Synthesis, Structure and Properties of a Mixed Mononuclear/Dinuclear Iron(II) Spin-Crossover Compound with the Ligand 4-(*p*-Tolyl)-1,2,4-triazole

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A new iron(II) compound with the formula $[Fe_2(L)_5(NCS)_4]_2$-$[Fe(L)_2(NCS)_2(H_2O)_2]$ (**I**) [where L = 4-(*p*-tolyl)-1,2,4-triazole] has been synthesized and subjected to X-ray structure determination. Compound **I** crystallizes in the triclinic space group *P*–1 (no. 2) with $a = 14.5785(11)$, $b = 16.1253(11)$, $c = 16.1963(8)$ Å, $\alpha = 80.930(5)$, $\beta = 85.796(5)$, $\gamma = 78.132(6)°$, $V = 3676.2(4)$ Å^3. The structure refinement converged to $wR2 = 0.172$, $R_F = 0.084$. The structure was found to consist of two types of iron-containing structural units, a mononuclear unit and a dinuclear one. The mononuclear unit has a crystallographic inversion centre, and is coordinated by two *N*CS anions, two triazole N1 nitrogen atoms, and two water molecules, each hydrogen-bonded to one of the two dinuclear units. The dinuclear units consist of two iron(II) ions bridged by three triazole ligands in a 1,2-fashion. The coordination spheres of both iron ions are completed by two *N*CS anions and one monodentate triazole ligand. The monodentate triazole ligands are connected through the non-coordinating N atom to the mononuclear iron unit by hydrogen bonds from its coordinated water molecule. Magnetic susceptibility measurements indicate a spin transition (ST) only for the iron ions in the dinuclear units, centred at around $T_{1/2} = 111$ K. The transition takes place within a relatively narrow *T* range. The mononuclear iron ion remains in the high-spin (HS) state even at very low temperature, yielding a ratio of 4:1 for the ST and HS iron ions. Temperature-dependent Mössbauer spectroscopy confirms these results.

Introduction

In the research on iron(II) compounds with a spin transition[1] (hereafter abbreviated as ST), the compounds with 4-substituted 1,2,4-triazoles have a special place. The variety of structural types and the physical properties of these compounds have been a topic of research for over 15 years. The structures characterized to date vary from mononuclear to trinuclear compounds with two triple bridges,[2–4] but one-, two-, and three-dimensional polynuclear compounds have also been found with various bridging triazole ligands.[5–7] Here, we focus on the linear structures obtained with 4-R-1,2,4-triazoles.

The variety of structural and physical properties leads to questions about the influences of variables such as the ligand substituents, the nature of the anion, and the metal-to-ligand ratio on the transition temperature, the form of the transition curve and the structure.[7] The substituents used to date have included primary and secondary alkyl and (substituted) phenyl groups.

The anions used in earlier research have varied from coordinating, e.g. NCS^- and $NCSe^-$, to non-coordinating, e.g. BF_4^-, ClO_4^- and triflate.[2–4] The effect of non-coordinating anions on the structure of the resulting compounds is usually restricted to effects related to hydrogen bonding. In an earlier paper, it was stated that the influence of non-coordinated anions is much more pronounced than the influence of the substituent used, although steric effects of the substituent can play an important role in the ST behaviour.[4] The effect of coordinating anions on the structure of divalent transition metal compounds with 1,2,4-triazole ligands is to block coordination sites. Therefore, coordinated anions limit the number of coordinated triazoles to four per metal core. For 1,2,4-triazoles having only two possible coordination sites, this leads to dinuclear units either with three bridging triazoles and one monodentate triazole per metal core,[8] or with NCS anions linking the dinuclear unit, yielding a polynuclear structure.[9] Because of this more pronounced influence on the structure, the influence on the ST behaviour can be expected to be rather large as well. It is, however, difficult to compare the influence of coordinated anions to the influence of non-coordinated anions, because of the difference in structural properties.

