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Preparation, Magnetic and Structural Study on Oxido-Bridged Diiron(III) Complexes with Open-Chain Tetrapyrrolic 2,2′-Bidipyrrin Ligands

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Four (μ-oxido)diiron(III) complexes of differently alkyl-substituted 2,2′-bidipyrrin ligands $[(L)Fe]_2O$ have been prepared by a one-pot approach from the respectively substituted 2,2′-bipyrroledialdehydes and 3,4-dialkylpyrroles, and from a suitable source of trivalent iron, under alkaline conditions. Four single-crystal X-ray diffraction studies were undertaken on three of the new compounds as different solvates. The iron atoms are five-coordinate in all cases, and the observed Fe–N and Fe–O distances are in the range of 2.024–2.082 Å and 1.761–1.818 Å, respectively. These bonds are (porphyrinato)iron-like, typical for *high spin* iron(III) complexes, and clearly distinct from those observed for the respective mononuclear (chlorido)-, (bromido)- and (iodido)iron(III)–2,2′-bidipyrrins, which contain a central *intermediate spin* iron(III) ion in the solid state. All complexes contain two helically distorted tetrapyrrolic ligands with the same sense of helicity, but pack quite differently from one case to the other. A cleft is present on one side of the connecting oxygen atom, which is occupied either by a self-complementary second molecule of the complex itself, or by a small molecule (dichloromethane, or pyrrole with N–H···O bond). The Fe–O-Fe subunits are bent and can be grouped with respect to the Fe–O–Fe bond angle range of either 153.91–156.89° or 131.89–132.97°. All new compounds were investigated by analytical, spectroscopic and magnetic means and found weakly paramagnetic and dynamic with respect to helix inversion at ambient temperature in solution. SQUID magnetometry revealed antiferromagnetically coupled *high spin* iron(III) species with exchange coupling constants of $J = -111$ to $-122\ \mathrm{cm}^{-1}$. The exchange coupling appears independent from the Fe–O–Fe angle as described earlier for related porphyrinoid and salen-type (μ-oxido)diiron(III) species.

Introduction

(μ-Oxido)(porphyrinato)diiron(III) complexes are the stable products of oxygenation and hydrolysis of sterically unhindered (porphyrinato)iron(II)- and -iron(III) complexes. Due to their ready availability, these dinuclear species have long been used as model compounds for biological (μ-oxido)diiron sites, and several spectroscopic, structural and magnetic studies have been undertaken in the past for different iron porphyrins and porphyrinoids.[1,2] Oxido-bridged iron(III) complexes of cofacial diporphyrins,[3] the so-called pacman porphyrins, have more recently gained further attention as photocatalysts for the reduction of molecular oxygen to water and the oxygenation of hydrocarbon substrates.[4] As a general rule, (μ-oxido)(porphyrinato)diiron(III) complexes, as well as the related salen species,[5] contain two *high spin* iron(III) ions which are antiferromagnetically coupled with $J = -92$ to $-147\ \mathrm{cm}^{-1}$. The Fe–O–Fe units display Fe–O bond lengths between 1.73 and 1.78 Å and Fe–O–Fe angles in the range 144.6–180°. It has been argued that these bond characteristics influence the strength of the magnetic exchange interaction between the iron atoms.[1f,1h,1o] A clear magnetostructural correlation, however, has not yet been found. The available data as well as theoretical considerations suggest that within a given set of compounds the Fe–O bond lengths do indeed influence the coupling constant in the predicted way,[6] whereas the Fe–O–Fe angle has a minor or no influence. Protonated forms, that is, (μ-hydroxido)(porphyrinato)diiron(III) cations, do also exist, but structural data on such species is rare.[7] Other than for the oxido-bridged examples the hydroxido-bridged complexes are known with both, *high spin* and *intermediate spin* iron(III) ions.

A conceptual bridge between porphyrin and salen complexes exists in metal chelates of open-chain tetrapyrrolic ligands. As a drawback, however, iron complexes of such ligands are usually unstable.[8] Nature indeed uses the ready hydrolysis of iron biliverdines for biological iron recovery.[9] The first stable example from this compound class was reported by Balch in 2004 and contains a helically distorted and strained biomimetic tetrapyrrole ligand.[10] We have recently reported a synthetic entry to a group of iron complexes with the open-chain tetrapyrrolic ligand 2,2′-bidipyr-

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rin,[11] which could be stabilized sufficiently by a ligand designed to reduce intramolecular strain.[12] 2,2′-Bidipyrrins[13] are simple tetrapyrroles consisting of two directly linked dipyrrin chelate subunits.[14] Because the dipyrrin fragments are free to rotate, metal chelates of 2,2′-bidipyrrins containing one,[15] two[16] and more metal atoms[17] have been obtained and structurally characterized. 2,2′-Bidipyrrins tend to undergo template-assisted oxidative macrocyclizations, yielding a number of different metallated porphyrinoids.[18] Iron derivatives are particularly active in these transformations.[19] A further peculiarity of (2,2′-bidipyrrinato)iron complexes is their often observed *intermediate spin* ground state in the solid state, manifested in Mössbauer and SQUID data as well as in short Fe–N bond lengths.[11] We have now prepared and studied the first series of oxido-bridged diiron(III) complexes with open-chain tetrapyrrolic ligands (Figure 1), that is, 2,2′-bidipyrrins with different β-pyrrolic substituents, by a one-pot procedure from pyrroles, bipyrrole dialdehydes and a source of iron, and report here preparative, structural, magnetic and spectroscopic aspects of the new species.

