

Surface induces different crystal structures in room temperature switchable spin crossover compound

Electronic Supplementary Information (ESI)

Characterization of thermally inert crystallites I

Below 295 K thermally inert crystallites (I) have the same morphology of the bulk phase crystallites and show the same Raman spectrum, however when heated up the transition temperature of the bulk material, they do not switch, even at 350 K (Fig S1a,b). The structure of these different crystals has been determined, using synchrotron X-ray diffraction, manually selecting them from a drop-casted sample.

Single crystal structure has been determined above and below the transition temperature of bulk material. The crystal packing is completely different from the known crystal form, with different space group ($I 2/c$) and a significantly smaller volume (~15% smaller at 100K). The unit cell contains four $[\text{Fe}(\text{L})_2]$ moieties and additional eight “free” ligand molecules. Iron ions lie on crystallographic twofold axis, this implies that the asymmetric unit contains half complex molecule and one neutral L, stacked to form a heterodimeric aggregate (Fig. S1c). Each free ligand is forming H-bonds, which involve the donor tetrazole ring N1-H atom, pointing to the acceptor N2 atom (2.85 Å) of the coordinated tetrazolate moiety of each L in the $\text{Fe}(\text{L})_2$ complex. These H-bonded free ligands form strong stacking interactions to neighbor ligand molecules,. This is leading to a very compact crystal packing, without solvent accessible voids. Fe^{II} sphere geometry reveals that Fe^{II} is in a low spin status in the whole temperature range explored (100-350K).

Thermally inert crystal form has no cavities and this result is compatible with insensitivity to alcohol exposure and better temperature resistance. Structural model obtained at 100K, 250K, 330K and 350K show the same iron coordination sphere, with bond lengths and angles consistent with low spin values found for bulk crystals below 300K¹. Essential crystal and refinement data are reported in Table 1SI. Full iron coordination sphere angles and bond lengths are reported in Table 2SI. Figure S1 shows an optical micrograph of the spin transition of the powder, in a zone particularly rich of thermally inert crystals (panels a and b – inert crystals encircled in b) and a picture of the crystal structure of thermally inert crystals (panel c).

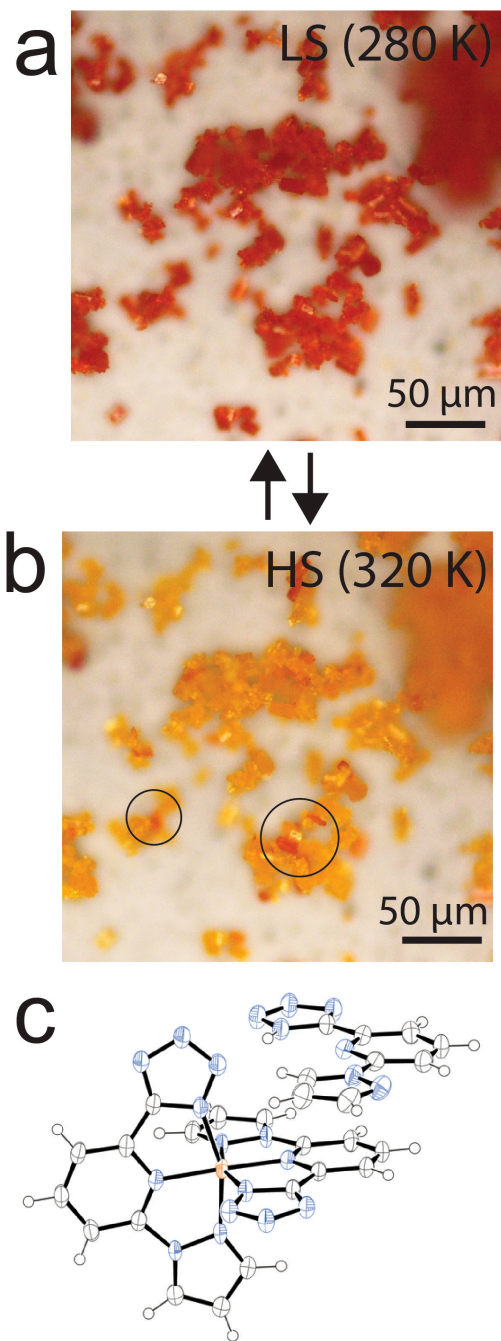


Figure S1. Optical micrograph of spin transition in the powder of **1**. The circles highlight some thermally inert crystallites that do not switch. The percentage of these crystals is normally < 1%, here we selected a zone exceptionally rich of these crystals. Images recorded at a) 280 K and b) 320 K. c) $[\text{Fe}(\text{L})_2]$ molecular assembly in thermally inert crystals, obtained by X-ray diffraction at 100 K. A free (not coordinated to iron) L molecule is present. Displacement ellipsoids are drawn at 50% probability.

