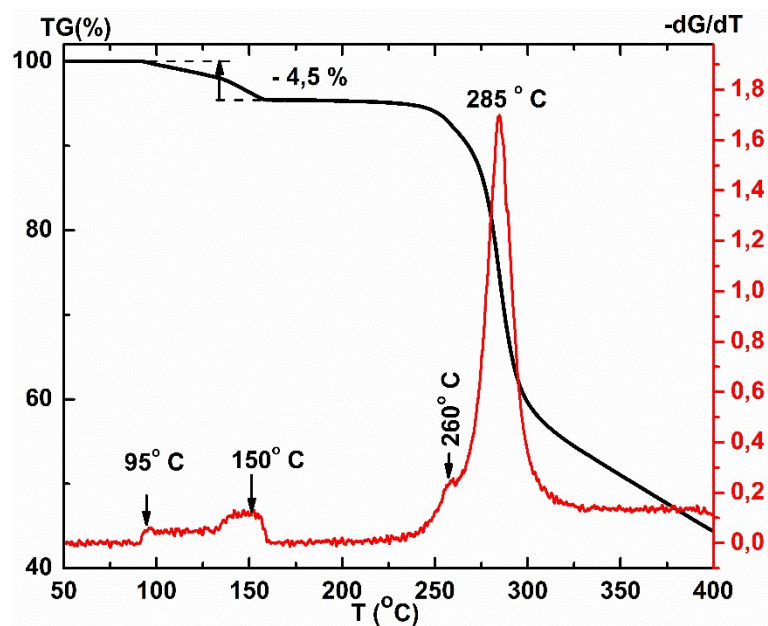
Figure S3. Thermogram (TG) of $[Fe^{III}(Hthpy)(thpy)]\cdot H_2O$ (normal curve (black) and 1st derivative of TG (red).
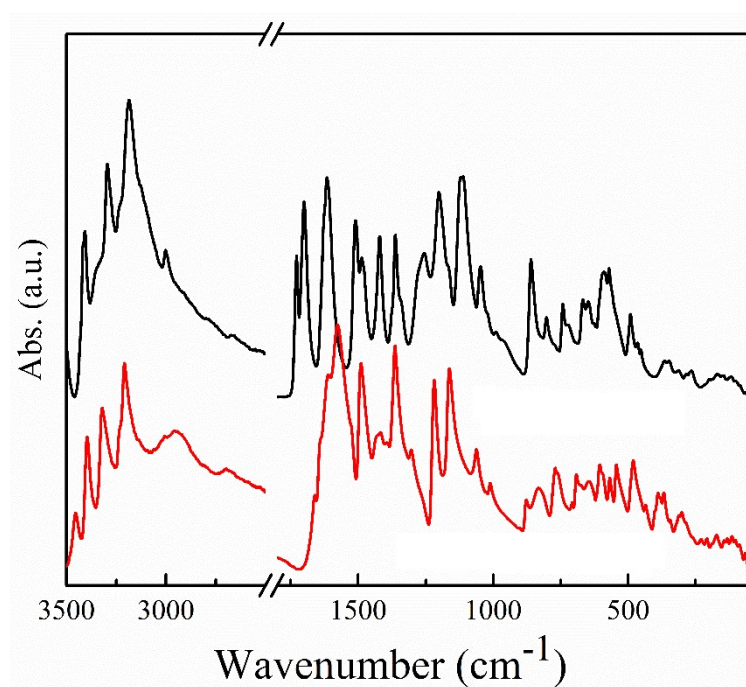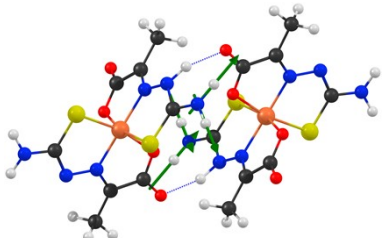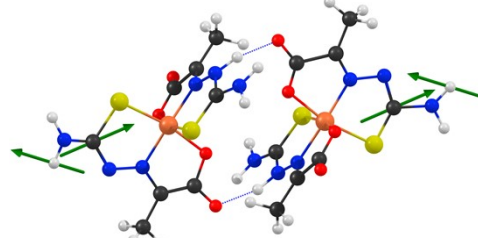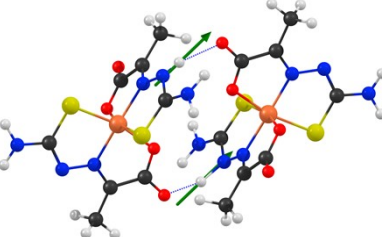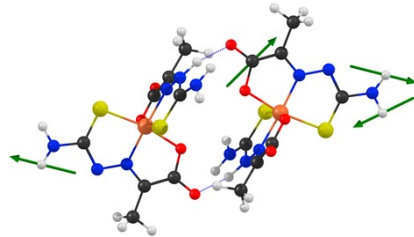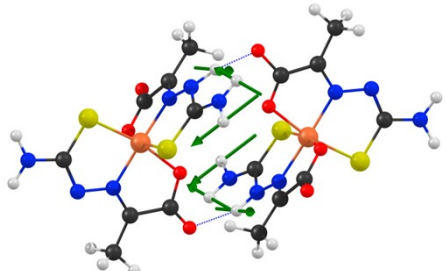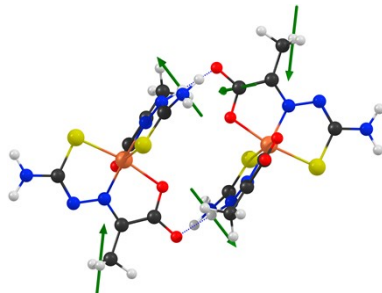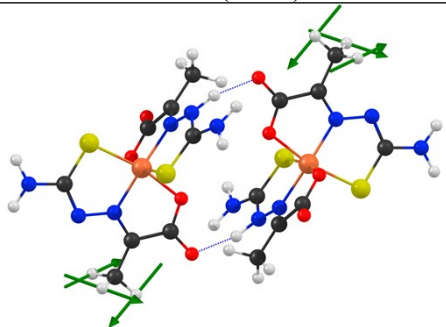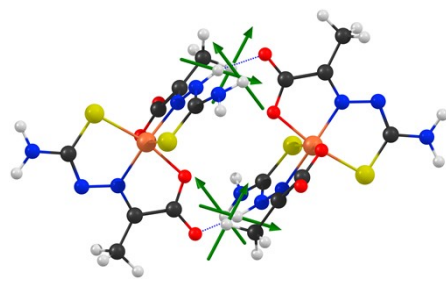
Figure S4. Experimental ATR FT-IR absorption spectra for the sample of the $H_2thpy\cdot\frac{1}{3}H_2O$ ligand (black line) and $[Fe^{III}(Hthpy)(thpy)]\cdot H_2O$ neutral complex (red line).

Table S1. The table of experimental IR vibrational modes for H_2thpy·⅓(H_2O) ligand and [Fe^{III}(Hthpy)(thpy)]·H_2O (**1**) neutral complex. Selected calculated (for **A** pair in LS state) IR vibrational modes of the **1** are showed in brackets.

Assignment of most essential vibrational mode	ν, cm^{-1}	
	H_2thpy·⅓H_2O	[Fe^{III}(Hthpy) (thpy)]·H_2O
ν(C-OH), ν(NH$_2$)	3501(m)	
ν(NH$_2$)	3407(s)	3453(m)/(*3469*) 3396(s)
ν(NH)	3294(s)	3319(s)
ν(OH)	3226(sh) 3186(s)	3228(sh) 3208(s)
ν(CH$_3$)	3001	2950(m)/(*3001*)
ν(C=O)	1728(m) 1701(s)	1661(w)
δ(NH) δ(NH$_2$)	1616(s)	1610(w) 1577(s)/(*1575*)
ν(C=N)	1511(s)	
δ(CH$_3$)	1485(m)	1489(s)/(*1482*)
ν(NCS)	1420(s)	1418(w)
δ(NH$_2$) δ(NH)	1362(m)	1364(s)/(*1364*) 1303(w)/(*1305*)
ν(C=S)	1256(m)	
δ(NCS) ν(C-C(=O)-O)	1200(s) 1168(sh) 1115(s) 1047(m)	1217(s) 1163(s) 1063(w)
ν(N-N)	860(s)	877(w)
δ(CH$_3$) ν(C-C)	802(m)	770(m)/(*764*) 762(m)
δ(NH)	742(m) 722(m) 671(w) 647(w)	 692(w) 645(m)
ν(COO-H)	590(m)	
ν(Fe-O)		568(w)
ν(Fe-N), ν(Fe-S)		543(m)/(*548*)

(w): weak, (m): middle, (s): strong, (sh): shoulder.

