Table 1. Experimental details

For all structures: $C_8H_{14}Fe_2NO_{12}$, M_r = 427.91. Experiments were carried out with Mo $K\alpha$ radiation using a Xcalibur, Atlas. H-atom parameters were constrained. Absorption correction: Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Computer programs: CrysAlis PRO 1.171.38.41 (Rigaku OD, 2015), CrysAlis PRO 1.171.38.34a (Rigaku OD, 2015), SHELXL2014/7 (Sheldrick, 2014).

Crystal data					
Crystal system, space group	Trigonal, *R*-3*c*:*H*	Trigonal, *R*-3*c*:*H*	Trigonal, *R*-3*c*:*H*	Trigonal, *R*-3*c*:*H*	Trigonal, *P*-31*c*
Temperature (K)	100	125	140	150	160
a, *c* (Å)	14.2916 (5), 41.4795 (17)	14.2896 (5), 41.4830 (15)	14.2909 (5), 41.5072 (16)	14.2991 (5), 41.5361 (13)	8.2603 (3), 13.8466 (4)
V (Å^3)	7337.1 (6)	7335.7 (6)	7341.3 (6)	7354.9 (5)	818.20 (6)
Z	18	18	18	18	2
μ (mm^{-1})	1.84	1.84	1.84	1.83	1.83
Crystal size (mm)	0.20 × 0.08 × 0.06	0.20 × 0.08 × 0.06	0.20 × 0.08 × 0.06	0.26 × 0.20 × 0.06	0.20 × 0.08 × 0.06
Data collection					
T_{min}, T_{max}	0.902, 1.000	0.896, 1.000	0.901, 1.000	0.904, 1.000	0.889, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] ref.	15149, 1558, 1297	15140, 1556, 1269	15136, 1558, 1262	15169, 1561, 1216	5752, 723, 641
R_{int}	0.031	0.031	0.031	0.029	0.022
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.610	0.610	0.610	0.610	0.691
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.070, 0.98	0.025, 0.072, 0.99	0.026, 0.069, 1.10	0.030, 0.078, 1.17	0.022, 0.050, 1.04
No. of reflections	1558	1556	1558	1561	723
No. of parameters	113	113	113	113	40
No. of restraints	3	3	3	3	2
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.24, -0.34	0.22, -0.35	0.25, -0.39	0.41, -0.50	0.26, -0.28

Table 2. Selected geometric parameters (Å)

	(100K)	(125K)	(140K)	(150K)		(160K)
Fe1—O4^{i}	2.0919 (12)	2.0895 (12)	2.0934 (12)	2.0955 (14)	Fe1—O1^{xi}	2.1205 (10)
Fe1—O4	2.0920 (12)	2.0896 (12)	2.0934 (12)	2.0955 (14)	Fe1—O1^{xii}	2.1205 (10)
Fe1—O2^{i}	2.1315 (12)	2.1309 (12)	2.1302 (12)	2.1304 (14)	Fe1—O1^{xiii}	2.1205 (10)
Fe1—O2	2.1315 (12)	2.1310 (12)	2.1302 (12)	2.1306 (14)	Fe1—O1	2.1205 (10)
Fe1—O1^{i}	2.1431 (11)	2.1431 (12)	2.1411 (12)	2.1391 (13)	Fe1—O1^{xiv}	2.1205 (10)
Fe1—O1	2.1432 (11)	2.1431 (12)	2.1412 (12)	2.1391 (13)	Fe1—O1^{xv}	2.1205 (10)
Fe2—O6^{ii}	2.0076 (11)	2.0069 (11)	2.0045 (11)	2.0069 (12)	Fe2—O2^{xvi}	2.0061 (9)
Fe2—O6^{iii}	2.0076 (11)	2.0069 (11)	2.0046 (11)	2.0069 (12)	Fe2—O2	2.0061 (9)
Fe2—O6	2.0076 (11)	2.0069 (11)	2.0046 (11)	2.0069 (12)	Fe2—O2^{xvii}	2.0062 (9)
Fe2—O6^{iv}	2.0077 (11)	2.0069 (11)	2.0046 (11)	2.0069 (12)	Fe2—O2^{xviii}	2.0062 (9)
Fe2—O6^{v}	2.0077 (11)	2.0069 (11)	2.0046 (11)	2.0069 (12)	Fe2—O2^{xix}	2.0062 (9)
Fe2—O6^{vi}	2.0077 (11)	2.0069 (11)	2.0046 (11)	2.0070 (12)	Fe2—O2^{xx}	2.0062 (9)
Fe3—O3^{vii}	1.9974 (11)	1.9960 (11)	1.9970 (11)	1.9994 (13)	O1—C1	1.2349 (17)
Fe3—O3^{viii}	1.9974 (11)	1.9960 (11)	1.9970 (11)	1.9994 (13)	O2—C1	1.2615 (17)
Fe3—O3	1.9974 (11)	1.9960 (11)	1.9970 (11)	1.9994 (13)	C2—N1	1.473 (8)
Fe3—O5	2.0199 (11)	2.0185 (11)	2.0156 (11)	2.0162 (13)	C21—N1	1.445 (8)
Fe3—O5^{viii}	2.0200 (11)	2.0186 (11)	2.0156 (11)	2.0162 (13)		
Fe3—O5^{vii}	2.0200 (11)	2.0186 (11)	2.0156 (11)	2.0162 (13)		
O1—C3	1.245 (2)	1.241 (2)	1.238 (2)	1.236 (2)		
O2—C2	1.2470 (19)	1.2447 (19)	1.2417 (19)	1.240 (2)		
O3—C3^{ix}	1.2641 (19)	1.2645 (19)	1.2660 (19)	1.263 (2)		
O4—C1	1.235 (2)	1.236 (2)	1.235 (2)	1.231 (2)		
O5—C2	1.2618 (19)	1.2624 (19)	1.2631 (19)	1.262 (2)		
O6—C1	1.2638 (19)	1.2616 (19)	1.2610 (19)	1.260 (2)		
C3—O3^{ix}	1.2641 (19)	1.2645 (19)	1.2659 (19)	1.263 (2)		
N11B—C10B	1.451 (7)	1.443 (7)	1.433 (7)	1.427 (8)		
N11B—C10A	1.457 (7)	1.458 (7)	1.449 (7)	1.447 (8)		
N1—C12^{x}	1.449 (6)	1.445 (6)	1.443 (6)	1.443 (7)		
N1—C12	1.449 (6)	1.445 (6)	1.443 (6)	1.443 (7)		