Structural models for data collected at 100 K have been deposited on The Cambridge Crystallographic Data Centre (access code is CCDC-1055435).

Synthesis thermally inert crystals

As it was already noted in the main article the powder of **1** contains a small percentage (we estimated < 2 %) of crystallites, which do not exhibit the spin transition, there we named these thermally inert crystals.

It was also possible to obtain thermally inert crystals as an exclusive convergent product of a chemical reaction. The chemical equation is shown in Fig. S2

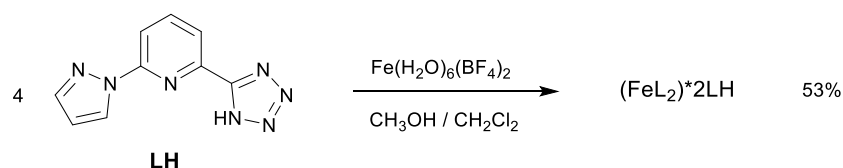


Figure S2. Synthesis of thermally inert crystals

LH (0.158 g, 0.74 mmol, 4 eq) and $\text{Fe}(\text{H}_2\text{O})_6(\text{BF}_4)_2$ (62.5 mg, 0.185 mmol, 1 eq) were added to a Ar-degassed solution of CH_2Cl_2 (25 ml) and MeOH (25 ml). The orange solution was stirred at 35°C. After 10 minutes time the stirring was stopped, the solution was filtered and the solvent was allowed to evaporate slowly over night. The next morning, the red crystals were collected by filtration and allowed to dry under an atmosphere of nitrogen. Yield:

Elemental analysis: calc. for **I** ($\text{C}_{36}\text{H}_{26}\text{FeN}_{28} = [\text{Fe}(\text{C}_9\text{H}_6\text{N}_7) \cdot 2(\text{C}_9\text{H}_7\text{N}_7)]$) C, 47.69; H, 2.89; N, 43.26; found C, 47.89; H, 2.88; N, 43.21.

Magnetic characterization of thermally inert crystals

Using an oven-setup for the high temperature range of the susceptibility measurement of unswitchable crystallites revealed a diamagnetic character until about 450K. Then the compound is gradually and irreversibly changing to the high spin state (see Fig. S3). This may be caused by the decomposition of the determined molecular structure of complex **I** due to thermal instability of the (H-bonded) N-rich ligand subunits. Structural models for data collected at 100 K have been deposited on The Cambridge Crystallographic Data Centre (access code CCDC-1055435).

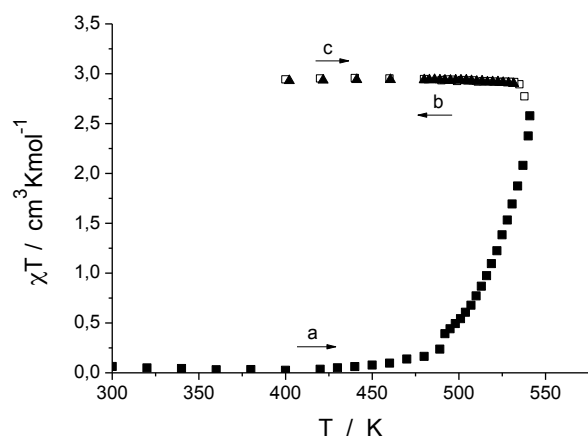


Figure S3 Magnetic properties of **I** ($B = 0.1$ T). Temperature dependence of the χT product: a) black squares: heating from 300 to 540 K; b) white squares: cooling to 400 K; c) black triangles: heating to 530 K.

Table 1SI. Crystal data and structure refinement for inactive crystals (**I**).

