Ligand-to-Metal Ratio Controlled Assembly of Tetra- and Hexanuclear Clusters Towards Single-Molecule Magnets**

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Dedicated to Professor Elmar Vilsmaier on the occasion of his 60th birthday

Abstract: A simple template-mediated route, starting from triethalolamine **1**, sodium hydride or caesium carbonate, and iron(III) chloride led to the six- and eight-membered iron coronates $[Na\subset\{Fe_6[N(CH_2CH_2O)_3]_6\}]^+$ (**2**) and $[Cs\subset\{Fe_8[N(CH_2CH_2O)_3]_8\}]^+$ (**3**). In the reaction of *N*-methyldiethanolamine **4** (H_2L^1) or *N*-(2,5-dimethylbenzyl)iminodiethanol **6** (H_2L^2) with calcium hydride followed by addition of a solution of iron(III) chloride, the neutral unoccupied coronands $[Fe_6Cl_6(L^1)_6]$ (**5**) and $[Fe_6Cl_6(L^2)_6]$ (**7**) were formed. Subsequent exchange of the chloride ions of **7** by bromide or thiocyanate ions afforded the ferric wheels $[Fe_6Br_6(L^2)_6]$ (**8**) or $[Fe_6(NCS)_6(L^2)_6]$ (**9**), respectively. Titration experiments of solutions of dianion $(L^1)^{2-}$ with iron(III) chloride in THF revealed interesting mechanistic details about the self-assembling process leading to **5**. At an iron/ligand ratio of 1:1.5 star-shaped tetranuclear $[Fe\{Fe(L^1)_2\}_3]$ (**11**) was isolated. However, at an iron/ligand ratio of 1:2, complex **11** was transformed into the ferric wheel **5**. It was shown, that the interconversion of **5** and **11** is reversible. Based on the mechanistic studies, a procedure was developed which works for both the synthesis of homonuclear **11** and the star-shaped heteronuclear clusters $[Cr\{Fe(L^1)_2\}_3]$ (**12**) and $[Al\{Fe(L^1)_2\}_3]$ (**13**). The structures of all new compounds were determined unequivocally by single-crystal X-ray analyses.

Keywords: cluster compounds • heteronuclear clusters • iron • metallacrown ethers • single-molecule magnets • supramolecular chemistry

Introduction

The formation of oxo-bridged polynuclear complexes of paramagnetic transition and rare earth metal ions, derived from polyalcoholato ligands is poorly understood.[1] However, despite of their unpredictable nature, oxo-bridged polynuclear iron and manganese metal clusters have been the subject of numerous detailed magnetic studies, which have been rewarded by the discovery of the so-called single-molecule magnets.[2] Recently, distinct supramolecular metal clusters have become accessible by rational design rather than by serendipity.[3]

In this context, we reported on the template-mediated self assembly of six- and eight-membered iron coronates.[4] The iron coronates $[Na\subset\{Fe_6[N(CH_2CH_2O)_3]_6\}]^+$ (**2**) and $[Cs\subset\{Fe_8[N(CH_2CH_2O)_3]_8\}]^+$ (**3**), with $Na\subset$[12]metallacrown-6 and $Cs\subset$[18]metallacrown-8 structures, were prepared from the reaction of triethanolamine (**1**) with iron(III) chloride and sodium hydride or caesium carbonate, respectively (Scheme 1).

A common feature of complexes **2** and **3** is that the μ_1-oxygen atoms do not participate in the formation of the hexa- or octanuclear structures. They solely function as ligands for the coordinative saturation of the iron centers. For this reason, further mono-anionic donors, such as chloride ions, could also be candidates for this function. As expected, reaction of *N*-methyldiethanolamine (**4**; H_2L^1) with calcium hydride and iron(III) chloride yielded the unoccupied neutral iron cryptand $[Fe_6Cl_6(L^1)_6]$ (**5**) with [12]metallacrown-6 structure (Scheme 2).[4]

In contrast to the iron coronates **2** and **3**, a variety of six-membered analogues of iron cryptate **5** is conceivable. In **5**, the μ_2-oxygen donors of the *N*-methyldiethanolamine ligands are structure-determining, whereas their *N*-methyl groups are innocent and are exchangeable by various alkyl and aryl