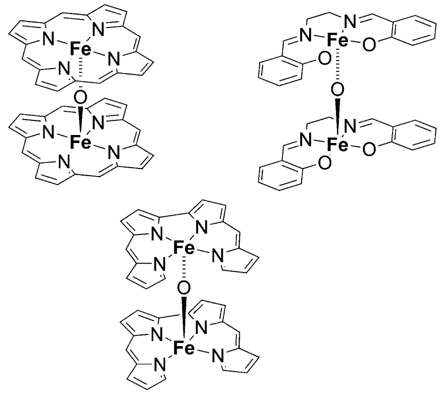
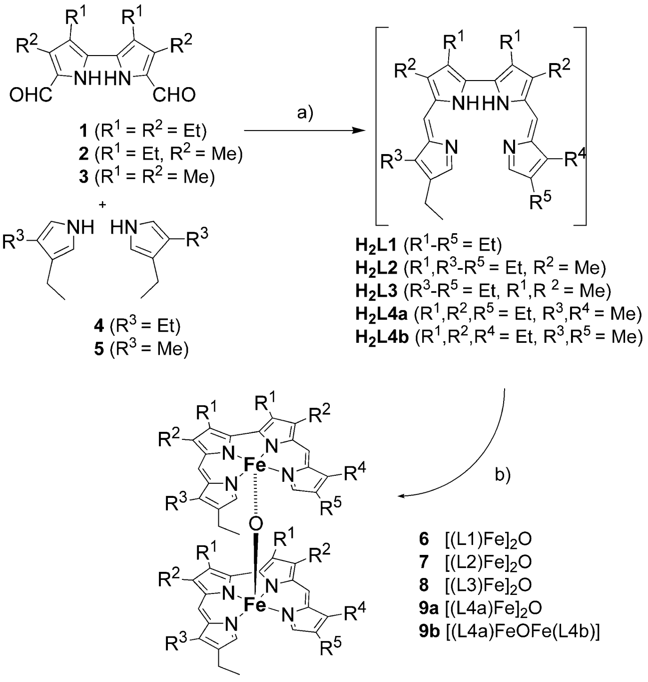


Figure 1. (μ-Oxido)diiron(III) complexes of porphyrin (top left), salen (top right) and 2,2′-bidipyrrin ligands (bottom).

Results and Discussion

Preparation and Spectroscopic Characterization

Scheme 1 summarizes the preparation of the (μ-oxido)diiron(III) complexes **6**–**9**, which differ from each other by the number and position of peripheral methyl- and ethyl substituents. Hexadecaethyl derivative **6** has been prepared earlier from the action of sodium hydroxide on the respective (chlorido)iron(III) complex. This strategy could not be transferred to other substitution pattern due to incompatible solubility properties. Therefore the one-pot strategy presented here was developed. The procedure is a variation of the preparation of the (chlorido)iron(III) complex of L1 and uses sodium hydroxide instead of ammonia as the alkaline reagent during the aqueous workup step. Other than for the chlorido derivative, however, which can be purified directly from the reaction mixture by several successive recrystallization steps, the oxido-bridged species are extremely soluble in nonpolar solvents like pentane or *n*-hexane and require a quick chromatographic separation step on deactivated alumina in order to remove decomposition products. Washing of the eluate with dilute sodium hydroxide and removal of the solvent yields the desired oxido-bridged compounds **6**–**9** in yields of 21–40%, depending on the substituent pattern.



Scheme 1. One-pot preparation of (2,2′-bidipyrrinato)(μ-oxido)diiron(III) complexes **6**–**9**. Reagents and conditions: (a) 1. $POCl_3$, CH_2Cl_2, room temp.; 2. NEt_3; (b) 1. $FeCl_2\cdot 4H_2O$, $FeCl_3$, dioxane; 2. NaOH, H_2O.

The identity of the new species was confirmed by a high-resolution measurement of the weak $[M + 1]^+$ signal for **6**, **7** and **8**. For **9**, only a strong signal for the $[(L4)Fe]^+$ fragment could be unambiguously identified. This observation is in agreement with the well-known breakdown of the Fe–O bond in similar porphyrin-based compounds.[20] Reproducible CHN data, in contrast, were not obtained for **6**–**9** due to the irregular co-crystallization of solvent molecules (see below).

The presence of oxido-bridged dinuclear species with strong antiferromagnetic interactions is apparent from the EPR silent behaviour of the compounds and from ^{1}H NMR spectroscopic investigation of **6**–**9** (Figure 2). Whereas the mononuclear halogenido derivatives show broad resonances over a range of 100–150 ppm, typical for paramagnetic (porphyrinato)iron(III) complexes,[21] the shifts for the protons of the weakly paramagnetic dinuclear species deviate only slightly from those expected for a closed-shell system. In addition, the line widths decrease significantly, although still no fine structure can be detected. Both effects are related to an efficient cancellation of the magnetic moments of the iron atoms. The signal number can be interpreted and understood for all derivatives if ABX_3 systems are taken into account for the diastereomerically split reso-