Symmetry code(s): (i) *x*-*y*+1/3, -*y*+2/3, -*z*+1/6; (ii) *x*-*y*, *x*, -*z*; (iii) -*x*+*y*, -*x*, *z*; (iv) -*x*, -*y*, -*z*; (v) -*y*, *x*-*y*, *z*; (vi) *y*, -*x*+*y*, -*z*; (vii) -*x*+*y*-1, -*x*, *z*; (viii) -*y*, *x*-*y*+1, *z*; (ix) -*x*, -*y*+1, -*z*; (x) *y*-2/3, *x*+2/3, -*z*+1/6; (xi) -*y*+1, -*x*+1, -*z*+1/2; (xii) *x*, *x*-*y*+1, -*z*+1/2; (xiii) -*x*+*y*, -*x*+1, *z*; (xiv) -*y*+1, *x*-*y*+1, *z*; (xv) -*x*+*y*, *y*, -*z*+1/2; (xvi) -*x*, -*y*+2, -*z*; (xvii) *y*-1, -*x*+*y*, -*z*; (xviii) -*y*+1, *x*-*y*+2, *z*; (xix) *x*-*y*+1, *x*+1, -*z*; (xx) -*x*+*y*-1, -*x*+1, *z*.

Table 3. Selected hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
(100K)				
N11B—H11A···O1	0.89	2.35	3.079 (6)	138.6
N11B—H11A···O2^{i}	0.89	2.35	3.101 (6)	141.5
N11B—H11B···O2^{ii}	0.89	2.05	2.880 (6)	154.7
C10B—H10D···O6^{iii}	0.96	2.59	3.488 (6)	155.1
C10B—H10F···O3^{iv}	0.96	2.55	3.390 (7)	145.6
N1—H1A···O2^{ii}	0.89	2.13	2.927 (4)	149.1
N1—H1B···O2^{i}	0.89	2.13	2.927 (4)	149.1
(125K)				
N11B—H11A···O1	0.89	2.34	3.073 (6)	139.2
N11B—H11A···O2^{i}	0.89	2.39	3.128 (6)	141.1
N11B—H11B···O2^{ii}	0.89	2.06	2.891 (6)	155.7
C10B—H10D···O6^{iii}	0.96	2.58	3.484 (6)	157.6
C10B—H10F···O3^{iv}	0.96	2.52	3.377 (7)	148.0
N1—H1A···O2^{ii}	0.89	2.14	2.935 (4)	148.6
N1—H1B···O2^{i}	0.89	2.14	2.935 (4)	148.6
(140K)				
N11B—H11A···O1	0.89	2.33	3.072 (6)	140.5
N11B—H11A···O2^{i}	0.89	2.42	3.150 (7)	139.8
N11B—H11B···O2^{ii}	0.89	2.08	2.910 (6)	154.9
C10B—H10D···O6^{iii}	0.96	2.55	3.468 (7)	159.6
C10B—H10F···O3^{iv}	0.96	2.52	3.395 (7)	151.1
N1—H1A···O2^{ii}	0.89	2.14	2.941 (4)	149.3
N1—H1B···O2^{i}	0.89	2.14	2.941 (4)	149.3
(150K)				
N11B—H11A···O1	0.89	2.35	3.085 (8)	140.1
N11B—H11A···O2^{i}	0.89	2.45	3.186 (8)	140.0
N11B—H11B···O2^{ii}	0.89	2.09	2.930 (8)	156.0
N1—H1A···O2^{ii}	0.89	2.15	2.952 (5)	149.1
N1—H1B···O2^{i}	0.89	2.15	2.952 (5)	149.1
(160K)				
N1—H1A···O1^{v}	0.89	2.43	3.174 (9)	141.7
N1—H1A···O1^{vi}	0.89	2.54	3.241 (10)	135.6
N1—H1B···O1^{vii}	0.89	2.15	2.982 (10)	155.8