	Inactive form (I)
Moiety Formula	C ₁₈ H ₁₂ FeN ₁₄ · 2C ₉ H ₇ N ₇
Empirical Formula	C ₃₆ H ₂₆ FeN ₂₈
Formula weight (Da)	906.70
Temperature (K)	100(2)
Wavelength (Å)	0.800
Crystal system	Monoclinic
Space Group	<i>I</i> 2/ <i>c</i>
<i>a</i> (Å)	16.407(3)
<i>b</i> (Å)	9.768(2)
<i>c</i> (Å)	23.226(5)
α (°)	90
β (°)	90.32(3)
γ (°)	90
<i>V</i> (Å ³)	3722.3(13)
<i>Z</i>	4
ρ (g·cm ⁻³)	1.618
<i>F</i> (000)	1856
μ (mm ⁻¹)	0.654
θ min,max (°)	2.0, 28.1
Resolution (Å)	0.85
Total refl. collectd	10920
Independent refl.	3051
Obs. Refl. [<i>F</i> _o >4 σ (<i>F</i> _o)]	2545
<i>I</i> / σ (<i>I</i>) (all data)	12.9
<i>I</i> / σ (<i>I</i>) (max resltn)	9.3
Completeness (all data)	0.95
Completeness (max resltn)	0.92
Rmerge (all data)	0.071
Rmerge (max resltn,)	0.118
Multiplicity (all data)	3.3
Multiplicity (max resltn)	3.1
Data/restraint/parameters	3051/0/308
Goof	1.024
<i>R</i> ₁ ^a [<i>I</i> >2.0 σ (<i>I</i>)], <i>wR</i> ₂ ^a [<i>I</i> >2.0 σ (<i>I</i>)]	0.0423, 0.1096
<i>R</i> ₁ ^a (all data), <i>wR</i> ₂ ^a (all data)	0.0532, 0.1175

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR_2 = \left[\frac{\sum w (F_o^2 - F_c^2)^2}{\sum w (F_o^2)^2} \right]^{1/2}.$$

Table 2SI. Bond lengths (Å) and angles (°) in iron coordination sphere.

	Dried Crystals ¹	Dried Crystals (1) ¹	Inactive form (I)
T (K)	180	300	100
Fe-N1	1.968(4)	1.978(1)	1.969(2)
Fe-N7	1.949(4)	1.962(1)	1.950(2)
Fe-N5	1.916(3)	1.912(1)	1.909(2)
Fe-N12	1.918(3)	1.912(1)	1.909(2)
Fe-N8	1.971(4)	1.980(1)	1.969(2)
Fe-N14	1.959(4)	1.971(1)	1.950(2)
N1-Fe-N7	160.04(14)	159.75(5)	160.30(8)
N1-Fe-N5	80.08(15)	79.85(5)	79.95(9)
N1-Fe-N12	101.77(15)	103.86(5)	103.52(9)
N1-Fe-N8	92.20(17)	92.41(5)	94.81(13)
N1-Fe-N14	92.34(16)	92.78(5)	90.23(9)
N7-Fe-N5	79.98(15)	79.92(5)	80.36(9)
N7-Fe-N12	98.19(14)	96.36(5)	96.10(9)
N7-Fe-N8	91.27(16)	92.30(5)	90.23(9)
N7-Fe-N14	91.14(16)	89.52(5)	91.39(13)
N5-Fe-N12	177.48(16)	176.22(5)	174.99(13)
N5-Fe-N8	102.26(14)	101.00(5)	103.52(9)
N5-Fe-N14	97.88(15)	99.07(5)	96.11(9)
N12-Fe-N8	79.45(15)	79.71(5)	79.94(9)
N12-Fe-N14	80.39(16)	80.15(5)	80.37(9)
N8-Fe-N14	159.83(14)	159.86(5)	160.30(8)
Colour	Deep Red	Deep Red	Bright Red
Spin Status	LS	LS	LS
CCDC	956141	1055429	1055435

Table 3. Calculated Raman frequencies E (cm^{-1}) and activities A ($\text{\AA}^4/\text{amu}$) of LS and HS states compared with the experimental ones at 280 K (LS) and 328 K (HS) reported within brackets. The assignments are based on the main contributions by the stretching (s), bending (b), and torsional (t) modes of **1** with **I** = pyridine, **II** = pyrazole, and **III** = tetrazole. The contributions given by Fe^{II} are evidenced.

