Supporting Information

Divergent Coordination Chemistry: Parallel Synthesis of [2 × 2] Iron(II) Grid-Complex Tauto-Conformers

Bernhard Schäfer, Jean-François Greisch, Isabelle Faus, Tilmann Bodenstein, Ivan Šalitroš, Olaf Fuhr, Karin Fink, Volker Schünemann, Manfred M. Kappes, and Mario Ruben*

anie_201603916_sm_miscellaneous_information.pdf
Table of content

1. Experimental section ................................................................. S4
2. Ligand synthesis ................................................................. S4
  2.1. Ethyl 6-(pyrazol-1-yl)picolinate (A) ....................................... S5
  2.2. 6-(pyrazol-1-yl)picolinic acid (B) ....................................... S6
  2.3. 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (L) ................................... S7
3. Synthesis of [2x2]-Fell grid complexes 1S and 1C .......................... S16
  3.1. ESI MS investigation of the reaction mixture of 1 ...................... S17
  3.2. 1H NMR spectroscopic investigation of the reaction mixture of 1 .......................... S18
  3.3. Purification of the reaction product by recrystallization ................. S19
  3.4. Isomerization of the S-[2x2] grid complex isomers under microwave irradiation .................. S20
4. X-ray diffraction analysis ...................................................... S21
  4.1. Detailed structural discussion of 1S and 1C ............................ S22
5. Magnetic susceptibility measurements ....................................... S26
6. Nuclear resonance vibrational spectroscopy (NRVS), nuclear forward scattering (NFS), and calculation of the partial density of iron phonon states (pDOS) ................................................................. S26
7. Mass spectrometry / ion mobility mass spectrometry as a tool for distinguishing complex isomers S30
8. Quantum chemical calculations ................................................ S33
9. References .............................................................................. S37

List of figures

SIFig.1 Synthesis of ligand L .......................................................... S4
SIFig.2 1H NMR spectrum of ethyl 6-(pyrazol-1-yl)picolinate A ...................... S5
SIFig.3 1H NMR spectrum of 6-(pyrazol-1-yl)picolinic acid B .......................... S6
SIFig.4 Mass spectrum of ligand L .................................................. S7
SIFig.5 1H NMR spectrum of L ..................................................... S8
SIFig.6 HH-cosy NMR spectrum of L .................................................. S9
SIFig.7 13C NMR spectrum of L ..................................................... S10
SIFig.8 dept135 NMR spectrum and 13C NMR spectrum of L .............................. S11
SIFig.9 HSQC NMR spectrum of L .................................................. S12
SIFig.10 HMBC NMR spectrum of L .................................................. S13
SIFig.11 HMBC NMR spectrum of L .................................................. S14
SIFig.12 NOESY NMR spectrum of L .................................................. S15
SIFig.13 ESI mass spectrum of the synthetic mixture of 1 ............................. S17
SIFig.14 1H NMR spectrum of the synthetic mixture 1 ................................ S18
SIFig.15 Purification of the reaction product 1 by recrystallization: $^1$H NMR spectra .......................... S19
SIFig.16 Isomerization of the grid complex isomers under microwave irradiation: $^1$H NMR spectra...... S20
SIFig.17 Molecular structure of a [2x2]-S-grid complex [Fe$_4$L$_4$](CF$_3$SO$_3$)$_8$ (1S) .......................... S23
SIFig.18 Molecular structure of a [2x2]-C-grid complex [Fe$_4$L$_4$](CF$_3$SO$_3$)$_6$F$_3$ (1C) .......................... S23
SIFig.19 Comparison of structural parameters of the grid isomers 1C and 1S .......................... S24
SIFig.20 Experimental nuclear resonance vibrational Spectroscopy (NRVS) data of 1S .......................... S27
SIFig.21 Experimental nuclear forward scattering (NFS) data of 1S .......................... S27
SIFig.22 Experimentally determined partial density of states (pDOS) obtained from the NRVS data of 1S... .......................... S28
SIFig.23 Simulated pDOS based on density functional theory calculations for 1S .......................... S28
SIFig.24 HR ESI Mass spectrum of the synthetic solution of 1 .......................... S30
SIFig.25 Arrival time distribution (ATD) for the species Fe$_4$C$_{96}$N$_{40}$H$_{58}$$_{2^+}$ ([Fe$_4$L$_4$-6H]$^{2+}$) .......................... S31
SIFig.26 Comparison of the experimental cross-sections with the computed ones for the Fe$_4$C$_{96}$N$_{40}$H$_{58}$$_{2^+}$ complex .......................... S32
SIFig.27 Computed structures for the intermediate state IS .......................... S33
SIFig.28 Model complexes for the two slightly differently coordinated Fe(II) centres in 1C .......................... S34
SIFig.29 Energies of the five lowest electronic states of model 1 in dependence of a magnetic field applied along the magnetic main axis .......................... S35
SIFig.30 Energies of the five lowest electronic states of model 2 in dependence of a magnetic field applied along the magnetic main axis .......................... S36
SIFig.31 Magnetic susceptibility of 1C, the measured data is compared to a direct simulation from five different sets of parameters using a spin Hamiltonian .......................... S37

List of tables
SiTab.1 Peak assignment of the ESI-MS of the synthetic mixture.......................... S17
SiTab.2 Crystal data and structure refinement for crystals of L, 1C, and 1S.......................... S21
SiTab.3 Bond lengths (pm), significant angles (°) and naming scheme adopted for iron coordination sphere.......................... S22
SiTab.4 Parameter sets used in the simulation of the magnetic susceptibility for 1C employing a spin Hamiltonian.......................... S37
1. **Experimental section**

**General:** Purchased chemicals and solvents as pyrazole, ethyl 6-bromopyridine-2-carboxylate, 1,2,4,5-benzenetetramine tetrahydrochloride, and polyphosphoric acid were obtained from commercial suppliers and used without purification. Diglyme was distilled of CaH$_2$. $^1$H and $^{13}$C NMR, COSY, HMQC correlation measurements were recorded using a Bruker Ultrashield plus 500 spectrometers with solvent-proton as internal standard. Elemental analyses were carried out on a Vario Micro Cube. FT-IR spectra were measured using KBr pellets (Magna FTIR 750, Nicolet) in the region of 4000–400 cm$^{-1}$. Mass data were acquired with a MicrOTOF-Q II Bruker for ESI-TOF. Travelling wave ion mobility mass spectrometry (see below: SI7)

2. **Ligand synthesis**

The preparation of the potassium pyrazolate salt and its reaction with the ethyl 6-bromopicolinate was carried out in a one-pot reaction. The ethyl 6-(pyrazol-1-yl)picolinate A could be isolated in a reasonably good yield of 65% after two steps. Ester cleavage under basic conditions gave 6-(pyrazol-1-yl)picolinic acid. Finally, two equivalents of this acid B and one equivalent of 1,2,4,5-benzenetetramine tetrahydrochloride took part in a condensation reaction in polyphosphoric acid at 220°C in the presence of air yielding 90 % of the product. With respect to all four reaction steps ligand L was isolated in about 54 % yield.

