Supplementary information

Spin Crossover in Iron(II) Hoffmann Clathrates Analogues with 1,2,3-triazole

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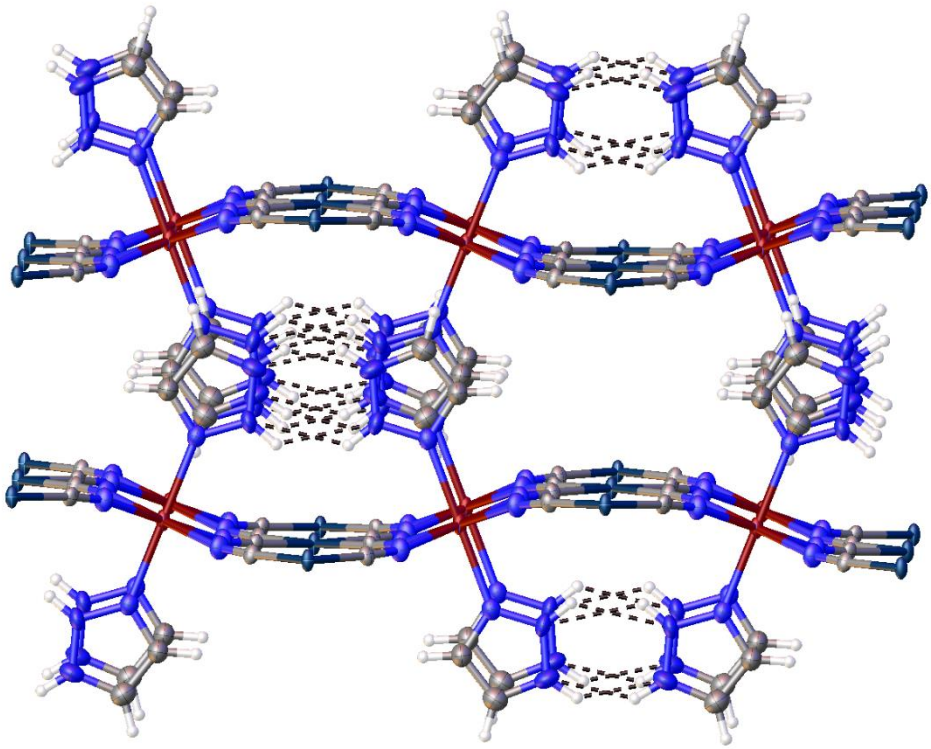

Figure S1. The view of crystal packing in **Pt-trz** showing hydrogen disorder. H(N) atoms are disordered by two positions with 0.5 occupancy each.

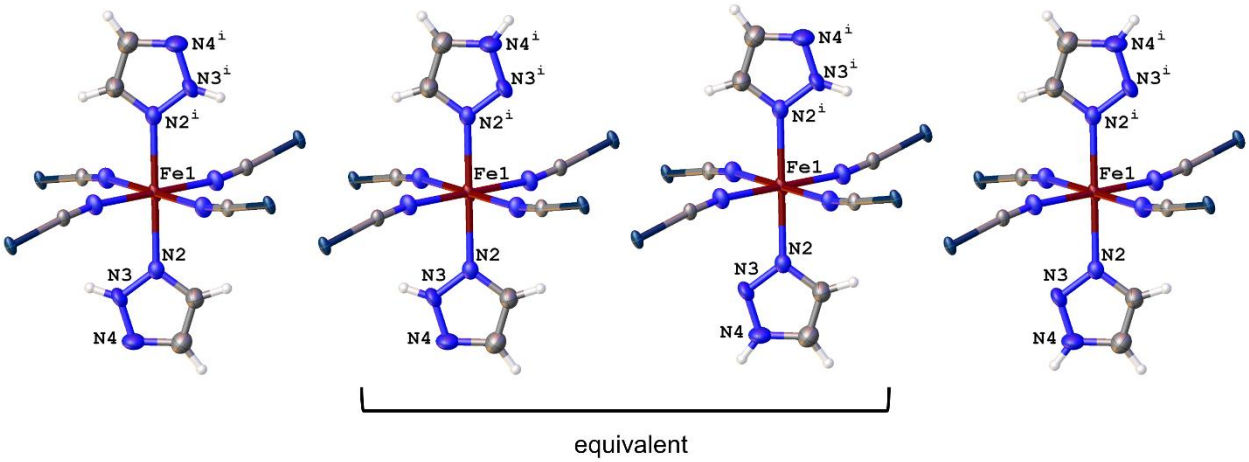

Figure S2. Demonstration of four possible environments of Fe^{II}, realized due to hydrogen disorder.