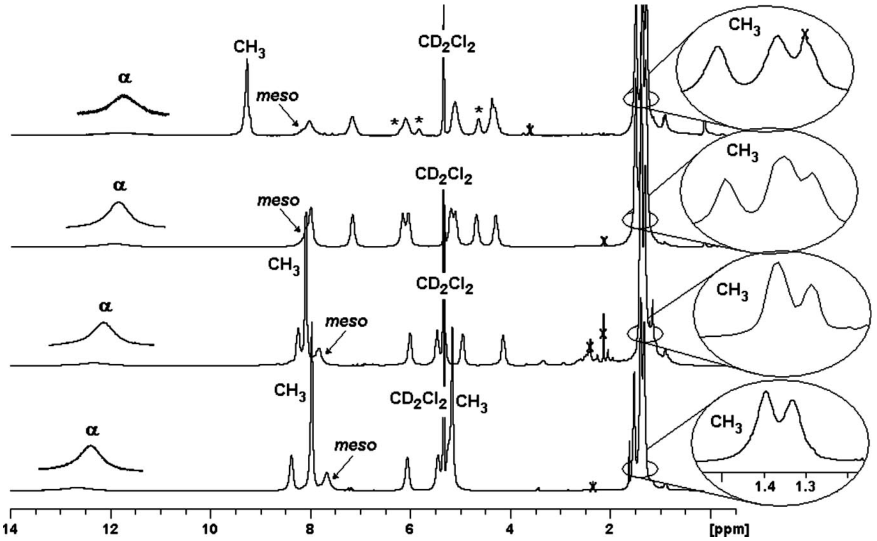
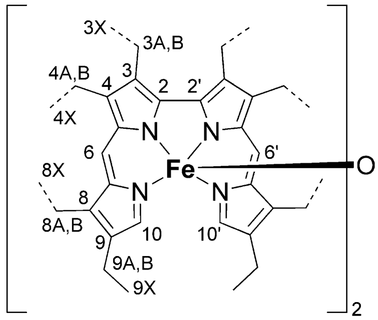


Figure 2. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, room temp.) of $[(L4)Fe]_2O$ (**9**), $[(L1)Fe]_2O$ (**6**), $[(L2)Fe]_2O$ (**7**) and $[(L3)Fe]_2O$ (**8**) (top to bottom), and assignment of the signals for special positions. Enlargements of the congested parts of the spectra around 1.5 ppm are inserted. The asterisks in the spectrum of **9** mark signals of the unsymmetrical minor isomer **9b**.

nances of the ethyl methylene protons. A possible helix inversion process of the two tetrapyrrolic ligands could not be observed, and because no additional signal splitting has been found in the ^{1}H NMR spectra down to 188 K it is assumed, that this process is very fast on the timescale of the experiment. The same result was obtained earlier for the mononuclear halogenido compounds.[11a] An assignment of the signals was undertaken by comparison of the different methyl- and ethyl-substituted derivatives and is presented in Table 1. Compound **9** consists of a mixture of two isomers, **9a** and **9b**, which are present in a ratio of 83:17. This observation relates to the unselective preparation of H_2L4 from 3-ethyl-4-methylpyrrole (**5**), where a symmetric H_2L4a and an unsymmetric derivative H_2L4b are formed in a ratio of 19:1. From statistics it can be derived that the second possible symmetric form of H_2L4 with methyl groups in the 9,9′-positions should be present in the mixture with only 0.25% abundance and can be neglected. A similar argument can be used for the possible, but not detected complex $[(L4b)Fe]_2O$, which should be present with ≤1% abundance only and in two isomeric forms.

Table 1. Assignment of ^{1}H NMR spectroscopic data for **6**, **7**, **8** and **9a**.



	6	**7**	**8**	**9a**
H-3A	5.09	5.45	5.15	5.11
H-3B	4.28	4.12	–	4.30
H-3X	1.35	1.37	–	1.34
H-4A	7.14	8.07	7.96	7.15
H-4B	6.14	–	–	6.10
H-4X	1.49	–	–	1.48
H-6 (*meso*)	8.05	7.81	7.66	8.02
H-8A	7.98	8.23	8.36	9.28
H-8B	6.03	5.99	6.04	–
H-8X	1.35	1.37	1.38	–
H-9A	5.17	5.29	5.43	5.11
H-9B	4.66	4.94	5.23	4.64
H-9X	1.28	1.28	1.32	1.27
H-10 (α)	11.90	12.29	12.64	11.80

Magnetic Measurements

SQUID measurements were undertaken on microcrystalline samples of **6**, **7** and **8** in a temperature range from 4–350 K (Figure 3). All three compounds show the expected behaviour for strong antiferromagnetic coupling in dinuclear iron(III) complexes. At 298 K the magnetic moments μ_{eff} of **6**, **7** and **8** per iron atom are determined to be only 1.22, 1.23 and 1.45 μ_B, far below the expected value for mononuclear $S = 5/2$ systems. Upon lowering the temperature to about 50 K the susceptibility of the samples drop in a fashion characteristic for (μ-oxido)(porphyrinato)diiron(III) compounds. Below 50 K the χ_{mol} values increase rapidly, presumably due to the presence of an unknown paramagnetic contamination in the samples. The temperature dependence of the molar magnetic susceptibility χ_{mol} could be fitted using the isotropic Heisenberg–Dirac–VanVleck model with the Hamiltonian $\hat{\mathbf{H}} = -2J\hat{\mathbf{S}}_1\times\hat{\mathbf{S}}_2$ and $S_1 = S_2 = 5/2$. The paramagnetic impurity was accounted for by a Curie–Weiss term. In addition, a temperature independent term was added to account for diamagnetic corrections, unknown solvent content and any temperature independent paramagnetism.[1k] With a g-factor fixed at 2.0 numerical values of the spin coupling constant J = –122 (for **6**), –121 (for **7**) and –111 cm^{-1} (for **8**) were obtained. These values are slightly smaller than those for (μ-oxido)(porphyrinato)diiron(III) complexes (J = –128 to –147 cm^{-1})[1j,1k] but larger than for the respective salen-type species (J = –92 to –100 cm^{-1}).[5] As expected, a fit with the assumption $S_1 = S_2 = 3/2$, that is, for a coupled *intermediate spin* system, did not result in meaningful parameters. This is in agreement with the earlier determination of *high spin* iron(III) ions in **6** by Mössbauer spectroscopy.[11a]