![Synthesis of ligand L](image)
2.1. Ethyl 6-(pyrazol-1-yl)picolinate (A)

A 250-mL-Schlenk-flask was charged with a magnetic stirrer bar and three vacuum-argon cycles were applied. Diglyme (100 mL, freshly distilled from CaH₂) was transferred to the flask. Potassium (1.07 g, 27.36 mmol, 0.85 eq.) was added followed by 1H-pyrazol (2.24 g, 32.9 mmol, 1 eq.). Hydrogen evolution was observed. The reaction was stirred and warmed up to 60 later to 70 °C overnight. After 14 hours, ethyl 6-bromopyridine-2-carboxylate (5 g, 21.7 mmol) was added at once and heated at 110°C for two days. The reaction was stopped. The solvent was removed by distillation. The remaining product was dissolved in CH₂Cl₂ and ice-water, followed by extraction with 3 x 50 mL CH₂Cl₂. The combined organic layer were dried over Na₂SO₄, filtered, solvent was removed by rotary evaporation. The product was dried at vacuo and used without further purification. Yield: 3.068 g (65%). ¹H-NMR (500 MHz, CDCl₃): δ=8.70 (d, 1H, ³J=2.6Hz, pz), 8.18 (d, 1H, ³J=1.0Hz, ³J=7.9Hz, py), 7.98 (d, 1H, ³J=1.2Hz, ³J=7.4Hz, py), 7.95 (dd, 1H, ³J=7.1Hz, ³J=14.9Hz, py), 7.75 (s, 1H, ³J=1.2Hz, pz), 6.48 (dd, 1H, ³J=1.7Hz, ³J=2.6Hz, pz), 4.47 (q, 2H, ³J=7.2Hz, CH₂), 1.45 (t, 3H, J=7.1Hz, CH₃) ppm.

![SIFig. 2]¹H NMR spectrum of ethyl 6-(pyrazol-1-yl)picolinate A in CDCl₃
2.2. 6-(pyrazol-1-yl)picolinic acid (B)

A (3.065 g, 14.1 mmol) was suspended and refluxed in a NaOH solution (2 mol/dm$^3$, 15 mL) and EtOH(20mL) for 2h. EtOH was removed by rotary evaporation and water (10 mL) was added. The pH value was adjusted to 3 with aqueous HCl. A white precipitate appeared and was collected by filtration. The white solid was washed with 3 x 2 mL of water and dried at 80°C in an oven. The product was used without further purification for the next reaction step. Yield: 92 %, 2.453 g, 12.97 mmol. $^1$H-NMR (500 MHz, (CD$_3$)$_2$SO): δ = 13.33 (s, 1H, COOH) ppm, 8.78 (d, 1H, $^3$J=2.5Hz, pz), 8.17 (m, 2H, py), 7.99 (d, 1H, $^4$J=1.5Hz, $^3$J=6.9Hz, py), 7.87 (d, 1H, $^3$J=1.1Hz, pz), 6.63 (dd, 1H, $^3$J=1.9Hz, $^3$J=2.4Hz, pz) ppm.

SIFig.3 $^1$H NMR spectrum of 6-(pyrazol-1-yl)picolinic acid B in CDCl$_3$
2.3. 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (L)

B (6-(pyrazol-1-yl)picolinic acid, 3.824 g, 20.21 mmol, 2.1 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (2.734 g, 9.62 mmol, 1 eq) and polyphosphoric acid (30 mL) was gently heated at 130°C until the polyphosphoric acid got viscous enough to allow the stirring with a magnetic stirrer bar. Then the temperature was set to 200°C. Caution: gas evolution leads to foam formation. After 4 h at 200°C the reaction was stopped, allowed to cool below 100°C and poured into crushed ice (100 g). The flask was rinsed with water. The aqueous suspensions were combined. The precipitate was filtered off. The solid was suspended in water and the pH value was altered to 10 using NaOH (3M). After the suspension was stirred for 1 h the precipitate was collected again. Afterward it was re-suspended in water, stirred, the pH was set to about 4 using HCl (1 mol/L). The precipitate was washed with water (1 L) later with MeOH (100 mL). The crude product was suspended in DMSO (20 mL), stirred for 1 h, and collected by filtration. Finally, the precipitate was suspended in MeOH (200 mL), stirred overnight, collected by filtration, dried in an oven at 120°C for 3 h and then at vacuo (T=90°C) over the weekend (60 h). Yield: 4.113 g (91%)

1H NMR (500 MHz, (CD$_3$)$_2$SO): δ=13.02 (s, 2H, NH-S), 12.96 (s, 2H, NH-C), 9.30 (d, 2H, J=2.3Hz, H5), 9.27 (d, 2H, J=2.3Hz, H5), 8.25 (d, 4H, J=0.7Hz, J=7.6Hz, H7), 8.17 (t, 4H, J=1.3Hz, J=8.0Hz, H8), 8.06 (s, 1H, Hβ), 8.01 (d, 4H, J=2.1Hz, J=8.0Hz, H9), 7.90 (s, 4H, H3), 7.87 (s, 2H, Hx), 7.72 (s, 1H, Hγ), 7.62 (dd, 4H, J=1.7Hz, J=2.5Hz, H4) ppm.

13C-NMR (126 MHz, (CD$_3$)$_2$SO): δ=151.46 (C11), 150.99 (C10), 147.49 (C6), 143.12 (C12-S), 143.10 (C3), 142.20 (C12-C), 141.33 (C8), 134.04 (C13-C), 133.14 (C13-S), 128.72 (C5), 128.64 (C5), 119.22 (C7), 119.14 (C7), 112.59 (C9), 108.72 (C4), 108.63 (Cβ), 100.22 (Cα), 92.40 (Cγ) ppm.

Elemental analysis [L*1.5H$_2$O with (C$_48$H$_38$N$_{20}$O$_3$)$_0.5$ (471.49)]: calc. C 61.14, H 4.06, N 29.71; found C 60.97, H 3.51, N 29.53; ES-MS (in DMSO): m/z= 445.19 (20%, [M+H]$^+$), m/z= 467.18 (100%, [M+Na]$^+$), m/z= 911.36 (67%, [2M+Na]$^+$); FT-IR (KBr): ν=3439, 3099.12, 1641, 1600, 1575, 1521, 1472, 1394, 1339, 1291, 1170, 1150, 1137, 1040, 992, 973, 937, 915, 882, 811, 762, 739, 711, 651, 624, 593, 521, 418 cm$^{-1}$.

In order to investigate L in solution a sample was subjected to 1H NMR spectroscopy, SIFig.5, where the expected signal sets for the peripheral pyrazol rings (green) as well as for the neighboring pyridine rings (blue) could be identified. The central benzene moiety exhibits three singlet signals for the two H atoms with integral ratios of 1:2:1 (SIFig.5C inset, red/black). Within the accuracy of 1H-NMR spectroscopy, the observed pattern is attributed to the presence of two tauto-conformers existing in a 1:1 ratio in solution. While the two benzene-based H atoms of the S conformer, called H$^S$, are chemically equivalent with an overall integrated value for 2H (SIFig.5C inset, red/black), the same two H atoms in the C conformer, here called H$^C$ and H$^γ$, are not equivalent and therefore lead to two separated singlet signals with integration values of 1 H atom each (SIFig.5C, red). Additional evidence for an 1:1 ratio of the S and C conformers on the NMR timescale was found in the signal of the
imidazole NH group (SI Fig.5C, purple) at about 13 ppm, which is split into two singlets; one coming from each tauto-conformer with overall integration values of four H-atoms in total. The color code of the $^1$H NMR resonances in SI Fig.5 is used to visually assign the respective H atoms in the structural formulas in SI Fig.5B:

**SI Fig.5** A) $^1$H NMR spectrum of L in D$_6$-DMSO; B) The structural formulas of C- and S-conformation of the ligand L are depicted, deconvoluting into S- and C-grid isomers up on coordination of Fe$^{II}$ ions. B) the ratio of C- and S-conformation of ligand in a solution of D$_6$-DMSO at 300K was determined to be one ($^1$H-NMR experiment). The H-signals of the central benzene ring are chemically equivalent for the S- ($H^\alpha$) but not equivalent for the C-conformation ($H^\beta$, $H^\gamma$) of the free grid ligand. The colour code of the $^1$H NMR resonances is visually assigned to the corresponding H atoms of the two tauto-conformers $\alpha_{15}$ and $\alpha_{20}$.
SI Fig. 6 HH-cosy NMR spectrum of L in deuterated DMSO and the employed numbering scheme.
SI Fig. 7 $^{13}$C NMR spectrum of L in deuterated DMSO and the employed numbering scheme
SIFig. 8 top: dept135 NMR spectrum, middle: $^{13}$C NMR spectrum of L in deuterated DMSO and bottom: the employed numbering scheme
SI Fig. 9 HSQC NMR spectrum of L in deuterated DMSO and the employed numbering scheme
SI Fig. 10 HMBC NMR spectrum of L in deuterated DMSO and the employed numbering scheme
SIFig.11 HMBC NMR spectrum of L in deuterated DMSO and the employed numbering scheme
SIFig. 12 NOESY NMR spectrum of L in deuterated DMSO and the employed numbering scheme
3. **Synthesis of [2x2]-Fe<sup>II</sup> grid complexes 1S and 1C**