We now wish to report a new triazole compound, in which the mononuclear moiety shows no ST, whereas the dinuclear part shows a clear ST. The ligand used in this study is 4-(*p*-tolyl)-1,2,4-triazole, which has not previously been used in this context.

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Results and Discussion

Structural Description of I

The structure was found to consist of two types of iron-containing structural units, i.e. a mononuclear unit (Figure 1) on a crystallographic inversion centre, hydrogen-bonded by two coordinated water molecules to two dinuclear units (Figures 2 and 3).

The mononuclear unit situated on a crystallographic inversion centre consists of an Fe^{II} ion, coordinated by two thiocyanate nitrogen atoms (N65) at a distance of 2.094(10) Å, two monodentate tolyl-triazole N1 atoms at 2.194(9) Å, and two water oxygen atoms (O1) at 2.185(9) Å, in an octahedral environment. The NCS anion is non-linear with the N65−C65−S5 angle 173.7(12)°; the angle of coordination to iron Fe3−N65−C65 is also non-linear being 168.8(10)°. An iron(II) centre with this chromophore of relatively weak ligand field strength can be expected to be in a high-spin (HS) state without an ST. The Fe−ligand distances are consistent with an HS state at room temperature.

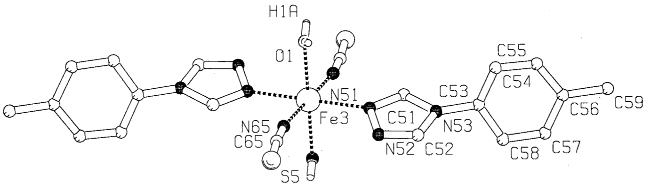

Figure 1. Structure of the mononuclear unit $Fe(L)_2(H_2O)_2(NCS)_2$ in **I**; non-water H atoms are omitted for clarity

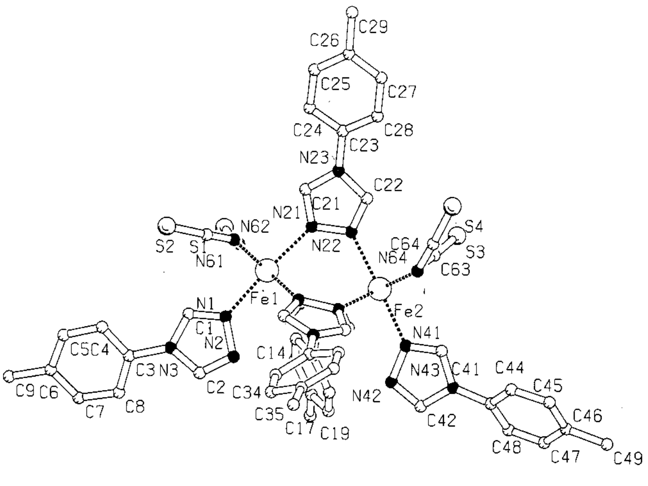

Figure 2. Structure of the dinuclear unit $[Fe_2(L)_5(NCS)_4]$ in **I**; H atoms are omitted for clarity

The unit cell also contains two dinuclear units. Both units consist of two iron ions linked by three 1,2-triazole bridges with Fe−N distances ranging from 2.151(8) Å to 2.223(8) Å, typical for an HS iron ion bound by triazole. The coordination spheres of both iron ions are completed by two thiocyanate N atoms at 2.092(9) to 2.188(9) Å, and a monodentate tolyl-triazole ligand at 2.152(8) and 2.173(8) Å, yielding a distorted octahedral N6 chromophore, which is known to produce ST compounds.