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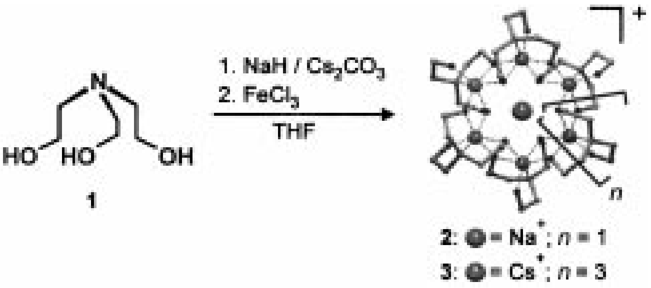
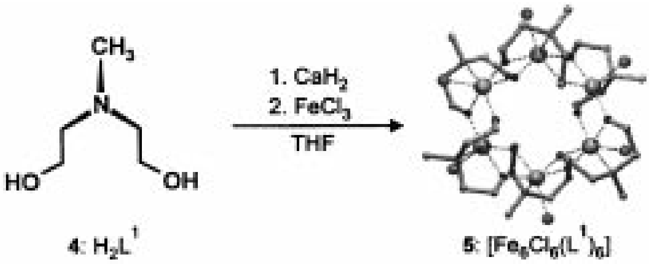


Scheme 1.



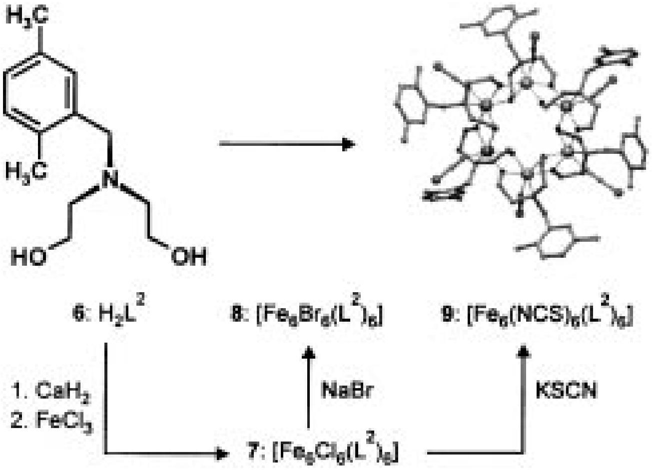
Scheme 2.

substituents. Additionally, chloride co-ligands necessary for iron center coordinative saturation and for charge compensation should be replaceable by diverse halogenato or pseudohalogenato donors.

Results and Discussion

In order to prove this hypothesis, we allowed *N*-(2,5-dimethylbenzyl)iminodiethanol (**6**; H_2L^2) to react with calcium hydride and iron(III) chloride to yield intermediate $[Fe_6Cl_6(L^2)_6]$ (**7**). Subsequent exchange of the chloride ions of **7** by bromide or thiocyanate ions afforded the unoccupied ferric wheels $[Fe_6Br_6(L^2)_6]$ (**8**)[5] or $[Fe_6(NCS)_6(L^2)_6]$ (**9**; Scheme 3).

Abstract in German: *Eine einfache Templat-gesteuerte Synthese führte, ausgehend von Triethalolamin* ***1****, Natriumhydrid oder Cäsiumcarbonat und Eisen(III)chlorid, zu den sechs- und achtkernigen Eisencoronaten* $[Na \subset \{Fe_6[N(CH_2CH_2O)_3]_6\}]^+$ (**2**) *und* $[Cs \subset \{Fe_8[N(CH_2CH_2O)_3]_8\}]^+$ (**3**). *Bei der Umsetzung von N-Methyldiethanolamin (**4**;* H_2L^1*) oder N-(2,5-Dimethylbenzyl)iminodiethanol (**6**;* H_2L^2*) mit Calciumhydrid und einer Eisen(III)chlorid Lösung, erhielten wir die neutralen, leeren Coronanden* $[Fe_6Cl_6(L^1)_6]$ (**5**) *und* $[Fe_6Cl_6(L^2)_6]$ (**7**). *Der anschließende Austausch der Chloridionen in* **7** *durch Bromid- oder Thiocyanationen führte zu den Eisenrädern* $[Fe_6Br_6(L^2)_6]$ (**8**) *bzw.* $[Fe_6(NCS)_6(L^2)_6]$ (**9**). *Titrationsexperimente von Lösungen des Dianions* $(L^1)^{2-}$ *mit Eisen(III)chlorid in THF lieferten einen interessanten Einblick in den Selbstorganisationsprozeß, der zu* **5** *führt. Bei einem Verhältnis Eisen zu Ligand von 1:1.5 wurde der sternförmige tetranucleare Cluster* $[Fe\{Fe(L^1)_2\}_3]$ (**11**) *isoliert. Dagegen wurde bei einem Verhältnis Eisen zu Ligand von 1:2 der Komplex* **11** *in das Eisenrad* **5** *umgewandelt. Zudem konnten wir zeigen, dass die Umwandlung von* **11** *in* **5** *reversibel ist. Auf der Basis dieser mechanistischen Studien haben wir eine Methode entwickelt, die sowohl für die Synthese des homonuclearen Clusters* **11** *als auch für die Synthese der heteronuclearen sternförmigen Cluster* $[Cr\{Fe(L^1)_2\}_3]$ (**12**) *und* $[Al\{Fe(L^1)_2\}_3]$ (**13**) *geeignet ist. Die Strukturen aller neuen Verbindungen wurden zweifelsfrei durch röntgenographische Kristallstrukturanalysen gesichert.*