2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d’]diimidazole (L) (0.2 g, 0.424 mmol, 1 eq., M·1.5H₂O) was suspended in freshly distilled CH₃CN (50 mL) sonicated and then degassed with argon. Afterwards Fe(DMSO)₄(CF₃SO₃)₂ (0.349 g, 0.424 mmol, 1 eq.) was added. The reaction was heated at 50°C for 14 hours under Ar atmosphere. It was allowed to cool to room temperature and filtered. The filtrate was reduced to about 5 mL. The product was precipitated by the addition of diethyl ether (30 mL) and collected by centrifugation (4000 Hz, 10 min). The ether was decanted and completely removed using pipette. The precipitate was dried at vacuo. Yield: m=0.326g, 96%. \(^\text{1H-NMR (500 MHz, CD₃CN): }\delta=68.3 (c), 66.7 (c), 65.0 (c), 62.7 (c), 58.3 (s), 56.3 (c), 54.0 (s), 53.2 (s), 48.7 (s), 42.4 (c), 37.0 (s), 33.5 (c), 30.5 (s), 28.6 (c), 20.4 (s), 15.5 (NH-c), 14.5 (NH-s) ppm.\)

The 1S grid complex isomer was isolated after several re-crystallization cycles: diisopropyl ether was allowed to diffuse into the nitromethane solution of the reaction product and the crystals were collected. After at least three cycles the 1S isomer was purified. Elemental analysis 1S [Fe₄L₄Tf₅·14H₂O with C₄₀H₃₂N₄₆O₂₅S₁₄Fe₄ (3445.94 g/mol): calc. (found) C, 36.25 (36.21); H, 2.69 (2.78); N, 16.26 (15.95); S, 7.44 (7.43). \(^\text{1H-NMR (500 MHz, CD₃CN): }\delta=54.0, 50.0, 48.7, 45.9, 34.2, 27.1, 21.7, 13.8 ppm.\)

FT-IR (KBr): v=3454, 3121, 2970, 2926, 1619, 1584, 1529, 1496, 1456, 1399, 1356, 1318, 1280, 1253, 1227, 1168, 1055, 1030, 988, 953, 895, 809, 765, 668, 639, 576, 518 cm⁻¹. The 1C isomer was isolated starting from 1S, which was dissolved in nitromethane. This solution was degassed with argon, heated in a micro-wave oven at 100°C for 30 min and allowed to cool to room temperature. The solvent was removed. Fractionized crystallization of 1C was accomplished using diisopropyl ether diffusing into a CH₃CN solution. Elemental analysis 1C [Fe₄L₄Tf₅·6H₂O·C₆H₁₂O with C₁₁₀H₇₈O₁₈N₄₀O₂₂S₁₄Fe₄ (4545.94 g/mol): calc. (found) C, 35.31 (35.34); H, 3.34 (3.35); N, 15.73 (15.72); S, 17.75 (17.77). \(^\text{1H-NMR (500 MHz, CD₃CN): }\delta=70.7, 66.5, 64.0, 61.9, 57.8, 43.6, 40.98, 10.2 ppm.\)

FT-IR (KBr): v=3437, 3120, 3085, 2973, 2932, 1616, 1583, 1559, 1528, 1495, 1457, 1400, 1349, 1321, 1279, 1254, 1226, 1165, 1085, 1057, 1030, 994, 952, 888, 842, 810, 764, 739, 715, 668, 639, 575, 518 cm⁻¹.\)

A \(^{57}\)Fe containing sample of 1S was prepared similar as described above starting from \(^{57}\)Fe(DMSO)₄(CF₃SO₃)₂ which was prepared from \(^{57}\)Fe as follows: \([\text{Fe(H₂O)}₄\text{Cl₂}]\). \(^{57}\)Fe (0.025g) was placed into a flask together with a few drops of water and cooled with ice (T=0 °C). The addition of concentrated aqueous HCl (0.1 cm³) was followed by the evolution of hydrogen. The reaction was stirred over night until the iron was dissolved completely. The water was removed under reduced pressure at a rotary evaporator almost to dryness. The white/off-white powder was suspended in diethyl ether and decanted, this was carefully repeated twice. The white solid, \([\text{Fe(H₂O)}₄\text{Cl₂}]\), was dried at vacuo. Yield 80-90%. \(^{57}\)Fe(DMSO)₄(CF₃SO₃)₂: \([\text{Fe(H₂O)}₄\text{Cl₂}] (0.153g, 0.769mmol, 1eq)\) was dissolved in deaerated CH₃CN (15 mL) and MeOH (4 mL). Ag(CF₃SO₃)₂ (0.395 g, 1.54 mmol, 2eq) was added and stirred for 1 h in darkness. The precipitated AgCl was removed by filtration and a slightly yellowish clear solution was gained. The solvent was removed completely and DMSO (1 mL) was added. The reaction product was precipitated by the addition of dried and freshly distilled diethyl ether, filtered and dried at vacuo. Yield 0.314 g.
3.1. ESI MS investigation of the reaction mixture of 1

(The high-resolution mass spectrometry and the ion mobility mass spectrometry are described below in the SI chapter 7.)

A drop of the synthetic solution was investigated by ESI-mass spectrometry in acetonitrile, SIFig.13 and SITab.1.

SIFig.13 a) ESI mass spectrum of the synthetic mixture of 1 sprayed from CH₃CN, b) comparison of the experimental and the simulated isotope pattern of [Fe₄L₄-3H]^{3+}, [Fe₆C₃0H₆3N₄0]^{5+} with a difference of the experimental and the simulated pattern of less than 3 mDa;

SITab.1 Peak assignment of the ESI-MS of the synthetic mixture sprayed from CH₃CN

| m/z      | intensity (%) | charge | Formula                  | mass   | Calculated | Δ / mDa |
|----------|---------------|--------|--------------------------|--------|------------|---------|
| 1447.526 | 31            | 2      | Fe₄L₄(Tf)₆               | 2894.08| 1447.539   | 13      |
| 1372.546 | 14            | 2      | Fe₄L₄(Tf)₅-3H            | 2744.12| 1372.559   | 13      |
| 1297.565 | 9             | 2      | Fe₄L₄(Tf)₄-2H            | 2594.16| 1297.579   | 14      |
| 915.364  | 12            | 3      | Fe₄L₄(Tf)₃               | 2745.12| 915.375    | 11      |
| 865.378  | 19            | 3      | Fe₄L₄(Tf)₃-H             | 2595.16| 865.388    | 10      |
| 815.393  | 89            | 3      | Fe₄L₄(Tf)₃-2H            | 2445.2 | 815.401    | 8       |
| 765.407  | 27            | 3      | Fe₄L₄(Tf)₃-3H            | 2295.2 | 765.415    | 8       |
| 715.419  | 29            | 3      | Fe₄L₄(Tf)₃-4H            | 2145.3 | 715.428    | 9       |
| 665.434  | 12            | 3      | Fe₄L₄(Tf)₃-H             | 1995.3 | 665.442    | 8       |
| 599.049  | 19            | 3      | Fe₄L₄(Tf)₂-3H            | 1797.1 | 599.056    | 7       |
| 549.065  | 98            | 3      | Fe₃L₃(Tf)₂-2H            | 1647.2 | 549.069    | 4       |
| 536.818  | 70            | 4      | Fe₃L₄(Tf)₂-3H            | 2146.3 | 536.823    | 5       |
| 499.079  | 100           | 4      | Fe₃L₄(Tf)₂-H             | 1996.3 | 499.083    | 4       |
| 451.002  | 4             | 3      | Fe₃L₂(Tf)₂-H             | 1353.0 | 451.004    | 2       |
| 399.670  | 45            | 5      | Fe₃L₃-3H                 | 1997.3 | 399.668    | 2       |
| 374.568  | 67            | 4      | Fe₃L₃-2H                 | 1498.3 | 374.564    | 4       |

