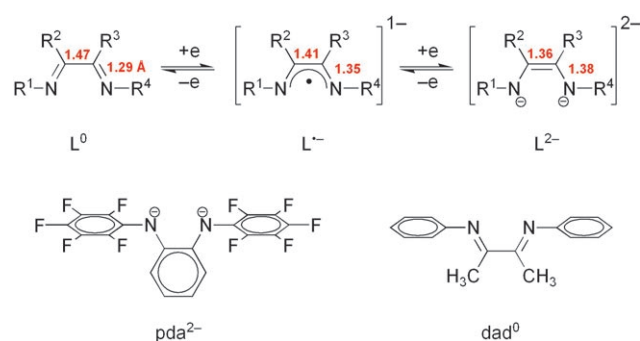


Reversible Electron Transfer Coupled to Spin Crossover in an Iron Coordination Salt in the Solid State**

Marat M. Khusniyarov,* Thomas Weyhermüller, Eckhard Bill, and Karl Wieghardt*

Mössbauer spectroscopy of a series of bis(α -diimine)iron complexes has recently unequivocally shown that these distorted tetrahedral complexes with a triplet ground state contain a high-spin ferrous ion ($S_{\text{Fe}} = 2$) and two monoanionic π radicals $L^{\cdot -}$ ($S_{\text{rad}} = 1/2$, Scheme 1), which are intramolecu-



Scheme 1. Ligand abbreviations used in this work.

larly antiferromagnetically coupled to the iron ion to yield the observed $S_{\text{t}} = 1$ ground state.^[1] The electronic structure of these complexes cannot be described as species containing a low-valent iron(0) center ($S_{\text{Fe}} = 1$, d^8) and two neutral α -diimine ligands as proposed^[2] in the literature. This^[1] and other^[3,4] recent studies have clearly established that α -diimines are noninnocent ligands with three accessible oxidation levels L^0 , $L^{\cdot -}$, and L^{2-} , which can be clearly discerned by their differing C–C and C–N bond lengths (Scheme 1).

In an attempt to synthesize such $[\text{FeL}_2]$ complexes with two different α -diimines (heteroleptic complexes), we prepared the extremely air-sensitive complex $[\text{Fe}^{\text{II}}(\text{pda}^{2-})(\text{dme})_2]$ (**1**; $\text{pda}^{2-} = N,N'$ -bis(pentafluorophenyl)-*o*-phenylenediamido(2 $-$) ligand, dme = dimethoxyethane). When **1** reacted

with 1 equivalent of N,N' -bis(phenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (dad^0), the EI mass spectrum indicated the presence of $[\text{Fe}(\text{pda})(\text{dad})]$, but the isolated main product turned out to be black crystals of $[\text{Fe}(\text{dad})_3][\text{Fe}(\text{pda})_2] \cdot (\text{toluene})$ (**2**; Figure 1). When the ratio $\text{dad}:\mathbf{1}$ was changed to 3:2, the yield of **2** increased to 43 %. As complex **2** possesses a very interesting temperature-dependent electronic structure (see below), its molecular structure was determined by single-crystal X-ray crystallography at 120 and 270 K.^[5]

