Self-Assembly

Influence of the Alkyl Chain Length on the Self-Assembly of Amphiphilic Iron Complexes: An Analysis of X-ray Structures

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Dedicated to Prof. Dr. I.-P. Lorenz on the occasion of his 70th birthday

Abstract: Several new amphiphilic iron complexes were synthesised and characterised by single crystal X-ray structure analysis. The Schiff-base-like equatorial ligands contain long alkyl chains in their outer periphery with chain lengths of 8, 12, 16 and 22 carbon atoms. As axial ligands methanol, pyridine, 4-aminopyridine, 4-(dimethylamino)pyridine and 1,2-bis(4-pyridyl)ethane were used. X-ray structure analysis of the products reveals different coordination numbers, depending on the combination of equatorial and axial ligand.

Introduction

Designing multifunctional materials is of great importance as they allow exploring many new potential applications. In this frame, adding additional properties to spin crossover (SCO) compounds would lead to materials that cannot only be switched from the low-spin (LS) to the high-spin (HS) state through thermal excitation, or induced by light, pressure or host inclusion,^[1-5] but exhibit further functionalities. One possibility to introduce additional properties to such materials is the synthesis of amphiphilic spin crossover complexes. This could result in liquid crystalline behaviour of the material, where synergetic effects between phase transition and spin transition (ST) are possible.^[6-12] Another interesting aspect is the self-assembly of such complexes in solution that might lead to the formation of micelles or inverse micelles and can influence the ST properties in solution.^[13, 14] Further the self-assembly of amphiphilic complexes on frontiers can be used for the formation of Langmuir-Blodgett (LB) films.^[15] Thus, such systems are not only of interest as bulk material but also for the nanostructuring of SCO materials. For a purposeful synthesis of such systems it is important to understand the self-assembly in solution as this will influence the behaviour on frontiers and the crystal packing in the bulk material.

For SCO complexes with iron(II), the most widely used metal ion in spin crossover research, $^{\scriptscriptstyle [3]}$ it is commonly necessary to

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304653.

Chem. Eur. J. **2014**, 20, 1–13

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The driving force for this is the self-assembly to lipid-layerlike arrangements. This can be controlled through the chain lengths and the dimension of the axial ligands in a crystalengineering-like approach. For this an empirical rule is introduced concerning the crystallisation behaviour of the complexes. The efficacy of this rule is confirmed with the crystallisation of an octahedral complex with two docosyl (C22) chains in the outer periphery. The rule is also applied to other ligand systems.



Scheme 1. General structure of the equatorial (top) and axial (bottom) ligands discussed in this work and their abbreviations.

synthesise octahedral complexes. Therefore, we designed N₂O₂-coordinating Schiff-base-like equatorial ligands with long alkyl chains in the outer periphery (Scheme 1). In combination with various axial ligands, octahedral iron(II) complexes with thermal spin crossover activity can be realised,^[16-18] and the influence of the hydrophobic substituents can be investigated. In a previous work we showed, that the amphiphilic complexes of this family can self-assemble to lipid-layer-like arrangements,^[16,17] with one of those complexes exhibiting a highly cooperative spin transition with a wide hysteresis loop.^[17] The X-ray structure of this complex was solved before and after the spin transition, revealing that the volume change of the unit cell is very small ($\Delta V/V \approx 2.9$ %),^[17] and in the region of thermal

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contraction. Despite this an up to 47 K wide thermal hysteresis loop is observed that can be explained with a hydrogen bond network between the polar head groups of the amphipilic complexes and significant changes in the structure of the complex upon spin transition.^[1,5,17] In contrast to this gradual spin transitions are observed for complexes with relatively short alkyl chain substituents.^[16,18] The X-ray structure of one of those complexes in the HS and the LS state reveals, that the volume change upon spin transition is higher compared to the example with the long alkyl chain. However, with $\Delta V/V \approx 4.0\%$ it is still small for a spin crossover complex.^[18] For this example with a very gradual spin transition no lipid-layer-like structure was observed.

There appears to be a connection between the appearance of lipid-layer-like (lamellar) structures and the cooperativity of the spin transition. Additionally, lamellar arrangements are interesting for further nanostructuring (e.g., LB film formation) or with regard to potential liquid crystalline properties. Thus, the question arises of whether there are factors which we can control in a crystal-engineering-like approach to obtain the desired lamellar structural motif. A second question to be answered is how to control the formation of octahedral complexes. First investigations on a system with short octyl chains demonstrated that often unwanted penta-coordinated products are obtained.^[18]

It is difficult to investigate the self-assembly of the highly air sensitive iron(II) complexes directly in solution. Therefore, we decided to have a look at the structures of the solid products that can be considered as the result of the self-assembly in solution. Thus, the X-ray structures of 15 complexes of the amphiphilic Schiff-base-like ligands used in our group were compared. The results lead to a rule which allows us to predict, under which conditions the purposeful synthesis of octahedral complexes with lamellar structures is possible. It will become clear why of the alkyl chain lengths used for the ligand (C8,

C12, C16 and C22), the longest chains were necessary for the synthesis of an octahedral complex with two bulky dmap (*N*,*N*-dimethylaminopyridine) as axial ligands. Application of this rule to other systems shows that it is not limited to the complexes investigated in our group. In Scheme 1 the general structure of the ligands together with the used abbreviations are given.

Results and Discussion

Synthesis of the complexes

An overview of the complexes discussed in this work is given in Table 1.

To obtain octahedral iron(II) complexes, the free Schiff-base-

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like ligands H₂L(a-d)(C*n*+1) were firstly converted with iron(II) acetate in methanol to give the penta- or hexa-coordinated [Fe(La-d)(C*n*+1)(MeOH)₁₋₂] complexes with methanol as axial ligand. Further treatment with aromatic N-donor ligands, like pyridine or imidazole that replace the methanol in the axial position, leads to a [N₄O₂] coordination sphere that shifts the iron(II) metal centre into the right energy region for the observation of thermal spin crossover.^[4, 19]

In the one hand, monomeric spin crossover complexes can be synthesised using axial ligands like pyridine (py), 4-aminopyridine (apy) or (4-dimethylamino)pyridine (dmap). These neutral compounds have been proved to be good candidates for SCO, but are also quite air sensitive and the thermal stability is not too high.^[4,19] On the other hand, coordination polymers can be realised using axial ligands like 4,4'-bipyridine (bipy), 1,2-bis(4-pyridyl)ethane (bpea) or 1,2-bis(4-pyridyl)ethene (bpee). These show an increased thermal stability as well as a dramatically increased stability against oxidation in comparison to monomeric SCO complexes and give higher yields due to low solubility.^[4,20] Additionally, such 1D polymeric SCO complexes are attractive for the formation of nanoparticles.^[21]