L : C₂₄H₁₆N₁₆0, Tf : CF₃SO₃
3.2. $^1$H NMR spectroscopic investigation of the reaction mixture of 1

1. Paramagnetically shifted
2. Two species present
3. Highly symmetric

SI_Fig. 14 $^1$H NMR spectrum of the crude reaction mixture after the grid complex formation in CD$_3$CN; each isomer of the [2x2] Fe$_4$ grid complex, 1S and 1C, gives a signal set in the spectrum, the C-type grid shows eight small signals (12%) and the S-type grid complex seven bigger signals (88%) the resonances of the H signals are paramagnetically shifted, the signals of the NH functions have a chemical shift of about 14.5 and 15.5 ppm.
3.3. Purification of the reaction product by recrystallization

Crude product in CD$_3$CN

Three re-crystallization cycles do remove the second component in CD$_3$NO$_2$

SIFig.15 Purification of the reaction product by recrystallization: $^1$H NMR spectrum of 1 top: reaction mixture, bottom: 1S after re-crystallization

The reaction product was re-crystallized at least three times from nitromethane and diisopropylether to remove the minor second component and to gain crystals suitable for X-ray diffraction. The crystals had to be handled quickly after removal of the mother liquid. It was noticed that they easily burst while they are dipped into N-patrone grease as a reaction of physical stress being moved from the tube to the goniometer head. The reason for this may be the loss of crystal-solvent.
3.4. Isomerization of the S-[2x2] grid complex isomers under microwave irradiation

5.7 mg in CD$_3$NO$_2$

SI Fig. 16 Isomerization of the S-[2x2] grid complex isomer under microwave irradiation, $^1$H NMR spectrum of 1S before (top) and after microwave irradiation
4. X-ray diffraction analysis

Single crystal X-ray diffraction data were collected on a STOE IPDS 2T diffractometer with graphite monochromated Mo-Kα radiation (0.71073 Å). Using Olex2,[1] the structure was solved with the ShelXS[2] structure solution program using Direct Methods and refined with the ShelXL[2] refinement package using Least Squares minimisation. Refinement was performed with anisotropic displacement factors for all non-hydrogen atoms (disordered atoms were refined isotropically). Hydrogen atoms were modelled on idealized positions.

Crystals suitable for X-ray diffraction were prepared
a) for the 1C grid complex from acetonitrile and diisopropyl ether,

Crystals suitable for X-ray diffraction were prepared
b) for the 1S grid complex from nitromethan and disisopropyl ether by fractionized crystallization.

### Table 2: Crystal data and structure refinement for crystals of L, 1C, and 1S

|            | L          | 1C         | 1S          |
|------------|------------|------------|-------------|
| Moiety     | C_{24}H_{16}N_{10}*(C_{3}H_{7}NO) | C_{48}H_{32}Fe_{2}N_{20} 5(CF_{3}O_{2}S), 3(F), 2(C_{3}H_{7}N), O | C_{96}H_{64}Fe_{4}N_{40}, 8(CF_{3}O_{2}S), 12(CH_{3}NO), C_{2}H_{4}O |
| Empirical  | C_{30}H_{32}N_{12}O_{2} | C_{48}H_{32}Fe_{2}N_{20}O_{10}S_{10} | C_{96}H_{64}Fe_{4}N_{40}, 8(CF_{3}O_{2}S), 12(CH_{3}NO), C_{2}H_{4}O |
| Formula    | 590.66 | 2901.73 | 4028.52 |
| Temperature/K | 180.2 | 180.2 | 180.2 |
| Crystal system | monoclinic | orthorhombic | monoclinic, |
| Space group | P2_1/c | Pbcn | C2/c |
| a / Å     | 11.0951(8) | 29.9052(9) | 28.2661(10) |
| b / Å     | 9.4388(4) | 25.8869(12) | 23.1942(9) |
| c / Å     | 14.7982(10) | 21.0840(6) | 26.8190(9) |
| α/°       | 90.00 | 90 | 90 |
| β/°       | 109.590(5) | 90 | 102.911(3) |
| γ/°       | 90.00 | 90 | 90 |
| Volume/Å³ | 1460.03(16) | 16322.2(10) | 17138.3(11) |
| Z          | 2 | 4 | 4 |
| ρcalc/mg/mm³ | 1.344 | 1.181 | 1.561 |
| μ/mm⁻¹    | 0.091 | 0.494 | 0.549 |
| F(000)    | 620.0 | 5872.0 | 8200 |
| Crystal size/mm³ | 0.23 × 0.18 × 0.18 | 0.2 × 0.18 × 0.17 | 0.28 × 0.20 × 0.18 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection | 5.22 to 51.28° | 4.378 to 47.998° | 4.128 to 49.410° |
| Index ranges | -13 ≤ h ≤ 11, -11 ≤ k ≤ 9, -17 ≤ l ≤ 17 | -32≤h≤34, -22≤k≤29, -24≤l≤22 | -33≤h≤33, -27≤k≤24, -25≤l≤31 |
| Reflections collected | 8503 | 43048 | 30899 |
| Independent reflections | 2742 [Rint = 0.0333, R_{sigma} = 0.0334] | 12749 [Rint = 0.1524, R_{sigma} = 0.1706] | 14073 [Rint = 0.0579, R_{sigma} = 0.0733] |
| Data/restraints/parameters | 2742/0/233 | 12749/25/783 | 14073 / 14 / 1135 |
| Data completeness | 0.993 | 0.994 | 0.963 |
| Goodness-of-fit on F² | 1.019 | 0.862 | 1.029 |
| Final R indexes [I>2σ(I)] | R₁ = 0.0435, wR₁ = 0.1052 | R₁ = 0.1040, wR₁ = 0.2495 | R₁ = 0.0828, wR₁ = 0.2294 |
| Final R indexes [all data] | R₁ = 0.0633, wR₁ = 0.1133 | R₁ = 0.2165, wR₁ = 0.3016 | R₁ = 0.1281, wR₁ = 0.2604 |
| Largest diff. peak/hole / e Å⁻³ | 0.42/0.22 | 0.72/0.70 | 1.167 / -0.813 |
| CCDC number | 1436806 | 1436807 | 1436808 |
4.1. Detailed structural discussion of 1S and 1C

SITab.3 Bond lengths (pm), significant angles (°) and naming scheme adopted for iron coordination sphere

| [2x2]Fe₄ grid isomer | 1S | 1C |
|-----------------------|----|----|
| T (K)                 | 180| 180|
| Fe(1)-N(18)'         | 190.6(5) | 214.5(8) |
| Fe(1)-N(3)           | 190.8(5)  | 217.6(8) |
| Fe(1)-N(1)           | 196.6(5)  | 225.0(9) |
| Fe(1)-N(20)'         | 196.9(6)  | 222.9(8) |
| Fe(1)-N(4)           | 198.2(4)  | 212.4(8) |
| Fe(1)-N(17)'         | 201.1(5)  | 220.8(9) |
| Fe(2)-N(13)          | 191.0(5)  | 211.0(9) |
| Fe(2)-N(8)           | 191.4(5)  | 212.8(9) |
| Fe(2)-N(11)          | 194.4(6)  | 219.4(11) |
| Fe(2)-N(10)          | 195.4(5)  | 221.0(8) |
| Fe(2)-N(7)           | 197.7(4)  | 215.0(8) |
| Fe(2)-N(14)          | 202.8(5)  | 219.4(8) |
| N(1)-Fe(1)N(4)       | 160.22(19)| 146.4(3) |
| N(20)′-Fe(1)-N(17)′  | 159.97(19)| 145.0(3) |
| N(11)-Fe(2)-N(14)    | 160.2(2)  | 146.0(3) |
| N(10)-Fe(2)-N(7)     | 160.7(2)  | 147.0(3) |
| ΣFe1                | 87   | 167 |
| ΣFe2*              | 85   | 152 |
| Colour              | Red  | Red |
| Spin Status         | LS   | HS  |

* \( \sum = \sum_{i=1}^{12} |\phi_i - 90^°| \) \( \phi_i \) is an N–Fe–N octahedron angle with two N atoms in cis.