Scheme 3.

Specifically, an X-ray crystallographic structure determination was carried out for **9**. According to this analysis, **9** is present in the crystal as unoccupied, neutral iron(III) complex with [12]metallacrown-6 structure (Figure 1). The six iron centers of the centrosymmetric molecule **9** are located in the corners of an almost regular hexagon. The Fe–Fe distances range from 3.15 to 3.16 Å, and the interior angles of the hexagon range between 118.11 and 121.98°. The diameter of the hexagon, defined as the mean distance between two opposite iron centers, is 6.20 Å. The distorted octahedral coordination sphere of the iron centers is completed by two nitrogen donors (one from $(L^2)^{2-}$ and one from NCS^-) and four μ_2-O donors. Thus, the $[Fe_6O_{12}]$ cores of $[Fe_6Cl_6(L^1)_6]$ (**5**) and $[Fe_6(NCS)_6(L^2)_6]$ (**9**) are nearly superimposible (Figure 1).

Until now, little is known about mechanistic aspects of self-assembling processes.[1f] In order to also shed light on this subject, we carefully studied the formation of compound **5**. After numerous attempts, *N*-methyldiethanolamine (**4**; H_2L^1) was now deprotonated with sodium hydride instead of calcium hydride. Careful titration of the dianion $(L^1)^{2-}$ with a solution of iron(III) chloride in THF afforded a colorless suspension of intermediate $[Fe(L^1)_2]^-$ (**10**) with an iron/ligand ratio of 1:2 (Scheme 4). Further addition of iron(III) chloride to the colorless suspension of **10** up to an iron/ligand ratio of 1:1.5 resulted in gradual color change to a brown suspension. After work-up, amber microcrystals were isolated. Based on the FAB-MS data (*m*/*z* 926, $[Fe_4(L^1)_6]$), the tetranuclear cluster **11** was generated rather than hexanuclear cluster **5**. However, when two equivalents of iron(III) chloride were added to $[Fe\{Fe(L^1)_2\}_3]$ (**11**), the known ferric wheel **5** with [12]metallacrown-6 structure was generated as the final product.[4] This process was shown to be reversible. When **5** was treated with three equivalents of $(L^1)^{2-}$, star-shaped cluster **11** was recovered. A similar tetranuclear iron(III) complex was reported recently by Gatteschi and co-workers.[2a,b]