For the synthesis of the final complexes similar reaction conditions were used as for the well investigated Schiff-base-like iron(II) complexes with no alkyl chains in the outer periphery.^[4] The combination of four different axial ligands with a total of sixteen different equatorial ligands (the lengths of the two alkyl chains are varied from 8, 12, and 16 up to 22 carbon atoms and four different substituents combinations for R¹ and R² are used) should allow the synthesis of a large pool of new octahedral complexes. It turned out, that the desired octahedral complexes were not obtained as easily as for the unmodified system.^[18] The difference is especially pronounced for the complexes with bridging axial ligands, which are readily formed for the unsubstituted Schiff-base-like ligands.^[4] In con-

Complex	Abbreviation	L_{eq}	L _{ax}	Oxidation state	Desired product	Ref.
[FeLa(C8)(dmap)]	1	La(C8)	dmap	iron(II)	no	this work
[FeLc(C8)(dmap)]	2 a	Lc(C8)	dmap	iron(II)	no	[7]
[FeLc(C8)(dmap)]	2 b	Lc(C8)	dmap	iron(II)	no	[7]
[(FeLc(C8)) ₂ O]	3	Lc(C8)	-	iron(III)	no	this work
[FeLc(C8)(dmap) ₂]×MeOH LS	4 aLS	Lc(C8)	dmap	iron(II)	yes	[7]
[FeLc(C8)(dmap) ₂]×MeOH HS	4 aHS	Lc(C8)	dmap	iron(II)	yes	[7]
$[FeLc(C8)(dmap)_2] \times 2 MeOH$	4 b	Lc(C8)	dmap	iron(II)	yes	[7]
[FeLc(C8)(apy)]	5	Lc(C8)	ару	iron(II)	no	this work
[FeLa(C12)(MeOH) ₂]	6	La(C12)	MeOH	iron(II)	yes ^[a]	[5]
[FeLc(C12)(MeOH) ₂]	7	Lc(C12)	MeOH	iron(II)	yes ^[a]	[5]
[FeLa(C12) ₂ (bpea)]	8	La(C12)	bpea	iron(II)	no	this work
[{FeLb(C12)(MeOH)} ₂ (bpea)]	9	Lb(C12)	bpea	iron(II)	no	this work
[FeLa(C12)(apy)]	10	La(C12)	ару	iron(II)	no	this work
[FeLb(C12)(dmap)(MeOH)]	11	Lb(C12)	dmap	iron(II)	no	this work
[FeLa(C16)(py) ₂]×0.25 H ₂ O LS	12LS	La(C16)	ру	iron(II)	yes	[6]
[FeLa(C16)(py) ₂]×0.25 H ₂ O HS	12 HS	La(C16)	ру	iron(II)	yes	[6]
[FeLd(C22)(dmap) ₂] × 0.5 EtOH	13	Ld(C22)	dmap	iron(II)	yes	this work

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Scheme 2. Exemplary reaction pathway with the desired (top) and obtained reaction product 9 (bottom).

trast to this, dimeric structures are obtained frequently, as illustrated in Scheme 2. Here, we focus on the synthetic approaches in which single crystals in high enough quality for an X-ray structure analysis of the product were obtained. whereas the other is methanol (from the solvent). For the parent Schiff-base-like complexes only one example for such an octahedral complex is known.^[22]

X-ray structure analysis

In the following the X-ray structures of eight new amphiphilic complexes are compared with those of seven previously published complexes of this ligand system. The focus is set on the

Chain length of eight carbon atoms

Crystals suitable for X-ray structure analysis were obtained quite frequently for the complexes with the C8 alkyl chains. However, in most cases the quality of the diffraction data was low. Thus, of the seven different structures (compounds 1, 2a,

analysis of the crystal packing, especially the arrangement of the alkyl chains and the van der Waals (vdW) interactions between them. For complexes 1, 2a, 3, 4b, 5 and 10, the quality of the diffraction data was low, so only the relative conformation of the complex and the orientation in the crystal is discussed. For the other examples intermolecular interactions are also considered. In the Supporting Information (Table S1), the crystallographic data of the newly presented complexes are summarised. Selected bond lengths and angles within the first coordination sphere are compared in Table 2. The iron centre of the complexes is either penta-coordinated or hexa-coordinated. For the latter case often mixed axial ligands were obtained, of which one is the desired N-heterocyclic ligand

complexes discussed in this work.						
	Fe—N _{eq} [Å]	Fe–O _{eq} [Å]	Fe—N _{ax} [Å]	0-Fe-0 [°]	Spin state	
1	2.1/2.0	1.9/2.0	2.1	101	HS	
2 a ^[7]	2.1/2.0	2.0/2.0	2.1	100	HS	
2 b ^[7]	2.073(4)/2.085(4)	2.002(3)/1.980(3)	2.127(4)	101.62(14)	HS	
3 ^[a]	2.0/2.0; 2.0/2.1	1.9/1.9; 1.9/2.0	Fe-O _{ax} : 1.8/1.8	91/94	HS	
4 aLS ^[7]	1.909(2)/1.915(2)	1.948(1)/1.957(1)	2.013(2)/2.018(2)	91.68(6)	LS	
4 aHS ^[7]	2.065(3)/2.080(3)	2.002(3)/2.012(3)	2.216(3)/2.217(3)	107.16(11)	HS	
4 b ^[7]	1.9/1.9	2.0/2.0	2.0/2.0	92	LS	
5	2.0/2.1	2.0/2.0	2.1	97	HS	
6 ^[5]	2.093(2)/2.095(2)	2.009(1)/2.030(1)	Fe-O _{ax} : 2.203(1)/2.230(2)	108.93(5)	HS	
7 ^[5]	2.088(2)/2.094(2)	2.007(2)/2.021(2)	Fe-O _{ax} : 2.201(2)/2.233(2)	109.37(8)	HS	
8 ^[b]	2.077(3)/2.075(3);	1.997(3)/1.978(3);	2.130(3); 2.132(5)	103.58(10);	HS	
	2.075(3)/2.077(3)	1.995(3)/1.977(3)		102.92(12)		
9 ^[c]	2.107(4)/2.101(5);	2.026(3)/2.040(3);	2.227(4); 2.242(4);	112.29(16);	HS	
	2.089(5)/2.102(4)	2.028(3)/2.026(3)	Fe-O _{ax} : 2.228(4)/2.227(4)	111.60(16)		
10 ^[d]	2.1/2.0; 2.1/2.0	2.0/2.0; 2.0/2.0	2.1; 2.1	107; 105	HS	
11	2.089(2)/2.095(2)	2.002(2)/2.026(2)	2.181(3); Fe–O _{ax} : 2.267(3)	108.87(9)	HS	
12 LS ^[6]	1.897(2)/1.907(2)	1.935(2)/1.947(2)	2.021(2)/2.014(2)	88.80(7)	LS	
12 HS ^[6]	2.059(3)/2.086(2)	2.001(2)/1.999(2)	2.284(3)/2.280(4); ^[f]	106.10(9)	HS	
			2.284(3)/2.288(7) ^[g]			
13 ^[e]	2.113(4)/2.120(4);	2.030(3)/2.075(3);	2.186(4)/2.224(4);	111.66(12);	HS	
	2.090(4)/2.134(4)	2.016(3)/2.062(3)	2.201(4)/2.235(4)	112.26(13)		
[a] Fe1; Fe3	. [b] Fe1; Fe2. [c] Fe1; F	e2. [d] Fe1; Fe2. [e] Fe1	; Fe2. [f, g] Disorder.			