Single crystals of the so purified grid complex were grown from nitromethane/ diisopropyl ether and investigated by X-ray diffraction. The experiment revealed the anticipated screw-like molecular structure of the proposed [2x2]Fe-grid complex 1S in the solid state (SiFig.17). The S-grid complex crystallizes in the monoclinic space group C2/c. The unit cell contains four grid complexes while the asymmetric unit consists of a [Fe₂L₂] moiety. The four FeII ions are situated at the corners of a square in a distorted octahedral \( \{N_{6}\} \) ligand environment that is composed of two orthogonal tridentate subunits of two different L ligands. The eight triflate anions form H-bonds to the NH functions of the imidazole units present in the ligand backbone. At 180 K four of the FeII ions have Fe-N bond lengths with typical values for the LS state (average bond lengths d [Å]: Fe1-N 1.96, Fe2-N 1.95, Si-Tab. 3). Other indicators of the spin state in related FeII-bis(pyrazol-1-yl)pyridine complexes are the \( \text{N}_{\text{pyrazole}}-\text{Fe}-\text{N}_{\text{imidazole}} \) angles (ca. 160° for LS and 145° for HS) and the Σ parameter (ca. 90° for LS and 160° for HS). According to the determined \( \text{N}_{\text{pyrazole}}-\text{Fe}-\text{N}_{\text{imidazole}} \) angles of N(1)-Fe(1)-N(4) 160.22(19)°, N(20)-Fe(1)-N(17) 159.97(19)°, N(10)-Fe(2)-N(7) 160.7(2)°, N(11)-Fe(2)-N(14) 160.2(2)°, and the calculated Σ = 87 for Fe(1) and Σ = 85 for Fe(2) one may conclude that 1S is in the LS state at 180 K.
Furthermore it was also possible to determine the molecular structure of the [2x2] C-grid complex **1C** in the solid state by XRD experiments (**SIFig.18**). The C-grid complex crystallizes in the orthorhombic space group *Pbcn* symmetry. The unit cell also contains four grid complexes while the asymmetric unit consists of a [Fe$_2$L$_2$] moiety. The eightfold positive charge of **1C** is balanced by five SO$_3$CF$_3$ anions and three F$^-$ anions. The F$^-$ ions may have formed by hydrolysis of SO$_3$CF$_3^-$ during the slow evaporation-diffusion process of diisopropylether into a solution of the [2x2] Fe$^{II}_4$ grid complex [6][7]. Only four SO$_3$CF$_3$ anions form H-bonds to the NH-functions of the imidazole units present in the ligand backbone. The reason for this might be the more compact arrangement of **1C** with respect to **1S**, see Fig. 2c, **SIFig.18** and **SIFig.19e-f**. The four Fe$^{II}$ ions of **1C** are situated at the corners of a square in a strongly distorted octahedral {N$_6$} ligand environment that is composed of two orthogonal tridentate subunits of two different L ligands. At 180 K all four of the Fe$^{II}$ ions have Fe-N bond lengths with typical values for the HS state (average bond lengths d [Å]: Fe1-N 2.19, Fe2-N 2.16). According to the determined N$_{pyrazole}$-Fe-N$_{imidazole}$ angles of N(4)-Fe(1)-N(1) 146.4(3)$^\circ$, N(20)-Fe(1)-N(17) 145.0(3)$^\circ$, N(7)-Fe(2)-N(10) 147.0(3)$^\circ$, N(11)-Fe(2)-N(14) 146.0(3)$^\circ$ and the calculated Σ = 167 for Fe(1) and Σ = 152 for Fe(2) one may conclude that **1C** is in the HS state at 180 K.
SI Fig. 19 Comparison of structural parameters of the grid isomers 1C and 1S (left and right column): Representation of the four Fe\textsuperscript{II} atoms together with selected angles and distances in Å (ligand backbone is omitted) a) 1C  b) 1S; c) the dieder angles show: the four Fe\textsuperscript{II} atoms of 1C are almost in-plane but the four of 1S are not (d); the distances of the centroids of the central benzene ring of opposite ligands is a measure for the pore size of the respective 1C (e) and 1S (f) grid isomer
The inspection of the general alignment of the four Fe$^{II}$ ions in the [2x2] grid-type arrangements illustrate differences in distance and position in respect to each other (SiFig.19). This has to be understood as a direct consequence deconvoluting L into divergent grid-type coordination assemblies. The four Fe$^{II}$ ions of 1C and 1S may be seen as the corners of a square. On average the side lengths (Fe1-Fe2 distances) in 1C are with about 7.3 Å twenty percent shorter then in 1S with about 9.1 Å (SiFig.19a/b). The four Fe$^{II}$ ions of 1C may be described to be in one plane with a torsion angle (Fe1Fe2Fe1’Fe2’) of about 0.8°. Nevertheless, this is not the case for 1S where a torsion angle (Fe1Fe2Fe1’Fe2’) of 11.2° is found (SiFig.19c/d). 1C may be described as a parallelogram with almost equal neighboring side lengths and two neighboring angles of 79.3° and 100.7°. While 1S exhibits a structure with almost right angles of 88.7° and 90.2° and equal distances between neighboring Fe$^{II}$ ions of 9.0 and 9.2 Å (SiFig.19a/b). These different steric parameters are also found in the diagonal Fe-Fe distances. They are almost identical in 1S [Fe1-Fe1’ (12.7 Å) and Fe2-Fe2’ (12.9 Å)] but different in 1C [Fe1-Fe1’ (11.2 Å) and Fe2-Fe2’ (9.3 Å)]. 1S develops a more relaxed situation compared to 1C. It is possible to point out two reasons for this behaviour. The first is a longer distance between the coordination pockets in the S-compared to the C-configuration of L. The second reason is the up-down coordination mode of the S-ligand itself that allows an almost parallel alignment of the two perpendicular-coordinated S-ligands in respect to each other. While in the case of a C-grid the backbone of two opposite C-ligands point towards each other due to the intrinsic up-up/down-down coordination mode. The steric hindrance is partially released by an additional distortion of the {N6} ligand environment of the Fe$^{II}$ ions in 1C. The two different geometries of the S-/C-ligand backbone translate into the two [2x2] 1C and 1S grid complex isomers with different structural parameter sets. We defined the centroid of the benzene moiety joining the two imidazole units of one L ligand (SiFig.19e/f). The centroids were determined choosing the six C atoms of the respective benzene ring and using the “calculate centroids” function of the Mercury 3.5.1 (Build RCS) software provided free of charge by the Cambridge Crystallographic Data Centre (CCDC), http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx. In 1C, the distance of two centroids of opposite C ligands is on average 4.6 Å and therefore almost half of the distance that was found for two centroids of opposite S ligands in 1S which is on average 8.9 Å. These distances defines also the space or pore size that is available surrounded by the grid arrangement. The two geometries of the S-/C-ligand backbone translate divergently into the two [2x2] 1C and 1S grid complex isomers with different structural parameter sets.
5. Magnetic susceptibility measurements

All herein reported magnetic measurements were performed on a SQUID magnetometer (Quantum Design, model MPMS-XL-5). In all cases, the temperature dependence of the magnetic moment was recorded at B=0.1 T as an external magnetic field. The temperature sweeping rate was 1 K min⁻¹ and it was the same for cooling and heating modes. Gelatine capsules as sample containers were used for the measurement in the temperature range 5-370 K. The very small diamagnetic contribution of the gelatine capsule and high temperature sample holder had a negligible contribution to the overall magnetisation, which was dominated by the sample. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal’s constants.[8] In the case of high temperature magnetic measurement (300 – 520 K), the experiment was carried out using a heating setup (oven for QD MPMS SQUID). High temperature sample holder consisted of Quartz glass tube and Teflon tape used as a pocket for the sample. All magnetic data were corrected for this background value and then processed into $\chi T$ product function.