Table S2. Selected experimental and calculated (in brackets for pair **A** in LS state) IR vibrational modes of the complex **1** (TPSSh/6-311+G(d,p)).

3453 (*3469*)	1364 (*1364*)
3009 (*3001*)	1300 (*1305*)
1577 (*1575*)	770 (*764*)
1489 (*1482*)	543 (*548*)

*Blue– nitrogen (N); yellow– sulfur (S); red- oxygen (O); black- carbon (C); white- hydrogen (H); orange- iron (Fe).

Table S3. Selected bond lengths (Å) and angles (°) in **1** at 150 and 350 K.

Bond	Bond length (Å)		Angle	Angle value (°)	
	150 K	350 K		150 K	350 K
Fe(1)-N(1)*	1.9096(9)	1.9205(12)	O(1)-Fe(1)-S(1)	168.40(3)	167.74(4)
Fe(1)-N(3)**	1.9152(9)	1.9246(12)	O(2)-Fe(1)-S(2)	168.32(3)	167.63(4)
Fe(1)-O(1)*	1.9318(8)	1.9328(12)	N(1)-Fe(1)-N(3)	173.55(4)	173.24(5)
Fe(1)-O(2)**	1.9608(9)	1.9629(12)	O(1)-Fe(1)-O(2)	86.80(4)	86.96(6)
Fe(1)-S(1)*	2.2262(3)	2.2288(5)	O(1)-Fe(1)-N(1)	83.42(4)	83.07(5)
Fe(1)-S(2)**	2.2354(3)	2.2480(5)	O(1)-Fe(1)-N(3)	90.40(4)	90.26(5)
N(2)-C(1)*d	1.334(1)	1.331(2)	O(1)-Fe(1)-S(2)	90.59(3)	90.75(4)
N(4)-C(4)**s	1.355(1)	1.349(2)	O(2)-Fe(1)-N(1)	95.77(4)	96.72(5)
S(1)-C(1)*s	1.752(1)	1.752(2)	O(2)-Fe(1)-N(3)	81.98(4)	81.78(5)
S(2)-C(4)**d	1.721(1)	1.717(2)	O(2)-Fe(1)-S(1)	90.65(3)	90.57(4)
			N(1)-Fe(1)-S(1)	85.59(3)	85.31(4)
			N(1)-Fe(1)-S(2)	95.24(3)	95.07(4)
			N(3)-Fe(1)-S(1)	100.45(3)	101.27(4)
			N(3)-Fe(1)-S(2)	86.66(3)	86.08(4)
			S(1)-Fe(1)-S(2)	94.083(13)	94.13(2)

(*) Bonds in $(thpy)^{2-}$ moiety, (**) bonds in $(Hthpy)^{-}$ moiety; (s) and (d) – single and double bonds, respectively.

Table S4. Octahedral distortion parameters in **1**.*

Octahedron, temperature	Σ, °	Θ, °	<Fe-O/N/S>, Å	ζ, Å	Δ, Å
$FeN_2O_2S_2$, 150K	52.7515	181.2127	2.0298	0.803789	0.004966
$FeN_2O_2S_2$, 350K	55.5750	192.4462	2.0362	0.808277	0.004976

*Σ is the sum of the deviation from 90° of the 12 *cis*-angles of the $FeN_2O_2S_2$ octahedron.

Θ is the sum of the deviation from 60° of the 24 trigonal angles of the projection of the $FeN_2O_2S_2$ octahedron onto the trigonal faces. ζ is the distance distortion parameter, which is the sum of deviation from individual M-X bond distances with respect to the mean metal-ligand bond distance. Δ is the scatter in metal-ligand bond lengths defined as normalized mean-square error.[1]

Reference: 1. R. Ketkaew, Y. Tantirungrotechai, P. Harding, G. Chastanet, P. Guionneau, M. Marchivie and D. J. Harding, *OctaDist*: a tool for calculating distortion parameters in spin crossover and coordination complexes, *Dalton Trans.* 2021, **50(3)**, 1086–1096.

Table S5. Hydrogen bond geometry in **1** at 150 K.

Donor--H..Acceptor			[Symmetry of A]	D-H, Å	H...A, Å	D...A, Å	D-H...A, °
N4	--H4	..O3	[-x,1-y,-z]	0.80(1)	2.07(1)	2.744(1)	142(2)
N5	--H5a	..O2	[-x,1-y,1-z]	0.83(1)	2.35(1)	3.099(1)	149(2)
N5	--H5b	..O4	[x+0.5,0.5-y,z+0.5]	0.84(1)	2.08(1)	2.908(1)	169(2)
N6	--H6a	..O5w	[0.5-x, y-0.5,0.5-z]	0.83(1)	1.97(1)	2.788(1)	166(2)
N6	--H6b	..O5w	[x+0.5,1.5-y,z-0.5]	0.84(1)	2.12(1)	2.847(1)	145(2)
O5w	--H5w1	..N2	[x,y,z]	0.77(1)	2.14(2)	2.900(1)	169(2)
O5w	--H5w2	..O4	[-x,1-y,1-z]	0.76(1)	2.13(2)	2.850(1)	158(2)

Table S6. The unit cell parameters of **1** in the temperature range of 150–350 K.

T,K	a, Å	b, Å	c, Å	β, °	V, Å³
150	11.1829(4)	10.4546(3)	12.7936(3)	102.816(3)	1458.47(8)
200	11.2079(2)	10.4490(2)	12.8107(2)	102.838(2)	1462.78(4)
250	11.2345(2)	10.4452(2)	12.8408(2)	102.874(2)	1468.95(4)
300	11.2600(3)	10.4459(2)	12.8763(3)	102.895(2)	1476.31(6)
350	11.2783(3)	10.4572(2)	12.9331(2)	102.933(2)	1486.62(5)

Table S7. Hydrogen bond geometry in **1** at 350 K.