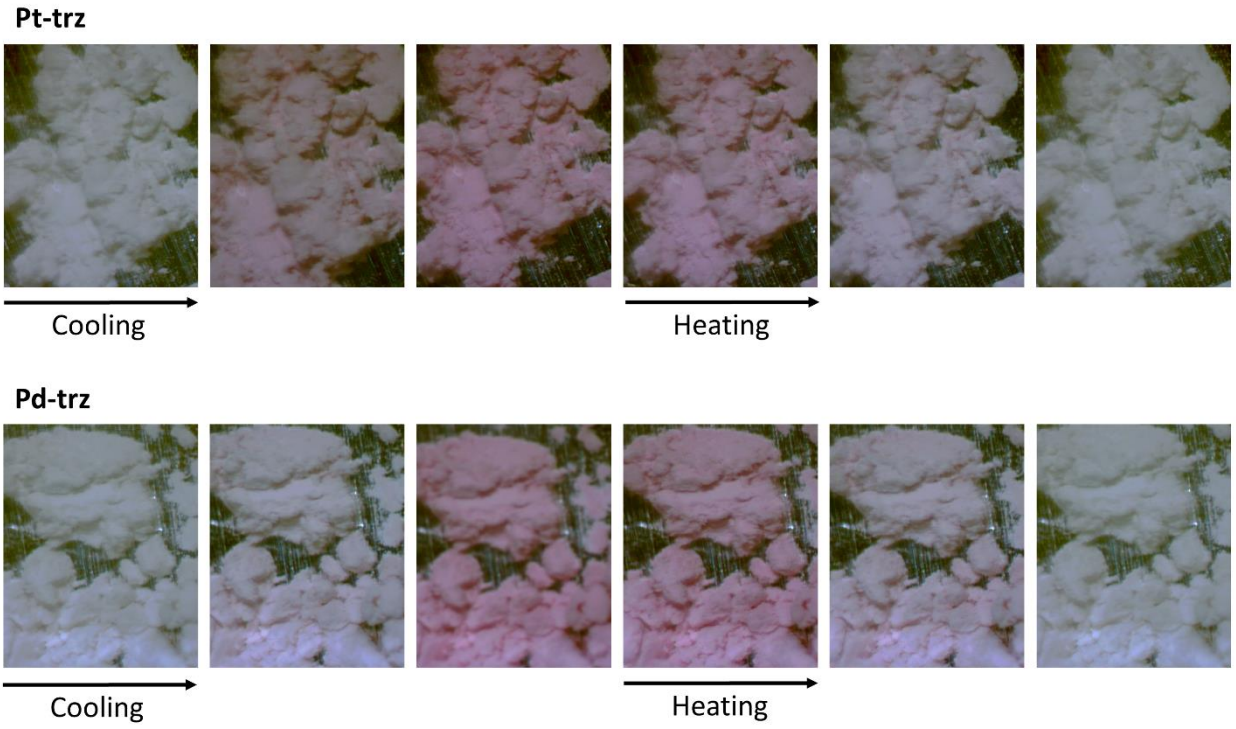

Figure S3. Images of **Pt-trz** and **Pd-trz** obtained during temperature dependent optical measurements, which show thermochromic effect upon SCO.