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2b, 3, 4a, 4b and 5), only two were of good enough quality to be discussed fully (2b and 4a), whereas for the others only the molecular setup and the relative orientation of the alkyl chains is discussed. The different products for the combination of Lc with dmap were presented recently.^[18] Two different samples were obtained for both, the octahedral complex 4, and the penta-coordinated complex 2.^[18] In all cases significant differences were observed for the relative orientation of the alkyl chains. For the penta-coordinated samples indications for vdW interactions were observed between the alkyl chains but not for the octahedral samples.^[18] Here, the motif of the crystal structures of the penta-coordinated complexes 1 and 5 and of the iron(III)- μ -oxido complex 3 are presented. The complexes crystallise in the space group $P\overline{1}$ (1) and (3) and $P2_1/c$ (5). The bond lengths around the iron centre are within the expected range for complexes of this type (Fe-O_{ea}/Fe-N_{ea}: 1.9-2.1 Å, Fe-N_{ax}: 2.1 Å).^[9] The distances to the bridging oxygen atom in the μ -oxido complex are clearly shorter (ca. 1.8 Å). This is also the case for the O-Fe-O angle (91–94°) in comparison to the Nsubstituted complexes (97–101°; Table 2).

The molecular setup of the complexes **1**, **3** and **5** is displayed in Figure 1. For the complexes with the C8 alkyl chains a wide variety of relative orientations of the alkyl chains is observed. They are either parallel to each other but bent down with regard to the equatorial Schiff-base-like ligand (Figure 1, top; **1** and **2b**), parallel to each other and in plane with the equatorial ligand (Figure 1, middle) or spread out and parallel with regard to the equatorial ligand (Figure 1, bottom; **5** and **2a**).

The packing of **1** is very similar to that of **2b** (Figure 2, top). The almost planar planes of the equatorial ligand including the iron are arranged above each other, the alkyl chains are bent in the direction of the dmap of the neighbouring molecule. Like **2b**, the dmap ligands in **1** are arranged parallel to each other and also almost parallel to the C8 alkyl chains, and the chains are also parallel to each other and form a lipid-layer-like arrangement. In the packing of **2b** vdW interactions between the alkyl chains and π - π interactions between the planes of the equatorial ligand are observed.

The arrangement of the molecules of **5** in the crystal (Figure 2, bottom) is very similar to the second modification of the penta-coordinated complex **2a**. As the quality of both structures is low, no discussion about the potential vdW interactions between the alkyl chains is possible.

In the μ -oxido sample of [FeLc(C8)] (**3**; Figure 2, middle), the only iron(III) complex in this study, two inequivalent molecules each with two iron centres (Fe-O-Fe angles: ca. 154°) are stacked above each other, shifted sideways in a small angle. The chains point in the same direction. Next to these two molecules, another pair is arranged, the alkyl chains of which point in the opposite direction, so the molecules form a zipper-type structure in which the polar head-groups are arranged next to each other as the nonpolar tail groups are.

For complexes with relatively short C8 alkyl chains the crystallisation mode is quite unpredictable. The strength of the vdW interactions increases with the dimension of the hydrophobic part of the molecule. For the complexes with C8 alkyl





Figure 1. Molecular setups of **1** (top), **3** (middle) and **5** (bottom). Hydrogen atoms are omitted for clarity. Ellipsoids for the crystal structures are drawn at the 50% probability level.

chains they are weak and do not dominate the crystal packing. They are easily surpassed by other, energetically more favourable conditions, such as hydrogen bonds or π - π interactions.

Chain length of twelve carbon atoms

Crystals suitable for X-ray structure analysis were obtained for six complexes with the chain length of 12 carbon atoms. The two precursor complexes with two methanol as axial ligands, **6** and **7**, crystallised readily out of the reaction mixture.^[16] The crystal structures of two dinuclear complexes with bpea (**8**, **9**), one complex with apy (**10**; motif) and one hexa-coordinated complex with one dmap and one methanol as axial ligands (**11**) were investigated and are discussed in the following. Crystallographic data and selected bond lengths and angles are summarised in Table S1 and Table 2, respectively. In all cases lipid-layer-like structures are observed. However, we did not succeed with the isolation of crystalline material with the de-





Figure 2. Packing in the crystal of 1 along [0 0 1] (top), 3 along [1 0 0] (middle) and 5 along [0 1 0] (bottom). Hydrogen atoms are omitted.

sired octahedral [N₄O₂] coordination sphere, which is interesting with regard to magnetic properties.

The mononuclear complex 10 crystallises in the triclinic space group P1 with four formula units in the unit cell and



Figure 3. Molecular setups of 11 (top), and 10 (bottom). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

two inequivalent iron centres whereas 11 crystallises in the monoclinic space group $P2_1/c$ with only one molecule in the asymmetric unit and four molecules in the unit cell. Figure 3 displays the molecular setup of the two mononuclear complexes and Figure 4 the packing of the molecules in the crystal.