Donor--H..Acceptor			[Symmetry of A]	D-H, Å	H...A, Å	D...A, Å	D-H...A, °
N4	--H4	..O3	[-x,1-y,-z]	0.78(2)	2.10(2)	2.770(2)	144(2)
N5	--H5a	..O2	[-x,1-y,1-z]	0.81(2)	2.46(2)	3.191(2)	151(2)
N5	--H5b	..O4	[x+0.5,0.5-y,z+0.5]	0.81(2)	2.15(2)	2.944(2)	167(2)
N6	--H6a	..O5w	[0.5-x, y-0.5,0.5-z]	0.82(2)	2.02(2)	2.825(2)	165(2)
N6	--H6b	..O5w	[x+0.5,1.5-y,z-0.5]	0.82(2)	2.21(2)	2.894(2)	142(2)
O5w	--H5w1	..N2	[x,y,z]	0.80(2)	2.18(2)	2.956(2)	164(3)
O5w	--H5w2	..O4	[-x,1-y,1-z]	0.79(2)	2.17(2)	2.902(2)	153(3)
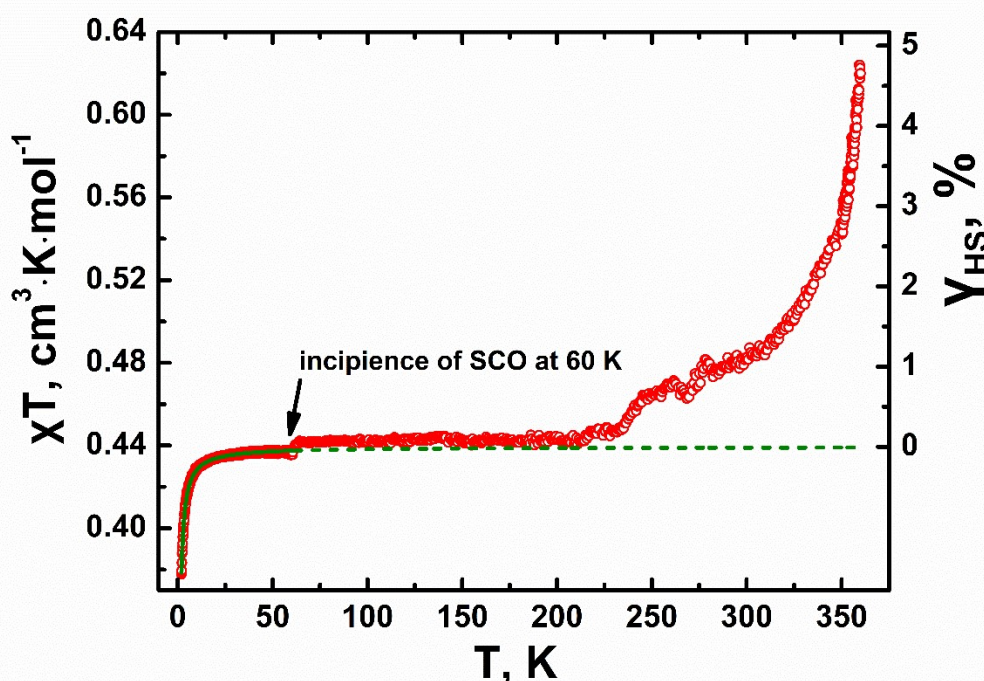
Figure S5. Temperature dependence of the χT product for [Fe^{III}(Hthpy)(thpy)]·H$_2$O (**1**) in the heating (red circles) mode in the temperature range of 2-360 K. The green solid line is the fit of experimental data in the heating mode (2–60 K) according to eqn (1). The parameters of the fitted curve: g=2.165(1); J/k$_B$= – 0.498(1) K, R^2=0.996.
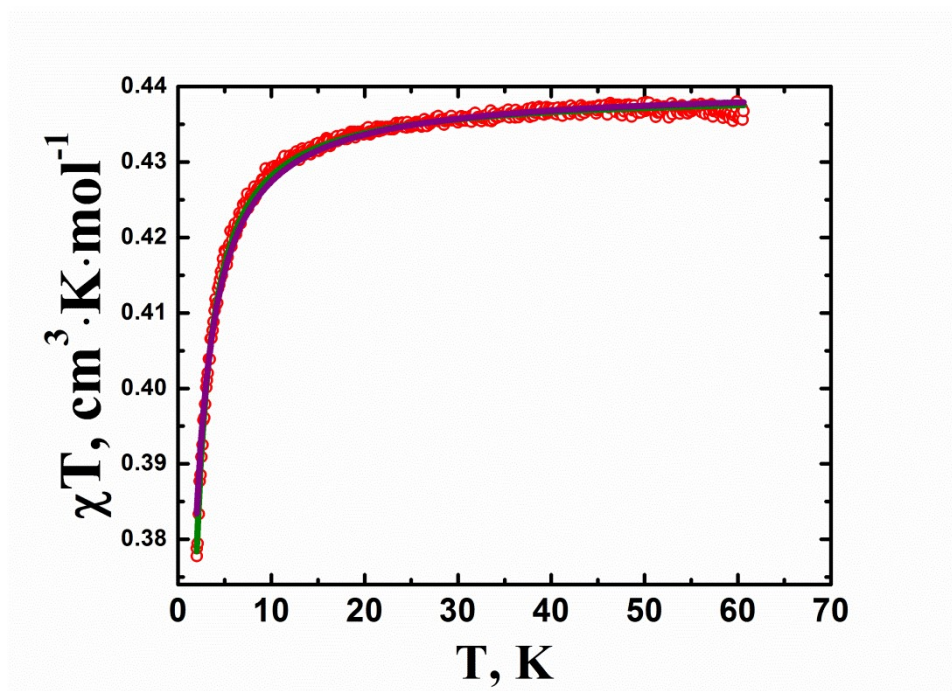
Figure S6. Comparison of Bleaney–Bowers (green line) and Curie–Weiss (purple line) fitting models for χT temperature dependence of [Fe^{III}(Hthpy)(thpy)]·H$_2$O (**1**) in the heating (red circles) mode in the temperature range of 2-60 K. The parameters of the fitted curve according to Curie–Weiss law: g_{LS}=2.166(1); θ= − 0.296(1) K, R^2=0.989.
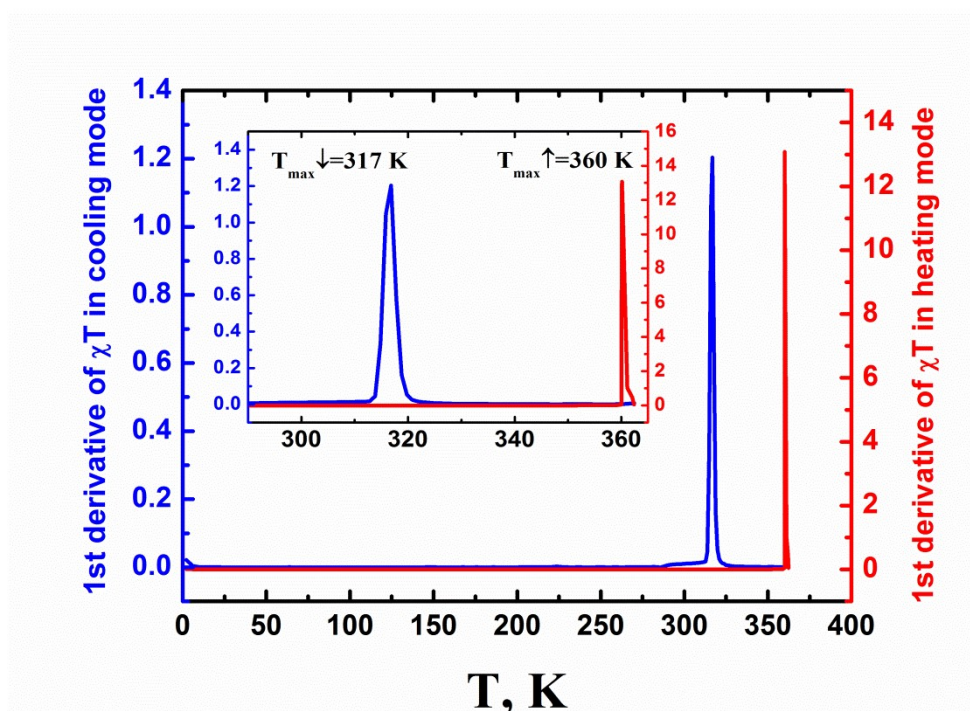
Figure S7. The first order differentiation of γ_{HS} *versus* T in cooling (blue line) and heating (red line) mode plots for [Fe^{III}(Hthpy)(thpy)]·H$_2$O.

Table S8. Mössbauer parameters for spectra of $[Fe^{III}(Hthpy)(thpy)]\cdot H_2O$ in temperature range of 80–365 K in heating and cooling modes.

