Dalton Transactions

Electronic Supplementary Information (ESI)

Two-step spin crossover in the mononuclear iron(II) complex $[Fe^{II}(L)_2(NCS)_2]$ (L = 2,5-di-(2-pyridyl)-1,3,4-thiadiazole)

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Additional Illustrations

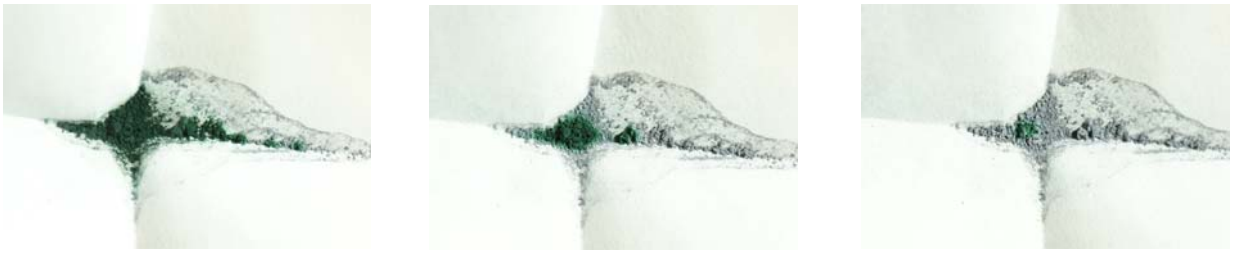

Fig. S1. Colour change of $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ from dark green to bluish grey upon gradual warming of a sample on filter paper after cooling with liquid nitrogen.

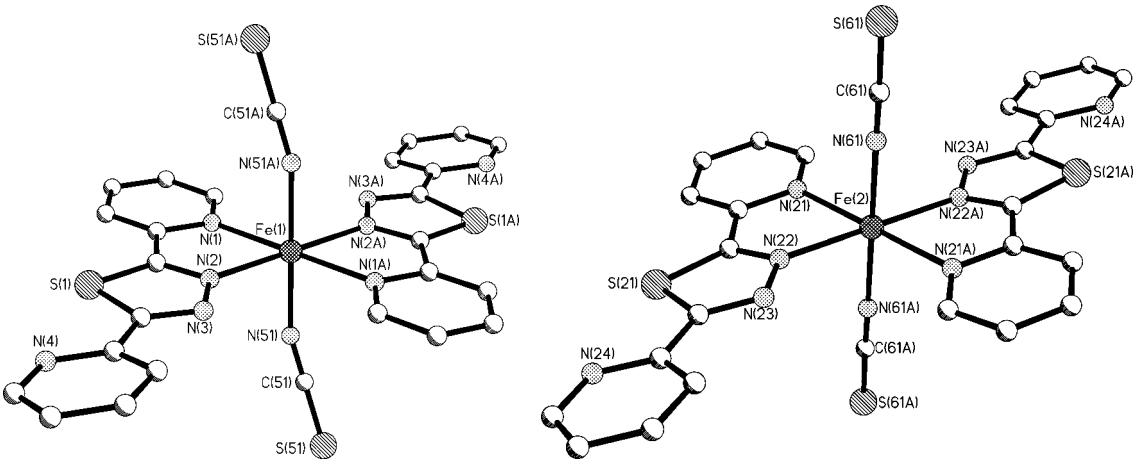

Fig. S2. View of the molecular structures of the two crystallographically independent iron(II) moieties of $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293 K. Hydrogen atoms have been omitted for clarity.

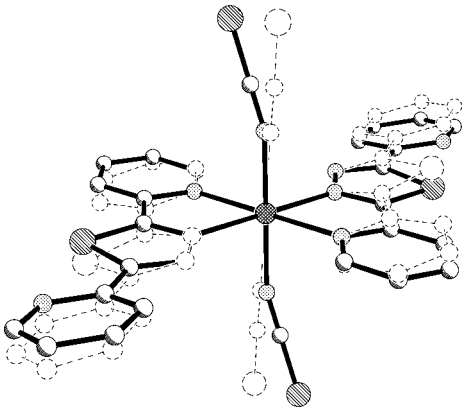

Fig. S3. Superposition of the two crystallographically independent iron(II) moieties of $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293 K: Fe(1) solid lines (HS); Fe(2) dotted line (HS).