The bond lengths to the equatorial coordinating N and O atoms are with about 2.1 and 2.0 Å very similar for both compounds and in the typical range for complexes of this ligand type, as are the O-Fe-O angles of about 105–109° that clearly indicate the high spin state in both complexes. In 11, the bond length to the O atom of the axially coordinating methanol is almost 0.1 Å longer than to the N atom of the axially attached dmap. One hydrogen bond between the O atom of the methanol and the O atom of one of the keto groups of the equatorial ligand of the neighboured complex molecule is observed (O7-H51-O3, Table 3). One non-classical hydrogen bond between C24-H24C-O1 connects the methyl group of a dmap pointing at the O-Fe-O site with the atom O1 of the complex shifted above. For both complexes the lipid-layer-like arrangement is supported by hydrogen bonds between the polar head-groups.

The dinuclear complexes 8 and 9 both crystallised out of the reaction mixtures of the corresponding iron-methanol complexes with the bidentade bridging bpea in an about 30 equiv excess after one day at room temperature (Scheme 2). For the

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Figure 4. Packing in the crystal of **10** (top) along [1 0 0] and **11** (bottom) along [0 0 1]. Hydrogen atoms are omitted for clarity. Hydrogen bonds in **11** are drawn in dashed lines.

Table bond	Table 3. Short contacts and hydrogen bonds and non-classical hydrogen bonds $[{\rm \AA}]$ of the obtained crystal structures.					
	D–H…A	D-H	H…A	D···A	D–H…A	
11	07–H51…O3 ^[a]	0.79(4)	1.95(4)	2.730(4)	170(4)	
	C24–H24…O1 ^[b]	0.98	2.57	3.395(5)	142	
9	017–H17…O26 ^[c]	0.82	1.87	2.686(4)	175	
	O27–H27…O15 ^[d]	0.82	1.90	2.689(4)	163	
8	C118–H11H…Fe1 ^[e]	0.98	2.90	3.491(4)	120	
	C15–H15B…Fe2 ^[f]	0.98	2.89	3.524(6)	123	
13	C137–H13H…O108 ^[g]	0.98	2.57	3.323(7)	134	
	C30–H30B…N106 ^[h]	0.98	2.58	3.381(11)	139	
	C32–H32···O105 ^[h]	0.95	2.36	3.266(6)	160	
	C45–H45B…O8 ^[i]	0.98	2.38	3.202(7)	141	
[a] x, y,1/2	[a] $x,-1/2-y,-1/2+z$; [b] $x,y,1+z$; [c] $1-x,1/2+y,1/2-z$; [d] $-x,-1/2+y,1/2-z$; [e] x,y,z ; [f] $-1+x,y,z$; [g] $1+x,y,z$; [h] $2-x,1-y,1-z$; [i] $-1+x,y,z$.					

corresponding parent compounds with no alkyl chains in the outer periphery those reaction conditions, even with a tenfold excess of axial ligand, always led to the corresponding coordination polymer.^[20, 23]

While **8** crystallises in the space group $P\overline{1}$ with two molecules in the unit cell, **9** crystallises in $P2_1/c$ with four molecules in the unit cell. Despite the comparably high excess of axial ligand, both complexes do not precipitate as coordination polymers but form dinuclear units with two iron centres per bridging ligand. For **9** the iron centre is saturated with methanol at the sixth coordination site whereas in **8** it is penta-coordinated. Figure 5 displays the molecular setup of **8** and **9** and Figure 6 their packing in the crystal. The average bond lengths and angles within the first coordination sphere do not differ much from the other complexes and are listed in Table 2. Like 11, in 9 two hydrogen bonds are formed between the O atoms of the coordinating methanols and the O atoms of the keto groups of the neighboured complexes. (O17-H17---O26 and O27-H27---O15, see Table 3 and Figure 6). For 8, no classical hydrogen bonds are possible. Surprisingly, a very short contact between atom Fe2 and H15B of atom C15 of one of the ethyl groups in the equatorial ligand surrounding the Fe1 metal centre is found that is shorter by 0.3 Å than the sum of the van der Waals radii (2.89 Å). The angle N13 (of the bpea)-Fe2-H15B is 168.1 $^{\circ}$ and the angle to the carbon atom C15 (N13-Fe2-C15) is 177.87(13)° (length Fe2-C15: 3.524(6) Å). Also, for Fe1 a contact shorter by 0.2 Å than the sum of the van der Waals radii is observed to C118 (Fe1-C118: 3.491(4) Å, **♦** N3-Fe1-C118: 177.89(10)°) and H11H (Fe1–H11H: 2.90 Å, AN3-Fe1-H11H: 168°) of one of the ethyl groups in the equatorial ligand surrounding Fe2. An intermolecular network is formed in which the carbon atoms of the CH₃ of the ethylester groups are connected with the iron atoms in a nearly ideal 180° angle.

All complexes with C12 alkyl chains, the four molecules discussed in this manuscript and the two methanol complexes already described,^[16] crystallise in a lipid-layer-like structure. The alkyl chains form layers with average layer–layer distances of about 4.8 (6), 4.8 (7), 4.1 (8), 4.4 (9), 4.2 (10) and 4.2 Å (11).

Stabilising van der Waals interactions between the alkyl chains (the London dispersion forces) can be considered, when the distances between the atoms are in the region of the sum of the van der Waals radii plus 0.3–0.4 Å. In the case of **8**, **10** and **11**, such stabilising interactions are dominant. Only few destabilising shorter contacts are observed and the average H– H distance is about 2.7 Å. In the case of **9**, the ratio of stabilising and destabilising interactions is around 1:1. It can be assumed that additional strong interactions (hydrogen bonds) influence the crystal packing. In the case of the methanol complexes **6** and **7** the layer–layer distance is relatively long. In agreement with this, fewer stabilising contacts between the alkyl chains are observed.

Chain length of sixteen carbon atoms

The structure of an octahedral spin crossover complex with two alkyl chains of 16 carbon atoms was published recently in the HS and the LS state (**12LS** and **12HS**).^[17] As for the complexes with C12 alkyl chains, a lipid-layer-like structure is observed in the crystal packing. The layer–layer distance between the alkyl chains is with an average of 4.3 Å (both spin states) in the same region as observed for most of the complexes with Cs12 alkyl chains. In agreement with this, numerous stabilising vdW contacts can be observed.