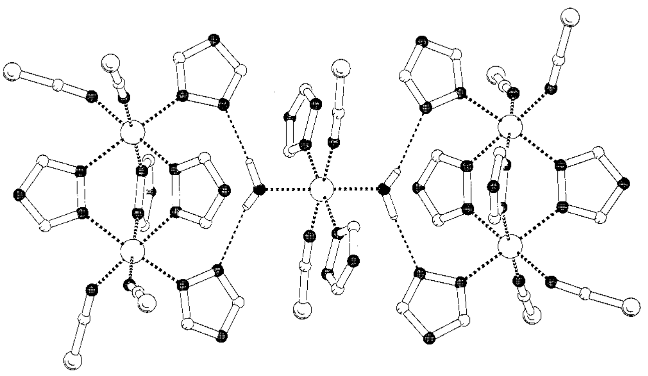

Figure 3. Pentanuclear assembly $[Fe_2(L)_5(NCS)_4]_2[Fe(L)_2(NCS)_2(H_2O)_2]$ (**I**), non-water H atoms and tolyl C atoms are omitted for clarity

Dinuclear units with this structure, M_2(1,2,4-triazole)$_5(NCS)_4$ (with M = divalent first-row transition metal ion), are known from the literature.[8][10] However, in these structures the monodentate triazoles are coordinated *trans* with respect to the metal−metal axis rather than *cis*, as is observed in the present structure. The *cis* configuration is clearly stabilized by a hydrogen-bonding network, which involves the water molecules coordinated by the mononuclear iron core. These water molecules form hydrogen bonds to the non-coordinated N atoms of the monodentate triazoles from the dinuclear unit (Table 1). The overall structure can thus be described as a pentanuclear unit, consisting of two dinuclear units linked by a mononuclear unit.

The overall structure contains four iron ions that might exhibit a temperature-induced ST, and one iron ion which is expected to be in an HS state at all temperatures.

Magnetic Measurements

At 290 K, χT was found to be 3.6 cm^3 K mol^{-1}, indicating all iron ions to be present in the HS state, as would be expected from the structure determination. On lowering the temperature, this value decreased only slightly, e.g. to 3.5 cm^3 K mol^{-1} at 150 K. On lowering the temperature still further, the sample showed a sharp drop in magnetization in the temperature range from 130 to 90 K. The $T_{1/2}$ was estimated to be 111 K. At 80 K, χT was found to be 0.7 cm^3 K mol^{-1} per iron ion, in agreement with one of the five iron ions being in an HS state and the other 4 being in low-spin (LS) state at low temperatures. This is in good agreement with the observed structure. Thus, a quantitative spin-state conversion $^5T_2 \rightarrow {}^1A_1$ occurs in 80% of all the iron(II) ions. This is shown clearly in Figure 4, where the fraction of HS molecules, derived from the magnetic measurements, is plotted as a function of temperature, $\gamma_{HS}(T)$. The conversion curves merge into a plateau at $\gamma_{HS} = 0.2$ at low temperatures, reflecting the expected 20% fraction of the iron ions, i.e. those localized in the centre of the pentanuclear assembly, that remain in the HS state at all temperatures. The compound did not show any variation of behaviour on cooling or heating, which is also apparent from

Table 1. Hydrogen bond geometries for **I**

	D···A [Å]	D−H [Å]	H···A [Å]	D−H···A [°]
O(1)−H(1A)···N(2) [1 − *x*,1 − *y*,−*z*]	3.031(13)	0.72(12)	2.36(13)	157(13)
O(1)−H(1B)···N(42) [1 − *x*,1 − *y*,−*z*]	3.128(13)	0.99(11)	2.15(11)	172(9)

Figure 4, where the transition curves for the cooling and heating directions are identical. No hysteresis is observed within the limits of experimental error.