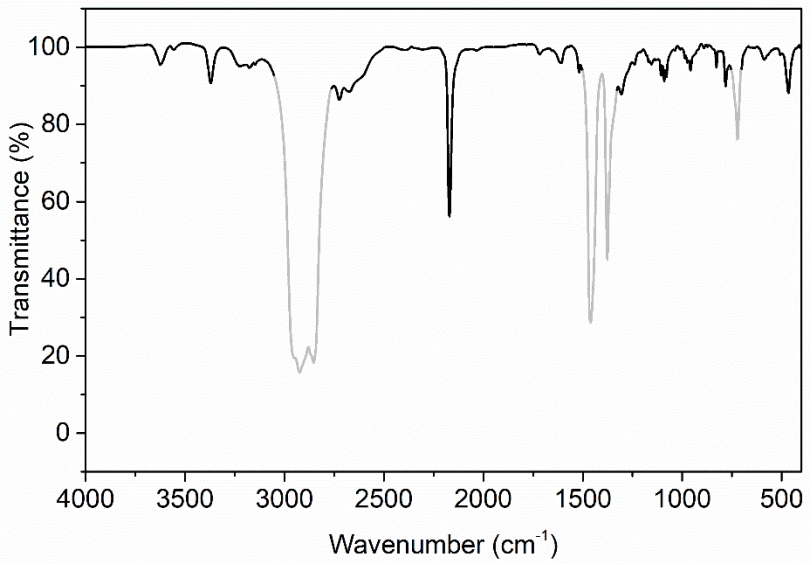

Figure S4. IR spectrum of **Pt-trz** measured in Nujol (IR bands of Nujol are marked as light grey).

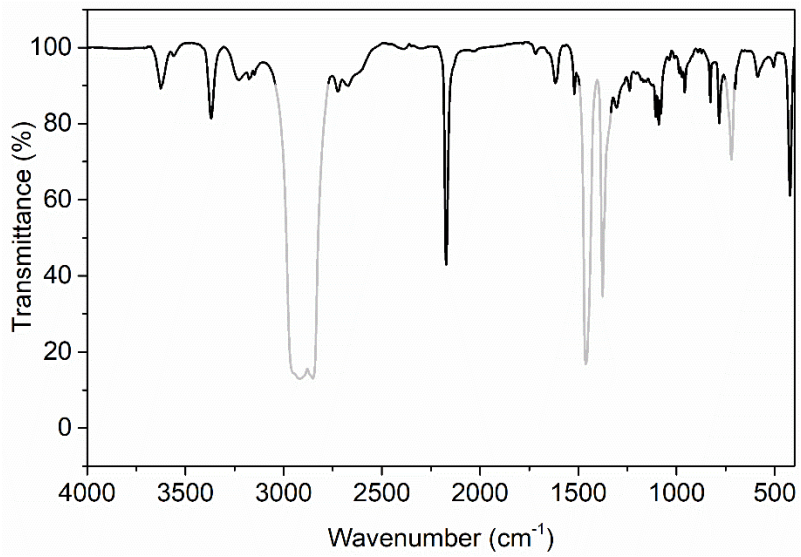

Figure S5. IR spectrum of **Pd-trz** measured in Nujol (IR bands of Nujol are marked as light grey).

Table S1. Spin transition and crystallographic characteristics of selected Fe^{II} Hofmann clathrate analogues.

2D complexes of general formula $[Fe(L)_2M(CN)_4]$										
	M = Pt					M = Pd				
L	Space group	Tr.	T↓	T↑	ΔT	Space group	Tr.	T↓	T↑	ΔT
Azines										
Pyridine[1]	*Cmmm*	ic	208	216	8	*Cmmm*	ic	208	213	5
Pyridazine*[2]	*Cmmm*	c	269	283	14	*Cmmm*	c	247	260	13
Pyrimidine *[3]	*Cmmm*	c	227	247	20	*Cmmm*	c	198	213	15
Azoles										
Proptrz*[4]	$P\bar{1}$	c	257	307	50	$P\bar{1}$	c	220	285	65
Thiome*[5]						$P\bar{1}$	c	184	204	20
Trz-py·$3H_2O$[6]	*C2/c*	50%	152	154	2					

Tr. – transition, c – complete, ic – incomplete, * - only temperatures for dehydrated forms are given, proptrz - (E)-3-phenyl-N-(4H-1,2,4-triazol-4-yl)prop-2-yn-1- imine, thiome - 4-[(E)-2- (5-methyl-2-thienyl)vinyl]-1,2,4-triazole, trz-py - 4-(2-pyridyl)-1,2,4,4H-triazole

Table S2. Spin transition temperatures for powder samples of **1** and **2**, obtained in different experiments.

