Self-Assembly of Tetrahedral and Trigonal Antiprismatic Clusters $[Fe_4(L^4)_4]$ and $[Fe_6(L^5)_6]$ on the Basis of Trigonal Tris-Bidentate Chelators**

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Dedicated to Professor Ernst Anders on the occasion of his 60th birthday

Abstract: In a one-pot reaction, the tetranuclear iron chelate complex $[Fe_4(L^4)_4]$ **6** was generated from benzene-1,3,5-tricarboxylic acid trichloride (**4**), bis-*tert*-butyl malonate (**5a**), methyllithium, and iron(II) dichloride under aerobic conditions. Alternatively, hexanuclear iron chelate complex $[Fe_6(L^5)_6]$ **7** was formed starting from bis-*para*-tolyl malonate (**5b**) by employing identical reaction conditions to those applied for the synthesis of **6**. The clusters **6** and **7** are present as racemic mixtures of homoconfigurational $(\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda)$-*fac* or $(\Delta,\Delta,\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)$-*fac* stereoisomers. The structures of **6** and **7** were unequivocally resolved by single-crystal X-ray analyses. The all-iron(III) character of **6** and **7** was determined by Mössbauer spectroscopy.

Keywords: cage compounds · cluster compounds · iron · self-assembly · supramolecular chemistry

Introduction

With the growing understanding of supramolecular chemistry, the harnessing of intermolecular interactions to routinely design and control complex architectures has become a reality. Increasingly, supramolecular structures are being invented and created rather than discovered. Self-assembly of Werner-type complexes features the participation of labile, reversible coordination bonds, which facilitate error-checking and self-correction under thermodynamic equilibration. Consequently, the predictable nature of coordination chemistry has been used to successfully generate a variety of different oligonuclear metal–ligand clusters.[1, 2]

The first *T*-symmetric cluster of type $[M_4(L^1)_6]$ **1** (Figure 1, top left) was discovered fortuitously in a one-pot reaction.[3] Only recently has there been progress towards developing a rational, symmetry-based synthetic approach to the formation of predesigned complex metal–ligand clusters[4] as a result of further examples of **1** by self-assembly.[5] Thus, four octahedral metal ions are located in the apices of a tetrahedron and each of the six edges are bridged by linear C_2-symmetric bischelating ligands. Comparatively, there are far fewer examples of *T*-symmetric clusters of type $[M_4(L^2)_4]$ **2** (Figure 1, top right).[6] The construction of symmetric tetrahedral clusters $[M_4(L^2)_4]$ **2** was realized with octahedral metal centers which occupy the vertices of the tetrahedron and trigonally symmetric tris-bidentate ligands which occupy the tetrahedral faces. The synergistic effect of serendipity and rational design in supramolecular chemistry, however, was highlighted again, as it was shown, that threefold symmetric tris-bidentate ligands do not exclusively generate $[M_4(L^2)_4]$ clusters **2**, as was demonstrated by the formation of trigonal-antiprismatic cluster $[M_6(L^3)_6]$ **3** (Figure 1, bottom).[7] In both structures **2** and **3**, three octahedral metal ions are linked by each of the C_3-symmetric

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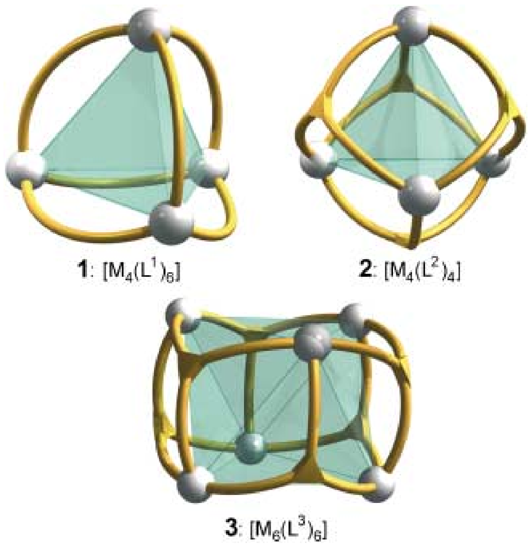
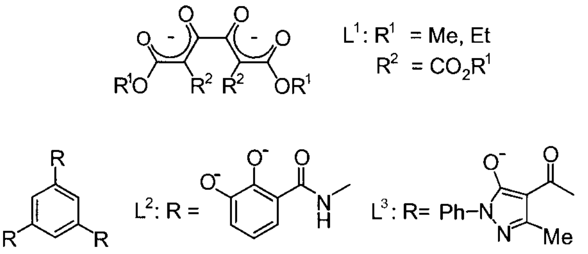


Figure 1. Schematic presentation, metal ions as corner units. Top left: Tetrahedron $[M_4(L^1)_6]$ **1**, edge-linked. Top right: Tetrahedron $[M_4(L^2)_4]$ **2**, face-linked. Bottom: Trigonal antiprism $[M_6(L^3)_6]$ **3**, face-linked.