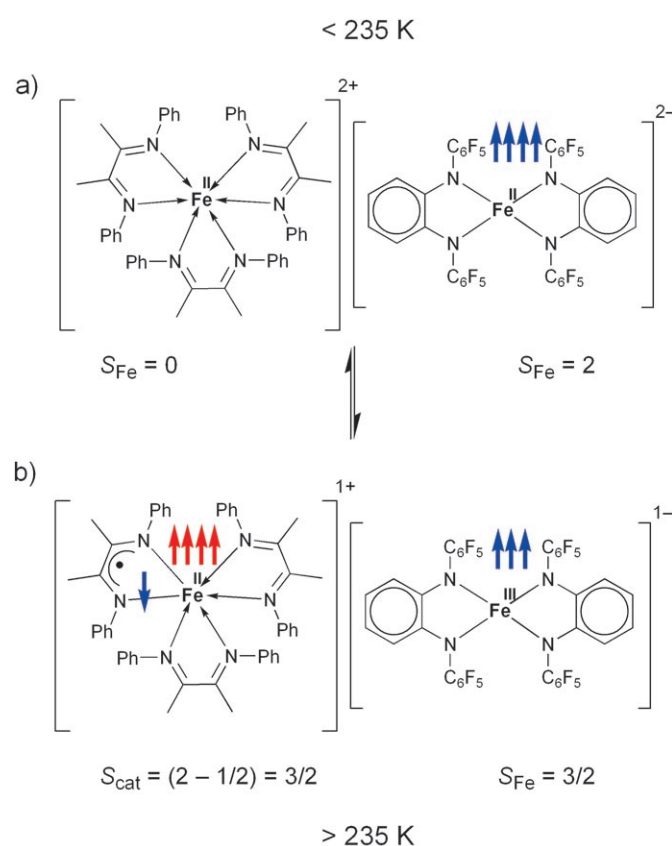


Figure 1. Electronic structure of **2**: a) below $T_{1/2} \approx 235$ K and b) above $T_{1/2}$.

The low-temperature structure of **2** consists of a cation-anion pair (Figure 2). Both the octahedral cation and the distorted tetrahedral anion contain one central iron ion; the charges of these ions are not specified at this point, because both dad and pda are noninnocent ligands. As shown in Scheme 1, their respective oxidation level can be determined by X-ray crystallography. The three dad ligands in **2** have long C–C bonds (av 1.473(4) Å) and short C–N bonds (av

[*] Dr. M. M. Khusniyarov, Dr. T. Weyhermüller, Dr. E. Bill, Prof. Dr. K. Wieghardt
Max Planck Institut für Bioanorganische Chemie
Stiftstrasse 34–36, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-3951
E-mail: marik@mpi-muelheim.mpg.de
wieghardt@mpi-muelheim.mpg.de
Homepage: http://ewww.mpi-muelheim.mpg.de/bac/index_en.php

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Supporting information for this article (details of physical measurements and spectroscopic characterization of **1**) is available on the WWW under <http://www.angewandte.org> or from the author.

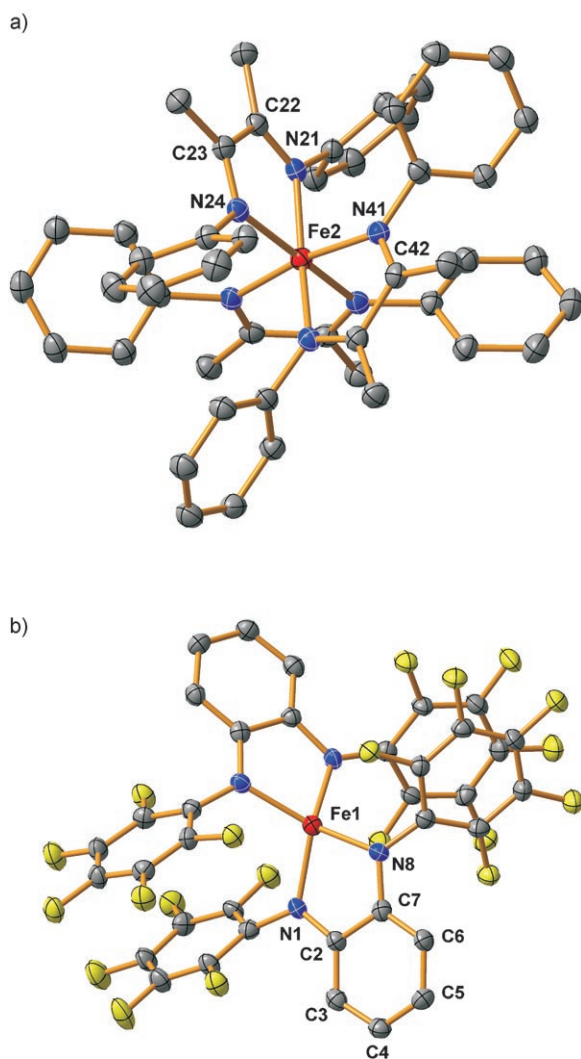


Figure 2. Crystal structure of **2** at 120 K: a) dication $[\text{Fe}^{\text{II}}(\text{dad}^0)_3]^{2+}$ (site symmetry C_2), b) dianion $[\text{Fe}^{\text{II}}(\text{pda}^{2-})_2]^{2-}$ (site symmetry C_2); thermal ellipsoids are drawn at the 30% probability level.