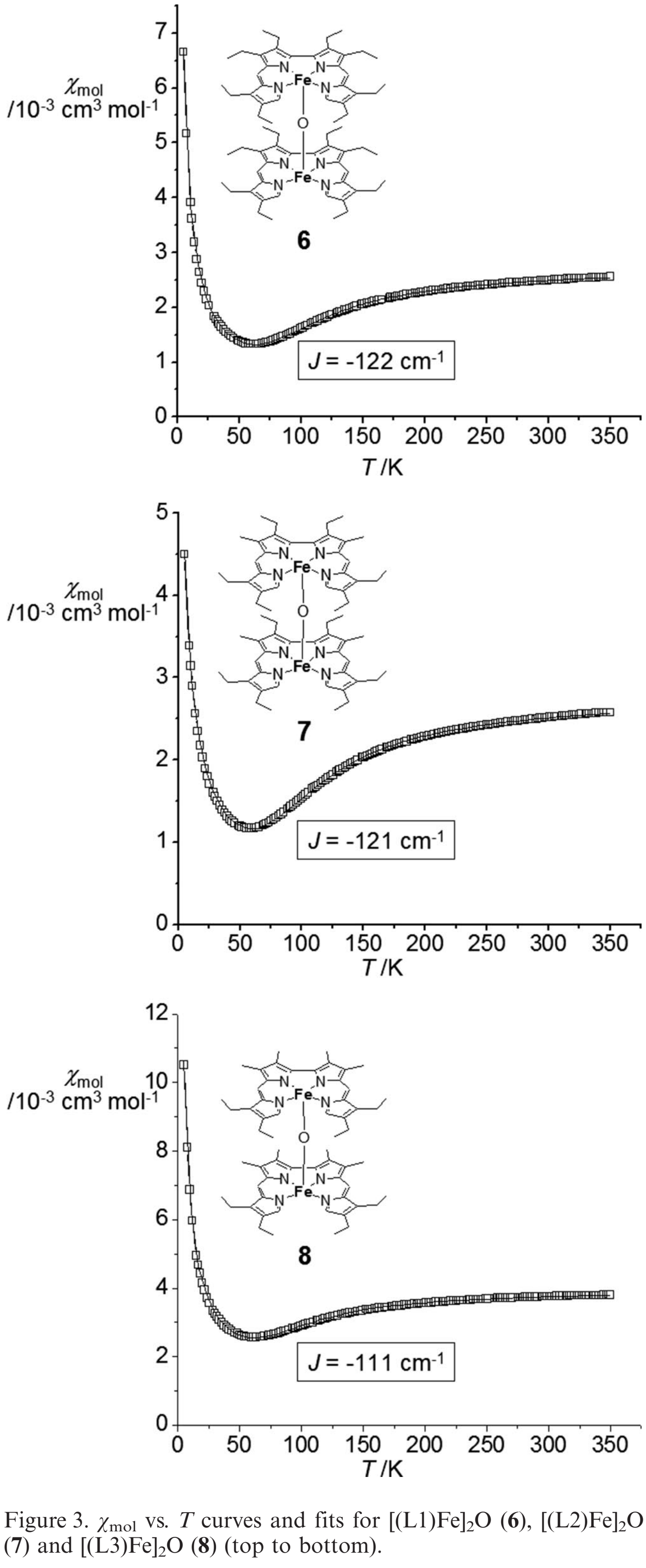


Figure 3. χ_{mol} vs. T curves and fits for $[(L1)Fe]_2O$ (**6**), $[(L2)Fe]_2O$ (**7**) and $[(L3)Fe]_2O$ (**8**) (top to bottom).

X-ray Crystallographic Determinations

Crystallographic analyses were undertaken on four single crystals obtained from the μ-oxido-bridged (2,2′-bidipyrrinato)iron complexes **6**, **7** and **8**. All four analyses reveal the presence of co-crystallized small molecules. Complexes **7** and **8** crystallize as dichloromethane solvates, whereas **6** was obtained either as a pyrrole adduct with intermolecular NH···O hydrogen bridge **6^{I}** or as a solvate **6^{II}** with a highly disordered solvent molecule (presumably thf) that could not be resolved and was therefore removed with the SQUEEZE command in Platon.[22] Selected metrical data of the coordination units are given in Table 2. Table 3 summarizes crystallographic data for the structure determinations. Figure 4 illustrates the molecular structures of the dinuclear units as well as their association behaviour in the crystal.

