# Pyridylmethylamines as Ligands in Iron Halide Complexes – Coordination Behaviour Depending on the Halide, the Denticity of the Amino Ligand and the Oxidation State of Iron

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Abstract. 2-Pyridylmethylamine (amp) and 8-aminochinoline (ach) readily form the following complexes with iron halides in methanol:  $[(amp)_2FeCl_2]$  (1a),  $[(amp)_2FeBr_2]$  (1b),  $[(ach)_2Fe(MeOH)_2]Br_2$  (1c), and  $[(amp)FeCl_2(\mu-OMe)]_2$  (2). Methanol was chosen as a solvent because these reactions are rather complex in ether. For example, FeCl\_3 forms the ionic complex pair  $[(dme)_2FeCl_2]$  [FeCl\_4] (3) with 1,2-dimethoxyethane (dme). The reaction of FeBr<sub>2</sub> with tridentate di(2-pyridylmethyl)amine (dpa) and tetradentate 1,2-dipyridyl-1,2-diaminoethane (dpdae) yields the complexes  $[(dpa)_2Fe]Br_2$ .

MeOH (4) and  $[(dpdae)_2Fe]$  [FeBr<sub>4</sub>] (5), respectively. Crystallographic and magnetochemical investigations show the high-spin configuration for the complexes 1 and 2, whereas the short Fe-N distances of 4 clearly indicate a low-spin state. Compound 2 exhibits an antiferromagnetic exchange interaction with a coupling constant J = -29.4 cm<sup>-1</sup> (H;af = -J S;af<sub>A</sub>·S;af<sub>B</sub>).

Keywords: Iron; Pyridyl complexes; Amino complexes; Pyridylmethylamines

#### Introduction

Iron plays a key role in many metalloenzymes such as lipoxygenases and methane monooxygenases. These nonhem iron enzymes are able to oxidize unsaturated fatty acids or methane with oxygen after activation of the appropriate C-H bonds. Furthermore, iron enzymes such as hemerythrin are responsible for the transport of oxygen. In all these metalloenzymes, the iron atoms are in an octahedral environment and partly coordinated by histidine groups. Therefore, in many biomimetic complexes, pyridine ligands are employed to mimic the reactivity of these iron enzymes.

Iron(II) readily forms the octahedral tris(2-pyridylmethylamine)iron(II) cation with couterions such as halide, perchlorate, or hexafluorophosphate [1]. These complexes show magnetic isomerism: With raising temperature the low-spin state changes into the high-spin state. Last year, *Törnroos* et al. [2] published the neutral complex dichlorobis(2-pyridylmethylamine)iron(II). The complexes with cis and the trans arrangement of the chloro substituents cocrystallized from 1-butanol. Other alcohols such as methanol [3], ethanol [4], propanol, tert-butyl alcohol and allyl alcohol lead to a substitution of the chloride ligands [3].

Institut für Anorganische und Analytische Chemie Friedrich-Schiller-Universität Jena August-Bebel-Str. 2 D-07743 Jena, Germany Tel.: +49 (0) 3641 948110 Fax: +49 (0) 3641 948102 e-mail: m.we@uni-jena.de These halide anions can also be substituted by nitrate if a stoichiometric amount of  $NaNO_3$  is added to a methanol solution of  $(H_2O)_2FeCl_2$  [5].

The tridentate ligand di(2-pyridylmethyl)amine forms the solvent-separated ion pair dichloro-bis(2-pyridylmethyl)amine]iron(II) [6], the iron atom shows low-spin configuration of the iron(II) center. A coordination at iron(III) leads only to an addition of this ligand and the formation of trichloro(2-pyridylmethyl)amine]iron(III) [7]. Iron(III) is also able to oxidize C-N bonds of the similar ligand N-(2pyridyl)methyl]pyridine-2-carboxamide [8]. It is well-known since decades that alkylamides of the late transition metals are not very stable [9]. Due to the oxidation force of iron there are also only very few examples of amides. An exception are the trialkylsilyl substituted amides. Thus, only the bis(trimethylsilyl)amides of iron(II) and iron(III) [10, 11] as well as the extremely reactive (2-pyridylmethyl)(trialkylsilvl)amides of iron(II) [12] are well-known. In order to compare the 2-pyridylmethylamides with the corresponding amines we prepared a series of compounds with bidentate 2-pyridylmethylamine, tridentate di(2-pyridylmethyl)amine and 1,2-dipyridyl-1,2-diaminoethane.