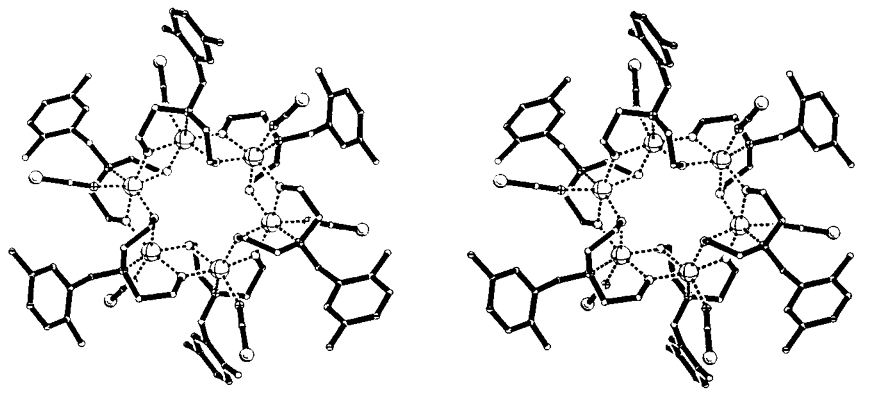
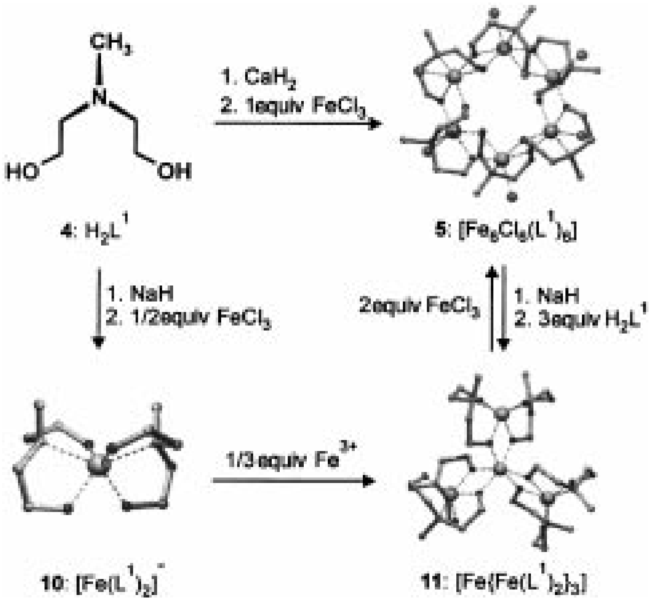


Figure 1. Stereoview of **9** in the crystal (PLUTON representation; H atoms omitted).



Scheme 4.

The single-crystal X-ray structure analysis indicated **11** as the star-shaped cluster $[Fe\{Fe(L^1)_2\}_3]$. In **11** the central iron ion is linked through two μ_2-alkoxo bridges from each of the three terminal building blocks $[Fe(L^1)_2]^-$ (**10**). The iron center in **10** is octahedrally coordinated through two nitrogen, μ_1-O , and μ_2-O donors. It is noteworthy, that during complexation of $(L^1)^{2-}$ to iron, nitrogen becomes a stereogenic center. From all the structures possible for $[Fe(L^1)_2]^-$, only (*R*,*R*)-(**10**) or (*S*,*S*)-(**10**) have the appropriate geometry to function as bidentate ligands to yield **11**. The central iron ion also becomes a stereogenic center with (*Δ*)- or (*Λ*)-configuration. Therefore, eight enantiomers of **11**, (*Δ*/*Λ*)-[(*R*,*R*)(*R*,*R*)(*R*,*R*)], (*Δ*/*Λ*)-[(*S*,*S*)(*S*,*S*)(*S*,*S*)], (*Δ*/*Λ*)-[(*R*,*R*)(*S*,*S*)(*S*,*S*)] and (*Δ*/*Λ*)-[(*S*,*S*)(*R*,*R*)(*R*,*R*)], are possible.[6] The X-ray structure analysis was carried out on a randomly selected single crystal of **11**, which featured the racemic isomers (*Δ*)-[(*S*,*S*)(*R*,*R*)(*R*,*R*)] and (*Λ*)-[(*R*,*R*)(*S*,*S*)(*S*,*S*)].[7] The two stereoisomers have a molecular C_2 axis. All four iron ions are located in a plane, with Fe-Fe-Fe angles of about 120° (Figure 2).

As a consequence of the afore-mentioned mechanistic study, it should be possible to generate heteronuclear species with different magnetic properties in addition to homonuclear **11**. In order to prove this hypothesis, intermediate **10** was treated with solutions of $[CrCl_3(THF)_3]$ or aluminium(III) chloride and after work-up $[Cr\{Fe(L^1)_2\}_3]$ (**12**) or $[Al\{Fe(L^1)_2\}_3]$ (**13**), respectively, were isolated (Scheme 5). According to single-crystal structure analyses, the heteronuclear clusters **12** and **13** are isostructural with **11**. They differ from **11** only by exchange of the central iron center by chromium(III) or aluminium(III), respectively.