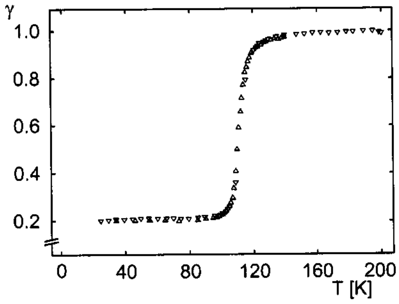

Figure 4. Molar fraction of the iron(II) HS molecules, γ_{HS}, in compound **I** as function of temperature; the conversion curves in cooling direction (▽) and heating direction (Δ) match perfectly

Mössbauer Spectroscopy

Mössbauer spectra of **I** were obtained in a temperature range between 80 K and 293 K. Figure 5 shows a selection of spectra recorded between 80 K and 200 K. At temperatures below $T_{1/2}$, the spectrum observed is indicative of two types of iron cores; at 80 K one core is in an LS state, as indicated by the apparent strong singlet absorption. The central core is in an HS state, yielding the doublet absorption (outer two signals) typical for an HS iron(II) complex denoted as HS^c. The ratio of the two states is 1 HS for every 4 LS cores, as one would expect from both the structural and magnetic data. Accordingly, one would expect a 1:4 intensity ratio (ratio of area fractions) of the LS and HS resonances in the low-temperature Mössbauer spectra. Inspecting the data of the relative area *A* (%) for the respective signals in Table 2, however, one notices that the HS area fraction at 80 K, for instance, is about 10% smaller than the expected value to match the 1:4 ratio. This discrepancy is due to the fact that the Lamb−Mössbauer factor of the LS state[11−13] differs from the HS state. The data collected in Table 2 are the results of the fitting procedure that included the thickness correction for the Mössbauer absorber.

The spectra obtained from the ST region show a clear transition from the LS state to two additional HS states; the new HS states HS1 and HS2 relate to the four iron(II) ions in the two dinuclear fragments. They are best fitted by two doublets with the same intensity and slightly different quadrupole splitting (see Table 2). This behaviour might be explained by the difference in the coordination spheres of the iron ions in the two dinuclear units. The intensity increase of the new HS quadrupole doublets is in line with the disappearance of the LS state. No change is observed in the central HS quadrupole doublet HS^c other than a normal temperature-dependent change in the splitting energy arising from the known temperature dependence of the valence electron contribution on the electric field gradient. At 200 K and above, broadened Mössbauer spectra were observed, which could satisfactorily be deconvoluted into three iron(II) HS doublets with intensity ratios of 2:2:1 at all temperatures as expected from the crystal structure. As an example, the spectrum measured at 200 K is depicted in Figure 6, together with the calculated subspectra of the three HS doublets derived from the fitting procedure.

Conclusion

The work described herein represents an important new example of the versatility of the 4-substituted 1,2,4-triazole ligand system. The new type of structural assembly is of interest from several points of view. Though the subunits of the assembly, especially the dinuclear unit, are not uncommon, and the hydrogen bonding through a non-coordinated triazole N atom has been described previously,[8] the re-

Table 2. Parameters of Mössbauer spectra at different temperatures: partial areas (%), isomer shift (I. S.) and quadrupole splitting (Q. S.)

		HS1				HS2				HS^c				LS				Impurity	
T K	%	I. S. mm/s	Q. S. mm/s	Γ mm/s	%	I. S. mm/s	Q. S. mm/s	Γ mm/s	%	I. S. mm/s	Q. S. mm/s	Γ mm/s	%	I. S. mm/s	Q. S. mm/s	Γ mm/s	%	I. S. mm/s	Q. S. mm/s	Γ mm/s
200	38.2	1.019	2.75	0.13	38.2	0.990	2.36	0.13	19.1	1.034	2.91	0.13	–	–	–	–	4.5	0.107	0.31	0.15
180	38.4	1.031	2.82	0.13	38.4	1.003	2.44	0.13	19.2	1.044	2.98	0.13	–	–	–	–	4.0	0.107	0.31	0.15
160	38.6	1.035	2.90	0.13	38.6	1.016	2.51	0.13	19.3	1.065	3.04	0.13	–	–	–	–	3.5	0.107	0.31	0.15
140	38.6	1.026	2.58	0.13	38.6	1.033	2.96	0.13	19.8	1.097	3.10	0.13	2.0	0.390	0.14	0.13	1.0	0.107	0.31	0.15
120	34.9	1.037	2.63	0.12	34.9	1.043	3.01	0.12	20.0	1.114	3.21	0.15	10.0	0.390	0.14	0.13	0.2	0.107	0.31	0.15
110	14.7	1.040	2.69	0.18	14.7	1.048	3.08	0.14	19.9	1.132	3.36	0.16	50.7	0.398	0.14	0.13	–	–	–	–
100	3.5	1.040	3.09	0.14	3.5	1.038	2.91	0.15	16.9	1.130	3.47	0.14	76.7	0.398	0.14	0.13	–	–	–	–
80	0.9	1.040	3.13	0.12	0.9	1.038	3.11	0.18	17.6	1.143	3.51	0.15	80.6	0.400	0.13	0.14	–	–	–	–