E^{LS} ($E^{280\text{K}}$)	A^{LS}	assignment ^{LS}	E^{HS} ($E^{328\text{K}}$)	A^{HS}	assignment ^{HS}
1620(1618)	0.315	s^{I}	1617(1615)	0.345	s^{I}
1570(1572)	0.285	s^{I}	1580(1579)	0.170	s^{I}
1536(1533)	0.460	$s^{\text{I,II}}$	1531(1534)	0.460	$s^{\text{I,II}}$
1513(1524)	0.633	$s^{\text{I,III}}$	1515(1524)	0.630	$s^{\text{I,II}}, b^{\text{I,III}}$
1490(1488)	0.397	$s^{\text{I,II}}$	1482(1477)	0.306	$s^{\text{I,III}}$
1411(1413)	0.213	$s^{\text{I,III}}$	1414(1411)	0.273	$s^{\text{I,III}}$
1372(1385)	0.950	$s^{\text{I}}, b^{\text{I-II,I-III}}$	1376(1395)	0.419	$s^{\text{I}}, b^{\text{I-II,I-III}}$
1349(1355)	0.425	$b^{\text{I-Fe-III}}$	1349(1353)	0.390	$b^{\text{I-Fe-III}}$
1292(1302)	0.219	s^{III}	1293(1313)	0.166	s^{III}
1211(1209)	0.418	b^{III}	1207(1206)	0.184	s^{II}
1173(1161)	0.135	$b^{\text{I}}, s^{\text{III}}$	1171(1187)	0.094	$s^{\text{II}}, b^{\text{I}}$
1154(1143)	0.188	b^{I}	1131(1146)	0.199	$b^{\text{I}}, s^{\text{III}}$
1129(1112)	0.302	b^{II}	1130(1102)	0.199	$s^{\text{Fe-I,II}}, b^{\text{I}}$
1061(1063)	0.133	b^{III}	1065(1062)	0.124	$b^{\text{III}}, s^{\text{III}}$
1037(1035)	0.693	$b^{\text{I}}, s^{\text{Fe-I}}$	1012(1012)	1.000	$s^{\text{Fe-I}}, b^{\text{I}}$
960(965)	0.119	b^{I}	954(965)	0.123	$s^{\text{Fe-III}}, b^{\text{III}}$
680(684)	0.166	$s^{\text{Fe-I}}, b^{\text{I}}$	666(667)	0.482	$s^{\text{Fe-I}}, b^{\text{I}}$
490(501)	0.131	t^{I}	460(472)	0.152	$s^{\text{Fe-I}}, b^{\text{I-Fe-II, I-Fe-III}}$
388(392)	0.118	$b^{\text{I-Fe-II, I-Fe-III}}$	375(383)	0.069	$b^{\text{I-Fe-II, I-Fe-III}}$
375(375)	0.124	$t^{\text{Fe-I, Fe-II, Fe-III}}$	356(358)	0.093	$s^{\text{Fe-I, Fe-II, Fe-III}}$
237(241)	0.189	$s^{\text{Fe-I, Fe-II, Fe-III}}$	270(263)	0.156	$t^{\text{I}}, s^{\text{Fe-I, Fe-II, Fe-III}}$

Table 4. Comparison among the electronic energies of the LS and HS states of complex **1** alone, calculated at the X-ray structures obtained at 100 K (LS) and 300 K (HS), in CH₃OH, and *in vacuo*. The zero-point correction to the electronic energy (ZPE) is calculated *in vacuo* with the standard ambient conditions without scaling of the force constants.

structure	E ^{LS} (au)	E ^{HS} (au)	ΔE ^(LS-HS) (cm ⁻¹)
X-ray	-2721.28855207	-2721.23372567	-12033.00
X-ray + H ₂ O ^{a)}	-2797.54179585	-2797.49369769	-10556.32
in CH ₃ OH	-2721.46437530	-2721.46617799	395.64
in CH ₂ Cl ₂	-2721.45749267	-2721.45923879	383.23
<i>in vacuo</i>	-2721.41547754	-2721.41754586	453.94
ZPE	0.32233000	0.31871500	793.40

^{a)}counterpoise corrected values (S. F. Boys and F. Bernardi, *Mol. Phys.*, **19** (1970) 553.)

Table 5. Comparison among the Natural Charges (δ) calculated for the LS and HS states of **1** at the X-ray geometry obtained at 100 K.