Conclusion

We described an efficient, simple route starting from triethanolamine and iron(III) chloride for the template-mediated self-assembly of six- and eight-membered iron coronates. Careful analysis of the structures of these systems was the basis for the rational design of various six-membered iron coronands, starting from *N*-alkyldiethanolamine and iron(III) chloride. Finally, the study of mechanistic aspects of the self-assembly processes operating during the cyclization, triggered our interest in tetranuclear homo- and heteronuclear star-shaped clusters. Magnetic studies on these compounds are currently being investigated and these results will be reported in a subsequent paper.

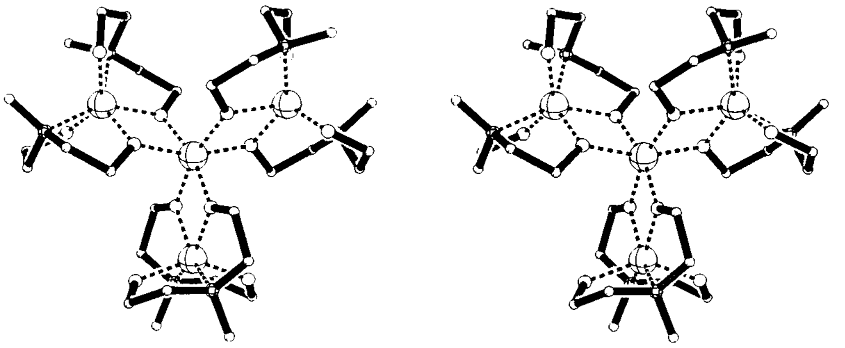
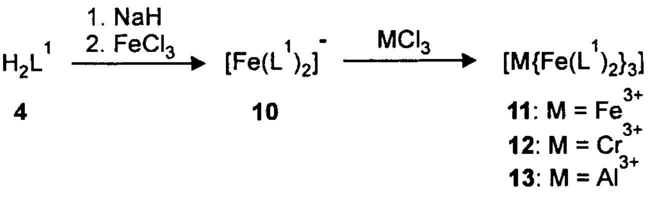


Figure 2. Stereoview of enantiomer [*Δ*-(*R*,*R*)(*S*,*S*)(*S*,*S*)]-**11** in the crystal, perpendicular to the C_2 axis running through the center and lower $[Fe(L^1)_2]^-$ module (*R*,*R*)-**10**. (PLUTON representation; H atoms omitted.)



Scheme 5.

Experimental Section

General techniques: Reagents, metal salts, and ligands were used as obtained from Aldrich, except **6** and **14**, which were prepared by standard procedures. IR spectra were recorded from KBr pellets on a Bruker IFS 25 spectrometer. FAB-MS spectra were recorded on a Micromass ZabSpec-E spectrometer. The microanalytical data deviate from theory due to the crystal solvents included and are not recorded here.

Preparation of [$Fe_6Cl_6(L^2)_6$] (7): *N*-(2,5-Dimethylbenzyl)iminodiethanol **6** (1.12 g, 5 mmol) was added to a suspension of calcium hydride (0.25 g, 6 mmol) in anhydrous THF (50 mL). After the mixture had been stirred for 30 minutes at 20 °C, a solution of iron trichloride (5 mmol, 0.81g) was added dropwise. The reaction mixture was stirred for one day at 20 °C, and the precipitate was subsequently collected on a glass frit. The solid was extracted with CH_2Cl_2 (100 mL). After evaporation of the solvent, a yellow microcrystalline powder of **7** was isolated which was recrystallized by dissolving in CH_2Cl_2 and later addition of CH_3OH. Yield: 0.62 g (33 %) yellow polycrystalline material; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2924$, 2863 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 1838 [$Fe_6Cl_5(L^2)_6$]$^+$.

Preparation of [$Fe_6Br_6(L^2)_6$] (8) and [$Fe_6(NCS)_6(L^2)_6$] (9): A solution of NaBr (0.61 g, 6 mmol for **8**) or KSCN (0.58 g, 6 mmol for **9**) in CH_3OH (100 mL) was added to a solution of crude **7** (0.94 g, 0.5 mmol) in CH_2Cl_2 (100 mL). The mixture was kept under reflux for 3 h. Subsequently the solvent was evaporated, and the remaining solid extracted with CH_2Cl_2. After evaporation of the solvent a yellow (**8**) or orange (**9**) microcrystalline product was obtained.