Chain length of 22 carbon atoms

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We succeeded with the crystallisation of an octahedral iron(II) complex with a Schiff-base-like ligand with two C22 alkyl

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Figure 5. Molecular setups of 8 (top) and 9 (bottom). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.



Figure 6. Packing in the crystal of 8 along [0 1 0] (top) and 9 along [1 1 0] (bottom). Hydrogen atoms are omitted for clarity. Hydrogen bonds in 9 are drawn in dashed lines.

chains and two dmap as axial ligands. Single crystals of high enough quality for X-ray structure analysis were obtained and the molecular setup could be elucidated. Compound 13 $([Fe(Ld)(C22)(dmap)_2] \times 0.5 EtOH)$ crystallises in the triclinic space group P1 with four molecules in the unit cell and two inequivalent iron centres bearing the desired octahedral [N₄O₂] coordination sphere. Selected bond lengths and angles are given in Table 2, and crystallographic data in Table S1 in the Supporting Information. Similar to the hexa-coordinated complex 9, the Fe-N_{eq} and Fe-O_{eq} bond lengths are with about 2.1 Å, respectively, 2.0 Å in the expected magnitude. The O-Fe-O angle of about 112° clearly indicates that the complex is in the HS state at 173 K. The molecular setup of 13 is displayed in Figure 7 (top). The coordination sphere around the iron(II) is a distorted octahedron. The Schiff-base-like ligand can be described as saddle shaped. The chelate six rings with the delocalised π system are bent in the direction of the phenylene substituents. The angles with the [N₂O₂] plane are 16°/23° (O1C1C2C3N1-plane and N2C10C11C12O2-plane) for Fe1 and $25^{\circ}/15^{\circ}$ for Fe2. The iron centre is slightly shifted out of the $[N_2O_2]$ plane by 0.08 Å.

The bond length to the N atom of the axial dmap ligand is slightly elongated at the more shielded site of the ligand. The planes of the dmap rings assume a staggered conformation with an angle of 74° for Fe1 and 52° for Fe2. The C22 alkyl chains are not arranged in plane with the equatorial ligand but point out of the [N₂O₂] plane with an angle of 22° at Fe1 and 28° at Fe2, bent about 45° sideward. This is different to the complexes with C12 and C16 alkyl chains.

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 $(dmap)_2$] is a low-spin complex in the entire temperature range (see Supporting Information, Figure S1). The difference to the spin state of **13** (HS at 173 K) can be explained with the missing additional ethanol molecule in the crystal packing.

Prediction of the molecular setup of amphiphilic complexes and their arrangement in the crystal

The results from X-ray structure analysis show clearly, that with an alkyl chain length of C12 or higher, lipid-layer-like arrangements are the preferred structural motif. However, often not the desired reaction product is obtained. This implies that the formation of lipid-layer-like arrangements prevents the formation of octahedral complexes. Thus, the question arises, what parameters control the formation of lipid-layer-like arrangements. In 1976, Israelachvili et al. predicted how amphiphiles selfassemble in solution, depending on the geometry of the molecules.^[24] For this, he introduced the critical packing parameter [*cpp*, Eq. (1)]:^[24]

$$cpp = V A^{-1} L^{-1}$$
 (1)

It correlates the volume of the hydrophobic part (V), in relation to the area of the head group (A) and the length of the hydrophobic part (L). If $cpp \approx 1$, in

Figure 7. Molecular setup (top) and packing in the crystal (bottom) of 13, packing along [1 0 0]. Hydrogen atoms are omitted for clarity. Ellipsoids for the crystal structures are drawn at the 50% probability level. Non-classical hydrogen bonds are drawn in dashed lines.

In the crystal packing, the molecules are clearly arranged in the lipid-layer-like structure with a layer–layer distance of about 4.00 Å (Figure 7, bottom). In comparison with the layer distances of the other complexes bearing this structure motif, this is short. Several non-classical hydrogen bonds are observed between the polar head-groups (C137–H13H···O108, C30–H30B···N106, C32–H32···O105 and C45–H45B···O8; see Table 3) indicating a dense packing. Most of the contacts between the alkyl chains are in the region of the sum of the van der Waals radii plus 0.3–0.4 Å. This indicates strong stabilising vdW interactions between the alkyl chains of this complex.

Unfortunately, the amount of crystals of **13** was not enough for magnetic measurements on the single crystals. A separately prepared powder sample with the composition [Fe(Ld)(C22)- a polar solvent the molecules bearing two alkyl chains will arrange in lipid layers. If the *cpp* is smaller than one, flexible micellar structures are realised, and if it is bigger than 1, in nonpolar solvents inverse micelles are formed. It should be pointed out, that for all of our reactions a polar solvent was used. On the basis of this, we tried to establish a rule for our complexes regarding how they will arrange in solution and thus in the solid. In order to obtain this rule, the broadness and the height of the polar head and the length of the whole molecule were measured (exemplarily shown for the complex **12LS** in Figure 8). The results are listed in Table 4.

First attempts to predict the crystal packing with the help of the critical packing parameter (*cpp*) of Israelachvili et al. were not successful. It then became obvious, that the following

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Figure 8. Dimensions of the compounds taken in account for the calculation of the *sap*. *L* denotes the length, *H* the height and *B* the broadness of the complex.

Table 4. Height (H), broadness (B) and length (L) of the complexes discussed in this work.						
	H [Å]	B [Å]	<i>L</i> [Å ⁻¹]	(H+B)/L		
1	8.10	17.13	16.19	1.56		
2a	8.11	14.68	16.02	1.42		
2b	8.12	14.24	15.90	1.41		
3	1.72	14.24	19.70	0.81		
4 aLS	15.90	14.40	19.15	1.58		
4 aHS	16.29	14.28	18.32	1.67		
4b	16.00	14.11	18.12	1.66		
5	6.74	14.31	17.50	1.20		
6	8.07	16.86	23.79	1.05		
7	8.07	14.91	23.98	0.96		
8	6.71	15.47	23.56	0.94		
9	10.87	13.26	24.25	1.00		
10	6.78	15.27	23.90	0.92		
11	12.22	12.83	23.86	1.05		
12LS	11.48	16.91	29.44	0.96		
12 HS	11.97	17.44	29.30	1.00		
13	16.26	16.36	32.20	1.01		

straight forward relation [the self-assembly parameter, *sap*, Eq. (2)] can be used. When the sum of the broadness (*B*) and the height (*H*) of the polar head-group, divided through the entire length of the molecule (*L*) is around 1, a lipid-layer-like packing in the crystal can be expected:

$$sap = (H+B)/L \tag{2}$$

The complexes with alkyl chains of eight carbon atoms have an entire length, *L*, of about 20.4 Å, when the chains are ideally arranged. Adding, for example, two dmap ligands in the axial positions would cause an inappropriate relation of (H+B)/L(substituent c: $B \approx 14.4$ Å, $H \approx 16.30$ Å; $sap \approx 1.50$). In agreement with this, other packing patterns are observed. Examples for this are the hexa-coordinated complexes **4a/4b**.