All compounds are composed from two oxygen-bridged (2,2′-bidipyrrinato)iron fragments with helically distorted tetrapyrrole ligands. The distortion is unequally distributed over the ligand perimeter in that one dipyrrin half contains two almost coplanar C_4N rings, whereas the terminal ring of the other half is largely bent away by an angle θ of either about 30° (**6^{I}**, **8**) or of about 40° (**6^{II}**, **7**). The metrics of the central FeN_4O coordination units are very similar in all observed cases. Typical Fe–N bond lengths for *high spin* iron(III) complexes in the range 2.024–2.082 Å are observed. The bonds towards the bipyrrolic N donor atoms are generally shorter than those to the terminal positions. The bond to the strongly tilted C_4N4 ring, however, is not generally the longest as observed in 2,2′-bidipyrrin complexes with pentacoordinate central ions before on *intermediate spin* iron(III) complexes.[11] The Fe–O bonds are found in the narrow range from 1.761–1.784 Å and fit well with the typical values for porphyrinoid and salen-type complexes of 1.73–1.78 Å. An exception is found for the H-bridged Fe–O–Fe unit of **6^{I}**, which displays slightly elongated Fe–O bonds of 1.785 and 1.818 Å. The coordination polyhedra around the iron atoms are distorted between trigonal bipyramidal and square pyramidal forms (closer to the latter form) and may be described by τ values of 0.23–0.35.[23] For the Fe–O–Fe subunit angles two cases are observed. In **6^{II}** and **7** this angle is as large as 153.91/154.41 and 156.89°, respectively, whereas for **6^{I}** and **8** values of 131.89 and 132.97° are observed. The grouping of the compounds is the same as that found above for the bending angle θ of the terminal C_4N ring.

Pi stacking is present between the two (2,2′-bidipyrrinato)iron fragments in all dinuclear complexes. Two types of stacking modes have been observed, either between the strongly bent C_4N rings (**6^{I}**, **8**) or between the planar dipyrrin halves of the ligands (**6^{II}**, **7**). There is an apparent coin-

Table 2. Selected metrical data (bond lengths, Å, and angles, °) for **6**^{I}, **6**^{II}, **7** and **8** from X-ray diffraction data.

	6^{I}·pyrrole		**6**^{II} molecule A		molecule B		**7**·CH_2Cl_2	**8**·CH_2Cl_2	
	Fe1[a]	Fe2[a]	Fe1	Fe2	Fe1	Fe2	Fe	Fe1	Fe2
Fe–N1[a]	2.055(3)	2.064(3)	2.080(8)	2.063(7)	2.074(8)	2.081(8)	2.049(3)	2.0617(18)	2.0659(18)
Fe–N2[a]	2.035(3)	2.050(3)	2.069(8)	2.061(7)	2.032(7)	2.050(8)	2.066(3)	2.0606(18)	2.0616(17)
Fe–N3[a]	2.025(3)	2.024(3)	2.052(7)	2.061(8)	2.045(7)	2.034(9)	2.045(3)	2.0433(19)	2.0479(18)
Fe–N4[a]	2.025(3)	2.065(3)	2.082(7)	2.064(7)	2.058(7)	2.056(6)	2.063(4)	2.0580(17)	2.0608(17)
Fe–O	1.818(3)	1.785(2)	1.784(5)	1.765(6)	1.761(6)	1.772(6)	1.7738(10)	1.7808(14)	1.7781(15)
N1–Fe–N2	85.57(13)	85.51(13)	84.9(3)	84.7(3)	86.0(3)	85.3(3)	85.11(14)	84.62(7)	84.83(7)
N1–Fe–N3	155.55(13)	154.19(12)	151.7(3)	153.0(3)	153.7(3)	154.4(3)	153.46(14)	153.49(7)	153.38(7)
N1–Fe–N4	102.04(12)	103.08(13)	101.8(3)	101.4(3)	102.7(3)	99.9(3)	101.08(14)	103.55(7)	103.39(7)
N1–Fe–O	99.51(11)	99.23(11)	101.6(3)	101.0(3)	103.0(3)	100.8(3)	98.86(11)	100.37(7)	100.00(7)
N2–Fe–N3	73.98(12)	73.49(13)	73.0(3)	73.4(3)	73.6(3)	74.1(4)	73.95(14)	73.90(8)	73.87(7)
N2–Fe–N4	136.32(12)	139.41(12)	138.1(3)	136.2(3)	137.3(3)	133.6(3)	135.64(13)	139.30(7)	138.30(7)
N2–Fe–O	119.69(11)	113.49(12)	114.5(2)	115.0(3)	113.2(3)	116.4(3)	115.36(16)	114.42(7)	114.07(7)
N3–Fe–N4	84.54(12)	84.44(13)	84.3(3)	84.6(3)	82.5(3)	84.0(3)	83.63(14)	83.94(7)	83.28(7)
N3–Fe–O	102.19(12)	102.78(11)	103.5(3)	102.5(3)	100.3(3)	102.1(3)	104.71(10)	102.56(7)	103.15(7)
N4–Fe–O	101.59(12)	104.27(12)	104.6(3)	106.3(3)	105.5(3)	107.8(3)	107.06(17)	103.36(7)	104.75(7)
θ[b]	30.58	27.23	40.56	39.35	40.34	42.04	41.44	26.20	29.26
τ^{23}	0.32	0.25	0.23	0.28	0.27	0.35	0.30	0.24	0.25
Fe···Fe	3.290		3.456		3.445		3.476	3.263	
Fe–O–Fe	131.89		153.91		154.41		156.89	132.96	
Δ_π[c]	3.458		3.207		3.259		3.509	3.286	
ϕ[d]	29.57		119.70		113.19		102.94	93.46	
Diastereom.[e]	unlike		like		like		like	like	