Temp., K	Spin state	ΔE_Q, mm/s	δ, mm/s	Γ, mm/s —	Γ, mm/s +	γ_{HS}, %
Heating mode						
80	LS	3.130(1)	0.205(1)	0.328(2)	0.267(1)	
296	LS	3.073(2)	0.127(1)	0.326(5)	0.270(4)	
358	LS	2.988(2)	0.105(1)	0.342(5)	0.281(4)	0
361	LS	2.958(3)	0.106(2)	0.361(7)	0.302(6)	
363	HS	0.95(1)	0.346(7)	0.57(2)	0.83(5)	68
363	LS	2.954(6)	0.108(3)	0.40(1)	0.29(1)	68
365	HS	0.95(1)	0.327(7)	0.54(2)	0.94(4)	100
Cooling mode						
353	HS	0.94(1)	0.350(8)	0.52(2)	0.82(5)	
343	HS	0.95(1)	0.369(8)	0.59(2)	0.84(4)	100
333	HS	0.945(8)	0.367(6)	0.58(2)	0.84(3)	
328	HS	0.93(1)	0.348(8)	0.61(2)	0.76(6)	76
328	LS	3.05(1)	0.119(7)	0.37(4)	0.35(3)	76
323	HS	0.81(3)	0.36(2)	0.54(4)	0.70(1)	15
323	LS	3.068(2)	0.119(1)	0.370(4)	0.305(3)	15
296	LS	3.060(2)	0.129(1)	0.362(5)	0.295(4)	0
80	LS	3.170(2)	0.207(1)	0.354(4)	0.306(3)	0
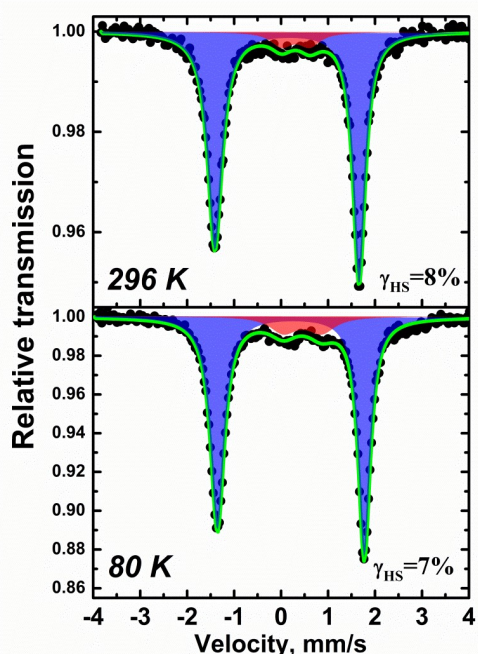
Figure S8. Mössbauer spectra of $[Fe^{III}(Hthpy)(thpy)]\cdot H_2O$ after heating up to 373 K at temperatures 80 and 296 K. An area of doublet highlighted in red corresponds to HS (S=5/2) Fe(III), whereas area of doublet highlighted in blue corresponds to the LS state. Green line denotes fit line.

Table S9. Mössbauer parameters for spectra of [Fe^{III}(Hthpy)(thpy)]·H$_2$O after heating up to 373 K at temperatures 80 and 296 K.

Temp., K	ΔE_Q, mm/s		δ, mm/s		γ_{HS}, %
	HS	LS	HS	LS	
296	0.60(2)	3.069(2)	0.31(2)	0.127(1)	8
80	0.81(2)	3.127(1)	0.45(2)	0.208(1)	7

Table S10. Comparison of bond lengths of the Fe(III) coordination octahedron of crystal structure **1** at 150 K and optimized structural fragments **A**, **B** pairs in the LS (S=1/2) state, as well as the isolated [Fe^{III}(Hthpy)(thpy)] molecule (TPSSh/6-311+G(d,p)).

Structure	Form ligand	Fe–S, Å	Δ(exp-calc), Å	Fe–Nim, Å	Δ(exp-calc), Å	Fe–O, Å	Δ(exp-calc), Å
X-ray (150K)	Hthpy⁻	2.2354(4)	_	1.915(1)	_	1.9611(9)	_
	thpy²⁻	2.2261(3)		1.909(1)		1.9319(8)	
Pair **A**	Hthpy⁻	2.3190	-0.0836(4)	1.920	-0.005(1)	1.9028	0.0583(9)
	thpy²⁻	2.2471	-0.021(3)	1.910	-0.001(1)	1.9282	0.0037(8)
Pair **B** (AFM)	Hthpy⁻	2.3332	-0.0978(4)	1.911	0.004(1)	1.9285	0.0326(9)
	thpy²⁻	2.2487	-0.022(3)	1.909	0	1.8913	0.0406(8)
Isolated complex	Hthpy⁻	2.3461	-0.1107(4)	1.912	0.003(1)	1.9045	0.0566(9)
	thpy²⁻	2.2650	-0.0389(3)	1.909	0	1.8883	0.0436(8)

Table S11. Comparison of bond lengths of the Fe(III) coordination octahedron in the HS (S=5/2) and LS (S=1/2) states for optimized structural fragments **A**, **B** pairs, and the isolated [Fe^{III}(Hthpy)(thpy)] molecule (TPSSh/6-311+G(d,p)). The relative change in bond lengths Δ^l is given in % relative to the LS state.

Structure	Form ligand	Fe–S, Å		Δ^l, %	Fe–N$_{im}$, Å		Δ^l, %	Fe–O, Å		Δ^l, %
		LS	HS		LS	HS		LS	HS	
Pair **A**	Hthpy⁻	2.3190	2.5030	7.9	1.920	2.209	15.1	1.9028	1.9610	3.1
	thpy²⁻	2.2471	2.3967	6.7	1.910	2.172	13.7	1.9282	2.0206	4.8
Pair **B**	Hthpy⁻	2.3332*	2.5728	10.3	1.911*	2.240	17.2	1.9285*	2.0069	4.1
	thpy²⁻	2.2487*	2.3701	5.4	1.909*	2.139	12.0	1.8913*	1.9589	3.6
Isolated complex	Hthpy⁻	2.3461	2.5712	9.6	1.912	2.233	16.8	1.9045	1.9660	3.2
	thpy²⁻	2.2650	2.3975	5.8	1.909	2.141	12.2	1.8883	1.9650	4.1

Rem: * – The bond lengths for pair **B** in the LS state are given, taking into account the AFM state.

Table S12. Comparison of the Fe···Fe distance in the HS (S=5/2) and LS (S=1/2) states for the crystal structure **1** at 150 K and optimized structural fragments **A**, **B** pairs, as well as the isolated [Fe^{III}(Hthpy)(thpy)] molecule (TPSSh/6-311+G(d,p)). The relative change in bond lengths Δ^l is given in % relative to the LS state.

Structure	Fe···Fe, Å				Δ^l, %
	LS	X-ray (150K)	Δ[exp-LS(calc)], Å	HS	
Pair **A**	6.1082	6.1534(4)	0.0452(4)	6.9457	13.7
Pair **B**	7.2158*	7.0599(4)	0.1559(4)	7.4772	3.6

Rem: * – The bond lengths for Pair **B** in the LS state are given, taking into account the AFM state.

Table S13. Electronic energy (E_{el}), zero-point vibration (E_{ZPV}) energy, total energy ($E_0=E_{el} + E_{ZPV}$), and total spin angular momentum ($<S^2>$) of the optimized molecular geometry, X-ray geometry with optimized hydrogen atoms, and X-ray geometry calculated and experimental values of exchange coupling constant J for two [Fe^{III}(Hthpy)(thpy)] complexes in TS ($S=S_1+S_2=1$) and BS ($S=S_1+S_2=0$) states (Pair **B**). The *J(calc)* values were calculated with formulas (eq. 2 and 3, see in text). *J(exp)= − 0.498(1) K.*

State	Parameter				*J(calc)*, K	
	E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	$<S^2>$	Noodleman	Yamaguchi
Optimized structure						
TS	-6003.030426	0.436815	-6002.593611	2.033278	-84.17	-84.18
BS	-6003.030414	0.436536	-6002.593878	1.033329		
X-ray geometry at 150K with optimized hydrogen atoms						
TS	-6002.938004	—		2.028684	-13.82	
BS	-6002.938048			1.028534		
X-ray geometry at 150K (SP calculations)						
TS	-6002.290379	—		2.028698	-0.92	
BS	-6002.290382			1.028571		

S14

Table S14. Optimized coordinates (TPSSh/6-311G+(d,p)) of [Fe^{III}(Hthpy)(thpy)] in the sextet (HS) state. Units are in Å.