The susceptibility measurements were performed with crystals grown (from nitromethan/diisopropyl ether) as described above. The crystals were collected from the mother solution via glass pipette, washed with diisopropyl ether and dried under a stream of nitrogen to remove the remaining “surface” solvent molecules. The sample was measured first in the temperature range between 5-370 K, several cycles; for the high temperature measurements the sample was measured and cycled from 300-520 K and vice versa. It has to be noted, that the nice shape crystals of 1S are very fragile to solvent loss, which was already noticed during the X-ray diffraction measurements.

6. Nuclear resonance vibrational spectroscopy (NRVS), nuclear forward scattering (NFS), and calculation of the partial density of iron phonon states (pDOS)

NRVS experiments were performed at the Dynamics Beamline P01 at Petra III, DESY in Hamburg, Germany under experiment No. 9556. The polycrystalline powdered sample was prepared on a thin glass fibre on a goniometer head. The storage ring operated at 40 bunch mode with a bunch separation of 192 ns and 6 GeV beam energy. For temperature control a cryogenic N₂ gas stream (Oxford Cryosystems Ltd) was used. The NRVS data were collected during several scans within the energy range -20 to 80 meV with a 0.25 meV step size. The experimental energy resolution of the set-up was ~ 1 meV (~ 8 cm⁻¹). The NRVS data and the pDOS were generated with a binning of 0.5 meV.

Results:

We have employed nuclear resonance vibrational spectroscopy (NRVS; also called nuclear inelastic scattering) in order to pin down the vibrational properties of complex 1S and to identify its spin marker bands. SIfig.20a and Fig. 4b shows NRVS data obtained at 80 K. From 150 up to 320 cm⁻¹, there are two broad bands with low intensity. The spectrum is dominated by a very intense band with two maxima at 380 and 399 cm⁻¹ and a band at 423 cm⁻¹ followed by bands at 464 and 492 cm⁻¹. SIfig.20b displays the NIS data obtained at 250 K. The spectrum shows similar positions of the aforementioned bands but with changed intensities. Now, the two bands in the 150 to 320 cm⁻¹ region have increased significantly compared to the NRVS signature obtained at 80 K. One band reaches from 150 to 230 cm⁻¹ with a maximum at 187 cm⁻¹. A second broad band feature can be observed from 230 up to 320 cm⁻¹ with a maximum at 246 cm⁻¹. The bands with maxima now at 384,
408, 460, and 501 cm\(^{-1}\) are decreased in intensity compared to the 80 K NRVS data (SI Fig. 20a). This trend is even more evident in the NRVS data obtained at T = 400 K (SI Fig. 20c). Now the NRVS data is dominated by the two broad band features in the region from 140 to 330 cm\(^{-1}\). From 330 up to 500 cm\(^{-1}\) a low intensity and broad band feature without any distinct structure is observed. Low spin (LS) iron(II) complexes have spin marker bands with significant intensities in the 300-500 cm\(^{-1}\) region whereas high spin (HS) iron(II) complexes show spin marker bands mainly from 200 up to 300 cm\(^{-1}\). This is due to the lower iron-ligand bond distances of the LS iron compared to the iron-ligand bond distances of the HS iron.\(^9\) Thus the NRVS data displayed in SI Fig. 20 show that 1S has a diamagnetic ground state with all four iron(II) ions being in the LS state. At 250 K there is an incomplete SCO observable which is almost complete at 400 K.

**SI-Fig. 20 left:** Experimental nuclear resonance vibrational spectroscopy (NRVS) data of 1S obtained at a) 80 K b) 250 K and c) 400 K. The solid black lines are guides to the eye.

**SI-Fig. 21 right:** a) Experimental nuclear forward scattering (NFS) data of 1S at 80 K (black) and simulation assuming 100 % LS iron(II) sites (red line). b) Experimental NFS data at 250 K (black) and simulation (orange line) assuming 70 % LS and 30 % HS iron(II) sites. The effective thickness of the sample for the simulation is 47 \(\mu\)m in both cases. For more parameters see text. c) Experimental NFS data at 400 K: Due to the low Lamb-Mössbauer-factor of compound 1S only electronic noise could be detected.

This observation is confirmed by the nuclear forward scattering (NFS) data displayed in SI Fig. 21. NFS can be regarded as synchrotron based Mössbauer spectroscopy in the time domain and allows similar to conventional Mössbauer spectroscopy the determination of the quadrupole splitting \(\Delta E_Q\). If
more than one iron species is present in the sample also differences of isomer shifts $\delta$ can be detected. The NFS data obtained at 80 K (SI Fig. 21a) shows a pattern which could be reproduced by a simulation assuming a single iron site with $\Delta E_{Q} = 0.66 \pm 0.01$ mms$^{-1}$. Such a value is characteristic for a LS iron(II) site. At 250 K (SI Fig. 21b) a beating structure is observed which can only be explained by the presence of a further second iron site with other Mössbauer parameters. In fact, it is possible to reproduce the experimental data by a simulation\,[10] assuming the presence of two types of iron sites: LS iron(II) sites with $\Delta E_{Q_{LS}} = 0.56 \pm 0.03$ mms$^{-1}$ and a relative contribution of 70 %; and HS iron(II) sites with $\Delta E_{Q_{HS}} = 1.87 \pm 0.05$ mms$^{-1}$ and a relative contribution of 30 %. In addition the difference of the isomer shifts of the LS iron(II) sites and the HS iron(II) sites could be obtained by the simulation of the NFS data as $|\delta_{HS} - \delta_{LS}| = 0.7 \pm 0.15$ mms$^{-1}$; This is consistent with isomer shifts reported for 6N coordinated HS iron(II) centers ($\delta_{HS}=0.9-1.05$ mms$^{-1}$ at room temperature) and reported for 6N coordinated LS iron(II) centers ($\delta_{LS}=0.3-0.4$ mms$^{-1}$ at room temperature).\,[11]

However, at 400 K it was not possible to obtain NFS data due to the low probability for coherent nuclear forward scattering events which is caused by the low Lamb-Mössbauer factor $f$ of chemical complexes at elevated temperatures resulting in extremely low count rates (SI Fig. 21c).

SI Fig. 22 left: Experimentally determined partial density of states (pDOS) obtained from the NVRS data displayed in SI Fig. 20 and Fig. 4 at a) 80 K b) 250 K and c) 400 K. The solid black lines are guides to the eye.

SI Fig. 23 right: a) Simulated pDOS for a) the low spin state (M=1), b) a 70:30 mixture of LS and HS state and c) the high spin state (M=17) based on density functional theory calculations using Gaussian 09 (Rev.C01/B3LYP*/CEP31-G).\,[12] The vertical lines highlight the quadratic displacement of the iron atoms as a function of the energy of the corresponding vibrations.