Compound 8: Yield: 0.64 g (60 %) yellow rhombic crystals from dichlormethane by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2925$, 2864 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 1348 [$Fe_4Br_3(L^2)_4$]$^+$.[5]

Compound 9: Yield: 0.60 g (60 %) orange rhombic crystals from dichlormethane by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2925$, 2868, 2036 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 1952 [$Fe_6(NCS)_5(L^2)_6$]$^+$.

Preparation of {Fe[Fe(L^1)$_2$]$_3$} (11), {Cr[Fe(L^1)$_2$]$_3$} (12), {Al[Fe(L^1)$_2$]$_3$} (13), and {Fe[Fe(L^3)$_2$]$_3$} (15)[7]

General method: *N*-Methyldiethanolamine **4** (0.70 g, 6 mmol for **11**, **12**, **13**) or *N*-benzyldiethanolamine **14** (1.17 g, 6 mmol for **15**) was added to a suspension of sodium hydride (0.34 g, 14 mmol) in anhydrous THF (100 mL). A solution of iron trichloride (0.59 g, 3 mmol) in THF (50 mL) was added dropwise. After the mixture had been stirred for one hour a solution of iron trichloride (0.16 g, 1 mmol for **11** and **15**), [$CrCl_3(THF)_3$] (0.37 g, 1 mmol for **12**), or aluminum trichloride (0.27 g, 1 mmol for **13**) in THF (50 mL) was added. The reaction mixture was stirred for one day at 20 °C. Subsequently the solvent was evaporated and the remaining solid extracted with $CHCl_3$ (100 mL). Pentane (50 mL) was added to this solution. After subsequent filtration the solvent was evaporated, and a brown (**11** and **15**), dark green (**12**) or light yellow (**13**) product was obtained.

Compound 11 · 4 $CHCl_3$: Yield: 1.02 g (71 %) amber rod-shaped crystals from $CHCl_3$ by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2965$, 2852 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 927 [$FeFe_3(L^1)_6$+H]$^+$.

Compound 12 · 4 $CHCl_3$: Yield: 0.63 g (45 %) green rod shaped crystals from $CHCl_3$ by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2963$, 2847 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 923 [$CrFe_3(L^1)_6$+H]$^+$.

Compound 13 · 4 $CHCl_3$: Yield: 0.89 g (65 %) light yellow rod-shaped crystals from $CHCl_3$ by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 2964$, 2651 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 898 [$AlFe_3(L^1)_6$+H]$^+$.

Compound 15 · 0.38 $CHCl_3$ · 1.24 Et_2O: Yield: 0.74 g (49 %) yellow rhombic crystals from $CHCl_3$ by diffusion of diethyl ether; m.p. > 240 °C; IR(KBr): $\tilde{\nu} = 3061$, 2857 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 1383 [$FeFe_3(L^3)_6$+H]$^+$.

Interconversion of 11 to 5: A solution of $FeCl_3$ (0.073 g, 0.45 mmol) in THF (20 mL) was added to a solution of **11** (0.21 g, 0.225 mmol) in THF (25 mL). The reaction mixture was stirred at room temperature overnight, and the yellow precipitate was collected on a frit and subsequently worked up as for compound **7**; 0.085 g (30 %) of polycrystalline **5** were obtained.

Interconversion of 5 to 11: Compound **4** (0.179 g, 1.5 mmol) was added to a suspension of sodium hydride (0.084 g, 3.5 mmol) in THF (50 mL). After stirring for 30 minutes a solution of (0.63 g, 0.5 mmol) **5** in CH_2Cl_2 (50 mL) was added. The reaction mixture was heated to reflux for 12 h and

Table 1. Details of X-ray structure determinations.