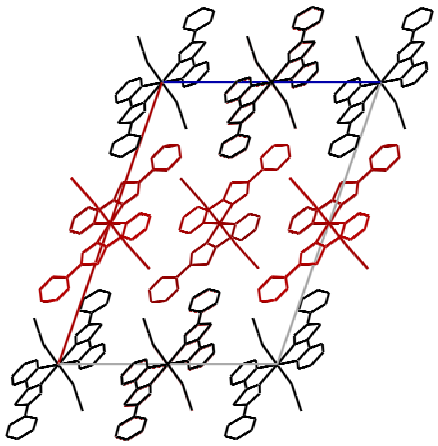

Fig. S4. View along the crystallographic *b* axis of $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293 K: Fe(1) black; Fe(2) red.

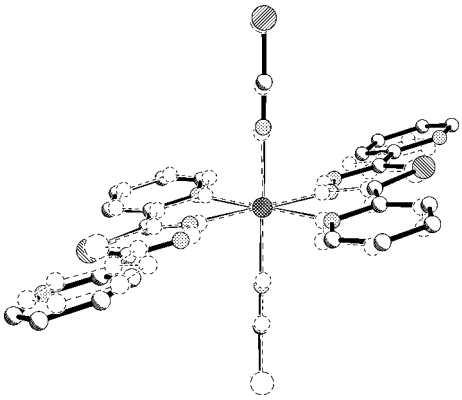

Fig. S5. Superposition of the Fe(2) moieties in the HS state at 293 K (solid lines) and in the LS state at 140 K (dotted lines).

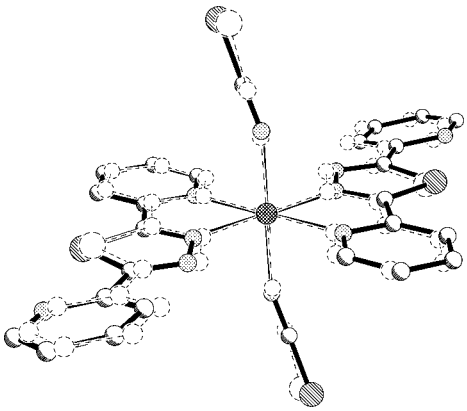

Fig. S6. Superposition of the Fe(1) moieties in the HS state at 140 K (solid lines) and in the LS state at 100 K (dotted lines).

Crystallographic Data

Table S1. Crystallographic data for $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293, 140 and 100 K.

	293 K	**140 K**	**100 K**
Empirical formula	$C_{26}H_{16}FeN_{10}S_4$	$C_{26}H_{16}FeN_{10}S_4$	$C_{26}H_{16}FeN_{10}S_4$
Formula weight [g·mol^{-1}]	652.58	652.58	652.58
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a [Å]	22.937(5)	22.760(5)	22.698(5)
b [Å]	8.0205(16)	7.8903(16)	7.8613(16)
c [Å]	16.694(3)	16.533(3)	16.210(3)
α [°]	90	90	90
β [°]	110.18(3)	110.84(3)	109.89(3)
γ [°]	90	90	90
V [Å^3]	2882.7(10)	2774.9(10)	2719.9(9)
Z	4	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.504	1.562	1.594
μ [mm^{-1}]	0.850	0.883	0.900
Temperature [K]	293(2)	140(2)	100(2)
F(000)	1328	1328	1328
Crystal colour and shape	bluish grey block	dark grey block	dark green block
Crystal size [mm^3]	0.25 × 0.10 × 0.06	0.25 × 0.10 × 0.06	0.25 × 0.10 × 0.06
$\Theta_{min.}$ / $\Theta_{max.}$ [°]	3.06 / 27.47	3.11 / 27.48	3.13 / 27.48
h	–29 → 29	–29 → 28	–29 → 28
k	–10 → 10	–10 → 10	–10 → 10
l	–21 → 21	–21 → 21	–20 → 21
Reflections collected	48179	47697	43709
Independent reflections	6599 [R_{int} = 0.0727]	6352 [R_{int} = 0.0923]	6163 [R_{int} = 0.1104]
Completeness to $\Theta_{max.}$ [%]	99.9	99.8	98.8
Data / restraints / parameters	6599 / 0 / 373	6352 / 0 / 373	6163 / 0 / 374
GOOF	1.049	1.078	1.063
*R*1 / *wR*2 [$I > 2\sigma(I)$]	0.0439 / 0.0855	0.0463 / 0.0966	0.0664 / 0.1614
*R*1 / *wR*2 (all data)	0.0930 / 0.1022	0.0714 / 0.1074	0.0968 / 0.1841
Max. peak / hole [e·Å^{-3}]	0.341 / –0.622	0.523 / –0.562	1.219 / –1.109