	Magnetic measurements		DSC		Optical measurements	
	T↓	T↑	T↓	T↑	T↓	T↑
Pt-trz	(1) 194 (2) 200	(1) 210 (2) 222	189	(1) 212 (2) 222	185	212
Pd-trz	202	(1) 212 (2) 220	198	(1) 215 (2) 222	193	218

Table S3. Summary of spin transition temperatures for single crystals of **Pt-trz** at different scan rates extracted from optical measurements.

Rate (K min^{-1})	$T_{\downarrow}$ (K)	$T_{\uparrow}$ (K)
0.5	199.3	227.4
1	198.6	226.4
5	199.1	228.2
10	197.7	224.7

Table S4. Crystal data and structure refinement for **Pt-trz** at 170 K.

Empirical formula	$C_8H_6FeN_{10}Pt$
Formula weight	493.17
Temperature/K	169.9(2)
Crystal system	orthorhombic
Space group	Imma
a/Å	13.8736(9)
b/Å	7.1949(4)
c/Å	12.8934(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1287.01(19)
Z	4
ρ_{calc}g/cm^3	2.545
μ/mm^{-1}	11.991
F(000)	912.0
Crystal size/mm^3	0.2 × 0.2 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.312 to 58.1
Index ranges	-17 ≤ h ≤ 17, -9 ≤ k ≤ 6, -8 ≤ l ≤ 17
Reflections collected	1729
Independent reflections	840 [R_{int} = 0.0335, R_{sigma} = 0.0580]
Data/restraints/parameters	840/0/57
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.0882
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.0937
Largest diff. peak/hole / e Å^{-3}	5.57/-2.67

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Pt-trz (LS). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	5000	2500	6971.2(5)	11.4(2)

Fe1	7500	7500	7500	10.3(5)
N2	7962(6)	7500	6052(7)	11.3(18)
N1	6567(4)	5600(9)	7151(5)	10.9(13)
N3	8884(6)	7500	5781(8)	21(2)
C1	6003(5)	4477(10)	7027(6)	11.5(14)
N4	8966(7)	7500	4769(8)	22(2)
C2	7455(9)	7500	5151(9)	25(3)
C3	8071(9)	7500	4339(10)	25(3)

Anisotropic Displacement Parameters ($Å^2×10^3$) for Pt-trz (LS). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	7.7(3)	4.1(3)	22.5(4)	0	0	0
Fe1	8.2(9)	5.1(10)	17.5(12)	0	-0.3(9)	0
N2	10(4)	7(4)	17(5)	0	-7(4)	0
N1	9(3)	9(3)	15(3)	1(3)	4(2)	3(2)
N3	14(4)	29(6)	18(6)	0	6(4)	0
C1	6(3)	11(3)	18(4)	5(3)	-3(3)	4(3)
N4	21(5)	26(6)	20(6)	0	5(4)	0
C2	27(6)	24(7)	22(7)	0	-3(6)	0
C3	32(6)	26(7)	17(7)	0	1(5)	0

Bond Lengths for Pt-trz (LS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	$C1^1$	1.991(7)	Fe1	$N1^4$	1.936(6)
Pt1	C1	1.991(7)	Fe1	$N1^6$	1.936(6)
Pt1	$C1^2$	1.991(7)	N2	N3	1.326(12)
Pt1	$C1^3$	1.991(7)	N2	C2	1.358(14)
Fe1	$N2^4$	1.974(9)	N1	C1	1.136(10)
Fe1	N2	1.974(9)	N3	N4	1.311(13)
Fe1	$N1^5$	1.936(6)	N4	C3	1.360(15)
Fe1	N1	1.936(6)	C2	C3	1.351(16)

^{1}1-X,1/2-Y,+Z; ^{2}+X,1/2-Y,+Z; ^{3}1-X,+Y,+Z; ^{4}3/2-X,3/2-Y,3/2-Z; ^{5}3/2-X,+Y,3/2-Z; ^{6}+X,3/2-Y,+Z

Bond Angles for Pt-trz (LS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
$C1^1$	Pt1	$C1^2$	91.2(4)	$N1^4$	Fe1	$N1^5$	90.2(3)
$C1^3$	Pt1	C1	91.2(4)	N1	Fe1	$N1^5$	89.8(3)
$C1^1$	Pt1	$C1^3$	88.7(4)	$N1^4$	Fe1	$N1^6$	89.8(3)