The values would match exactly, for example, for a penta-coordinated complex [FeLc(C8)(MeOH)]. Indeed, the synthesised fine crystalline powder of the methanol precursor has this composition. Additionally it is extremely air sensitive—a further indication for penta-coordination. Unfortunately, no crystals of high enough quality could be isolated. For the penta-coordinated complexes with one N-heterocyclic axial ligand (2a/2b, 1 and 5) the ratio is closer to 1 compared to the octahedral systems. Thus, lipid-layer-like structures, for example, with bent alkyl chains as for 1 and 2b, are observed. For the μ -oxido complex 3 the ratio is smaller than 1 and again another structural motif is observed.

For the complexes with alkyl chain lengths of 12 carbon atoms the situation is different. Penta- and hexa-coordinated products are obtained. Due to the longer hydrophobic tails the importance of the vdW interactions as structure determining element increases and lipid-layer-like structures are observed for every complex. The alkyl chains are arranged along the [N₂O₂] plane without significant differences in the angles. However, reactions with dmap, apy or the bridging bpea did not give the desired hexa-coordinated products. Only spin crossover inactive methanol complexes 6 and 7,^[16] mixed derivatives like 11, dinuclear complexes as 8 and 9 or penta-coordinated compounds (10) crystallised. Application of Equation (2) explains this behaviour. As can be seen in Table 4, for all of the crystallised complexes with C12 alkyl chains the values for (H+B)/L are almost exactly around 1. The two penta-coordinated complexes with slightly smaller values reveal both short contacts to other atoms at the empty coordination site. Adding bigger axial ligands (for example, two dmap and substituent b: $B \approx 13.0$ Å, $H \approx 16.30$ Å, $L \approx 23.89$ Å; $sap \approx$ 1.23) would cause a loss of the ability of the complex to crystallise in the lipid-layer-like structure. This is the reason why 11, for example, crystallises in this unusual modification bearing one methanol instead of a second dmap. It also explains the formation of dinuclear complexes instead of coordination polymers, despite the large excess of axial ligand.

For complexes with C16 alkyl chains the situation is very similar. Unfortunately, only the crystal structure of one complex **12** (HS and LS) could be obtained so far.^[17] The axial pyridine ligands fit exactly in combination with substituent a and the C16 alkyl chains ((H+B)/L for the complex in HS: 1.00) to give a lipid-layer-like structure in the crystal.

To add more bulky ligands, like dmap, following Equation (2), the chain length had to be elongated. Consequently, the corresponding ligand and the methanol precursor with alkyl chain lengths of 22 carbon atoms was synthesised and converted with dmap. The complex **13** is hexa-coordinated and exhibits a lipid-layer-like arrangement of the molecules in the crystal. The structural situation for the C22 compound is more complicated. The calculated length of **13** is 40.6 Å (Figure 9). This is too long for the dmap ligands, even if the high steric demand of the equatorial ligand is considered (calculated *sap* = 0.81). This can be the reason, why the nonpolar chains are bent quite strongly sideward. As shown in Figure 9,

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Figure 9. Measurement of the length taken in account for the calculation of (H+B)/L for complex 13. *L* denotes the length of the complex. The plane on the left is spanned by the ultimate four hydrogen atoms of the complex.

a plane was spanned at the outer H atoms of the two phenylene rings of the equatorial ligand. Measuring the distance between the plane and the latest H atoms of the alkyl chains leads to an average length of 32.2 Å, which denotes the actual length of the complex in the crystal, and a *sap* of 1.01. Consequently, it should be possible to add more bulky axial ligands like phenylpyridine without losing the lipid-layer-like arrangement.

The next question to be answered is, whether this concept can be transferred to other amphiphilic complexes.^[12,25] In the field of spin crossover research, amphiphilic systems are so far reported for iron(II),^[8,26] cobalt(II),^[9] iron(III)^[11,13,14,27] and manganese(III).^[10]

A few X-ray structures are available for complexes with alkyl chains \leq C8. In contrast to our system, in all cases counter ions are involved. For manganese(III) complexes with the bapen ligand and C6 alkyl chains different orientations of the alkyl chains in the crystal packing are observed.^[10] For a similar iron(III) complex with the sal₂trien ligand and C8 alkyl chains already a layered structure is observed with interactions between the polar heads (and the counter ions) and interactions between the nonpolar chains.^[27] A similar situation is observed for an iron(II) complex of the C₆tren ligand with three C6 alkyl chains.^[74]

The cobalt(II) complexes investigated by Hayami and coworkers differ from our system as the two alkyl chains point in opposite directions and again counter ions are involved.^[6,28] Layered structures are observed that differ, however, quite strongly from lipid-layer-like arrangements.

An iron(III) complex of a Schiff base ligand with *n*-dodecyl chains showed a very similar behaviour to our complexes with C12 alkyl chains. X-ray structure analysis revealed self-assembly to lipid-layer-like structures for this neutral complex in the solid state.^[29] Between the polar head-groups a network of hydrogen bonds is observed. For this system, the calculated value of (H+B)/L is with 0.87 significantly smaller than 1 and

a better result is obtained if only the length of the alkyl chain is considered (1.08). This illustrates the influence of the different numbers of alkyl chains on the *sap*.

Conclusion

In this work, the crystal structures of seven published and eight new amphiphilic iron complexes with Schiff-base-like ligands and nonpolar alkyl chain groups with lengths of 8, 12, 16 and 22 carbon atoms are presented and discussed. With regard to the spin transition properties of the central metal atom, a [N₄O₂] coordination sphere and self-assembly to lipidlayer-like structures is desired. This can be achieved, if the newly introduced sap (self-assembly parameter) is considered. The sap allows us to predict, which general requirements have to be fulfilled for the observation of octahedral complexes with lipid-layer-like structures in the solid. For the synthesis of octahedral complexes with rather bulky axial ligands as the dmap, long alkyl chains are necessary. The synthesis of a ligand with C22 alkyl chains allowed the crystallisation of a corresponding octahedral iron(II) complex with dmap. This is, to the best of our knowledge, the complex with the longest alkyl chains in which crystallisation succeeded.