	δ^{LS}	δ^{HS}	$\Delta(\delta^{\text{LS}} - \delta^{\text{HS}})$
2 x pyridyl-	0.6769	0.4492	0.2277
2 x diazoly-	0.1682	-0.0036	0.1718
2 x tetrazolyl-	-0.9762	-1.1892	0.2130
Fe ^{II}	0.1311	0.7435	-0.6124

Table 6. Comparison among the Natural Charges (δ) calculated for the LS and HS states of **1** at the X-ray geometries obtained at 100 K and 300 K.

atom	100 K			300 K		
	δ^{LS}	δ^{HS}	$\Delta(\delta^{\text{LS}}-\delta^{\text{HS}})$	δ^{LS}	δ^{HS}	$\Delta(\delta^{\text{LS}}-\delta^{\text{HS}})$
C (1)	0.0073	0.0165	-0.0092	0.0056	0.0147	-0.0091
N (2)	-0.1616	-0.1571	-0.0045	-0.1606	-0.1558	-0.0048
N (3)	-0.1741	-0.2841	0.1100	-0.1760	-0.2860	0.1100
C (4)	0.0351	0.0482	-0.0131	0.0378	0.0507	-0.0129
C (5)	-0.2935	-0.2957	0.0022	-0.2930	-0.2953	0.0023
C (6)	0.4190	0.4210	-0.0020	0.4194	0.4207	-0.0013
N (7)	-0.3690	-0.4893	0.1203	-0.3700	-0.4894	0.1194
C (8)	0.2319	0.2357	-0.0038	0.2310	0.2340	-0.0030
C (9)	-0.2153	-0.2140	-0.0013	-0.2145	-0.2131	-0.0014
C(10)	-0.1409	-0.1404	-0.0006	-0.1409	-0.1410	0.0001
C(11)	-0.2743	-0.2721	-0.0022	-0.2753	-0.2731	-0.0022
C(12)	0.2555	0.2637	-0.0082	0.2551	0.2633	-0.0082
N(13)	-0.2508	-0.3713	0.1204	-0.2531	-0.3730	0.1199
N(14)	-0.0838	-0.0791	-0.0047	-0.0850	-0.0808	-0.0042
N(15)	-0.0960	-0.0952	-0.0008	-0.0940	-0.0932	-0.0008
N(16)	-0.3131	-0.3125	-0.0007	-0.3136	-0.3131	-0.0005
Fe(17)	0.1311	0.7435	-0.6124	0.1388	0.7501	-0.6113
N(18)	-0.2520	-0.3713	0.1192	-0.2517	-0.3701	0.1184
N(19)	-0.0850	-0.0808	-0.0042	-0.0843	-0.0800	-0.0043
N(20)	-0.0967	-0.0961	-0.0006	-0.0964	-0.0960	-0.0004
N(21)	-0.3127	-0.3128	0.0001	-0.3109	-0.3109	0.0000
C(22)	0.2584	0.2662	-0.0078	0.2547	0.2617	-0.0069
C(23)	0.2305	0.2346	-0.0041	0.2282	0.2330	-0.0048

atom	100 K			300 K		
	δ^{LS}	δ^{HS}	$\Delta(\delta^{LS}-\delta^{HS})$	δ^{LS}	δ^{HS}	$\Delta(\delta^{LS}-\delta^{HS})$
C(1)	0.0073	0.0165	-0.0092	0.0056	0.0147	-0.0091
N(24)	-0.3690	-0.4896	0.1206	-0.3701	-0.4906	0.1205
C(25)	0.4185	0.4204	-0.0019	0.4212	0.4238	-0.0026
C(26)	-0.2764	-0.2747	-0.0018	-0.2768	-0.2756	-0.0012
C(27)	-0.1423	-0.1417	-0.0005	-0.1432	-0.1417	-0.0015
C(28)	-0.2207	-0.2191	-0.0016	-0.2183	-0.2170	-0.0013
N(29)	-0.1638	-0.1598	-0.0040	-0.1629	-0.1595	-0.0033
N(30)	-0.1755	-0.2854	0.1099	-0.1772	-0.2849	0.1077
C(31)	0.0433	0.0579	-0.0146	0.0426	0.0566	-0.0140
C(32)	-0.2903	-0.2928	0.0025	-0.2924	-0.2948	0.0024
C(33)	0.0063	0.0163	-0.0100	0.0056	0.0149	-0.0094
H(34)	0.2409	0.2398	0.0011	0.2410	0.2398	0.0011
H(35)	0.2245	0.2242	0.0004	0.2236	0.2232	0.0004
H(36)	0.2275	0.2257	0.0018	0.2277	0.2258	0.0019
H(37)	0.2220	0.2215	0.0004	0.2220	0.2216	0.0004
H(38)	0.2289	0.2284	0.0005	0.2292	0.2288	0.0004
H(39)	0.2173	0.2168	0.0005	0.2164	0.2159	0.0004
H(40)	0.2412	0.2401	0.0011	0.2405	0.2395	0.0010
H(41)	0.2238	0.2235	0.0004	0.2242	0.2239	0.0003
H(42)	0.2270	0.2251	0.0018	0.2273	0.2256	0.0017
H(43)	0.2213	0.2209	0.0004	0.2218	0.2215	0.0004
H(44)	0.2291	0.2287	0.0004	0.2294	0.2290	0.0003
H(45)	0.2164	0.2161	0.0004	0.2172	0.2168	0.0004