1.301(3) Å) in the ligand N-C-C-N backbone; this situation is only consistent with the neutral form of the ligand.^[1,3,4] The short Fe–N bonds (1.973–1.983(2) Å) indicate the presence of a low-spin (LS) iron ion. At low temperature, the cation $[\text{Fe}(\text{dad}^0)_3]^{n+}$, containing three neutral dad^0 ligands and a LS ferrous or ferric center, carries therefore a 2+ or 3+ charge. Note that the bond lengths in $[\text{Fe}(\text{dad}^0)_3]^{n+}$ are very close to those reported for diamagnetic $[\text{Fe}^{\text{II}}(\text{CH}_3\text{-dad}^0)_3](\text{ClO}_4)_2$.^[6]

If $[\text{Fe}(\text{dad}^0)_3]^{n+}$ is a cation, then $[\text{Fe}(\text{pda})_2]^{m-}$ must be an anion and $n=m$. The anion shows a highly distorted tetrahedral geometry and a dihedral angle of 57.1° between the two planes of the two ligand $\text{C}_6\text{H}_4\text{N}_2$ backbones, which results from the four bulky C_6F_5 substituents involved in intramolecular π – π interactions.^[4a,7] The anion possesses C_2 symmetry rendering the two pda ligands crystallographically identical. The six C–C bond lengths in the *o*-phenylene unit are consistent with those in an aromatic ring, whereas the C–N lengths correspond to single bonds (av 1.399(4) Å). These parameters imply the presence of two dianionic closed-shell pda^{2-} ligands.^[7,8] The four long Fe–N bonds (1.988–

2.004(2) Å) point to a high-spin (HS) configuration of the iron ion (+II or +III oxidation state). The charge of the anion is then 2– for a $[\text{Fe}^{\text{II}}(\text{pda}^{2-})_2]^{2-}$ or 1– for a $[\text{Fe}^{\text{III}}(\text{pda}^{2-})_2]^{-}$ species. As the cation $[\text{Fe}(\text{dad}^0)_3]^{n+}$ has a 2+ or 3+ charge and the anion $[\text{Fe}(\text{pda}^{2-})_2]^{m-}$ has a 1– or 2– charge, it follows that in **2** the cation and the anion possess 2+ and 2– charges, respectively. Thus, the electronic structure of **2** at low temperature is best described as $[\text{Fe}^{\text{II}}(\text{dad}^0)_3]^{2+}[\text{Fe}^{\text{II}}(\text{pda}^{2-})_2]^{2-}$, in which the dication contains a LS Fe^{II} center ($S_{\text{Fe}} = 0$) in an octahedral ligand field and the dianion contains a HS Fe^{II} center ($S_{\text{Fe}} = 2$) in a twisted tetrahedral environment. At low temperature neither the dication nor the dianion contain ligand π radicals.

This assignment of the oxidation and the spin states of the iron ions in **2** is fully confirmed by ^{57}Fe Mössbauer spectroscopy. The zero-field Mössbauer spectrum measured at 80 K shows two main quadrupole doublets of about equal intensities^[9] (Figure 3a). The quadrupole doublet with an isomer shift $\delta = 0.38 \text{ mm s}^{-1}$ and a quadrupole splitting $|\Delta E_Q| = 0.53 \text{ mm s}^{-1}$ is assigned to the LS Fe^{II} center in the octahedral dication, whereas the doublet with $\delta = 0.68 \text{ mm s}^{-1}$ and an enormously large quadrupole splitting $|\Delta E_Q| = 5.20 \text{ mm s}^{-1}$ is assigned to the HS Fe^{II} ion in the dianion (only one example