Table S2. Selected distances [Å] for $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293, 140 and 100 K.

	293 K (HS)	140 K (HS, LS)	100 K (LS)
Fe(1)–N(1)	2.216(2)	2.215(2)	2.019(3)
Fe(1)–N(2)	2.188(2)	2.176(2)	1.986(3)
Fe(1)–N(51)	2.098(3)	2.087(3)	1.946(3)
Fe(2)–N(21)	2.206(2)	2.011(2)	2.008(3)
Fe(2)–N(22)	2.192(2)	1.986(2)	1.984(3)
Fe(2)–N(61)	2.088(3)	1.940(2)	1.940(3)

Table S3. Selected angles [°] for $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293, 140 and 100 K.

	293 K (HS)	140 K (HS, LS)	100 K (LS)
N(1)–Fe(1)–N(2)	75.15(8)	75.30(8)	80.42(13)
N(1)–Fe(1)–N(2A)	104.85(8)	104.70(8)	99.58(13)
N(1)–Fe(1)–N(51)	91.75(10)	91.38(9)	91.98(13)
N(2)–Fe(1)–N(51)	90.35(9)	91.06(9)	91.40(13)
Fe(1)–N(51)–C(51)	161.5(3)	160.2(2)	168.6(3)
N(21)–Fe(2)–N(22)	75.67(8)	80.75(9)	80.91(13)
N(21)–Fe(2)–N(22A)	104.33(8)	99.25(9)	99.09(13)
N(21)–Fe(2)–N(61)	92.62(9)	91.17(9)	90.84(13)
N(22)–Fe(2)–N(61)	91.52(9)	91.08(9)	91.88(13)
Fe(2)–N(61)–C(61)	175.7(3)	177.8(2)	175.8(3)

Table S4. Structural parameters for $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ at 293, 140 and 100 K.

	293 K		140 K		100K	
	Fe(1)	Fe(2)	Fe(1)	Fe(2)	Fe(1)	Fe(2)
spin state	HS	HS	HS	LS	LS	LS
octahedral volume [Å^3] [a]	13.107	13.031	12.970	10.195	10.250	10.173
average trigonal distortion angle Φ [°] [b]	6.05	5.69	5.88	3.62	3.74	3.56
octahedral distortion parameter Σ [°] [c]	67.8	73.9	68.6	46.0	51.82	47.23
mean octahedral quadratic elongation λ_{oct} [d]	1.024	1.023	1.024	1.009	1.010	1.009

[a] octahedral volume[1]
[b] average trigonal distortion angle $\Phi = \Sigma_1^{24}(|60–\theta_i|)/24$ [$\Phi = 0°$ for an ideal octahedron; θ_i represents the individual trigonal angles of the eight faces of the octahedron][2]
[c] octahedral distortion parameter $\Sigma = \Sigma_1^{12}(|90–\varphi_i|)$ [$\Sigma = 0°$ for an ideal octahedron; φ_i represents the twelve smallest L–M–L angles][3]
[d] mean octahedral quadratic elongation $\lambda_{oct} = \Sigma_1^{6}(l_i/l_0)^2/6$ [$\lambda_{oct} = 1$ for an ideal octahedron; l_0 represents the centre-to-vertex distance of an octahedron with O_h symmetry whose volume is equal to that of the distorted octahedron with distances l_i][4]