Table 7. X-ray cartesian coordinates (Å) of **1**.

atom	100 K			300 K		
	x	y	z	x	y	z
C (1)	3.95257	14.00586	1.41526	3.94962	14.06983	1.45172
N (2)	3.59343	13.09599	0.46211	3.60094	13.16270	0.49614
N (3)	4.69666	12.61338	-0.20038	4.70610	12.71199	-0.17900
C (4)	5.72924	13.22165	0.35222	5.73305	13.33531	0.36917
C (5)	5.31861	14.08520	1.35838	5.30779	14.19212	1.39013
C (6)	2.35658	12.54726	0.09796	2.37618	12.59779	0.13447
N (7)	2.50760	11.58299	-0.81122	2.53778	11.65860	-0.79497
C (8)	1.42926	10.90461	-1.26753	1.47406	10.95876	-1.24925
C (9)	0.15974	11.19418	-0.79852	0.20237	11.20632	-0.76294
C (10)	0.01401	12.22425	0.12068	0.04803	12.21668	0.17751
C (11)	1.11494	12.92530	0.58797	1.13097	12.93133	0.64475
C (12)	1.86408	9.92907	-2.24658	1.91260	10.01159	-2.25640
N (13)	3.18496	9.90548	-2.52245	3.23102	10.00594	-2.53391
N (14)	3.34324	8.93783	-3.43567	3.39823	9.06971	-3.47670
N (15)	2.15158	8.42195	-3.70877	2.21754	8.54314	-3.74987
N (16)	1.19464	9.03340	-2.96489	1.25996	9.11687	-2.99253
Fe(17)	4.25110	11.20504	-1.49078	4.28567	11.31233	-1.48780
N (18)	4.34379	12.47046	-3.00036	4.35393	12.59186	-2.99707
N (19)	3.54581	13.31190	-3.66978	3.55403	13.43225	-3.65558
N (20)	4.26437	13.86126	-4.64312	4.26016	13.98010	-4.63183
N (21)	5.53677	13.39273	-4.63045	5.52365	13.51497	-4.62938
C (22)	5.54444	12.54240	-3.60695	5.55090	12.66818	-3.61191
C (23)	6.58724	11.69267	-3.03676	6.60009	11.82102	-3.06625
N (24)	6.04874	10.91411	-2.06481	6.08055	11.03746	-2.08774

atom	100 K			300 K		
	x	y	z	x	y	z
C (25)	6.81367	10.06334	-1.38863	6.85247	10.17621	-1.43741
C (26)	8.16728	9.91460	-1.64585	8.19943	10.01586	-1.72727
C (27)	8.71612	10.73050	-2.62397	8.73000	10.81776	-2.71259
C (28)	7.94119	11.64676	-3.32270	7.94323	11.74248	-3.39477
N (29)	6.09872	9.41616	-0.38805	6.15748	9.52237	-0.41753
N (30)	4.80647	9.85382	-0.18267	4.86935	9.94774	-0.19111
C (31)	4.39244	9.22815	0.91796	4.47996	9.31974	0.90533
C (32)	5.40925	8.39283	1.43049	5.50858	8.49537	1.40152
C (33)	6.47982	8.53419	0.59001	6.55162	8.64440	0.54875
H (34)	-0.59399	10.69973	-1.09950	-0.54419	10.69981	-1.06332
H (35)	-0.85404	12.45276	0.43551	-0.81915	12.41973	0.50489
H (36)	1.02474	13.63361	1.21539	1.02777	13.62272	1.28878
H (37)	3.37428	14.48508	1.99738	3.36262	14.52623	2.04343
H (38)	5.87732	14.62606	1.90333	5.85574	14.74774	1.93190
H (39)	6.63355	13.08690	0.09600	6.63717	13.21780	0.10633
H (40)	8.32558	12.22085	-3.97565	8.31728	12.30240	-4.06581
H (41)	9.64403	10.66092	-2.81942	9.65169	10.73838	-2.93157
H (42)	8.69520	9.28175	-1.17410	8.73368	9.38018	-1.26595
H (43)	7.32292	8.10455	0.66920	7.39800	8.21801	0.61272
H (44)	5.36096	7.84420	2.20435	5.47848	7.94660	2.17544
H (45)	3.53227	9.33037	1.30567	3.62200	9.41169	1.30506