[a] Unified numbering system used for all (2,2′-bidipyrrinato)iron(III) units; N4 denotes the nitrogen atom of the tilted C_4N moiety. [b] Interplanar angle between the rms plane of the dipyrrin unit containing N1,N2 with the rms plane of the C_4N4 ring. [c] Minimum distance of an atom of the juxtaposed π-stacked unit to the rms plane of the other. [d] Torsion angle defined by the iron atoms and the centroids of the central five-membered Fe–N2–C–C–N3 rings. [e] Derived from the sense of helicity of the two tetrapyrrole subunits in a molecule.

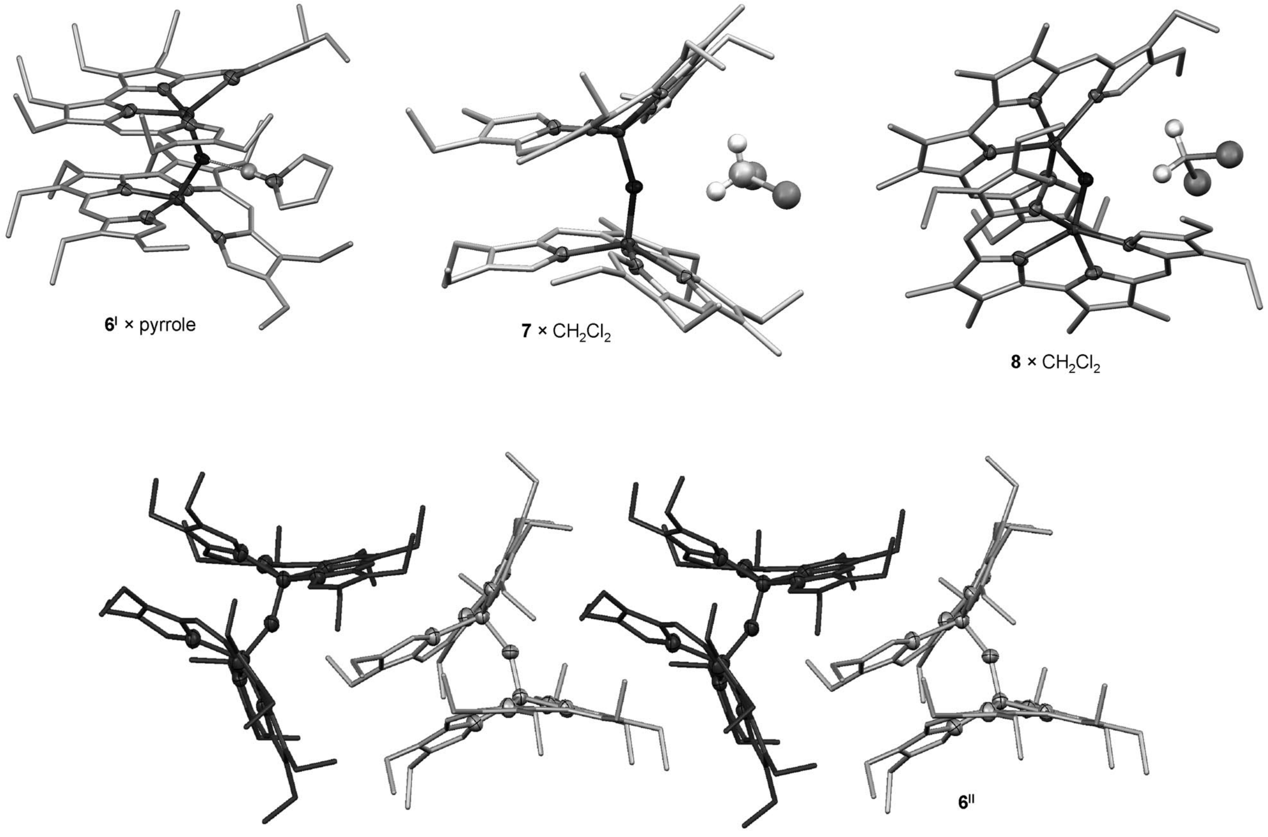


Figure 4. Molecular structures of **6**^{I}, **6**^{II}, **7** and **8**, and association of small molecules (top) or self recognition pattern (bottom, light grey: molecule A, dark grey: molecule B) in the crystal (selected hydrogen atoms displayed only; ellipsoids set at 50% probability).

cidence with the structure groups assigned above. In contrast, the observed π–π distances Δ_π of about 3.46, 3.21/3.26, 3.51 and 3.29 Å as well as the torsion angle ϕ of two juxtaposed 2,2′-bidipyrrin ligands of 29.57, 119.70/113.19, 102.94 and 93.46° for **6**$^{\mathbf{I}}$, **6**$^{\mathbf{II}}$, **7** and **8**, respectively, do not correlate with other structural parameters. In combination with the helicity of the tetrapyrroles these π-stacking arrangements on one side of the chelate ligands open a pocket on the other side of the complexes. For **6**$^{\mathbf{I}}$, **7** and **8** these pockets house the small molecules, that is, the H-bonded pyrrole moiety and the dichloromethane units. Complex **6**$^{\mathbf{II}}$ fills the void space in the gap by a self-complementary binding of peripheral ethyl substituents of the neighbour molecule, thus forming supramolecular chains of alternating molecules **A** and **B** in the crystal.