C1[2]	Pt1	C1	88.7(4)	N1	Fe1	N1[4]	180.0
C1[2]	Pt1	C1[3]	175.8(4)	N1[5]	Fe1	N1[6]	180.0(3)
C1[1]	Pt1	C1	175.8(4)	N1	Fe1	N1[6]	90.2(3)
N2[4]	Fe1	N2	180.0	N3	N2	Fe1	124.2(7)
N1[5]	Fe1	N2[4]	90.2(2)	N3	N2	C2	106.0(9)
N1	Fe1	N2	89.8(2)	C2	N2	Fe1	129.9(7)
N1	Fe1	N2[4]	90.2(2)	C1	N1	Fe1	174.6(6)
N1[5]	Fe1	N2	89.8(2)	N4	N3	N2	110.3(9)
N1[4]	Fe1	N2[4]	89.8(2)	N1	C1	Pt1	174.0(7)
N1[6]	Fe1	N2[4]	89.8(2)	N3	N4	C3	109.0(10)
N1[6]	Fe1	N2	90.2(2)	C3	C2	N2	109.5(10)
N1[4]	Fe1	N2	90.2(2)	C2	C3	N4	105.2(11)

[1]1-X,1/2-Y,+Z; [2]1-X,+Y,+Z; [3]+X,1/2-Y,+Z; [4]3/2-X,3/2-Y,3/2-Z; [5]+X,3/2-Y,+Z; [6]3/2-X,+Y,3/2-Z

Hydrogen Bonds for Pt-trz (LS).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H1A	N3[1]	0.86	2.50	3.097(18)	127.4
N4	H1B	N4[1]	0.86	2.17	2.868(19)	137.9

[1]2-X,3/2-Y,+Z

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Pt-trz (LS).

Atom	*x*	*y*	*z*	U(eq)
H1A	9359.38	7500	6208.92	25
H1B	9500.67	7500	4430.29	26
H2	6785.93	7500	5099.96	29
H3	7916.05	7500	3637.01	30

Atomic Occupancy for Pt-trz.

Atom	*Occupancy*
H1A	0.5
H1B	0.5

Table S5. Crystal data and structure refinement for **Pt-trz** at 255 K.

Empirical formula	$C_8H_6N_{10}FePt$
Formula weight	493.17

Temperature/K	255.00(10)
Crystal system	orthorhombic
Space group	Imma
a/Å	14.3717(6)
b/Å	7.4268(3)
c/Å	13.1817(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1406.96(16)
Z	4
ρ_{calc}g/cm^3	2.328
μ/mm^{-1}	10.969
F(000)	912.0
Crystal size/mm^3	0.2 × 0.2 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.192 to 58.49
Index ranges	-18 ≤ h ≤ 12, -5 ≤ k ≤ 9, -10 ≤ l ≤ 17
Reflections collected	2112
Independent reflections	940 [R_{int} = 0.0272, R_{sigma} = 0.0453]
Data/restraints/parameters	940/0/57
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0742
Final R indexes [all data]	R_1 = 0.0449, wR_2 = 0.0789
Largest diff. peak/hole / e Å^{-3}	3.62/-2.04

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Pt-trz (HS). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pt1	5000	2500	1952.1(4)	16.85(17)
Fe1	7500	7500	2500	17.4(4)
N2	6949(5)	7500	4056(6)	25.8(17)
N1	6520(4)	5474(7)	2073(4)	26.7(13)
N3	6073(5)	7500	4338(7)	33(2)
C1	5972(4)	4396(8)	1991(5)	18.7(12)
N4	5999(7)	7500	5324(7)	44(2)
C3	6864(8)	7500	5706(9)	43(3)
C2	7439(7)	7500	4912(8)	40(3)

Anisotropic Displacement Parameters (Å^2×10^3) for Pt-trz (HS). The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U_{11}+2hka*b*U_{12}+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