# **Results and Discussion**

# **Synthesis**

The THF adducts of FeCl<sub>2</sub> and FeBr<sub>2</sub> reacted with 2pyridylmethylamine (amp) in methanol to give the bis(amp) complexes with the halide ligands in trans arrangement according to equation 1. The complexes  $[(amp)_2FeX_2]$  with X = Cl (1a) and Br (1b) formed regardless of the chosen



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stoichiometry of the starting materials in the shape of yellow cuboids and yellow-green platelets, respectively. A similar reaction of  $[(thf)_2FeBr_2]$  with less flexible 8-aminochinoline (ach) led also to the 1:2 complex **1c**, however, the bromide ions were substituted by the solvent molecules, giving an ion triple with the  $[(ach)_2(MeOH)_2Fe]^{2+}$  cation.



#### Formula 1

The reaction of FeCl<sub>3</sub> with Amp in methanol gave the dimeric complex **2** with the methanolate anions in the bridging positions. The single crystals appeared to be light brown, in pulverized form they were yellow. A powder diffractogram confirmed that these substances were identical. If the solvent was changed to an ether the reaction of FeCl<sub>3</sub> with Amp gives no pure products but an inseparable mixture. In order to understand the difficulties arising from the solvent change, the ether adduct was investigated. Anhydrous iron(III) chloride was dissolved in hot 1,2-dimethoxyethane (dme). During cooling to room temperature, orange platelets of  $[(dme)_2 \text{FeCl}_2]^+$  [FeCl<sub>4</sub>]<sup>-</sup> (**3**) precipitated.

Whereas FeCl<sub>3</sub> formed a 1:1 complex with di(2-pyridylmethyl)amine (dpa) [7], FeCl<sub>2</sub> and dpa yielded the 1:2 compound [6]. The reaction of  $[(thf)_2FeBr_2]$  with Dpa gave the 1:2 complex **4** according to equation 2 regardless of the stoichiometry of the starting materials. This compound precipitated in the shape of red platelets. The crystalline compound contains methanol molecules in the cavities between the iron(II) complexes.

Due to steric strain the tetradentate ligand 1,2-dipyridyl-1,2-diaminoethane (dpdae) cannot bind with all of the nitrogen donor atoms to a single metal atom. The reaction of  $[(THF)_2FeBr_2]$  with dpdae yielded the ion pair



#### Formula 2

 $[(dpdae)_2Fe]^{2+}$   $[FeBr_4]^{2-}$  (5) in the shape of orange-red platelets, regardless of the stoichiometry of the starting materials. The iron(II) ion of the cation is in a distorted octahedral environment whereas the the anion forms a  $[FeBr_4]^{2-}$  tetrahedron.

# **Molecular Structures**

The compounds of the type  $(amp)_2FeX_2$  with X as Cl (1a) and Br (1b) show the same molecular inversion symmetry, however, they crystallize in different space groups. Data of these complexes are listed in Table 1 together with those of  $[(ach)_2Fe(MeOH)_2]Br_2$  (1c) in comparison to well-known compounds [2, 5]. The compounds 1a, 1b and 1c are represented in Figures 1, 2 and 3, respectively.

The centrosymmetric compounds of the type [(amp)<sub>2</sub>FeX<sub>2</sub>] are very similar: The bite angle N1-Fe-N2 of all of these compounds is very small and varies between 75.7° and 79.6°. Due to these small angles, the octahedral geometry at the iron centers is distorted. The Fe-N bonds vary between 215 and 220 pm for the amino group as well as for the pyridyl ligand. The data of the 8-aminochinoline complex 1c fit very well into this scheme. For the C<sub>2</sub>-symmetric cis-[(amp)<sub>2</sub>FeCl<sub>2</sub>], the Fe-N bond lengths are slightly elongated but here the Fe-Cl distances are smaller [2]. An exception is the nitrate  $[(amp)_2Fe(NO_3)_2]$  [5], which shows very short Fe-N bonds. On the other hand, the Fe-O distances to the monodentate nitrate anion are extremely large despite an electrostatic attraction. Even the neutral methanol molecule in 1c shows a closer contact to the iron(II) center (214.1(2) pm) than the nitrate with a value of

	[(amp) <sub>2</sub> FeX <sub>2</sub> ]	[(ach) <sub>2</sub> FeX <sub>2</sub> ]				
x	Cl (1a)	Br (1b)	Cl (trans) [2]	Cl (cis) [2]	NO <sub>2</sub> [5]	MeOH (1c)
Fe-X	250.08(6)	273.86(4)	249.39(4)	246.13(5)	229.7(4)	214.1(2)
Fe-N1	218.5(2)	215.1(3)	217.5(1)	222.0(1)	212.8(6)	219.4(2)
Fe-N2	218.9(2)	217.2(3)	219.7(1)	222.7(1)	207.6(5)	218.6(2)
N1-Fe-N2	76.57(8)	77.9(1)	77.13(5)	75.68(5)	79.6(2)	76.77(8)
N1-Fe-X	90.25(5)	87.08(7)	89.57(4)	91.76(4) 99.68(4)	88.8(2)	93.20(7)
N1-Fe-N2 '	103.43(8)	102.2(1)	102.87(5)	91,94(5)	100.4(2)	103.23(8)
N2-Fe-X	89.19(6)	92.04(9)	91.35(4)	89.77(4) 167.06(4)	94.2(2)	93.14(8)

Table 1 Selected bond lengths/pm and angles/° of [(Amp)<sub>2</sub>FeX<sub>2</sub>] and related complexes in comparison to literature data.