This empirically derived rule to design octahedral SCO complexes can also be successfully applied to explain the crystallisation behaviour of other ligand systems. Depending on the system, slight adjustments may be necessary. Additionally, we gain a further insight into the self-assembly of such complexes in solution. This is of great importance for the nanostructuring of SCO systems (e.g., micelles or inverse micelles) or the creation of thin layers (e.g., Langmuir–Blodgett films).

Experimental Section

Synthesis

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The synthesis of the iron complexes and syntheses with the diamino precursor were carried out under an argon atmosphere using Schlenk-tube techniques. The solvents therefore were purified as described in the literature,^[30] and distilled under an atmosphere of argon. The synthesis of 1,2-dioctyloxybenzene, 1,2-didodecyloxybenzene, 1,2-dihexadecyloxybenzene, 1,2-didocosyloxybenzene, 4,5-dioctyloxy-1,2-dinitrobenzene, 4,5-didodecyloxy-1,2dinitrobenzene, 4,5-dihexadecyloxy-1,2-dinitrobenzene, 4,5-didocosyloxy-1,2-dinitrobenzene, 1,2-diamino-4,5-dioctyloxybenzene, 1,2diamino-4,5-didodecyloxybenzene, 1,2-diamino-4,5-dihexadecyloxybenzene, 1,2-diamino-4,5-didocosyloxybenzene,[16,17] ethoxymethyleneethylacetoacetate,^[31] methoxymethylenemethylacetoacetate,^[32] ethoxymethyleneacetylacetone,^[31] ethoxymethylenephenylacetoacetate,^[33] H₂La-c, [Fe(La-c)(Cn+1)(MeOH)₁₋₂],^[16,17] and iron(II) acetate^[34] are described in the literature. Pyridine (py), 4-aminopyridine (apy; Alfa Aesar, 98%), 4-(dimethylamino)pyridine (dmap; Merck, \geq 99%) and 1,2-bis(4-pyridyl)ethane (bpea; Aldrich, 99%) were purchased and used as received. For the complexes 5, 9 and 13 the amount of crystals was not enough to perform elemental analysis.

[Fe(La)(C8)(dmap)] (1): [Fe(La)(C8)(MeOH)₂] (0.40 g, 0.52 mmol) and dmap (2.1 g, 17.19 mmol, 33.1 equiv) were dissolved in methanol (17 mL) and heated to reflux for 90 min. After storing at -30 °C

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black crystalline precipitate was filtered and washed two times with methanol (2.5 mL). In the residual solution black needle-like crystals were formed at 7 °C within few days. Yield: 0.02 g (5%; 820.84 g mol⁻¹). Elemental analysis calcd (%) for $C_{43}H_{64}FeN_4O_8$: C 62.92, H 7.86, N 6.83; found: C 62.97, H 8.09, N 7.32.

[(Fe(Lc)(C8))₂O] (3): [Fe(Lc)(C8)(MeOH)₁₋₂] (0.3 g, 0.41 mmol) was dissolved in pyridine (6 mL) and heated to reflux for 15 min. After cooling to RT, H₂O (4 mL) was added and the mixture was shortly heated again until it boiled. After cooling to RT, fine crystalline brown precipitate was filtrated. Yield: 0.27 g (79%; 828.81 g mol⁻¹). Elemental analysis calcd (%) for C₄₄H₆₀FeN₄O₈: C 63.76, H 7.30, N 6.76; found: C 63.66, H 7.21, N 7.27. Needle-like crystals of μ -oxido complex were formed in the remaining solution standing in air.

[Fe(Lc)(C8)(apy)] (5): [Fe(Lc)(C8)(MeOH)₁₋₂] (0.29 g, 0.39 mmol) and apy (1.11 g, 11.79 mmol, 30.2 equiv) were dissolved in methanol (10 mL) and heated to reflux for 1 h. After storing the black solution for 4 d at 6 °C, black block-like crystals were isolated. Yield: 0.08 g (25%; 858.84 g mol⁻¹).

[{Fe(La)(C12)}₂(bpea)] (8): [Fe(La)(C12)(MeOH)₂] (0.34 g, 0.39 mmol) and bpea (2.15 g, 11.67 mmol, 29.9 equiv) were dissolved in methanol (10 mL) and heated to reflux for 75 min. After 1 d at RT, greenish-black needles were filtrated and washed with methanol (3 mL). Yield: 0.06 g (16%; 1806.00 g mol⁻¹). Elemental analysis calcd (%) for C₁₀₀H₁₅₂Fe₂N₆O₁₆: C 66.50, H 8.48, N 4.65; found: C 66.64, H 8.70, N 4.72.

 $[{Fe(Lb)(C12)(MeOH)}_2(bpea)]$ (9): [Fe(Lb)(C12)] (0.27 g, 0.36 mmol) and bpea (1.83 g, 9.93 mmol, 27.5 equiv) were suspended in methanol (10 mL) and heated to reflux for 1 h. After 1 d at RT, black platelet-like crystals were filtrated. Yield: 0.02 g (3%; 1749.98 g mol⁻¹).

[Fe(La)(C12)(apy)] (10): [Fe(La)(C12)(MeOH)₂] (0.22 g, 0.37 mmol) and apy (1.03 g, 10.94 mmol, 29.6 equiv) were dissolved in methanol (10 mL) and heated to reflux for 1 h. After cooling to RT, black platelet-like crystals were isolated. Yield: 0.13 g (39%; 904.99 g mol⁻¹). Elemental analysis calcd (%) for C₄₉H₇₆FeN₄O₈: C 65.03, H 8.46, N 6.19; found: C 65.34, H 8.55, N 6.33.

[Fe(Lb)(C12)(dmap)(MeOH)] (11): [Fe(Lb)(C12)] (0.26 g, 0.35 mmol) and dmap (1.17 g, 9.58 mmol, 27.4 equiv) were dissolved in methanol (10 mL) and heated to reflux for 1 h. After 14 d at 6 °C black needle-like crystals were filtrated and washed with methanol (3 mL). Yield: 0.01 g (3%; 905.04 g mol⁻¹). Elemental analysis calcd (%) for $C_{s0}H_{80}FeN_4O_7$: C 66.35, H 8.91, N 6.19; found: C 66.64, H 9.09, N 6.15.