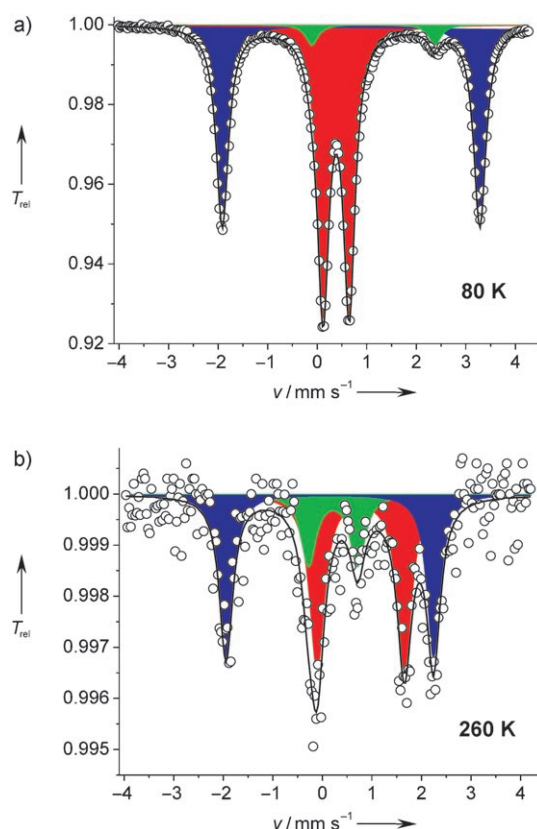


Figure 3. Zero-field ^{57}Fe Mössbauer spectra of **2**: a) at 80 K, simulated with $\delta = 0.38 \text{ mm s}^{-1}$, $|\Delta E_Q| = 0.53 \text{ mm s}^{-1}$ (cation); $\delta = 0.68 \text{ mm s}^{-1}$, $|\Delta E_Q| = 5.20 \text{ mm s}^{-1}$ (anion); $\delta = 1.13 \text{ mm s}^{-1}$, $|\Delta E_Q| = 2.48 \text{ mm s}^{-1}$ (HS Fe^{II} impurity);^[11] b) at 260 K, simulated with $\delta = 0.76 \text{ mm s}^{-1}$, $|\Delta E_Q| = 1.80 \text{ mm s}^{-1}$ (cation); $\delta = 0.16 \text{ mm s}^{-1}$, $|\Delta E_Q| = 4.19 \text{ mm s}^{-1}$ (anion); $\delta = 0.22 \text{ mm s}^{-1}$, $|\Delta E_Q| = 0.99 \text{ mm s}^{-1}$ (impurity).^[12] Color scheme: blue anion, red cation, green impurities.

with a larger $|\Delta E_O|$ in ^{57}Fe Mössbauer spectroscopy has been reported^[10].

Magnetic susceptibility measurements of solid **2** revealed an effective magnetic moment $\mu_{\text{eff}} = 4.86\text{--}4.99 \mu_B$ in the temperature range 50–230 K, which is in agreement with a quintet spin state (Figure 4). In full agreement with the X-ray

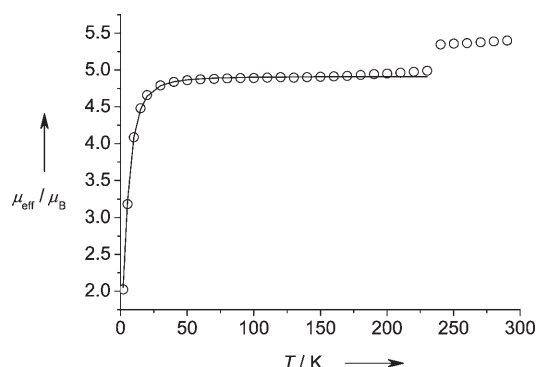


Figure 4. Magnetic susceptibility measurements of **2** performed at 7 T; the best fit for the temperature range 2–230 K was obtained with $g = 2.005$, $|D| = 4.5 \text{ cm}^{-1}$, $E/D = 0$.

data at 120 K, the $S = 2$ state is only due to the paramagnetic $[\text{Fe}^{\text{II}}(\text{pda}^{2-})_2]^{2-}$ dianion; the ferrous ion in the octahedral dication is diamagnetic. Surprisingly, the magnetic moment μ_{eff} increases abruptly to $5.35 \mu_B$ in the small temperature range 230–240 K. This transition is reproducible and independent of the applied field (0.01, 1, and 7 T). No significant hysteresis was found by changing the direction of the temperature sweep.