**Fig. 1** Molecular structure of [(amp)<sub>2</sub>FeCl<sub>2</sub>] (1a). The ellipsoids represent a probability of 30 %. The N-bound hydrogen atoms are represented with arbitrary radii, all other H atoms are neglected for clarity reasons.



**Fig. 2** Molecular structure of [(amp)<sub>2</sub>FeBr<sub>2</sub>] (**1b**). The ellipsoids represent a probability of 30 %. The N-bound hydrogen atoms are shown with arbitrary radii, all C-bound H atoms are omitted for clarity reasons.

229.7(4) pm [5]. These Fe-N bond lengths show a characteristic elongation of approximately 20 pm compared with low-spin complexes. For example, the octahedral complex  $[Fe(Py-C(O)-N-C_6H_4-S-CH_2)_2]$  shows average Fe-N distances of 196.8 pm for the pyridyl unit and of 197.3 pm for the amido fragment [13].

Figure 4 shows the molecular structure of  $[(dme)_2FeCl_2]^+$ [FeCl<sub>4</sub>]<sup>-</sup> (3) as well as selected structural parameters. The tetrahedral tetrachloroferrate(III) anion shows Fe2-Cl bond



Fig. 3 Molecular structure of  $[(ach)_2Fe(MeOH)_2]Br_2$  (1c). The ellipsoids represent a probability of 30 %. The N- and O-bound hydrogen atoms are drawn with arbitrary radii, all other H atoms are neglected for clarity reasons.



Fig. 4 Molecular structure of  $[(dme)_2FeCl_2]$  [FeCl<sub>4</sub>] (3). The ellipsoids represent a probability of 30 %. The H atoms are neglected for clarity reasons.

Selected bond lengths/pm: Fe1-Cl1 222.26(8), Fe1-O1 212.7(2), Fe1-O2 207.4(2), Fe2-Cl2 220.0(1), Fe2-Cl3 219.7(1), Fe2-Cl4 218.95(9); angles/°: O1-Fe-O2 78.07(7), Cl1-Fe1-Cl1A 100.85(5).

lengths of approximately 220 pm whereas those of the octahedral cation (Fe1-Cl1) are slightly increased. Due to the high-spin configuration no distortion can be expected for the anion. The cation shows two different Fe1-O distances to the ether ligand (207.4(2) and 212.7(2) pm). Due to the higher oxidation state of the iron atom, these values are smaller than for the methanol-iron contact in **1c**.



Fig. 5 Molecular structure of  $[(amp)_2FeCl_2(\mu-OMe)]_2$  (2). The ellipsoids represent a probability of 30 %. The N-bound hydrogen atoms are represented with arbitrary radii, all other H atoms are neglected for clarity reasons.

Selected bond lengths/pm: Fe-Cl1 236.69(8), Fe-Cl2 230.37(7), Fe-N1 216.4(2), Fe-N2 217.4(2), Fe-O1M 195.5(2), Fe-O1MA 203.3(2); angles/°: N1-Fe-N2 75.69(9), N1-Fe-Cl1 93.27(6), N1-Fe-Cl2 95.20(5), Fe-O1M-FeA 104.44(7).



**Fig. 6** Molecular structure of the centrosymmetric  $[(dpa)_2Fe]^{2+}$  cation of **4**. The ellipsoids represent a probability of 30 %. The N-bound hydrogen atoms are represented with arbitrary radii, all other H atoms are neglected for clarity reasons.

Selected bond lengths/pm: Fe-N1 199.2(4), Fe-N2 203.1(4), Fe-N3 199.5(4); angles/°: N1-Fe-N2 83.4(2), N1-Fe-N3 , N2-Fe-N3 82.9(2), N1-Fe-N2A 96.6(2), N1-Fe-N3A 94.4(2), N2-Fe-N3A.

The molecular structure of the centrosymmetric dinuclear complex 2 is represented in Figure 5. In the di-



Fig. 7 Molecular structure of  $[(dpdae)_2Fe]$  [FeBr<sub>4</sub>] (5). The ellipsoids represent a probability of 30 %. The N-bound hydrogen atoms are drawn with arbitrary radii, all C-bound H atoms are neglected for clarity reasons.