Table 8. Cartesian coordinates (Å) of **1** calculated *in vacuo* for LS and HS.

	LS			HS		
	x	y	z	x	y	z
C (1)	-0.08812	3.58756	-2.02273	-0.26884	3.61361	-2.48983
N (2)	0.02649	2.26305	-1.75169	-0.03631	2.33567	-2.09501
N (3)	0.11079	2.03979	-0.41512	0.15086	2.25636	-0.75876
C (4)	0.04967	3.23359	0.15324	0.03356	3.49668	-0.31206
C (5)	-0.07356	4.24692	-0.81717	-0.22959	4.39719	-1.36199
C (6)	0.03788	1.13575	-2.58706	0.01020	1.14994	-2.85483
N (7)	0.14921	0.01675	1.88150	0.12872	0.06033	-2.11343
C (8)	0.13657	-1.19263	-2.48098	0.20011	-1.15669	-2.68153
C (9)	0.04990	-1.28495	-3.86890	0.14972	-1.29964	-4.06910
C (10)	-0.04282	-0.10699	-4.60206	0.02295	-0.14980	-4.83737
C (11)	-0.05529	1.13907	-3.97108	-0.04566	1.11143	-4.24258
C (12)	0.21037	-2.23621	-1.48735	0.33648	-2.22099	-1.71071
N (13)	0.19604	-1.82955	-0.20187	0.29004	-1.92374	-0.39917
N (14)	0.30216	-2.91991	0.52817	0.49094	-3.07330	0.22736
N (15)	0.37541	-3.95444	-0.28941	0.64860	-4.02024	-0.67145
N (16)	0.32011	-3.55687	-1.55903	0.55790	-3.51519	-1.90238
Fe(17)	0.14016	0.09962	0.02966	-0.01474	0.12179	0.03553
N (18)	-1.79324	0.14381	0.22573	-2.00090	0.38442	0.59124
N (19)	-2.87011	0.25957	-0.52265	-3.16016	0.63927	-0.00370
N (20)	-3.92013	0.31344	0.27648	-4.09352	0.69167	0.91474
N (21)	-3.54629	0.23569	1.55212	-3.57409	0.47150	2.12682
C (22)	-2.22407	0.13233	1.50334	-2.28227	0.28554	1.90284
C (23)	-1.19906	0.04373	2.51493	-1.19424	0.03645	2.82764
N (24)	0.02131	0.07227	1.93874	-0.00097	0.02721	2.21035

	LS			HS		
	x	y	z	x	y	z
C (25)	1.12730	-0.04812	2.66309	1.10681	-0.18925	2.89692
C (26)	1.10497	-0.16739	4.04493	1.11242	-0.41117	4.27007
C (27)	-0.15277	-0.17156	4.65239	-0.12462	-0.40393	4.91256
C (28)	-1.31712	-0.06948	3.89899	-1.29711	-0.17703	4.20057
N (29)	2.27015	-0.03946	1.84909	2.26625	0.15437	2.09880
N (30)	2.07172	0.06921	0.51037	2.14078	0.16762	0.79450
C (31)	3.27624	0.02336	-0.03640	3.36566	0.11218	0.29540
C (32)	4.27165	-0.11433	0.95049	4.30310	0.24698	1.28213
C (33)	3.58979	-0.15414	2.14289	3.55868	-0.41193	2.42512
H (34)	0.04149	-2.25994	-4.34138	0.20654	-2.28912	-4.50698
H (35)	-0.11918	-0.15127	-5.68395	-0.02087	-0.22610	5.91965
H (36)	-0.14761	2.05804	-4.53709	-0.13239	2.00953	-4.84167
H (37)	-0.17556	3.95151	-3.03476	-0.45439	3.86489	-3.52267
H (38)	-0.14998	5.31096	-0.65552	-0.37991	5.46410	1.30251
H (39)	0.08494	3.31598	1.22991	0.13637	3.69412	0.74571
H (40)	-2.30077	-0.09051	4.35273	-2.27201	-0.16768	4.67341
H (41)	-0.21708	-0.26851	5.73162	-0.16680	-0.57743	5.98345
H (42)	2.01351	-0.26690	4.62636	2.02898	-0.58123	4.82161
H (43)	3.93500	-0.25931	3.15979	3.84605	-0.69829	3.42480
H (44)	5.33884	0.18364	0.80754	5.36872	0.37678	0.17253
H (45)	3.37873	0.07927	-1.11047	3.52654	0.32450	0.75226