In order to understand the vibrational properties of the LS and HS states we have performed density functional theory (DFT) calculations using Gaussian09 (Rev. C01/B3LYP/CEP-31G).\,[12] With a
subsequent normal mode analysis it is possible to calculate the partial density of iron phonon states (pDOS). The pDOS as obtained from the experimental NRVS data is shown in SIFig.22. For comparison the simulated pDOS based on the crystal structure data is displayed in SIFig.23. SIFig.23a shows a pDOS calculated under the assumption that all four iron(II) sites are in the LS state. The calculated pDOS shows an intense band ca at 178 cm$^{-1}$ and five bands with lower intensity at 204, 226, 252, 278 and 298 cm$^{-1}$. The experimental pDOS obtained at 80 K (SIFig.22a) does also show low intensity features in this region from 150 to 320 cm$^{-1}$. Strong intensity bands are calculated to occur from 340 up to 380 cm$^{-1}$ with two maxima at 358 and 368 cm$^{-1}$, but composed out of several modes. These modes correspond to the bands at 380, 399 and 423 cm$^{-1}$ in the experimental pDOS at 80 K (SIFig.22a). Furthermore, the theoretical pDOS shows two closed maxima at 398 and 410 cm$^{-1}$ and a strong maximum at 438 cm$^{-1}$. The corresponding modes forming these two bands are very likely representing the band at 464 cm$^{-1}$ in the experimental pDOS obtained at 80 K. The modes, which contribute to the band at 438 cm$^{-1}$, can be assigned to the band at 492 cm$^{-1}$ in the experimental pDOS.

In order to simulate the experimental pDOS obtained at 400 K (SIFig.22c), it was assumed that all iron(II) sites are in the HS state. The result of this calculation is shown in SIFig.23c. The calculated pDOS for the all HS complex shows a very strong band from 170 up to 220 cm$^{-1}$ with two maxima at 186 and 204 cm$^{-1}$. This band corresponds to the band from 140 up to 240 cm$^{-1}$ in the experimental pDOS obtained at 400 K. There are even more intense bands with maxima at 246, 264 und 280 cm$^{-1}$, which in the experimental pDOS correspond to the broad second band observable from 240 up to 330 cm$^{-1}$ at 400 K. There are also some small bands calculated at 334 and 350 cm$^{-1}$ corresponding to the very broad band without any structure from 330 to 500 cm$^{-1}$ in the experimental pDOS displayed in SIFig.23c. However, it cannot be excluded that there is also a small contribution from LS iron(II) sites even at 400 K, which might also contribute to the experimental pDOS obtained at 400 K.

The experimental pDOS obtained at 250 K as shown in SIFig.22b has contributions of both HS and LS modes. For the simulated pDOS displayed in SIFig. 23b a mixture of 70 % LS and 30 % HS iron(II) sites has been supposed, which is based on the analysis of the NFS data displayed in SIFig.21b. The calculated pDOS shows one broad band from 150 up to 220 cm$^{-1}$ and several less strong bands at 248, 268 and 280 cm$^{-1}$. These four bands correspond to the first region from 140 to 330 cm$^{-1}$ in the experimental pDOS obtained at 250 K (SIFig.22b). There is one more very strong band from 340 up to 380 cm$^{-1}$ with maxima at 358 and 368 cm$^{-1}$ and several smaller bands at 400, 412 and 438 cm$^{-1}$ as well. These bands correspond to the second region from 330 up to 500 cm$^{-1}$ of the experimental pDOS obtained at 250 K. Overall there is a good agreement between experimental and calculated pDOS which confirms the results of the NFS analysis, namely a LS:HS ratio of 70:30.
7. Mass spectrometry / ion mobility

Structural information about gas-phase ions can be obtained using ion mobility mass spectrometry. Ion mobility is a technique that spatially separates ions under the influence of an electric field by affecting their motion via collisions with a buffer gas. In the present work, travelling-wave ion-mobility (as implemented on a SYNAPT G2S-HDMS, Waters) is used to distinguish isomers with an identical mass over charge ratio. Assuming comparable ionization efficiency, the relative amount of some of the species in the synthetic solution is reported. Identification of the C and S isomers is achieved by converting the arrival time distributions obtained using nitrogen as a buffer gas to helium-converted cross-sections using polyalanine dications as calibrants and comparing them to those of model structures. In order to account for the relaxation of the gas-phase ion structures compared to those of species packed in a crystal, to sample the complexes’ conformational space, as well as to account for the charge state of the species observed using mass spectrometric techniques, both crystal structures and additional structures generated using the educated guess method and pre-optimized using OpenMopac (as low spin structures) were refined as high spin (multiplicity = 17) structures at the RI-BP86-D3-BJ/basis def2-tzvp (Fe), def2-svp (rest) level [13],[14],[15],[16],[17],[18],[19],[20] using TURBOMOLE. [21] Minimum structures were confirmed by calculating harmonic force constants. A reasonably good agreement between the experimentally inferred and the computed cross-sections as displayed below in SIFig.26 (cross-sections computed using Mobcal [22],[23],[24] with the parameter set of Campuzano et al. [25] for the trajectory method) is observed.

In order to characterize the species formed in the reaction medium, a drop of synthetic solution (diluted in acetonitrile) was electrosprayed using nano-electrospray and the ion-mobility spectrum of the species present recorded concurrently to their mass spectrum (SIFig.24).

![SI-Fig. 24](image)

SI-Fig. 24 High resolution ESI mass spectrum of the synthetic solution of 1. The experimental and theoretical isotopic patterns of the [Fe₄L₄-6H]²⁺ (sum formula: Fe₄C₉₆N₄₀H₅₈²⁺) species are provided in inset.

The ion mobility data for the doubly charged Fe₄C₉₆N₄₀H₅₈²⁺ complexes is displayed in SIFig.25. The C-form/S-form data was obtained by solubilizing crystals identified to correspond to species with the
ligands forming C-type/S-type bridges. The S-form appears to convert in acidic media on the experiment timescale into a C-form with one of the irons hydrated (Fe\(^{III}\)H) a species not observed when the synthetic solution is sprayed (in absence of formic acid addition). Comparison between the experimentally inferred He-corrected cross sections and the theoretical cross-sections is provided in SI Fig. 26. The experimental cross-sections were calibrated against doubly-charged polyalanine cations using the references cross-sections for doubly-charged species provided by Bush and coworkers.\(^{[26]}\)

**SI-Fig. 25** Arrival time distribution (ATD) for the species [Fe\(_4\)L\(_4\)-6H]\(^{2+}\) (sum formula: [Fe\(_4\)C\(_{96}\)N\(_{40}\)H\(_{58}\)]\(^{2+}\)).

1C ATD (top, in red), 1S ATD (middle, in blue), and synthetic mixture (bottom, in black); black arrows show an intermediate species at an AT of 5.3 ms (* small peaks correspond to species with the same m/z=997 like [M\(_x\)]\(^{2+}\); x=0.25, 0.5; M=Fe\(_4\)C\(_{96}\)N\(_{40}\)H\(_{58}\)).
SI Fig. 26 Comparison of the experimental cross-sections with the computed ones for the Fe₄C₃₈N₄₀H₅₈²⁺ complex; experimental cross-sections: 1Cexp (dissolved crystal in CH₃CN), 1Sexp (dissolved crystal in CH₃CN/HCOOH), RP (reaction product in CH₃CN); computed cross-sections in the green colour code: 1Ccalc, 1Scalc, IS (intermediate state) for SCSC and SSCC.

The agreement between the experimentally inferred cross-sections and the theoretical ones (see SI-Fig. 26) is so that unambiguous assignment is possible. Furthermore, the structure associated with the peak at ~5.3 ms in SI Fig. 25 (black arrow) appears to correspond to a mixed S/C form either of the SCSC or of the SSCC type. Those species are observed for the synthetic solution as well as when 1S crystals are re-solubilized. They may thus correspond to transient species involved in dynamical equilibria or interconversion processes occurring either in solution or upon electronebulization. The solubilized crystals of 1C on the other hand appear to yield a single species upon electronebulization. By integrating the arrival time distributions one can assess, at a given time, the relative amount of 1C and 1S, and intermediate present in the present case, their relative amounts in percent are about 65, 25, and 10, respectively.
SI Fig. 27 Computed (RI-BP86-D3-BJ/basis def2-tzvp (Fe), def2-svp (rest) level using TURBOMOLE) structures for the intermediate state, IS, associated with the peak at ~5.3 ms in SI-Fig. 25 and corresponding to a mixed S/C form either of the SSCC or of the SCSC type as shown in A and B respectively. (Fe: green, C: black, N: blue, H: white)

8. Quantum chemical calculations

Zero field splittings$^{[27]}$ and G-tensors were calculated for two mononuclear model complexes of the grid complex 1C shown in SI Fig. 28. The model complexes were obtained by cutting the C-C bonds of the bridging ligands after the first aromatic ring and saturating them by H-atoms. The atomic positions were taken from the X-ray structures, only the positions of the H atoms were optimized at DFT-level using the BP86 functional. For the model complexes, complete active space self-consistent field (CASSCF) calculations$^{[28]}$ and spin orbit configuration interaction (SOCl) calculations$^{[29]}$ in the active space were performed. The active space (6,5) contained six electrons in the Fe(II) 3d orbitals. The orbitals were obtained by a state average calculation on the five quintet states of the 3d$^6$ configuration.