Selected bond lengths/pm: FeA-N1A 206.6(6), FeA-N3A 207.8(6), FeA-N4A 210.5(6), Fe-Br1 240.3(1), Fe-Br2 238.7(1), Fe-Br3 242.7(1), Fe-Br4 246.0(1); angles/°: N1A-FeA-N3A 80.7(2), N1A-FeA-N4A 82.9(2), N3a-FeA-N4A 79.0(2).

nuclear unit the Fe<sup>3+</sup> ions are symmetrically bridged by two methanolate groups with Fe-O bond lengths of 195.5(2) and 203.3(2) pm, which are within the usually observed range [14, 15]. Moreover, also the bond angle at the bridging oxygen atom with 104.44(7)° is found within the expected range. The Fe-N bonds are only slightly shortened compared to the iron(II) derivatives discussed earlier. The two chlorine atoms are in a cis-arrangement and show distances to the iron center of 230.37(7) and 236.69(8) pm, which are drastically smaller than those listed in Table 1 for iron(II) complexes.

The molecular structure of  $[(dpa)_2Fe]Br_2 \cdot 2$  MeOH (4) is represented in Figure 6 and is very similar to the structure of the corresponding chloride complex which was described earlier by *Davies* et al. [6]. The Fe-N bond lengths of 4 lie at 199 and 203 pm for the pyridyl unit and the amino moiety, respectively. The smaller distance to the pyridyl groups results from a higher s-orbital participation at the nitrogen atom. The magnetic measurements confirm the low-spin state of this complex in agreement with the investigations of *Davies* et al. [6].

Figure 7 shows the molecular structure of  $[(dpdae)_2Fe]^{2+}$ [FeBr<sub>4</sub>]<sup>2-</sup> (5). The Fe-N bonds lengths show values of 206.6(6) pm for the pyridyl fragment and 207.8(6) and 210.5(6) pm for the amino functions. The fused five-membered metallacycles induce intramolecular strain and lead to the variation of these values. Due to this fact, small bite angles N-Fe-N between 79 and 83° are observed and reflect the deviation from an octahedral geometry at the iron center.

The tetrahedral tetrabromoferrate(II) anion displays an average Fe-Br distance of 241.9 pm which is smaller than in the octahedral complex **1b**. A comparison with the very few literature-known tetrabromoferrate(II) (average Fe-Br 244 pm [16] and 245 pm [17]) and the very common tetrabromoferrate(III) anions (average Fe-Br bond length 232 pm, min./max. Fe-Br distances 228/238 pm) allows an



Fig. 8 Plot of  $\chi_M$  and  $\chi_M T$  vs. T for complex 2 at an applied field of 2 kOe. The corresponding fit functions are drawn as solid lines (for parameters see text).

unambiguous assignment of the oxidation state and confirms that the anion of **5** contains an iron(II) ion.

# Magnetochemical Investigations of 2

The magnetic properties of compound **2** were determined by magnetic susceptibility measurements of polycrystalline samples with a SQUID-susceptometer as a function of temperature in the range from 2 to 300 K. The  $\chi_M$  and  $\chi_M T$ plots of the obtained data are given in Figure 8. At room temperature complex **2** exhibits a nearly paramagnetic behavior with  $\chi_M T$  values of about 6.0 cm<sup>3</sup> K mol<sup>-1</sup>, which approaches the theoretical spin-only value for two independent S = 5/2 centers per molecule expected for the high temperature limit [18]. Upon lowering the temperature complex **2** shows an antiferromagnetic coupling of the two iron(III) ions, leading to a decrease of the  $\chi_M T$  values. The sharp increase of the  $\chi_M$  values at very low temperatures is indicative for the presence of paramagnetic impurities.

A quantitative analysis of the susceptibility data has been performed with the assumption of an isotropic interaction by using the Heisenberg-Dirac-Van Vleck Hamiltonian  $\hat{H} = -J \hat{S}_A \cdot \hat{S}_B$  with  $S_A = S_B = 5/2$ . The least-squares fit was carried out including a term representing possible paramagnetic impurities. A good fit to the data was obtained with a coupling constant J = -29.4 cm<sup>-1</sup>, g = 2.085 and a fraction of paramagnetic impurities of  $\rho = 0.018$ . This fit is illustrated in Figure 8 and corresponds to a coefficient of determination of  $r^2 = 0.99997$ .