H₂Ld(C22): 1,2-Diamino-4,5-didocosyloxybenzene (1.2 g, 1.58 mmol) was suspended in ethanol (200 mL) saturated with argon and ethoxymethylenephenylacetoacetate (0.94 g, 3.80 mmol, 2.4 equiv) was added dropwise. The yellow suspension was heated to reflux for 90 min and then stored at -30 °C, overnight. The precipitate was filtered and washed with ethanol (20 mL). The orange product was recrystallised from ethanol (30 mL). Yield: 1.42 g (77%; 1161.72 g mol⁻¹). ¹H NMR (296 K, CDCl₃): $\delta = 0.87$ (t, 6H, ³J= 8 Hz, CH₃), 1.20-1.64 (m, 80 H, CH₃(CH₂)₁₉, CH₃(Et)), 1.75-1.90 (m, 4H, CH₂CH₂O), 3.95–4.11 (m, 8H, CH₂O), 6.82 (s, 2H, NHC_aCH), 7.30– 7.75 (m, 10 H, Phenyl-CH), 8.30 (dd, 2 H, ${}^{3}J = 12.9$ Hz, C=CH), 12.14 ppm (dd, 2H, ${}^{3}J = 12.9$ Hz, NH); elemental analysis calcd (%) for C74H116N2O8: C 76.51, H 10.06, N 2.41; found C 76.76, H 9.96, N 2.71.

 $[Fe(Ld)(C22)(MeOH)_2]$: H₂Ld(C22) (1.14 g, 0.98 mmol) and iron(II) acetate (0.36 g, 2.06 mmol, 2.1 equiv) were mixed in methanol (160 mL) and heated to reflux for 5 h. The brown precipitate was filtered, washed with methanol (2×15 mL) and dried in vacuum. Yield: 0.93 g (74%; 1279.63 g mol⁻¹). Elemental analysis calcd (%)

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ike N 2.48. %; [Fe(Ld)(C22)(dmap),]×0.5 EtOH (13): [Fe(Ld)(C22)(MeOH),] (0.25 g,

0.20 mmol) and dmap (1.22 g, 10.02 mmol, 50.0 equiv) were dissolved in a mixture of toluene (8 mL) and ethanol (2 mL) and heated to reflux for 90 min. After cooling to -30 °C ethanol (5 mL) were added and the green solution again stored at -30 °C for 11 d. The brown precipitate was filtered and dried in vacuum. Yield: 0.13 g (45%; 1482.92 g mol⁻¹). In the residual solution black needle-like crystals were formed.

for C₇₆H₁₂₂FeN₂O₁₀: C 71.33, H 9.61, N 2.19; found: C 71.45, H 10.05,

 $\label{eq:constraint} \begin{array}{ll} \mbox{[Fe(Ld)(C22)(dmap)_2]} & (powder): & [Fe(Ld)(C22)(MeOH)_2] & (0.17 \mbox{ g}, 0.13 \mbox{ mmol}) and dmap & (0.81 \mbox{ g}, 6.65 \mbox{ mmol}, 50 \mbox{ equiv}) were heated to reflux in ethanol (30 \mbox{ mL}) for 90 \mbox{ min}. After 3 \mbox{ d} the brown precipitate was filtered, washed with ethanol (3 \mbox{ mL}) and dried in vacuum. Yield: 0.19 \mbox{ g} (98\%; 1459.89 \mbox{ g} \mbox{ mol}^{-1}). Elemental analysis calcd (%) for $C_{88}H_{134}FeN_6O_8: C 72.40, \mbox{ H} 9.25, \mbox{ N} 5.76; found: C 72.20, \mbox{ H} 9.45, \mbox{ N} 5.97. \end{array}$

X-ray diffraction

The intensity data of 1, 2, 3, 9, 10 and 11 were collected with a Stoe IPDS II diffractometer, the intensity data of 5 with a Bruker Nonius Kappa CCD diffractometer and the intensity data of 13 with a Bruker D8 Venture diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SIR97: 1, 10, 11,^[35] SIR2004: 3, 5,^[36] and SHELXS-97: 8, 9, 13^[37]) and refined by full-matrix least-square techniques against F_0^2 (SHELXL-97, SHELXH-97 for 3, 10 and 13).^[37] The hydrogen atoms were included at calculated positions with fixed displacement parameters, allowed to ride on their parent atoms. If not denoted differently, for methyl and hydroxyl groups the torsion angles were allowed to be refined according to the electron density. In the structure of 11, the proton of the methanol hydroxyl group was directly located according its electron density. If not denoted differently in the ciffile, all non-hydrogen atoms were refined anisotropically. Due to bad guality of the data of 1, 3, 5 and 10 only the general molecular setup could be investigated. For 3 and 5, twin refinement was conducted based on twin law:

$$\begin{pmatrix} -1.000 & 0.000 & 0.000 \\ 0.026 & 1.000 & -0.188 \\ 0.000 & 0.000 & -1.000 \end{pmatrix}$$
 for **3**
$$\begin{pmatrix} -1.000 & 0.000 & 0.000 \\ 0.000 & -1.000 & 0.000 \\ 0.224 & 0.000 & 1.000 \end{pmatrix}$$
 for **5**

found by PLATON.^[38] ORTEP-III^[39] was used for the structure representation, Schakal-99^[40] and Mercury^[41] for the representation of the molecule packing. CCDC-952444 (1), 952445 (3), 952442 (5), 952449 (8), 952446 (9), 952447 (10), 952448 (11) and 952443 (13) 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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Acknowledgements

Financial supports from the German Science Foundation (SFB840; project A10) and the University of Bayreuth are acknowledged. We thank S. Albrecht and P. Mayer (University of Munich) for the collection of the single crystal X-ray data of **5** and **13**.

Keywords: crystal engineering \cdot head-tail compounds \cdot iron \cdot N,O ligands \cdot self-assembly

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Received: November 27, 2013 Revised: February 4, 2014 Published online on

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FULL PAPER

Looking ahead: Based on the X-ray structures of 15 amphiphilic iron complexes the self-assembly parameter, *sap*, is introduced that allows to predict when lipid-layer-like structures are observed (see figure). This was used for the crystallisation of a complex with two C22 alkyl chains and can also be applied to other systems.



Self-Assembly

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Influence of the Alkyl Chain Length on the Self-Assembly of Amphiphilic Iron Complexes: An Analysis of X-ray Structures