SI Fig. 28 Model complexes for the two slightly differently coordinated Fe(II) centres in 1C.
The numerical D-tensors $D_1$ and $D_2$ for the model complexes are obtained from the SOCI wave functions as

$$
D_1 = \begin{pmatrix}
-11.98 & -4.69 & -12.18 \\
-4.69 & 8.74 & 9.79 \\
-12.18 & 9.79 & 7.52
\end{pmatrix}
$$

$$
D_2 = \begin{pmatrix}
-13.63 & 3.51 & -14.16 \\
3.51 & 17.70 & -7.10 \\
-14.16 & -7.10 & 1.00
\end{pmatrix},
$$

the values are given in cm$^{-1}$. The $D$ values given in the main body are obtained by diagonalization of the tensors. The g-factors ($g_1=4.50$, $g_2=0.76$, $g_3=0.10$, with an average of $g=1.78$ for model 1 and $g_1=7.93$, $g_2=0.47$, $g_3=0.16$ with an average of $g=2.85$ for model 2, respectively) were obtained from the energy splittings of the two lowest electronic states assuming an effective spin of $S=1/2$. The average value for the two models amounts to $g_{av}=2.32$.

The magnetic main axes were determined by applying the magnetic field on a hemisphere and determining the direction which shows the maximal energy splitting. In SI-Fig. 29 and 30, the field dependence of the five lowest electronic states (lowest $S=2$ state) along the magnetic main axes are shown for the two models.

SI-Fig.29 Energies of the five lowest electronic states of model 1 in dependence of a magnetic field applied along the magnetic main axis. For B=0 T the zero field splittings can be extracted.
**SIFig.30** Energies of the five lowest electronic states of model 2 in dependence of a magnetic field applied along the magnetic main axis. For B=0T the zero field splittings can be extracted.
SI Fig. 31 Magnetic susceptibility of 1C. The measured data is compared to a simulation from five different sets of parameters (see Si-Tab. 4) using a spin Hamiltonian of the form
\[
\hat{H} = \sum_{i \neq j=1} -2J_{ij}\hat{S}_i\hat{S}_j + \sum_{i=1}^4 \left(D\hat{S}_{z,i}^2 + E\left(\hat{S}_{x,i}^2 + \hat{S}_{y,i}^2\right) + \beta g\hat{S}_iB\right)
\]

\(J_{ij}\) are the magnetic exchange coupling, \(S\) spin operators and \(\beta\) is Bohr’s magneton.

SI Tab. 4 Parameter sets used in SI-Fig. 31. \(D, E\) and \(J\) are given in cm\(^{-1}\). J13 and J24 are assumed to be negligible.

| parameter set | D     | E     | \(g\)  | J12=J34 | J14=J23 |
|---------------|-------|-------|--------|---------|---------|
| 1             | -6    | 2     | 2.11   | -0.1    | 0.1     |
| 2             | -6    | 2     | 2.11   | 0       | 0       |
| 3             | -6    | 0     | 2.11   | 0       | 0       |
| 4             | 0     | 0     | 2.11   | -0.1    | -0.1    |
| 5             | -6    | 2     | 2.11   | 0.1     | 0.1     |

The distance of the Fe centres in the grid complex is rather large (see SI 4.1, SI-Fig. 19a/b). Therefore, the magnetic exchange couplings \(J_{ij}\) are assumed to be close to zero. We found reasonable agreement with the experimental data by assuming that all centres have the same values for \(g\) (2.11) and \(D\) (-6 cm\(^{-1}\)) and an E/D value of 1/3. Introducing an exchange coupling constant different from zero did not improve the results.
9. References

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
[2] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112–122.
[3] I. Šalitroš, O. Fuhr, R. Kruk, J. Pavlík, L. Pogány, B. Schäfer, M. Tatarko, R. Boča, W. Linert, M. Ruben, Eur. J. Inorg. Chem. 2013, 49, 10986.
[4] B. Schäfer, C. Rajnák, I. Šalitroš, O. Fuhr, D. Klar, C. Schmitz-Antoniak, E. Weschke, H. Wende, M. Ruben, Chem. Commun. 2013, 339–341.
[5] D. Gentili, N. Demitri, B. Schäfer, F. Liscio, I. Bergenti, G. Ruani, M. Ruben, M. Cavallini, J Mater Chem C 2015, 3, 7836–7844.
[6] P. Wasserscheid, A. Boesmann, R. Van Hal, Preparation and Use of Halogen-free Ionic Liquids, 2003, WO 2003074494.
[7] K. F. Konidaris, C. D. Polyzou, G. E. Kostakis, A. J. Tasiopoulos, O. Roubeau, S. J. Teat, E. Manessi-Zoupa, A. K. Powell, S. P. Perlepes, Dalton Trans 2012, 41, 2862–2865.
[8] O. Kahn, Molecular Magnetism, VCH, New York, NY, 1993.
[9] J. A. Wolny, S. Rackwitz, K. Achterhold, K. Muffler, V. Schünemann, Hyperfine Interact. 2012, 204, 129–132.
[10] Y. Shvyd’ko, Hyperfine Interact. 2000, 125, 173–188.
[11] N. N. Greenwood, T. C. Gibb, Mössbauer Spectroscopy, p. 196–197, table 8.1 (Chapman and Hall Ltd. London, 1971).
[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., Gaussian 09, Gaussian, Inc., Wallingford, CT, USA, 2009.
[13] F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057.
[14] A. D. Becke, Phys. Rev. A 1988, 38, 3098–3100.
[15] O. Treutler, R. Ahlrichs, J. Chem. Phys. 1995, 102, 346.
[16] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.
[17] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[18] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456–1465.
[19] J. P. Perdew, Phys. Rev. B 1986, 33, 8822–8824.
[20] J. P. Perdew, Phys. Rev. B 1986, 34, 7406–7406.
[21] TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[22] M. F. Mesleh, J. M. Hunter, A. A. Shvartsburg, G. C. Schatz, M. F. Jarrold, J. Phys. Chem. 1996, 100, 16082–16086.
[23] M. F. Mesleh, J. M. Hunter, A. A. Shvartsburg, G. C. Schatz, M. F. Jarrold, J. Phys. Chem. A 1997, 101, 968–968.
[24] A. A. Shvartsburg, M. F. Jarrold, Chem. Phys. Lett. 1996, 261, 86–91.
[25] I. Campuzano, M. F. Bush, C. V. Robinson, C. Beaumont, K. Richardson, H. Kim, H. I. Kim, Anal. Chem. 2012, 84, 1026–1033.
[26] M. F. Bush, I. D. G. Campuzano, C. V. Robinson, Anal. Chem. 2012, 84, 7124–7130.
[27] R. Maurice, R. Bastardis, C. de Graaf, N. Suaud, T. Mallah, N. Guihéry, J. Chem. Theory Comput. 2009, 5, 2977–2984.
[28] U. Meier, V. Staemmler, Theor. Chim. Acta 1989, 76, 95–111.
[29] K. Fink, C. Wang, V. Staemmler, Inorg. Chem. 1999, 38, 3847–3856.