Pt1	10.3(2)	8.2(2)	32.0(3)	0	0	0
Fe1	12.3(8)	8.7(7)	31.2(11)	0	-0.9(8)	0
N2	23(4)	23(4)	31(4)	0	-2(4)	0
N1	24(3)	18(3)	38(3)	-1(2)	-1(3)	-4(2)
N3	16(4)	49(5)	35(5)	0	5(4)	0
C1	16(3)	15(3)	25(3)	3(3)	-3(3)	1(2)
N4	40(5)	66(7)	25(5)	0	9(4)	0
C3	40(6)	52(7)	36(6)	0	-4(6)	0
C2	28(5)	57(7)	35(6)	0	-1(5)	0

Bond Lengths for Pt-trz (HS).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	C1	1.984(6)	Fe1	$N1^{4}$	2.136(5)
Pt1	$C1^{1}$	1.984(6)	Fe1	$N1^{6}$	2.136(5)
Pt1	$C1^{2}$	1.984(6)	N2	N3	1.313(10)
Pt1	$C1^{3}$	1.984(6)	N2	C2	1.330(12)
Fe1	N2	2.199(8)	N1	C1	1.129(8)
Fe1	$N2^{4}$	2.199(8)	N3	N4	1.303(11)
Fe1	$N1^{5}$	2.136(5)	N4	C3	1.342(14)
Fe1	N1	2.136(5)	C3	C2	1.333(15)

^{1}+X,1/2-Y,+Z; ^{2}1-X,+Y,+Z; ^{3}1-X,1/2-Y,+Z; ^{4}3/2-X,3/2-Y,1/2-Z; ^{5}3/2-X,+Y,1/2-Z; ^{6}+X,3/2-Y,+Z

Bond Angles for Pt-trz (HS).

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Pt1	$C1^{1}$	177.0(4)	$N1^{4}$	Fe1	$N1^{5}$	90.4(3)
$C1^{2}$	Pt1	$C1^{3}$	177.0(4)	N1	Fe1	$N1^{5}$	89.6(3)
C1	Pt1	$C1^{2}$	89.5(3)	$N1^{4}$	Fe1	$N1^{6}$	89.6(3)
$C1^{1}$	Pt1	$C1^{3}$	89.5(3)	N1	Fe1	$N1^{4}$	180.0
$C1^{1}$	Pt1	$C1^{2}$	90.4(3)	$N1^{5}$	Fe1	$N1^{6}$	180.0(3)
C1	Pt1	$C1^{3}$	90.4(3)	N1	Fe1	$N1^{6}$	90.4(3)
N2	Fe1	$N2^{4}$	180.0	N3	N2	Fe1	127.6(6)
$N1^{5}$	Fe1	N2	90.5(2)	N3	N2	C2	105.5(8)
N1	Fe1	$N2^{4}$	89.5(2)	C2	N2	Fe1	126.9(6)
N1	Fe1	N2	90.5(2)	C1	N1	Fe1	170.0(6)
$N1^{5}$	Fe1	$N2^{4}$	89.5(2)	N4	N3	N2	111.1(9)
$N1^{4}$	Fe1	N2	89.5(2)	N1	C1	Pt1	176.0(6)
$N1^{6}$	Fe1	N2	89.5(2)	N3	N4	C3	107.4(9)
$N1^{6}$	Fe1	$N2^{4}$	90.5(2)	C2	C3	N4	106.2(10)
$N1^{4}$	Fe1	$N2^{4}$	90.5(2)	N2	C2	C3	109.8(9)

^{1}1-X,1/2-Y,+Z; ^{2}1-X,+Y,+Z; ^{3}+X,1/2-Y,+Z; ^{4}3/2-X,3/2-Y,1/2-Z; ^{5}+X,3/2-Y,+Z; ^{6}3/2-X,+Y,1/2-Z

Hydrogen Bonds for Pt-trz (HS).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H1A	N3[1]	0.86	2.48	3.084(15)	128.2
N4	H1B	N4[1]	0.86	2.19	2.872(19)	136.5

[1]1-X,3/2-Y,+Z

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Pt-trz (HS).

Atom	*x*	*y*	*z*	U(eq)
H1A	5608.44	7500	3926.94	40
H1B	5489.64	7500	5665.85	52
H3	7029.75	7500	6388.34	51
H2	8085.08	7500	4951.39	48

Atomic Occupancy for Pt-trz (HS).

Atom	*Occupancy*
H1A	0.5
H1B	0.5

References

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