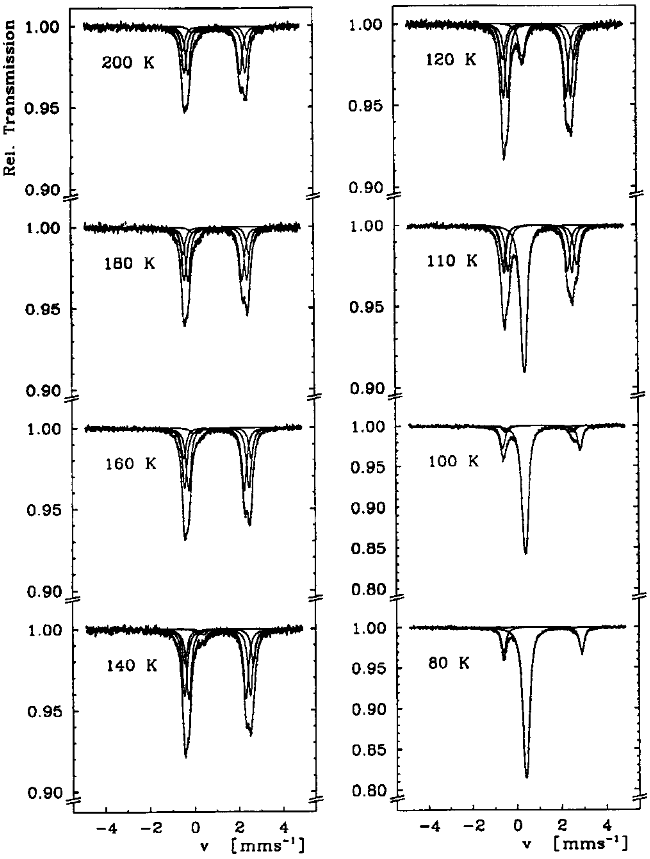

Figure 5. Selected Mössbauer spectra of compound **I** as function of temperature

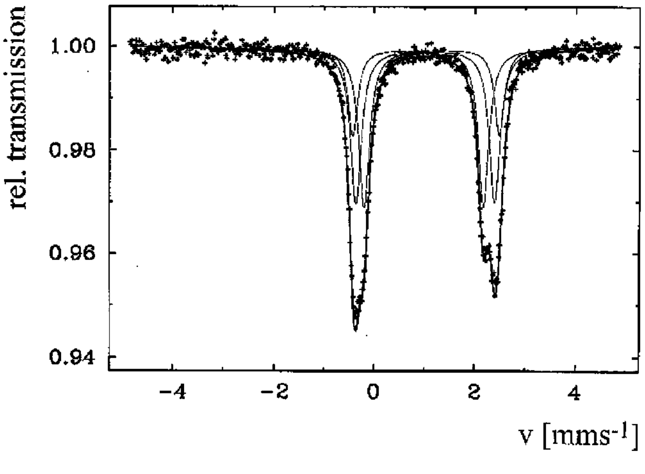

Figure 6. Mössbauer spectrum of compound **I** measured at 200 K; the broadened doublet is composed of three iron(II) HS doublets with intensity ratios of 2:2:1; the two with equal intensity relate to the four iron ions in the dinuclear units; the doublet with lowest intensity but largest splitting energy arises from the central iron(II) ion, which remains in the HS state at all temperatures