Experimental Details

General remarks. All solvents used were laboratory reagent grade. 2,5-Di-(2-pyridyl)-1,3,4-thiadiazole (**L**) was prepared as described in the literature.[5] Elemental analyses were carried out with a Elementar Vario EL analyzer. IR spectra were recorded over the range 4000–400 cm^{-1} using a Nicolet Magna 760 FTIR spectrometer. Single crystal X-ray data were collected using a Rigaku R-AXIS Spider IP area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97[6] and refined against F^2 using all data by full-matrix least-squares techniques with SHELXL-97.[6] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions using a riding model. CCDC 748038 (293 K), 748039 (140 K) and 748040 (100 K) contain the supplementary crystallographic data for the structures reported in this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Variable-temperature cell parameter determination was carried out over the range of 270–100 K in steps of 30 K (270–210 K), 10 K (210–180 and 150–120 K) and 2 K (178–150 K and 120–100 K) by slowly cooling the single crystal. Four frames were measured with a wide scan area allowing an equilibration time of 1 minute. Refined standard cell parameters were noted. Variable-temperature magnetic susceptibility measurements were carried out on a microcrystalline, ground sample using a Quantum Design MPMS*XL* SQUID susceptometer over the range 300–2 K (1.0 T) in both the cooling and heating mode. Mössbauer spectra were recorded using a WissEL alternating constant-acceleration spectrometer on microcrystalline samples. Isomer shifts are given relative to iron metal at ambient temperature. The experimental data were fitted with Lorentzian line shapes using the program Mfit.[7]

Synthesis of $[Fe^{II}(L)_2(NCS)_2]$: Under a protective atmosphere of argon a solution of KSCN (87.5 mg, 900 μmol) in MeOH (4 ml) was added to a cloudy solution of $FeSO_4 \cdot 7H_2O$ (125.0 mg, 450 μmol) in MeOH (4 ml). After stirring at room temperature for 5 minutes, the reaction mixture was evaporated to dryness under reduced pressure. The residue was triturated with MeOH (10 ml) and the resulting suspension was filtered. The clear MeOH solution of $Fe(NCS)_2$ thus obtained was added completely to a suspension of **L** (216.3 mg, 900 μmol) in MeOH (70 ml), whereupon a dark red solution formed. On standing at room temperature overnight without stirring a blue crystalline solid formed, which was filtered off, washed with MeOH (2 × 2 ml) and dried in vacuo. Single crystals suitable for X-ray diffraction and an analytically pure, crystalline sample of $[Fe^{II}(\mathbf{L})_2(NCS)_2]$ were obtained straight from the reaction mixture. Yield: 156 mg (239 μmol, 53

%). Elemental analysis (%) found: C 47.62, H 2.12, N 21.52, S 19.53; calcd. for $C_{26}H_{16}N_{10}S_4Fe$ [Fe^{II}(**L**)$_2$(NCS)$_2$] (M = 652.57 g·mol^{-1}): C 47.86, H 2.47, N 21.46, S 19.65. IR (diamond ATR): $\tilde{\upsilon}$ = 3086.2, 3054.9, 3009.4, 2105.5, 2050.5 (vs), 1597.6, 1584.0, 1567.1, 1476.2, 1457.5, 1442.4, 1431.2 (s), 1406.7, 1317.8, 1304.8, 1252.2, 1159.1, 1086.3, 1055.4, 1025.4 (s), 1013.8, 1002.2, 970.9, 906.4, 813.7, 784.3 (vs), 739.5, 715.2 (s), 648.5, 636.7, 608.4, 479.0, 414.8, 402.0 cm^{-1}. IR (ZnSe ATR): $\tilde{\upsilon}$ = 3084.7, 3052.9, 3009.0, 2049.9 (vs), 1596.3, 1582.7, 1566.1, 1475.3, 1456.8, 1441.0, 1429.5 (s), 1406.2, 1316.9, 1303.5, 1249.7, 1158.3, 1085.2, 1054.0, 1024.4 (s), 1013.0, 1000.8, 970.6, 812.4, 782.9 (vs), 738.4, 713.9 (s).

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