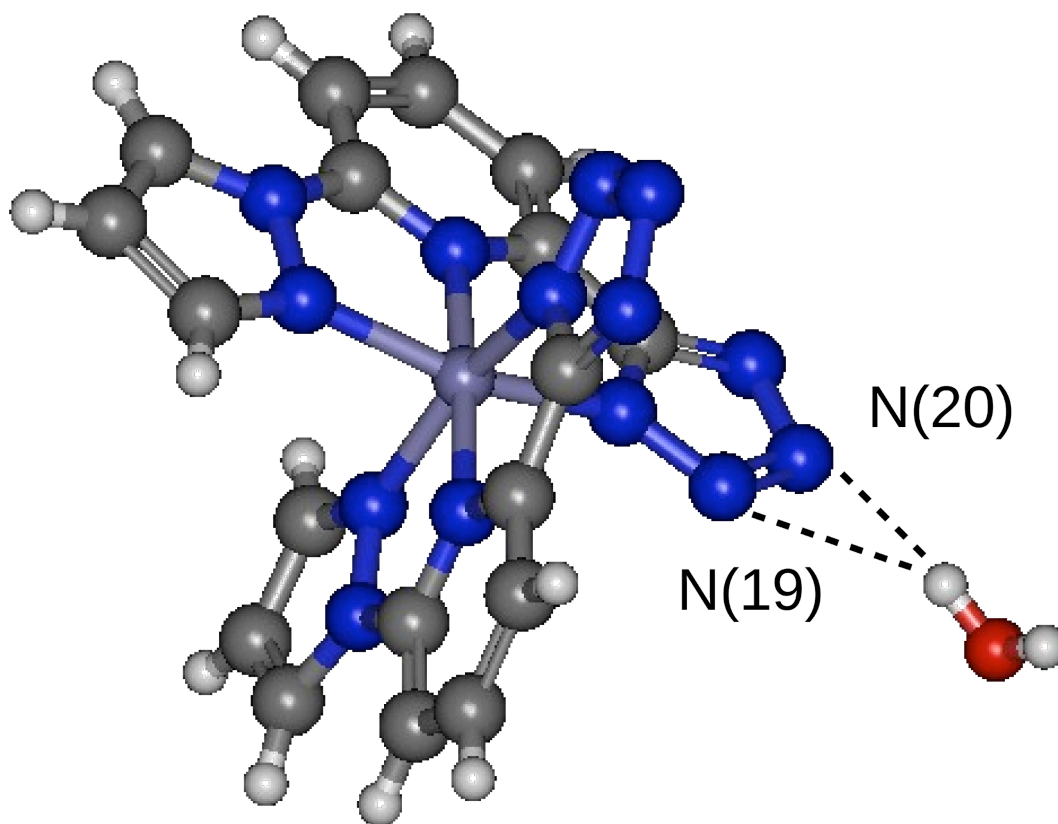


Figure S4. Hydrated complex in crystal **1**. N(20)-H = 2.10485 Å, N(19)-H = 2.63899 Å (drawn by Gabedit: A.R. Allouche, *J. Comput. Chem.*, 32, 174-182(2011)).

1. D. Gentili, N. Demitri, B. Schafer, F. Liscio, I. Bergenti, G. Ruani, M. Ruben and M. Cavallini, *Journal of Materials Chemistry C*, 2015, 3, 7836-7844.