Conclusions

In summary we have developed a one-pot synthesis for a series of unprecedented μ-oxido-bridged diiron(III) complexes with open-chain tetrapyrrolic ligands and characterized the new compounds by means of spectroscopy, magnetic measurements and X-ray diffraction. The magnetic data suggests that the new complexes can be interpreted to lie between the related porphyrin and salen systems, and the magnetostructural correlation confirms the earlier finding on other oxido-bridged systems that the Fe–O bond lengths has a profound influence on the magnetic exchange coupling, whereas other structural parameters are of minor importance. In the solid the new species form supramolecular aggregates through weak intermolecular interactions. The helicity of the bound tetrapyrrolic ligands and the intramolecular π-stacking modes observed for the dinuclear compounds result in the formation of inner voids that are filled either with different small molecules, or with the side chains of an adjacent molecule, thus forming a 1D chain. The (2,2′-bidipyrrinato)(μ-oxido)diiron(III) complexes discussed here are valuable precursors for the further development of the hitherto almost unknown coordination chemistry of iron with open-chain tetrapyrroles related to the natural bilines, and will be used for studies upon the reactivity and electronic properties of these rare iron species in the near future.

Experimental Section

General: Reagents were purchased from commercial sources and used as received without any further purification. Solvents were purified using standard procedures and stored under an atmosphere of Argon in the dark. The following starting materials were prepared from literature procedures: tetraalkylbipyrroledialdehydes **1**,[24] **2**[25] and **3**[26] and dialkylpyrroles **4**[27] and **5**.[28] Spectroscopic and analytical data of **6** has been reported earlier.[11a] ^{1}H NMR spectra were obtained at 400 MHz with a Bruker AMX 400 spectrometer at room temperature in CD_2Cl_2. High-resolution ESI+ mass spectra were recorded with a Finnigan TSQ 700 instrument. *m*/*z* values are given for the most abundant isotopomers only. UV/Vis spectra were obtained with a Shimadzu UV-1601-PC spectrophotometer in concentrations of ca. 10^{-5} mol^{-1}. IR spectra were measured in KBr matrix with a Bruker IFS 88 instrument. SQUID measurements were performed with a Quantum Design MPMS R2 magnetometer using gelatine capsules and an applied external field of 500 G.

General Procedure for the Preparation of (μ-Oxido)diiron(III) Complexes 6–9: 3,4-Dialkylpyrrole (0.81 mmol) was treated under an atmosphere of nitrogen with a solution of 3,3′,4,4′-tetraalkyl-5,5′-diformyl-2,2′-bipyrrole (0.33 mmol) in dichloromethane (15 mL) and $POCl_3$ (0.25 mL, 2.72 mmol), whereupon the colour of the reaction mixture changed from yellow to violet. The reaction mixture was stirred at ambient temperature for 20 min until the colour became blue-green. Triethylamine (2.0 mL) was added in air, and the resulting solution was immediately treated with a suspension of $FeCl_2\cdot 4H_2O$ and $FeCl_3$ in dry dioxane (3 mL) and additional dioxane (80 mL) and stirred until the colour of the reaction mixture changed to brown. Dichloromethane (150 mL) and aqueous sodium hydroxide (1 M, 50 mL) were then added quickly, and the reaction mixture was shaken until the organic layer became orange-brown. The organic layer was separated, dried with sodium sulfate and filtered, and the solvent was removed in vacuo. The pure product was obtained from the residue by a quick chromatographic separation on neutral alumina (Brockmann grade V) with dichloromethane/*n*-hexane (1:1) and evaporation of all volatiles. After drying in high vacuo, the title compound was obtained as a violet-black, microcrystalline solid.

μ-Oxidobis[3,3′,8,8′,9,9′-hexaethyl-4,4′-dimethyl-2,2′-bidipyrrinatoiron(III)] (7): Prepared from **2** (95 mg) and **4** (100 mg, 33%). MS (ESI+): calcd. for $C_{64}H_{80}N_8Fe_2O$ $[M + 1]^+$ 1089.5227; found 1089.5267 (Δ = 0.42 mmu). UV/Vis (CH_2Cl_2): λ (ε, dm^3 mol^{-1} cm^{-1}) = 395 (58200), 791 (20200) nm. IR: $\tilde{\nu}$ = 818 (ν_{asym} Fe–O–Fe) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.28 (br. s, 12 H, H-9X, H-9′X), 1.37 (br. s, 24 H, H-3X, H-3′X, H-8X, H-8′X), 4.12, 5.45 (br., 8 H, AB, H-3AB, H-3′AB), 4.94, 5.29 (br., 8 H, AB, H-9AB, H-9′AB), 5.99, 8.23 (br., 8 H, AB, H-8AB, H-8′AB), 7.81 (br. s, 4 H, H$_{meso}$), 8.07 (br. s, 12 H, H-4a, H-4′a), 12.29 (br. s, 4 H, H-10, H-10′) ppm.