C	-3.070257000000	0.425665000000	-1.292432000000
C	-2.057920000000	-0.629639000000	1.798312000000
C	-0.679823000000	-0.961553000000	2.314608000000
C	1.330587000000	2.531976000000	0.351877000000
C	2.479983000000	1.527445000000	0.254752000000
C	2.446299000000	-1.825589000000	-0.834651000000
C	-3.278818000000	-0.843081000000	2.623786000000
H	-3.787792000000	0.111813000000	2.792357000000
H	-2.996450000000	-1.287802000000	3.577677000000
H	-3.985413000000	-1.490076000000	2.094713000000
C	3.854524000000	1.886428000000	0.709557000000
H	4.060759000000	1.435505000000	1.688764000000
H	3.907811000000	2.969653000000	0.821200000000
H	4.618622000000	1.550936000000	-0.000627000000
N	-3.227141000000	0.156939000000	-0.009381000000
N	-2.054776000000	-0.172506000000	0.584321000000
N	2.094289000000	0.395247000000	-0.212858000000
N	2.940365000000	-0.665480000000	-0.313853000000
H	3.823098000000	-0.644067000000	0.188273000000
N	-4.188363000000	0.746010000000	-1.993075000000
H	-5.028008000000	0.942736000000	-1.466825000000
H	-4.088333000000	1.155071000000	-2.907848000000
N	3.291349000000	-2.874254000000	-0.848491000000
H	4.202259000000	-2.849950000000	-0.413144000000
H	2.932018000000	-3.767087000000	-1.148497000000
O	0.280366000000	-0.695004000000	1.457918000000
O	0.171974000000	2.029944000000	0.054814000000
O	-0.519065000000	-1.440372000000	3.426372000000
O	1.581780000000	3.678182000000	0.687293000000
Fe	-0.120141000000	0.116006000000	-0.286475000000
S	-1.567276000000	0.325620000000	-2.186472000000
S	0.892722000000	-1.919152000000	-1.487926000000

Table S15. Optimized coordinates (TPSSh/6-311G+(d,p)) of [Fe^{III}(Hthpy)(thpy)] in the doublet (LS) state. Units are in Å.

S15

C	-2.291018000000	-0.237450000000	-1.931906000000
C	-2.278493000000	0.080880000000	1.485049000000
C	-1.110738000000	0.158743000000	2.428389000000
C	1.082836000000	2.459157000000	-0.271682000000
C	2.258554000000	1.490317000000	-0.214330000000
C	2.194429000000	-2.030513000000	0.131131000000
C	-3.688386000000	0.176840000000	1.952664000000
H	-4.155581000000	1.085032000000	1.557119000000
H	-3.697632000000	0.206473000000	3.042526000000
H	-4.274273000000	-0.672429000000	1.589068000000
C	3.670512000000	1.965142000000	-0.183213000000
H	4.133935000000	1.761267000000	0.790688000000
H	3.664472000000	3.044710000000	-0.338819000000
H	4.274660000000	1.492402000000	-0.966638000000
N	-2.847488000000	-0.132418000000	-0.742634000000
N	-1.914329000000	-0.066122000000	0.246768000000
N	1.858176000000	0.263665000000	-0.176691000000
N	2.730984000000	-0.791381000000	-0.076833000000
H	3.697565000000	-0.589970000000	0.159454000000
N	-3.122196000000	-0.348370000000	-3.003204000000
H	-4.096895000000	-0.129817000000	-2.852274000000
H	-2.744121000000	-0.178633000000	-3.921613000000
N	3.082004000000	-3.032751000000	0.328476000000
H	4.046012000000	-2.945370000000	0.039941000000
H	2.712751000000	-3.968711000000	0.403910000000
O	0.068584000000	0.078870000000	1.829151000000
O	-0.086783000000	1.884605000000	-0.206670000000
O	-1.259337000000	0.270628000000	3.633543000000
O	1.300774000000	3.655848000000	-0.367289000000
Fe	-0.029648000000	-0.012920000000	-0.054314000000
S	-0.561614000000	-0.311199000000	-2.235628000000
S	0.529603000000	-2.283533000000	0.135076000000

Table S16. Optimized coordinates (TPSSh/6-311G+(d,p)) of **A** pair of [Fe^{III}(Hthpy)(thpy)] in HS-HS state. Units are in Å.

C	0.257404000000	0.641283000000	6.429856000000
C	-1.563955000000	2.001126000000	3.868434000000
C	-1.414988000000	1.812566000000	2.397487000000
C	-1.100819000000	-2.332509000000	2.624133000000
C	-0.025506000000	-2.379937000000	1.547503000000
C	2.816277000000	-0.364516000000	1.107435000000
C	-2.612744000000	2.874066000000	4.468956000000
H	-3.296667000000	2.273262000000	5.078003000000
H	-3.169230000000	3.379645000000	3.680357000000
H	-2.154706000000	3.608698000000	5.138205000000
C	-0.105327000000	-3.347305000000	0.417112000000
H	-0.360331000000	-2.818578000000	-0.508881000000
H	-0.884160000000	-4.077741000000	0.633958000000
H	0.853243000000	-3.852425000000	0.259464000000
N	-0.722794000000	1.357112000000	5.888831000000
N	-0.694899000000	1.311214000000	4.546600000000
N	0.885669000000	-1.486339000000	1.729653000000
N	1.905906000000	-1.332600000000	0.851392000000
H	1.917515000000	-1.778783000000	-0.096549000000
N	0.317594000000	0.635083000000	7.779060000000
H	-0.426630000000	1.076588000000	8.299254000000
H	0.962143000000	0.024246000000	8.252690000000
N	3.767492000000	-0.211028000000	0.178305000000
H	3.722359000000	-0.748301000000	-0.685073000000
H	4.429261000000	0.542747000000	0.272676000000
O	-0.432558000000	1.074531000000	2.009160000000
O	-0.889332000000	-1.431330000000	3.541322000000
O	-2.217626000000	2.355186000000	1.601717000000
O	-2.053262000000	-3.093288000000	2.558147000000
Fe	0.511852000000	-0.068733000000	3.381675000000
S	1.499022000000	-0.225680000000	5.560002000000
S	2.784688000000	0.560074000000	2.542722000000
C	-0.017972000000	-0.367384000000	-6.555616000000
C	1.802708000000	-1.727958000000	-3.994099000000
C	1.653650000000	-1.539456000000	-2.523152000000
C	1.340629000000	2.605334000000	-2.748977000000
C	0.265069000000	2.652963000000	-1.672604000000
C	-2.577464000000	0.638380000000	-1.233522000000
C	2.851391000000	-2.601052000000	-4.594582000000
H	3.535471000000	-2.000337000000	-5.203540000000
H	3.407722000000	-3.106775000000	-3.805967000000
H	2.393276000000	-3.335564000000	-5.263910000000
C	0.344990000000	3.620073000000	-0.542000000000
H	0.599749000000	3.091078000000	0.383908000000

H	1.124040000000	4.350354000000	-0.758586000000
H	-0.613471000000	4.125404000000	-0.384368000000
N	0.961927000000	-1.083575000000	-6.014533000000
N	0.933876000000	-1.037798000000	-4.672300000000
N	-0.646371000000	1.759711000000	-1.855127000000
N	-1.666846000000	1.606135000000	-0.977116000000
H	-1.678513000000	2.052121000000	-0.029092000000
N	-0.078000000000	-0.361049000000	-7.904826000000
H	0.666135000000	-0.802763000000	-8.424971000000
H	-0.722296000000	0.250035000000	-8.378482000000
N	-3.528907000000	0.485017000000	-0.304604000000
H	-3.483758000000	1.022106000000	0.558892000000
H	-4.190946000000	-0.268478000000	-0.399295000000
O	0.671236000000	-0.801385000000	-2.134859000000
O	1.128972000000	1.704497000000	-3.666460000000
O	2.456246000000	-2.082112000000	-1.727363000000
O	2.293415000000	3.365647000000	-2.682531000000
Fe	-0.272683000000	0.342306000000	-3.507356000000
S	-1.259401000000	0.499928000000	-5.685839000000
S	-2.545872000000	-0.285949000000	-2.668974000000

Table S17. Optimized coordinates (TPSSh/6-311G+(d,p)) of **A** pair of [Fe^{III}(Hthpy)(thpy)] in LS-LS (TS) state. Units are in Å.