sulting species is a quite unique pentanuclear assembly, with two dinuclear units hydrogen-bonded to a mononuclear unit. The iron ion in the bridging, mononuclear unit remains in an HS state throughout the temperature range from 20 to 300 K, and does not show any variation in its Mössbauer spectra other than the normal temperature-dependent variation. On the other hand, a spin transition is observed, which is attributed to the iron ions in the dinuclear units. The Mössbauer spectra show two doublets for the iron ions with a spin transition; the slight differences in the splitting energy might be explained by the slight differences in the coordination spheres of these iron ions. This difference is mainly due to a difference in the metal−ligand bond lengths in the dinuclear unit. Though the iron ions seem to be slightly different, this has no observable influence on the spin transition temperature ($T_{1/2}$), as this is observed at a sharp T of 111 K.

Experimental Section

Preparation of I: The ligand 4-(*p*-tolyl)-1,2,4-triazole (L) was prepared according to a modified literature procedure.[14] $[Fe_2(L)_5(NCS)_4]_2[Fe(L)_2(NCS)_2(H_2O)_2]$ H_2O (**I**) was synthesized by adding a solution of 2.5 mmol of L in 25 mL of hot water to a solution of 1 mmol of FeCl2·2H2O and 2 mmol of NH_4NCS in 25 mL of hot water. Crystals appeared upon slow cooling to room temperature; single crystals suitable for X-ray diffraction structure determination were collected from this solution. − $C_{118}H_{114}Fe_5N_{46}O_3S_{10}$ (2824.5): calcd. C 50.18, H 4.07, N 22.81, S 11.35, Fe 9.89; found C 50.21, H 4.05, N 22.93, S 10.72, Fe 9.10.

Crystal Structure Determination of I: A block-shaped crystal of approximate dimensions 0.2 × 0.3 × 0.3 mm, suitable for X-ray structure determination, was sealed in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit cell parameters and an orientation matrix were obtained from a least-squares fitting of the setting angles of 25 well-centred reflections (SET 4[15]) in the range $8.42° < \theta < 15.11°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[16] Crystal data and details of the data collection are presented in Table 1. Data were collected at ambient temperature in $\omega/2$ scan mode, with scan angle $\Delta\omega = 0.82 + 0.35 \tan\theta°$. Total data of 10732 reflections were collected, 10102 of which were independent. Data were corrected for L_P effects and for 1% instability in the three periodically measured reference reflections (2 0 4, 4 2 0, −3 1 2) during 37 h of X-ray exposure time, but not for absorption. The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[17]). Refinement on F^2 was carried out using full-matrix least-squares techniques (SHELXL-93[18]); no observance criterion was applied during refinement. Hydrogen atoms, except the water hydrogen atoms [H(1A) and H(1B)], were included in the refinement in calculated positions, riding on their carrier atoms. The coordinates of the water hydrogen atoms were allowed to refine freely. The methyl hydrogen atoms were refined as a rigid group, allowing for rotation about the C−C bond. At this stage of the refinement, a difference Fourier map revealed a number of residual density peaks (approx. height 1.5 e $Å^{-3}$) in a channel running parallel to the b axis and located at $x = 1/2$, $z = 0$, with a volume of 491.9 $Å^3$. No discrete solvent model could be refined. The BYPASS procedure,[19] as implemented in the program PLATON,[20] was used to take this electron density into account. A total number of 123 electrons was found in the channel, which is probably occupied by water. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with fixed isotropic thermal parameters related to the value of the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.5 for the methyl and water hydrogen atoms, and of 1.2 for the aromatic hydrogen atoms. Convergence was reached at $wR2 = 0.172$, $w^{-1} = \sigma^2(F^2) + (0.0574P)^2$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$, $R_F = 0.084$ for 3501 $F_o > 4\,\sigma\,(F_o)$, $S = 0.84$ for 829 parameters. The residual density was in the range -0.48 to 0.42 e Å^{-3}. The relatively high R values and the rather high U_1/U_3 ratios for some atoms are related to the weak scattering that is most probably a consequence of the disorder in the solvent-filled channels. Selected bond lengths and angles are given in Table 4. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[21] Geometrical calculations and illustrations were performed with PLATON. All calculations were performed with a DEC5000 cluster. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-100926. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for **I**