The observed antiferromagnetic interaction between the high-spin iron(III) ions is consistent with the usually observed superexchange through alcoholate bridges [14, 19]. Moreover, for dinuclear iron(III) units bridged by ligand oxygen atoms (oxo, hydroxo, alkoxo, etc.) a magnetostructural correlation has been established between the magnetic coupling and the shortest superexchange pathway between the iron(III) ions [15]. For 2 this shortest average length of the coupling pathway is  $\langle \text{Fe-O} \rangle = 199.4 \text{ pm}$ , leading to a predicted coupling constant of  $J = -19 \text{ cm}^{-1}$ . It is worth noting here that the observed experimental value is well within the predictive range of the reported relationship. This is corroborated by the fact that other alcoholate bridged dinuclear iron(III) complexes with only slightly smaller values for the shortest average length of the exchange pathway of 199.1 and 198.9 pm exhibit coupling constants of -30.8 and 32.6 cm<sup>-1</sup>, respectively [14, 19].

## **Summary and Perspectives**

Selected physical data of iron complexes with pyridylmethylamino ligands are given in Table 2. The oxidation state of the iron atom shows only a minor influence on the Fe-N bond lengths. However, the spin state strongly affects



Formula 3

 Table 2
 Comparison of selected characterization data of the compounds 1, 2, 4, and 5.

	[(amp) <sub>2</sub> FeCl <sub>2</sub> ]	[(amp) <sub>2</sub> FeBr <sub>2</sub> ]	[(ach) <sub>2</sub> Fe(MeOH) <sub>2</sub> ] <sup>2+</sup>	[(amp)FeCl <sub>2</sub> (µ-OMe)] <sub>2</sub>	[(dpa) <sub>2</sub> Fe]Br <sub>2</sub> ·2 MeOH	[(dpdae) <sub>2</sub> Fe] <sup>2+</sup>
x	1a	1b	1c	2	4	5
$n(Fe^{n+})^{a}$	2	2	2	3	2	2
Fe-N(pyridyl)	218.5	215.1	219.4	216.4	199.2, 199.5	206.6
Fe-N(amine)	218.9	217.2	218.6	217.4	203.1	207.8, 210.5
Spin <sup>b)</sup>	h.s.	h.s.	h.s.	h.s.	1.s.	h.s.
v(NH)	3337, 3233	3277, 3228	3157 (broad)	3302, 3245	3346 (broad)	3277, 3247

a) Oxidation state of the iron center; b) high spin h.s., low spin l.s.

the Fe-N distances. The low-spin configuration leads to a shortening of the Fe-N bonds of nearly 20 pm.

Trialkylsilyl substituted 2-pyridylmethylamines can easily be deprotonated (A) and oxidized (B) by tin(II) and at elevated temperatures by zinc(II) compounds. These reactions lead to a C-C coupling and after protonation to the formation of 1,2-dipyridyl-1,2-bis(trialkylsilylamino)ethane (C). The reaction sequence is illustrated in equation 3. The standard potentials  $E^0(Fe^{2+}/Fe^{3+})$  of +0.77 V,  $E^0(Fe/Fe^{2+})$ of -0.44 V and  $E^0(Fe/Fe^{3+})$  of -0.04 V offer a broad window for electron transfer reactions. In order to perform the C-C coupling reaction, a deprotonation of the amino group is required as the first reaction step. Therefore, the 2-pyridylmethylamides of iron [12] are far less stable than these amine complexes. Future investigations are in progress in order to show to what extent these complexes can serve as precursors for the C-C coupling reactions.

# **Experimental Section**

*General procedure*: All manipulations were carried out in an anhydrous argon atmosphere and the solvents were thoroughly dried. Starting 1,2-dipyridyl-1,2-bis(tert-butyldimethylsilylamino)ethane was prepared according to a literature procedure [20].

 $[(amp)_2FeCl_2]$  (1a): On a solution of 0.07 g of (thf)<sub>1.5</sub>FeCl<sub>2</sub> (0.3 mmol) in 20 ml of THF a second solution of 0.07 g of 2-aminomethylpyridin (amp, 0.6 mmol) in 2 ml of methanol was layered.Within 4 days the first crystals formed. Now the mixture was stored at 5 °C and 0.03 g of yellow cuboids of 1 (0.1 mmol, 29 %) precipitated. M.p. 219 °C (dec.).