To understand the origin of this transition, we determined the structure of **2** at high temperature (270 K).^[5] The space group remains the same but the unit-cell lengths increase slightly relative to those of the low-temperature structure; the unit-cell volume increases by 7%. In the octahedral cation two dad ligands preserve the geometry of the fully oxidized neutral form dad^0 as can clearly be seen from the bond lengths within the N–C–C–N backbone, whereas the oxidation level of the third dad ligand has changed: its C–N and C–C bond lengths at 1.350(7) and 1.412(11) Å, respectively, are indicative of the presence of one monoanionic π radical $\text{dad}^{\cdot-}$. Furthermore, the Fe–N bond lengths in the cation have increased considerably (from av 1.977(2) at low temperature to av 2.121(5) Å at high temperature). We interpret this behavior as an indication for LS $\leftrightarrow$ HS transition at the Fe^{II} center within the cation. Note that in the high-temperature structure the Fe–N bond lengths for the $\text{dad}^{\cdot-}$ ligand are shorter than those for the two neutral dad^0 ligands.

The anion $[\text{Fe}(\text{pda})_2]^{m-}$ shows a slightly decreased twist angle of 52.7° at high temperature. The bond lengths within the pda units closely resemble those found in the low-temperature structure, that is, both ligands remain in the fully reduced pda^{2-} form. In contrast, the Fe–N bonds in the anion are significantly shorter in the high-temperature structure (av 1.890(5) Å) than in the low-temperature structure (av 1.996(2) Å). Does this observation also point to a spin-crossover transition? This situation would not be in accord

with the observation that the HS state is favored at high temperature for spin-crossover complexes.^[13] The only alternative interpretation involves internal oxidation of the HS Fe^{II} ion in the dianion of **2** at low temperature to an intermediate-spin (IS) ferric ion with formation of the monoanion $[\text{Fe}^{\text{III}}(\text{pda}^{2-})_2]^-$ at high temperature.

The zero-field ^{57}Fe Mössbauer spectrum of **2** recorded at 260 K shows two quadrupole doublets (Figure 3b). The doublet with $\delta = 0.76 \text{ mm s}^{-1}$ and $|\Delta E_O| = 1.80 \text{ mm s}^{-1}$ is characteristic of a HS Fe^{II} that we assign to the cation. Thus, the isomer shift δ of the cation increases from 0.38 to 0.76 mm s^{-1} by increasing the temperature, indicating a spin transition (crossover) $S_{\text{Fe}} = 0 \leftrightarrow S_{\text{Fe}} = 2$ of this iron ion. On the basis of the results of the crystal structure determination and Mössbauer spectroscopy, we assign the electronic structure of the monocation at 260 K as $[\text{Fe}^{\text{II}}(\text{dad}^0)_2(\text{dad}^{\cdot-})]^+$. The cation now has the charge 1+, that is, it is reduced by electron transfer from the dianion at $T > 240 \text{ K}$. As the anion must have the charge 1– at high temperature, that is, it is oxidized at 260 K, and it contains two pda^{2-} ligands, then the oxidation state of the iron in the anion must be +III. The second doublet with $\delta = 0.16 \text{ mm s}^{-1}$ and a large value of $|\Delta E_O| = 4.19 \text{ mm s}^{-1}$ is assigned to an IS Fe^{III} center. Thus, the electronic structure of **2** at temperatures above 240 K is $[\text{Fe}^{\text{II}}(\text{dad}^0)_2(\text{dad}^{\cdot-})]^+[\text{Fe}^{\text{III}}(\text{pda}^{2-})_2]^-$.