C	0.351265000000	0.317725000000	5.877499000000
C	-1.510606000000	2.011510000000	3.542348000000
C	-1.588078000000	1.774971000000	2.081074000000
C	-1.335734000000	-2.294106000000	2.400363000000
C	-0.069419000000	-2.449024000000	1.578116000000
C	2.555613000000	-0.140635000000	1.187302000000
C	-2.335650000000	3.025849000000	4.256153000000
H	-2.994525000000	2.536954000000	4.981292000000
H	-2.934246000000	3.578127000000	3.531495000000
H	-1.697134000000	3.715758000000	4.816353000000
C	0.121557000000	-3.596474000000	0.648845000000
H	-0.119966000000	-3.297271000000	-0.377357000000
H	-0.565880000000	-4.391228000000	0.940667000000
H	1.152005000000	-3.963257000000	0.663062000000
N	-0.475648000000	1.265871000000	5.456003000000
N	-0.653285000000	1.209596000000	4.117614000000
N	0.740265000000	-1.457824000000	1.761859000000
N	1.909433000000	-1.327878000000	1.067657000000
H	2.064242000000	-1.856082000000	0.176728000000
N	0.626085000000	0.292513000000	7.201421000000
H	0.093210000000	0.891492000000	7.814590000000
H	1.120299000000	-0.491439000000	7.594896000000
N	3.614046000000	0.025595000000	0.383257000000
H	3.732482000000	-0.613996000000	-0.399790000000
H	4.030684000000	0.942378000000	0.321214000000
O	-0.794992000000	0.864650000000	1.607792000000
O	-1.367458000000	-1.219515000000	3.150186000000
O	-2.371554000000	2.419855000000	1.343920000000
O	-2.233508000000	-3.116294000000	2.304186000000
Fe	0.158098000000	-0.094748000000	2.982309000000
S	1.132636000000	-0.868961000000	4.853241000000
S	2.069690000000	1.040488000000	2.323033000000
C	-0.112094000000	-0.044328000000	-6.003078000000
C	1.749736000000	-1.738153000000	-3.667924000000
C	1.827202000000	-1.501623000000	-2.206648000000
C	1.574914000000	2.567448000000	-2.525896000000
C	0.308592000000	2.722379000000	-1.703663000000
C	-2.316476000000	0.414021000000	-1.312898000000
C	2.574774000000	-2.752498000000	-4.381729000000
H	3.233663000000	-2.263606000000	-5.106857000000
H	3.173355000000	-3.304790000000	-3.657070000000
H	1.936254000000	-3.442393000000	-4.941942000000
C	0.117622000000	3.869820000000	-0.774381000000
H	0.359123000000	3.570600000000	0.251822000000
H	0.805079000000	4.664565000000	-1.066182000000

H	-0.912818000000	4.236623000000	-0.788610000000
N	0.714802000000	-0.992489000000	-5.581582000000
N	0.892430000000	-0.936225000000	-4.243192000000
N	-0.501105000000	1.731192000000	-1.887426000000
N	-1.670281000000	1.601255000000	-1.193237000000
H	-1.825094000000	2.129453000000	-0.302306000000
N	-0.386903000000	-0.019103000000	-7.327003000000
H	0.145967000000	-0.618087000000	-7.940171000000
H	-0.881103000000	0.764858000000	-7.720476000000
N	-3.374917000000	0.247799000000	-0.508862000000
H	-3.493342000000	0.887383000000	0.274194000000
H	-3.791571000000	-0.668977000000	-0.446834000000
O	1.034118000000	-0.591299000000	-1.733366000000
O	1.606628000000	1.492869000000	-3.275735000000
O	2.610669000000	-2.146515000000	-1.469493000000
O	2.472704000000	3.389617000000	-2.429693000000
Fe	0.081054000000	0.368121000000	-3.107884000000
S	-0.893454000000	1.142363000000	-4.978819000000
S	-1.830560000000	-0.767097000000	-2.448637000000

Table S18. Optimized coordinates (TPSSh/6-311G+(d,p)) of **B** pair of [Fe^{III}(Hthpy)(thpy)] in HS-HS state. Units are in Å.

C	0.218044000000	6.240470000000	5.988290000000

C	-1.236881000000	7.426440000000	3.124835000000
C	-1.002265000000	7.053984000000	1.686308000000
C	-0.881462000000	2.687266000000	2.434446000000
C	0.150690000000	2.713349000000	1.313201000000
C	2.923101000000	4.833785000000	0.812854000000
C	-2.134125000000	8.548998000000	3.517252000000
H	-2.899325000000	8.195777000000	4.215924000000
H	-2.596406000000	8.972607000000	2.625885000000
H	-1.562472000000	9.319507000000	4.045697000000
C	0.036238000000	1.786875000000	0.148892000000
H	-0.326804000000	2.327079000000	-0.734961000000
H	-0.691923000000	1.013516000000	0.393570000000
H	0.998288000000	1.321469000000	-0.093786000000
N	-0.671458000000	6.929958000000	5.287838000000
N	-0.563526000000	6.696734000000	3.964231000000
N	1.044583000000	3.618976000000	1.489213000000
N	2.006644000000	3.854046000000	0.558130000000
H	1.905208000000	3.452624000000	-0.369444000000
N	0.209436000000	6.369402000000	7.323781000000
H	-0.583330000000	6.802866000000	7.797577000000
H	0.816361000000	5.779546000000	7.869398000000
N	3.813032000000	5.074818000000	-0.169624000000
H	3.757564000000	4.639843000000	-1.079316000000
H	4.451177000000	5.846049000000	-0.049970000000
O	-0.165802000000	6.047845000000	1.530799000000
O	-0.730886000000	3.628205000000	3.317877000000
O	-1.550220000000	7.653729000000	0.773892000000
O	-1.747346000000	1.825498000000	2.420284000000
Fe	0.587584000000	5.123127000000	3.084635000000
S	1.467329000000	5.211289000000	5.283648000000
S	2.979426000000	5.641474000000	2.291247000000
C	-3.055929000000	4.214127000000	6.486590000000
C	-1.601005000000	3.028156000000	9.350046000000
C	-1.835622000000	3.400613000000	10.788572000000
C	-1.956422000000	7.767331000000	10.040432000000
C	-2.988575000000	7.741250000000	11.161677000000
C	-5.760989000000	5.620819000000	11.662026000000
C	-0.703761000000	1.905598000000	8.957629000000
H	0.061439000000	2.258819000000	8.258958000000
H	-0.241481000000	1.481989000000	9.848996000000
H	-1.275415000000	1.135089000000	8.429184000000
C	-2.874125000000	8.667728000000	12.325983000000
H	-2.511084000000	8.127527000000	13.209839000000
H	-2.145964000000	9.441086000000	12.081304000000
H	-3.836176000000	9.133135000000	12.568658000000

N	-2.166427000000	3.524638000000	7.187042000000
N	-2.274360000000	3.757863000000	8.510649000000
N	-3.882469000000	6.835624000000	10.985666000000
N	-4.844531000000	6.600558000000	11.916748000000
H	-4.743098000000	7.001983000000	12.844321000000
N	-3.047320000000	4.085194000000	5.151099000000
H	-2.254554000000	3.651730000000	4.677304000000
H	-3.654244000000	4.675050000000	4.605481000000
N	-6.650924000000	5.379792000000	12.644502000000
H	-6.595459000000	5.814772000000	13.554193000000
H	-7.289070000000	4.608561000000	12.524850000000
O	-2.672085000000	4.406752000000	10.944081000000
O	-2.106998000000	6.826391000000	9.157002000000
O	-1.287667000000	2.800868000000	11.700989000000
O	-1.090538000000	8.629098000000	10.054593000000
Fe	-3.425469000000	5.331470000000	9.390244000000
S	-4.305214000000	5.243308000000	7.191231000000
S	-5.817313000000	4.813126000000	10.183635000000

Table S19. Optimized coordinates (TPSSh/6-311G+(d,p)) of **B** pair of [Fe^{III}(Hthpy)(thpy)] in LS-LS (TS) state. Units are in Å.