 $IR/cm^{-1}:~3337~s,~3233~s,~3149~m,~3014~m,~1603~s,~1568~m,~1491~m,~1331~w,~1290~m,~1254~w,~1212~w,~1152~m,~1104~w,~1060~m,~1013~s,~979~w,~921~m,~896~w,~810~w,~766~s,~730~m,~646~w,~633~m,~552~m,~474~w.~MS~(DEI,~m/z):~234~([Fe(amp)Cl_2]^+,~1~\%),~199~([Fe(amp)Cl]^+,~2~\%),~108~([amp]^+,~100~\%),~79~([py]^+,~88~\%).$ 

 $[(amp)_2FeBr_2]$  (1b): A solution of 0.34 g of 2-aminomethylpyridin (3.2 mmol) in 2 ml of methanol was added dropwise to a solution of 0.57 g of (thf)<sub>2</sub>FeBr<sub>2</sub> (1.6 mmol) in 5 ml of methanol. A yellowbrown solution formed and already after 30 minutes, the crystallization of began. Within 17 hours yellow-green microcrystalline **2** precipitated. This solid was collected, the volume of the mother liquor reduced and another crop of crystals were obtained. Recrystallization from hot methanol gave 0.51 g of **2** (1.2 mmol, 75 %) in the shape of yellow-green platelets. M.p. 260 °C (dec.). Elemental analysis (C<sub>12</sub>H<sub>16</sub>Br<sub>2</sub>FeN<sub>4</sub>; 431.94 g mol<sup>-1</sup>): calcd.: C 33.37, H 3.73, N 12.97; found: C 33.37, H 3.82, N 13.08 %.

 $IR/cm^{-1}:~3277~vs,~3228~vs,~3149~s,~3055~w,~2026~w,~1944~w,~1653~w,~1602~vs,~1568~m,~1481~s,~1283~m,~1189~w,~1144~s,~1106~s,~1093~s,~1051~w,~1019~vs,~973~w,~932~m,~809~w,~771~vs,~668~w,~645~w,~630~m,~551~m,~476~m.$  MS (DEI, m/z): 324 ([Fe(amp)Br\_2]<sup>+</sup>, 1 %), 243 ([Fe(amp)Br]^+, 3 %), 108 ([amp]^+,~100~\%), 80 ([py+H]^+,~97~\%).

 $[(ach)_2Fe(MeOH)_2]Br_2$  (1c): A solution of 0.32 g of 2-aminochinoline (2.22 mmol) in 7 ml of methanol was dropped at r.t. to a solution of 0.40 g of (thf)\_2FeBr<sub>2</sub> (1.11 mmol) in 3 ml of methanol. The reaction mixture turned red immediately. Storage at 5 °C afforded the precipitation of a microcrystalline powder of 1c. Reduction of the volume of the mother liquor and storage at 5 °C yielded another crop of crystals of 1c. Recrystallization from boiling methanol gave 0.54 g of orange-brown platelets of 1c (1.0 mmol, 87 %). M.p. 110 °C (dec.). Elemental analysis ( $C_{20}H_{24}Br_2FeO_2N_4$ , 568.08 g mol<sup>-1</sup>): calcd.: C 41.97, H 4.09, N 9.84; found: C 42.29, H 4.26, N 9.86 %.

 $IR/cm^{-1}$ : 3157 br, vs, 2752 m, 2488 w, 1999 w, 1947 w, 1885 w, 1816 w, 1743 w, 1678 w, 1622 m, 1592 m, 1576 s, 1503 vs, 1425 m, 1406 m, 1320 s, 1264 w, 1248 w, 1223 m, 1196 w, 1174 w, 1134 m, 1075 vs, 1061 s, 1030 m, 1001 vs, 895 m, 831 vs, 793 s, 769 vs, 668 br, w, 633 m, 580 m, 566 m, 525 m, 500 w, 491 m, 466 w. MS (DEI, m/z): only the fragmentation pattern of the ligand was observed, 144 ([ach]<sup>+</sup>, 100 %), 117 ([ach-NH2-CH]+, 52 %).

 $[(amp)FeCl_2(\mu-OMe)]_2$  (2): A solution of 0.80 g of anhydrous FeCl<sub>3</sub> (4.9 mmol) in 10 ml of methanol was prepared. Within 10 minutes a solution of 0.53 g of 2-aminomethylpyridine (amp, 4.9 mmol) was added. A yellow-brown microcrystalline solid of 2 (1.29 g, 4.8 mmol, 99 %) precipitated. M.p. 180 °C (dec.). Elemental analysis (C<sub>14</sub>H<sub>22</sub>Cl<sub>4</sub>Fe<sub>2</sub>O<sub>2</sub>N<sub>4</sub>, 531.85 g mol<sup>-1</sup>): calcd.: C 31.66, H 4.14, N 10.37; found: C 31.62, H 4.17, N 10.53 %.