Generally, tetrahedral ferric complexes possess a HS state. The highly distorted twisted environment of the four-coordinate iron center in $[\text{Fe}^{\text{III}}(\text{pda}^{2-})_2]^-$ completely removes the degeneracy of the t_2 and e orbital sets, yielding an IS Fe^{III} center, which is observed for four-coordinate Fe^{III} centers.^[14] The IS state of Fe^{III} is confirmed by magnetic susceptibility measurements (Figure 4). As the HS Fe^{II} center ($S_{\text{Fe}} = 2$) would be strongly antiferromagnetically coupled to the N, N' -coordinated radical $\text{dad}^{\cdot-}$, the monocation possesses a total spin $S_{\text{cat}} = 3/2$. The total spin of the monoanion containing IS Fe^{III} is again $S_{\text{an}} = 3/2$. A simple model for two noninteracting paramagnetic centers gives $\mu_{\text{eff}} = (\mu_{\text{cat}}^2 + \mu_{\text{an}}^2)^{1/2} = (2 \times 3.87^2)^{1/2} = 5.47 \mu_B$ (spin-only value), which is in good agreement with the experimental value $\mu_{\text{eff}} = 5.35\text{--}5.40 \mu_B$ observed at high temperature.

Thus, electron transfer within a cation–anion pair coupled to spin crossover has been observed for the first time. This multiple, thermally induced process is abrupt and reversible without noticeable hysteresis. By increasing the temperature, electron transfer from the HS Fe^{II} center in the dianion to a dad^0 ligand in the dication yields a monocation $[\text{Fe}^{\text{II}}(\text{dad}^0)_2(\text{dad}^{\cdot-})]^+$. Concomitantly, the HS Fe^{II} center in the dianion is converted into an IS Fe^{III} center in the monoanion $[\text{Fe}^{\text{III}}(\text{pda}^{2-})_2]^-$. The electron transfer is accompanied by a spin transition $S_{\text{Fe}} = 0 \leftrightarrow S_{\text{Fe}} = 2$ within the cation, which is not involved in the electron transfer process.

$S_{\text{Fe}} = 0 \leftrightarrow S_{\text{Fe}} = 2$ spin transitions have been observed in several closely related $[\text{Fe}^{\text{II}}\text{L}_3]^{2+}$ systems ($\text{L} = \alpha$ -iminopyridine derivatives).^[15] Taking these results into consideration we could envisage that prior to electron transfer thermally induced spin crossover occurs in $[\text{Fe}^{\text{II}}(\text{dad}^0)_3]^{2+}$. If, on the other hand, electron transfer occurs first, then the one-electron reduction of dad would reduce the energy gap between the t_{2g} and e_g sets of d orbitals and induce the

following spin crossover. Furthermore, the localization of a π electron on one dad ligand would lower the symmetry of the cation, which in turn would remove the orbital degeneracy. Both these factors are highly favorable for Fe^{II} to form a HS state. At present we have no evidence for which of the two scenarios is actually valid.

Experimental Section

1: $[\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2]^{[16]}$ (1.694 g, 4.498 mmol) dissolved in dme (15 mL) was slowly added to a solution of H_2pda (1.800 g, 4.089 mmol) in dme (15 mL) at -80°C . The reaction mixture was allowed to warm to room temperature and was stirred for an additional 1 h. The reaction volume was decreased to 15 mL by evaporation in vacuo, and hexane (ca. 15 mL) was added. After the reaction mixture was stirred for 1.5 h at room temperature, the red solution was decanted and a bright-yellow, extremely air-sensitive powder was dried in vacuo. Yield: 2.63 g (95 %). Anal. calcd (%) for $\text{C}_{26}\text{H}_{24}\text{F}_{10}\text{FeN}_2\text{O}_4$: C 46.31, H 3.59, F 28.17, Fe 8.28, N 4.15; found: C 45.20, H 3.41, F 27.40, Fe 8.07, N 4.08; UV/Vis (dme): $\lambda_{\text{max}}(\epsilon) = 351$ (8200), 292 (7300), 247 nm (10700); magnetic moment $\mu_{\text{eff}} = 5.28 \mu_{\text{B}}$ ($T = 290$ K, $B = 1$ T); ^{57}Fe Mössbauer ($T = 80$ K, $B = 0$ T): $\delta = 1.19$ mm s^{-1} , $|\Delta E_{\text{Q}}| = 2.44$ mm s^{-1} .