Symmetry code(s): (i) *x*-*y*+1/3, -*y*+2/3, -*z*+1/6; (ii) -*y*, *x*-*y*+1, *z*; (iii) -*x*+*y*, -*x*+1, *z*; (iv) -*x*, -*y*+1, -*z*; (v) *x*-*y*+1, -*y*+1, *z*+1/2; (vi) *y*, -*x*+*y*, -*z*+1; (vii) -*x*, -*y*+1, -*z*+1; (viii) *x*-*y*+1, *x*+1, -*z*+1.

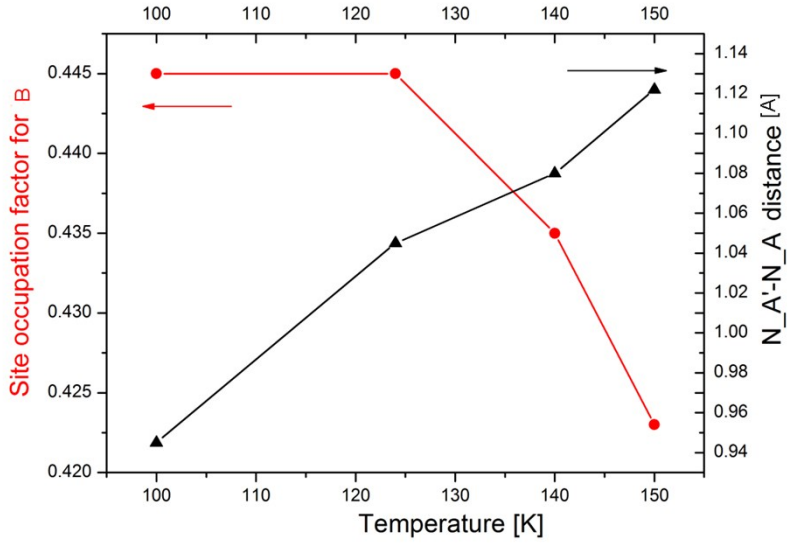

Figure S1. Temperature induced changes in the site occupation factor for B position and the distance between the split nitrogen atoms from A and A' states. The s.o.f for A and A' = (1-s.o.f.(B))/2.

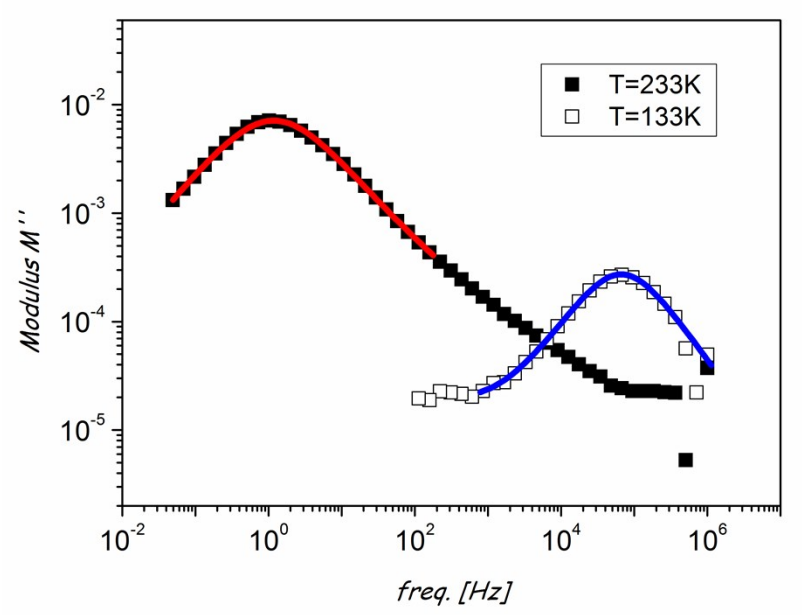

Figure S2: The exemplary fitting of relaxation time.