 $IR/cm^{-1}:$  3302 s, 3245 m, 3155 w, 3078 w, 1601 m, 1569 w, 1483 m, 1521 w, 1282 m, 1164 m, 1111 w, 1080 s, 1035 vs, 1023 vs, 977 w, 930 m, 889 w, 815 w, 770 s, 653 m, 643 m , 586 m, 509 s. **MS** (DEI, m/z): only the fragmentation of amp was observed, 107 ([amp-H]<sup>+</sup>, 100 %), 79 ([py]<sup>+</sup>, 93 %).

 $[(dme)_2FeCl_2]$  [FeCl<sub>4</sub>] (3): Anhydrous FeCl<sub>3</sub> was dissolved in boiling 1,2-dimethoxyethane (dme). Cooling to r.t. afforded quantitatively the precipitation of orange platelets. M.p. 194 °C (dec.). Elemental analysis (C<sub>8</sub>H<sub>20</sub>O<sub>4</sub>Cl<sub>8</sub>Fe<sub>2</sub>, 504.65 g mol<sup>-1</sup>): calcd.: C 19.04, H 3.99; found: C 19.16, H 4.08 %.

 $\mathbf{IR}/\mathrm{cm}^{-1}$ : 3422 br, m, 2991 w, 2943 m, 2842 w, 1617 w, 1450 s, 1438 m, 1287 m, 1243 m, 1204 w, 1184 m, 1113 m, 1065 s, 1016 vs, 979 m, 859 m, 847 vs, 803 m, 552 s.

 $[(dpa)_2Fe]Br_2$ ·2 MeOH (4): A solution of 0.70 g of bis(2-pyridylmethyl)amine (dpa, 3.6 mmol) in 3 ml of methanol was added to a stirred solution of 0.63 g of (thf)\_2FeBr\_2 (1.8 mmol) in 5 ml of methanol. A red solid of 4 (0.86 g, 1.3 mmol, 72 %) precipitated from this brown solution. M.p. 250 °C (dec.). Elemental analysis (C<sub>26</sub>H<sub>34</sub>Br<sub>2</sub>FeO<sub>2</sub>N<sub>6</sub>, 678.24 g mol<sup>-1</sup>): calcd.: C 46.04, H 5.05, N 13.39; found: C 45.66, H 5.03, N 12.18 %.

 $IR/cm^{-1}: 3346 \ br, \ s, \ 3131 \ vs, \ 3017 \ m, \ 1608 \ m, \ 1569 \ w, \ 1485 \ m, \ 1312 \ m, \ 1248 \ w, \ 1155 \ m, \ 1120 \ m, \ 1070 \ m, \ 1027 \ s, \ 911 \ m, \ 820 \ w, \ 781 \ m, \ 792 \ s, \ 565 \ br, \ w, \ 492 \ w, \ 458 \ w. \ MS \ (DEI, \ m/z): \ 415 \ ([Fe(dpa)Br_2-H]^+, \ 0, 3\ \%), \ 336 \ ([Fe(dpa)Br])^+, \ 6\ \%), \ 200 \ ([dpa+H]^+, \ 17\ \%), \ 107 \ ([amp-H]^+, \ 59\ \%), \ 93 \ ([picolyl]^+, \ 100\ \%), \ 78 \ ([py-H]+, \ 14\ \%).$ 

 $[(dpdae)_2Fe]$  [FeBr<sub>4</sub>] (5): 1,2-Dipyridyl-1,2-bis(tert-butyldimethylsilylamino)ethane (0.28 g, 0.63 mmol) was dissolved in 2 ml of methanol which yielded quantitatively the formation of MeOSit-BuMe<sub>2</sub> and 1,2-dipyridyl-1,2-diaminoethane (dpdae). This solution was layered on the solution of 0.23 g of (thf)<sub>2</sub>FeBr<sub>2</sub> (0.63 mmol) in 5 ml of methanol. At the border of these two solutions a red ring formed. Within 4 days orange-red platelets precipitated from this mixture. After reduction of the volume and storage of the mother liquor at 5 °C afforded another crop of orange-red crystals. M.p. 148 °C (dec.).

 $IR/cm^{-1}:$  3277 m, 3247 m, 1607 w, 1591 m, 1572 w, 1302 w, 1160 w, 1012 m, 799 w, 756 m, 632 w. MS (DEI, m/z): 448 ([2dpdae+Fe-2NH<sub>3</sub>]<sup>+</sup>, 1 %), 429 ([dpdae+Fe+2Br-H]<sup>+</sup>, 2 %), 289 ([dpdae+Fe+NH<sub>3</sub>-H]+, 100 %), 196 ([dpdae-NH<sub>3</sub>-H]<sup>+</sup>, 36 %), 108 ([amp]<sup>+</sup>, 84 %), 79 ([py]<sup>+</sup>, 44 %).