Empirical formula	$C_{118}H_{112}N_{46}Fe_5O_2S_{10}$ [a]
Molecular mass	2806.39[a]
Space group	$P-1$
a [Å]	14.5785(11)
b [Å]	16.1253(11)
c [Å]	16.1963(8)
α [°]	80.930(5)
β [°]	85.796(5)
γ [°]	78.132(6)
V [Å^3]	3676.2(4)
Z	1
$\rho_{\mathrm{calcd.}}$ [g cm^{-3}]	1.2677(1)[a]
μ (Mo-K_α) [cm^{-1}]	6.8[a]
R_F[b]	0.084
$wR2$[c]	0.172
S	0.84
λ [Å]	0.71073 (Mo-K_α, graphite monochromator)

[a] Without disordered solvent contribution. – [b] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 4. Selected bond lengths [Å] and angles [°] for **I**

(a) Distances [Å]			
Fe(1)–N(1)	2.152(8)	Fe(2)–N(32)	2.193(8)
Fe(1)–N(11)	2.202(9)	Fe(2)–N(41)	2.173(8)
Fe(1)–N(21)	2.180(8)	Fe(2)–N(63)	2.092(9)
Fe(1)–N(31)	2.195(8)	Fe(2)–N(64)	2.148(9)
Fe(1)–N(61)	2.100(10)	Fe(3)–O(1)	2.185(9)
Fe(1)–N(62)	2.188(9)	Fe(3)–N(51)	2.194(9)
Fe(2)–N(12)	2.151(8)	Fe(3)–N(65)	2.094(10)
Fe(2)–N(22)	2.223(8)		
(b) Angles [°]			
N(1)–Fe(1)–N(11)	88.8(3)	N(12)–Fe(2)–N(22)	93.3(3)
N(1)–Fe(1)–N(21)	173.6(3)	N(12)–Fe(2)–N(32)	87.9(3)
N(1)–Fe(1)–N(31)	87.2(3)	N(12)–Fe(2)–N(41)	89.5(3)
N(1)–Fe(1)–N(61)	93.2(4)	N(12)–Fe(2)–N(63)	90.2(3)
N(1)–Fe(1)–N(62)	89.9(4)	N(12)–Fe(2)–N(64)	176.6(3)
Fe(1)–N(61)–C(61)	154.1(9)	Fe(2)–N(63)–C(63)	172.0(9)
Fe(1)–N(62)–C(62)	152.6(9)	Fe(2)–N(64)–C(64)	142.7(8)
O(1)–Fe(3)–N(51)	90.0(3)	N(51)–Fe(3)–N(65)	89.9(4)
O(1)–Fe(3)–N(65)	88.2(4)	Fe(3)–N(65)–C(65)	168.8(10)

Magnetic Properties: The magnetic susceptibility of **I** was measured over the temperature range 4.2–300 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at ca. 1.4 T, and over the temperature range 20–200 K with a FONER-type magnometer (PAR 155) equipped with a Cryovac continuous-flow cryostat and a Bruker electromagnet, operating at 1 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Mössbauer Spectra: These were measured with a ^{57}Co(Rh) source using a constant acceleration spectrometer in a cryostat with exchange gas. The obtained spectra of polycrystalline samples were fitted with Lorentzian-shaped lines using a non-linear iterative minimization routine (MOSFUN).

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