	9	**11**	**12**	**13**	**15**
formula	$C_{84}H_{114}Fe_6N_{12}O_{12}S_6 \cdot 4\,CHCl_3$	$C_{30}H_{66}Fe_4N_6O_{12} \cdot 4\,CHCl_3$	$C_{30}H_{66}CrFe_3N_6O_{12} \cdot 4\,CHCl_3$	$C_{30}H_{66}AlFe_3N_6O_{12} \cdot 0.38\,CHCl_3 \cdot 1.24\,Et_2O$	$C_{66}H_{90}Fe_4N_6O_{12}$
M_r	2011.33	1403.76	1399.91	1374.89	1520.13
crystal size [mm]	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.20	0.50 × 0.20 × 0.20	0.30 × 0.30 × 0.10	0.70 × 0.60 × 0.40
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
space group	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	$P4_12_12$
T [K]	173(2)	173(2)	173(2)	293(2)	133(2)
a [Å]	15.2673(2)	25.621(3)	25.594(5)	25.590(4)	13.953(3)
b [Å]	16.0292(3)	13.158(2)	13.135(3)	13.1048(19)	13.953(3)
c [Å]	19.5276(4)	21.067(3)	21.056(4)	20.9260(12)	37.370(6)
α [°]	90	90	90	90	90
β [°]	101.2618(7)	124.49(2)	124.40(3)	124.058(2)	90
γ [°]	90	90	90	90	90
V [Å^3]	4689.75(14)	5854.0(12)	5841(2)	5813.9(12)	7280(10)
Z	2	4	4	4	4
ρ_{calcd} [Mg m^{-3}] 1.424	1.593	1.592	1.571	1.388	
θ range [°]	1.36 – 25.05	2.35 – 24.97	2.34 – 24.97	5.94 – 21.60	1.82 – 24.79
reflections collected	28 381	5265	5287	10 790	76 876
unique reflections	8299	5143	5143	5646	6240
[R_{int}]	0.0604	0.0507	0.0958	0.0484	0.0629
reflections observed [$I > 2\sigma(I)$]	5780	3009	3953	5036	5455
parameters	541	308	308	504	481
final $R1$ [$I > 2\sigma(I)$]	0.0481	0.0490	0.0515	0.0453	0.0383
$wR2$ (all data)	0.1514	0.1215	0.1850	0.1183	0.0962
Flack x[10]	–	–	–	–	0.03(2)
largest residuals [e Å^{-3}]	1.172/ – 0.808	0.962/ – 0.789	1.207/ – 1.024	1.014/ – 0.643	0.590/ – 0.509

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subsequently worked up as for **11**; 0.60 g (86 %)of polycrystalline **11** were obtained.

Single-crystal X-ray structure analyses: Details for crystal data, data collection, and refinement are given in Table 1. X-ray data were collected on an Nonius MACH3 diffractometer (**9**, **11**, and **12**) and on a Stoe–Siemens–Huber four-circle diffractometer equipped with a Siemens SMART CCD detector (**15**) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). For **13** rotation images were taken using a Bruker Smart CCD camera mounted on beamline ID11 at the ESRF. A wavelength of $\lambda = 0.5166$ Å was selected with a double-crystal sagitally-focussing Si(111) monochrometer. Semi-empirical absorption corrections using ψ scans (**9**, **11** and **12**) or equivalents (**13** and **15**) were employed. The structures were solved by direct methods with SHELXS-97[8] and refined with full-matrix least-squares against F^2 with SHELXL-97.[9] Hydrogen atoms were attached in idealized positions and refined by using the riding model. Except for **13**, where due to the high quality of the data, hydrogen atom positions and isotropic thermal factors were refined without constraints. All other atoms were refined anisotropically. The disorder in the intercalated chloroform in **13** is probably due to large librational motion which cannot be accounted for with thermal ellipsoids. In **15** the solvent is disordered. It was refined as a mixture of diethyl ether (site occupation factor 0.619(7)) and chloroform (site occupation factor 0.191(7)) with distance restraints and restraints for the anisotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151611 to CCDC-151613 (for **9**, **11**, **12**), CCDC-153853 (**13**), and CCDC-151497 (**15**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[5] $[Fe_6Br_6(L^2)_6]$ (**8**) is isostructural with $[Fe_6(NCS)_6(L^2)_6]$ (**9**). However, due to pronounced solvent disorder the structure of **8** could not be refined unambiguously.

[6] We thank one of the referees for bringing the complexity of the stereochemistry to our attention.

[7] In order to prove the generality of our new method for the synthesis of star-shaped $[Fe(FeL_2)_3]$ clusters, instead of *N*-methyldiethanolamine **4** (H_2L^1) we also used *N*-benzyldiethanolamine (**14**; H_2L^3) and isolated product $[Fe\{Fe(L^3)_2\}_3]$ (**15**). For the X-ray structure analysis we randomly picked out a single crystal which revealed homochiral (Λ)-[(*R*,*R*)(*R*,*R*)(*R*,*R*)] configuration for **15**.

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