# Magnetic measurements

The magnetic susceptibility data were measured on a MPMSR-5S-SQUID magnetometer from Quantum Design in the range from 2 to 400 K at an applied magnetic field of 2 kOe. Diamagnetic corrections were estimated according to Pascal's constants. The suscepti-

Compound	1a	1b	1c	2	3	4	5
Formula	C12H16Cl2FeN4	C <sub>12</sub> H <sub>16</sub> Br <sub>2</sub> FeN <sub>4</sub>	C <sub>20</sub> H <sub>24</sub> Br <sub>2</sub> FeN <sub>4</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>22</sub> Cl <sub>4</sub> Fe <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>8</sub> H <sub>20</sub> Cl <sub>6</sub> Fe <sub>2</sub> O <sub>4</sub>	C <sub>24</sub> H <sub>26</sub> Br <sub>2</sub> FeN <sub>6</sub> * 2 CH <sub>4</sub> O	C <sub>24</sub> H <sub>28</sub> Br <sub>4</sub> Fe <sub>2</sub> N <sub>8</sub>
fw /g·mol <sup>−1</sup>	343.04	431.96	568.10	531.86	504.64	678.26	859.88
<i>T</i> /°C	-90(2)	-90(2)	-90(2)	-90(2)	-90(2)	-90(2)	-90(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	Pbcm	$P\bar{1}$	$P\overline{1}$
al À	6.1016(5)	6.6820(5)	9.4902(4)	11.0055(6)	6.775(2)	8.7387(6)	9.9256(6)
b/ Å	12.8559(10)	7.0774(3)	13.0177(9)	8.1195(3)	14.9714(7)	9.2175(9)	11.0407(8)
c/ Å	9.3085(6)	8.5467(5)	9.7133(7)	12.2240(8)	19.3557(9)	9.7053(9)	15.9915(10)
$\alpha$ /°		112.255(3)				76.643(4)	74.469(4)
β/°	98.552(5)	96.085(3)	105.242(4)	108.920(3)		84.627(6)	74.956(4)
γ/°		96.600(4)				67.888(5)	64.936(4)
$V/Å^3$	722.05(9)	366.65(4)	1157.78(13)	1033.31(10)	1963.3(7)	704.64(11)	1507.87(17)
Ζ	2	1	2	2	4	1	2
$\rho (g \cdot cm^{-3})$	1.578	1.956	1.630	1.709	1.707	1.598	1.894
$\mu ({\rm cm}^{-1})$	14.05	64.68	41.25	19.37	22.99	34.05	62.91
measured data	4639	2588	7975	7128	11975	4731	10495
data with $I > 2\sigma(I)$	1413	1528	2193	1763	1568	2423	4822
unique data (R <sub>int</sub> )	1640	1662	2637	2363	2319	3070	6810
$WR_2$ (all data, on $F^2$ ) <sup>a)</sup>	0.0951	0.0806	0.0750	0.0801	0.0815	0.1617	0.1582
$R_1 \ (I \ge 2\sigma(I))^{\rm a)}$	0.0353	0.0308	0.0306	0.0329	0.0350	0.0576	0.0578
s <sup>b)</sup>	1.135	1.093	1.041	0.989	1.033	1.070	1.024
Res. dens./e·A <sup>-3</sup>	0.399/-0.431	0.652 / -0.862	0.643/-0.608	0.305/-0.373	0.417/-0.416	1.296/-0.710	1.947/-1.274
Absorpt. method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr T min/max	0.7884/0.8475	0.5888/0.8075	0.4703/0.5089	0.7305/0.7701	0.6228/0.7769	0.4923/0.6800	0.3669/0.4580
CCDC No.	611357	611358	611359	611360	611361	611362	611363

 Table 3
 Crystal data and refinement details for the X-ray structure determinations

<sup>a)</sup> Definition of the *R* indices:  $\mathbf{R}_1 = (\Sigma ||F_o| + |F_c||) / \Sigma ||F_o| = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$  with  $w^{-1} = \sigma^2 (F_o^2) + (aP)^2$ . <sup>b)</sup>  $s = \{\Sigma [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$ .

bility data were further corrected for the presence of paramagnetic impurity. For details see refs. [21, 22].

#### X-ray structure determinations

The intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda =$  0.71073 Å). Data were corrected for Lorentz polarization and for absorption effects [23–25]. The crystal data and refinement details are summarized in Table 3. The structures were solved by direct methods (SHELXS [26]) and refined by full-matrix least squares techniques against  $F_0^2$  (SHELXL-97 [27]).

*Supporting Information available:* Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-611357 for 1a, CCDC-611358 for 1b, CCDC-611359 for 1c, CCDC-611360 for 2, CCDC-611361 for 3, CCDC-611362 for 4, and CCDC-611363 for 5. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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