C	0.381407000000	5.800300000000	5.904103000000
C	-1.411392000000	7.377410000000	3.430060000000

C	-1.496536000000	7.062543000000	1.967554000000
C	-1.274203000000	2.921303000000	2.587730000000
C	-0.047141000000	2.796465000000	1.701716000000
C	2.593142000000	5.101493000000	1.229696000000
C	-2.175802000000	8.489787000000	4.059956000000
H	-2.697018000000	8.140140000000	4.956083000000
H	-2.879713000000	8.893850000000	3.331476000000
H	-1.494265000000	9.284944000000	4.382841000000
C	0.135489000000	1.647156000000	0.770514000000
H	0.095297000000	1.974486000000	-0.276414000000
H	-0.680404000000	0.943725000000	0.940456000000
H	1.089923000000	1.135569000000	0.942896000000
N	-0.443098000000	6.711453000000	5.412538000000
N	-0.609171000000	6.578857000000	4.075021000000
N	0.756752000000	3.795831000000	1.857165000000
N	1.912899000000	3.920004000000	1.129144000000
H	2.044987000000	3.303291000000	0.333536000000
N	0.622220000000	5.806544000000	7.226613000000
H	-0.025986000000	6.291632000000	7.850029000000
H	1.146889000000	5.040877000000	7.618936000000
N	3.670907000000	5.232257000000	0.419865000000
H	4.131237000000	4.421110000000	0.031528000000
H	4.240298000000	6.056213000000	0.544278000000
O	-0.731609000000	6.045893000000	1.591542000000
O	-1.309638000000	4.017333000000	3.300896000000
O	-2.209722000000	7.696465000000	1.205662000000
O	-2.119185000000	2.040843000000	2.581367000000
Fe	0.184439000000	5.203117000000	3.015972000000
S	1.219870000000	4.593591000000	4.916902000000
S	2.109157000000	6.308608000000	2.296972000000
C	-3.219292000000	4.654300000000	6.570776000000
C	-1.426495000000	3.077190000000	9.044820000000
C	-1.341351000000	3.392056000000	10.507325000000
C	-1.563683000000	7.533297000000	9.887149000000
C	-2.790745000000	7.658135000000	10.773162000000
C	-5.431029000000	5.353108000000	11.245182000000
C	-0.662085000000	1.964813000000	8.414923000000
H	-0.140867000000	2.314459000000	7.518798000000
H	0.041825000000	1.560748000000	9.143404000000
H	-1.343622000000	1.169656000000	8.092037000000
C	-2.973374000000	8.807444000000	11.704365000000
H	-2.933183000000	8.480114000000	12.751293000000
H	-2.157482000000	9.510875000000	11.534423000000
H	-3.927809000000	9.319031000000	11.531983000000
N	-2.394788000000	3.743146000000	7.062341000000
N	-2.228716000000	3.875743000000	8.399859000000
N	-3.594638000000	6.658770000000	10.617714000000
N	-4.750785000000	6.534597000000	11.345734000000
H	-4.882874000000	7.151310000000	12.141342000000
N	-3.460106000000	4.648056000000	5.248266000000
H	-2.811900000000	4.162968000000	4.624850000000
H	-3.984775000000	5.413723000000	4.855942000000

N	-6.508794000000	5.222344000000	12.055013000000
H	-6.969123000000	6.033491000000	12.443351000000
H	-7.078186000000	4.398389000000	11.930600000000
O	-2.106278000000	4.408707000000	10.883337000000
O	-1.528248000000	6.437267000000	9.173983000000
O	-0.628166000000	2.758134000000	11.269218000000
O	-0.718701000000	8.413756000000	9.893512000000
Fe	-3.022325000000	5.251483000000	9.458907000000
S	-4.057755000000	5.861009000000	7.557977000000
S	-4.947044000000	4.145993000000	10.177907000000

Table S20. Optimized coordinates (TPSSh/6-311G+(d,p)) of **B** pair of $[Fe^{III}(Hthpy)(thpy)]$ in BS $(S_1+S_2=0)$ state. Units are in Å.

C	1.051542000000	0.615828000000	1.467773000000
C	2.375622000000	2.366789000000	-1.178669000000
C	3.672712000000	2.164241000000	-1.900983000000

C	1.398884000000	3.423819000000	-1.562478000000
H	0.391456000000	3.006029000000	-1.648296000000
H	1.716027000000	3.874375000000	-2.503689000000
H	1.353242000000	4.198827000000	-0.788941000000
N	1.067478000000	1.556808000000	0.537147000000
N	2.204438000000	1.526450000000	-0.197950000000
N	-0.030475000000	0.520706000000	2.259327000000
H	-0.907541000000	0.953488000000	1.963472000000
H	-0.098654000000	-0.269926000000	2.880331000000
O	4.416678000000	1.184475000000	-1.404461000000
O	3.999239000000	2.849835000000	-2.857158000000
S	2.390827000000	-0.504542000000	1.760179000000
Fe	3.599777000000	0.241381000000	0.016942000000
C	3.509863000000	-2.007579000000	-1.548243000000
C	4.850171000000	-2.056598000000	-0.835599000000
C	6.260074000000	0.288697000000	1.404775000000
C	5.847793000000	-3.128710000000	-1.112304000000
H	6.744671000000	-2.720709000000	-1.595966000000
H	5.389385000000	-3.847385000000	-1.792569000000
H	6.148278000000	-3.647640000000	-0.194233000000
N	4.989882000000	-1.069282000000	-0.014214000000
N	6.138181000000	-0.884213000000	0.713265000000
H	6.953183000000	-1.438303000000	0.469254000000
N	7.446344000000	0.485445000000	2.028153000000
H	8.052995000000	-0.291537000000	2.249318000000
H	7.523614000000	1.299347000000	2.619899000000
O	2.775282000000	-0.971232000000	-1.235655000000
O	3.209309000000	-2.889653000000	-2.336101000000
S	5.006282000000	1.408495000000	1.467189000000
C	-3.509851000000	2.007574000000	1.548250000000
C	-4.850156000000	2.056604000000	0.835602000000
C	-6.260071000000	-0.288674000000	-1.404783000000
C	-5.847771000000	3.128723000000	1.112306000000
H	-6.744654000000	2.720729000000	1.595965000000
H	-5.389360000000	3.847395000000	1.792572000000
H	-6.148251000000	3.647657000000	0.194234000000
N	-4.989872000000	1.069291000000	0.014214000000
N	-6.138170000000	0.884234000000	-0.713270000000
H	-6.953168000000	1.438330000000	-0.469261000000
N	-7.446340000000	-0.485411000000	-2.028165000000
H	-8.052985000000	0.291576000000	-2.249330000000
H	-7.523614000000	-1.299312000000	-2.619913000000
O	-2.775277000000	0.971222000000	1.235661000000
O	-3.209294000000	2.889643000000	2.336112000000
S	-5.006288000000	-1.408483000000	-1.467194000000
Fe	-3.599777000000	-0.241381000000	-0.016941000000
C	-1.051542000000	-0.615844000000	-1.467770000000
C	-2.375639000000	-2.366800000000	1.178668000000
C	-3.672728000000	-2.164245000000	1.900979000000
C	-1.398908000000	-3.423838000000	1.562476000000
H	-0.391477000000	-3.006055000000	1.648294000000
H	-1.716055000000	-3.874391000000	2.503687000000

H	-1.353273000000	-4.198846000000	0.788939000000
N	-1.067486000000	-1.556825000000	-0.537145000000
N	-2.204447000000	-1.526460000000	0.197950000000
N	0.030476000000	-0.520726000000	-2.259322000000
H	0.907540000000	-0.953513000000	-1.963466000000
H	0.098662000000	0.269908000000	-2.880322000000
O	-4.416687000000	-1.184474000000	1.404457000000
O	-3.999261000000	-2.849839000000	2.857153000000
S	-2.390819000000	0.504537000000	-1.760174000000

Table S21. H-Optimized coordinates (TPSSh/6-311G+(d,p)) of **B** pair of [Fe^{III}(Hthpy)(thpy)] in LS-LS (TS) state. Units are in Å.