μ-Oxidobis[8,8′,9,9′-tetraethyl-3,3′,4,4′-tetramethyl-2,2′-bidipyrrinatoiron(III)] (8): Prepared from **3** (89 mg) and **4** (100 mg, 29%). MS (ESI+): calcd. for $C_{60}H_{72}N_8Fe_2O$ $[M + 1]^+$ 1033.4601; found 1033.4645 (Δ = 0.44 mmu). UV/Vis (CH_2Cl_2): λ (ε, dm^3 mol^{-1} cm^{-1}) = 394 (58900), 797 (20400) nm. IR: $\tilde{\nu}$ = 816 (ν_{asym} Fe–O–Fe) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.32 (br. s, 12 H, H-9X, H-9′X), 1.38 (br. s, 12 H, H-8X, H-8′X), 5.15 (br., 12 H, AB, H-3, H-3′), 5.23, 5.43 (br., 8 H, AB, H-9AB, H-9′AB), 6.08, 8.36 (br., 8 H, AB, H-8AB, H-8′AB), 7.66 (br. s, 4 H, H$_{meso}$), 7.96 (br. s, 12 H, H-4a, H-4′a), 12.64 (br. s, 4 H, H-10, H-10′) ppm.

μ-Oxidobis[3,3′,4,4′,9,9′/8′-hexaethyl-8,8′/9′-dimethyl-2,2′-bidipyrrinatoiron(III)] (Mixture of 9a and 9b): Prepared from **1** (100 mg) and **5** (89 mg, 20%). MS (ESI+): calcd. for $C_{32}H_{40}N_4Fe$ [M – O]/2$^+$ 536.2602; found 536.2610 (Δ = 0.08 mmu). UV/Vis (CH_2Cl_2): λ = 388, 794 nm. IR: $\tilde{\nu}$ = 816 (ν_{asym} Fe–O–Fe)cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2; only **9a**): δ = 1.27 (br. s, 12 H, H-9X, H-9′X), 1.34 (br. s, 12 H, H-3X, H-3′X), 1.48 (br. s, 12 H, H-4X, H-4′X), 4.30, 5.11 (br., 8 H, AB, H-3AB, H-3′AB), 4.64, 5.11 (br., 8 H, AB, H-9AB, H-9′AB), 6.10, 7.15 (br., 8 H, AB, H-4AB, H-4′AB), 8.02 (br. s, 4 H, H$_{meso}$), 9.28 (br. s, 12 H, H-8a, H-8′a), 11.80 (br. s, 4 H, H-10, H-10′) ppm.

X-ray Crystallography: Suitable single crystals of **6**–**8** were obtained by slow evaporation of solutions of the compounds in dichloro-

Table 3. Crystallographic data collection and refinement parameters of **6^{I}**, **6^{II}**, **7** and **8**.

Compound	**6^{I}**·pyrrole	**6^{II}**	**7**·CH_2Cl_2	**8**·CH_2Cl_2
Empirical formula	$C_{72}H_{93}Fe_2N_9O$	$C_{68}H_{88}Fe_2N_8O$	$C_{56.78}H_{83.56}Cl_{3.56}Fe_2N_8O$	$C_{61}H_{74}Cl_2Fe_2N_8O$
M_r	1212.25	1145.16	1240.40	1117.88
T [K]	100(2)	193(2)	193(2)	193(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	tetragonal	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{4}2_1/c$	$Pbca$
a [Å]	16.0055(7)	16.3678(18)	15.7060(5)	24.5904(15)
b [Å]	16.0104(8)	18.600(2)	15.7060(5)	17.2154(8)
c [Å]	25.3923(12)	24.364(4)	26.2060(13)	27.1781(12)
α [°]	90	76.130(16)	90	90
β [°]	91.060(4)	82.569(15)	90	90
γ [°]	90	72.393(13)	90	90
V [Å^3]	6505.8(5)	6850.8(15)	6464.5(4)	11505.4(10)
Z	4	4	4	8
$D_{calcd.}$ [Mg m^{-3}]	1.238	1.110	1.275	1.291
μ [mm^{-1}]	0.496	0.470	0.643	0.645
θ range [°]	1.49–26.02	1.87–26.26	2.59–26.07	2.08–25.96
h	–19 to 19	–20 to 20	–18 to 19	–30 to 30
k	–19 to 19	–23 to 23	–3 to 16	–21 to 21
l	–29 to 31	–29 to 30	–30 to 29	–32 to 33
Reflections collected	29222	63501	9931	87072
Independent	12284	25208	5723	11152
Observed [$I > 2\sigma(I)$]	5070	6690	4984	7388
Final R_1 [$I > 2\sigma(I)$]	0.0485	0.0807	0.0642	0.0380
Final wR_2 [$I > 2\sigma(I)$]	0.0683	0.2048	0.1616	0.0844

methane/*n*-hexane mixtures (1:1) at –20 °C, and in the presence of small amounts of pyrrole (for **6^{I}**) or thf (for **6^{II}**). Diffraction data for compounds **6^{I}**, **7** and **8** were collected with a STOE IPDS-1, data for **6^{II}** with a STOE IPDS-2, using monochromated Mo-K_α radiation. The structures were solved by direct methods using SIR 92[29] (**6^{I}**, **7**, **8**) or SHELXS 97[30] (**6^{II}**) and refined on all F^2 using SHELXL 97.[31] Further details are given in Table 3. Graphics were prepared using Mercury 1.4.2.[32] CCDC-698946 (for **6^{II}**), -698947 (for **6^{I}**), -698948 (for **7**) and -698949 (for **8**) 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.

Supporting Information (see footnote on the first page of this article): Mathematical expression and fitting parameters of the magnetic study.

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