2: A solution of dad (179 mg, 0.756 mmol) in toluene (5 mL) was slowly added to a suspension of **1** (340 mg, 0.504 mmol) in toluene (9 mL) at -45°C . The reaction mixture was stirred for 40 min at room temperature and then filtered. The blue solution was left to stand overnight, during which time a black crystalline solid formed. The toluene solution was decanted and black crystals, suitable for X-ray crystallography, were washed with toluene and dried in vacuo. Yield: > 182 mg (> 43 %). Anal. calcd (%) for $\text{C}_{91}\text{H}_{64}\text{F}_{20}\text{Fe}_2\text{N}_{10}$: C 61.09, H 3.61, F 6.24, N 7.83; found: C 60.79, H 3.59, Fe 6.18, N 7.70. ESI-MS (CH_2Cl_2): m/z 932 $[\text{Fe}(\text{pda})_2]^-$ (neg.); 765 $[\text{Fe}(\text{dad})_3 + \text{H}]^+$, 528 $[\text{Fe}(\text{dad})_2]^+$, 264 $[\text{Fe}(\text{dad})]^{2+}$ (pos.).

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$c = 71.670(3)$, $V = 11876.8(8) \text{ \AA}^3$, $Z = 6$, $\rho_{\text{calcd}} = 1.501 \text{ g cm}^{-3}$, $\mu = 0.469 \text{ mm}^{-1}$, 61205 refl. collected, 6293 independent refl., $R_{\text{int}} = 0.0706$, $R = 0.0346$ ($I \geq 2\sigma(I)$), $R(\text{all}) = 0.0580$, $wR(\text{all}) = 0.0837$; Fe1–N8 1.988(2), Fe1–N1 2.004(2), N1–C2 1.401(3), C2–C3 1.392(4), C2–C7 1.428(4), C3–C4 1.394(4), C4–C5 1.364(4), C5–C6 1.394(4), C6–C7 1.390(4), C7–N8 1.396(4); Fe2–N24 1.973(2), Fe2–N41 1.976(2), Fe2–N21 1.983(2), N21–C22 1.307(3), C22–C23 1.473(4), C23–N24 1.301(3), N41–C42 1.296(4), C42–C42#2 1.472(5) $\text{\AA}$. Crystal data of **2** at $T = 270(2)$ K: $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$), $\text{C}_{91}\text{H}_{64}\text{F}_{20}\text{Fe}_2\text{N}_{10}$, $M_r = 1789.22$, dimensions $0.22 \times 0.13 \times 0.11 \text{ mm}^3$, hexagonal, space group $P6_122$, $a = b = 14.241(2)$, $c = 72.189(14)$, $V = 12679(4) \text{ \AA}^3$, $Z = 6$, $\rho_{\text{calcd}} = 1.406 \text{ g cm}^{-3}$, $\mu = 0.440 \text{ mm}^{-1}$, 12427 refl. collected, 3633 independent refl., $R_{\text{int}} = 0.0577$, $R = 0.0564$ ($I \geq 2\sigma(I)$), $R(\text{all}) = 0.0789$, $wR(\text{all}) = 0.1456$; Fe1–N1 1.875(5), Fe1–N8 1.905(5), N1–C2 1.411(7), C2–C3 1.379(8), C2–C7 1.387(8), C3–C4 1.396(8), C4–C5 1.386(10), C5–C6 1.392(8), C6–C7 1.377(8), C7–N8 1.395(7); Fe2–N41 2.092(5), Fe2–N21 2.127(5), Fe2–N24 2.143(6), N21–C22 1.318(8), C22–C23 1.463(8), C23–N24 1.297(7), N41–C42 1.350(7), C42–C42#2 1.412(11). CCDC-665127 and CCDC-665128 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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