C	1.737160000000	0.252227000000	-0.268341000000
C	-0.006582000000	1.995156000000	-2.676734000000
C	-0.144859000000	1.677127000000	-4.132553000000

C	0.170002000000	-2.501472000000	-3.755813000000
C	1.388308000000	-2.532211000000	-4.641774000000
C	3.958453000000	-0.150117000000	-4.869909000000
C	-0.713834000000	3.138471000000	-2.042886000000
H	-1.090993000000	2.863636000000	-1.054250000000
H	-1.516333000000	3.464831000000	-2.706007000000
H	-0.022785000000	3.977617000000	-1.897346000000
C	1.605446000000	-3.647505000000	-5.592364000000
H	1.495484000000	-3.312288000000	-6.631797000000
H	0.842982000000	-4.401839000000	-5.393163000000
H	2.597487000000	-4.100227000000	-5.474089000000
N	1.004803000000	1.270240000000	-0.722671000000
N	0.776342000000	1.153772000000	-2.067715000000
N	2.153546000000	-1.518912000000	-4.421439000000
N	3.324273000000	-1.323917000000	-5.101790000000
H	3.531670000000	-1.913091000000	-5.901731000000
N	1.986143000000	0.186365000000	1.037872000000
H	1.487383000000	0.802550000000	1.680156000000
H	2.498818000000	-0.593828000000	1.413856000000
N	5.039069000000	0.108516000000	-5.565413000000
H	5.455797000000	-0.546363000000	-6.210684000000
H	5.530705000000	0.973400000000	-5.397750000000
O	0.550018000000	0.685087000000	-4.569926000000
O	0.022767000000	-1.442071000000	-3.036306000000
O	-0.897391000000	2.346849000000	-4.858466000000
O	-0.595820000000	-3.471241000000	-3.732110000000
Fe	1.539285000000	-0.205967000000	-3.169990000000
S	2.397714000000	-1.014937000000	-1.282040000000
S	3.373693000000	0.959840000000	-3.692443000000
C	-1.737160000000	-0.252227000000	0.268341000000
C	0.006582000000	-1.995156000000	2.676734000000
C	0.144859000000	-1.677127000000	4.132553000000
C	-0.170002000000	2.501472000000	3.755813000000
C	-1.388308000000	2.532211000000	4.641774000000
C	-3.958453000000	0.150117000000	4.869909000000
C	0.713834000000	-3.138471000000	2.042886000000
H	1.090993000000	-2.863636000000	1.054250000000
H	1.516333000000	-3.464831000000	2.706007000000
H	0.022785000000	-3.977617000000	1.897346000000
C	-1.605446000000	3.647505000000	5.592364000000
H	-1.495484000000	3.312288000000	6.631797000000
H	-0.842982000000	4.401839000000	5.393163000000
H	-2.597487000000	4.100227000000	5.474089000000
N	-1.004803000000	-1.270240000000	0.722671000000
N	-0.776342000000	-1.153772000000	2.067715000000
N	-2.153546000000	1.518912000000	4.421439000000
N	-3.324273000000	1.323917000000	5.101790000000
H	-3.531670000000	1.913091000000	5.901731000000
N	-1.986143000000	-0.186365000000	-1.037872000000
H	-1.487383000000	-0.802550000000	-1.680156000000
H	-2.498818000000	0.593828000000	-1.413856000000
N	-5.039069000000	-0.108516000000	5.565413000000

H	-5.455797000000	0.546363000000	6.210684000000
H	-5.530705000000	-0.973400000000	5.397750000000
O	-0.550018000000	-0.685087000000	4.569926000000
O	-0.022767000000	1.442071000000	3.036306000000
O	0.897391000000	-2.346849000000	4.858466000000
O	0.595820000000	3.471241000000	3.732110000000
Fe	-1.539285000000	0.205967000000	3.169990000000
S	-2.397714000000	1.014937000000	1.282040000000
S	-3.373693000000	-0.959840000000	3.692443000000

Table S22. H-Optimized coordinates (TPSSh/6-311G+(d,p)) of **B** pair of [Fe^{III}(Hthpy)(thpy)] in BS ($S_1+S_2=0$) state. Units are in Å.

C	-0.957165000000	-0.351855000000	1.453743000000
C	-2.153895000000	-2.282718000000	-1.138215000000
C	-3.435124000000	-2.125733000000	-1.895499000000

C	-1.145852000000	-3.317224000000	-1.488622000000
H	-0.131730000000	-2.920176000000	-1.395686000000
H	-1.349385000000	-3.676826000000	-2.498345000000
H	-1.219748000000	-4.166631000000	-0.798714000000
N	-0.927027000000	-1.383775000000	0.609199000000
N	-2.046254000000	-1.410697000000	-0.179147000000
N	0.096815000000	-0.149083000000	2.241645000000
H	0.959878000000	-0.667458000000	2.076350000000
H	0.117719000000	0.644309000000	2.860460000000
O	-4.243949000000	-1.218716000000	-1.469588000000
O	-3.680950000000	-2.841776000000	-2.879691000000
S	-2.299846000000	0.764648000000	1.596517000000
Fe	-3.523290000000	-0.216526000000	0.016561000000
C	-3.732881000000	2.052267000000	-1.498723000000
C	-5.053362000000	1.932859000000	-0.783045000000
C	-6.078275000000	-0.562966000000	1.464720000000
C	-6.130669000000	2.923841000000	-1.011109000000
H	-6.975889000000	2.477303000000	-1.550635000000
H	-5.715854000000	3.723751000000	-1.625982000000
H	-6.501651000000	3.349748000000	-0.070860000000
N	-5.064229000000	0.920453000000	0.014363000000
N	-6.153315000000	0.602119000000	0.778619000000
H	-7.029278000000	1.086534000000	0.611142000000
N	-7.134528000000	-0.942498000000	2.141965000000
H	-7.968127000000	-0.380752000000	2.233912000000
H	-7.092107000000	-1.801765000000	2.668948000000
O	-2.898945000000	1.087817000000	-1.308130000000
O	-3.498177000000	3.049039000000	-2.190727000000
S	-4.640476000000	-1.507975000000	1.459185000000
C	3.732881000000	-2.052267000000	1.498724000000
C	5.053362000000	-1.932859000000	0.783045000000
C	6.078275000000	0.562966000000	-1.464721000000
C	6.130669000000	-2.923841000000	1.011109000000
H	6.975889000000	-2.477303000000	1.550634000000
H	5.715855000000	-3.723751000000	1.625983000000
H	6.501650000000	-3.349748000000	0.070860000000
N	5.064228000000	-0.920453000000	-0.014362000000
N	6.153315000000	-0.602119000000	-0.778619000000
H	7.029278000000	-1.086533000000	-0.611141000000
N	7.134528000000	0.942498000000	-2.141965000000
H	7.968127000000	0.380752000000	-2.233911000000
H	7.092107000000	1.801765000000	-2.668947000000
O	2.898946000000	-1.087817000000	1.308130000000
O	3.498177000000	-3.049039000000	2.190728000000
S	4.640476000000	1.507975000000	-1.459185000000
Fe	3.523290000000	0.216526000000	-0.016562000000
C	0.957164000000	0.351855000000	-1.453743000000
C	2.153895000000	2.282718000000	1.138215000000
C	3.435124000000	2.125733000000	1.895498000000
C	1.145852000000	3.317224000000	1.488621000000
H	0.131730000000	2.920177000000	1.395685000000
H	1.349385000000	3.676825000000	2.498344000000

H	1.219749000000	4.166631000000	0.798714000000
N	0.927027000000	1.383775000000	-0.609199000000
N	2.046254000000	1.410697000000	0.179147000000
N	-0.096816000000	0.149083000000	-2.241645000000
H	-0.959879000000	0.667457000000	-2.076350000000
H	-0.117720000000	-0.644310000000	-2.860460000000
O	4.243949000000	1.218716000000	1.469587000000
O	3.680950000000	2.841776000000	2.879691000000
S	2.299846000000	-0.764648000000	-1.596516000000