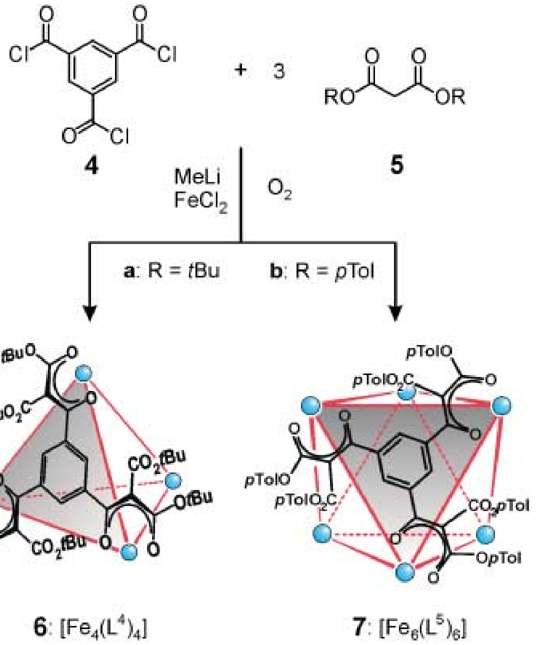


tris-bidentate ligands $(L^{2/3})^{3-}$ thereby occupying a central position in the respective equilateral triangles generated.

Results and Discussion

In an attempt to generalize the methodology for the construction of three-dimensional (3D) clusters with $[M_4(L^2)_4]$ or $[M_6(L^3)_6]$ stoichiometry, as realized in **2** and **3**, respectively, the threefold symmetric tris-bidentate ligands H_3L^4 and H_3L^5 were designed. They are formally accessible by the coupling of benzene-1,3,5-tricarboxylic acid trichloride **4** with three monoanions of dialkyl- or diaryl malonate **5**. Treatment of di-*tert*-butyl malonate **5a** (R = *t*Bu) with methyllithium/iron(II) dichloride and **4** at −78 °C in tetrahydrofuran was followed by workup under aerobic conditions and subsequent thin-layer chromatography, affording bordeaux red crystals from acetone (Scheme 1).

Abstract in German: *In einer Eintopf-Reaktion entstand bei der Umsetzung von Benzol-1,3,5-tricarbonsäuretrichlorid* ***4****, Malonsäure-bis-tert-butyl-ester* ***5a****, Methyllithium und Eisen(II)-chlorid unter aeroben Bedingungen der vierkernige Eisenchelatkomplex $[Fe_4(L^4)_4]$* ***6****. Im Gegensatz dazu erhielten wir, ausgehend von Malonsäure-bis-para-tolyl-ester* ***5b****, unter ansonsten völlig identischen Bedingungen, wie sie zur Synthese von* ***6*** *angewandt wurden, den sechskernigen Eisenchelatkomplex $[Fe_6(L^5)_6]$* ***7****. Die Cluster* ***6*** *und* ***7*** *liegen als racemische Gemische vor, die aus den homo-konfigurierten (Δ,Δ,Δ,Δ)/(Λ,Λ,Λ,Λ)-fac bzw. (Δ,Δ,Δ,Δ,Δ,Δ)/(Λ,Λ,Λ,Λ,Λ,Λ)-fac Stereoisomeren bestehen. Die Struktur der Cluster* ***6*** *und* ***7*** *wurde zweifelsfrei durch Einkristall Röntgen Strukturanalyse bestimmt. Der all-Eisen(III) Charakter von* ***6*** *und* ***7*** *wurde mit Hilfe der Mössbauer Spektroskopie aufgeklärt.*



Scheme 1. Synthesis of the tetra- and hexanuclear iron clusters $[Fe_4(L^4)_4]$ **6** and $[Fe_6(L^5)_6]$ **7**.

According to the elemental analysis and fast atom bombardment (FAB) MS data the compound was of composition $[Fe(L^4)]_n$ with $n = 4$. The UV/Vis spectrum of **6** in dichloromethane, exhibited a ligand-to-metal charge-transfer (LMCT) absorption at $\lambda_{max} = 457$ nm. Structural characterization of the tetranuclear iron chelate complex $[Fe_4(L^4)_4]$ **6** by NMR spectroscopic techniques was inconclusive due to strong signal broadening by paramagnetic iron. Consequently a single-crystal X-ray crystallographic structural determination of this complex was carried out (Figure 2).[8] According to this

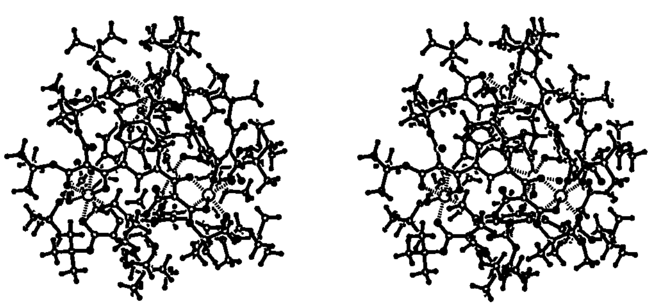


Figure 2. Stereo representation of $[Fe_4(L^4)_4]$ **6**. Solvent molecules are not depicted for clarity.

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analysis, **6** crystallizes as a neutral, tetranuclear iron(III) chelate complex with twofold crystallographic symmetry in the space group *C*2/*c* with four molecules per unit cell. In **6** four iron centers constitute the apices of a tetrahedron and the four tris-bidentate ligands $(L^4)^{3-}$ are located above the triangular faces of the tetrahedron. The four homoconfigurated iron centers in **6** are octahedrally coordinated by six oxygen donors and the mean Fe–Fe distance is 8.57 Å. Hence, the complex has nearly *T*-molecular symmetry (characterized by three C_2 and four C_3 axes) and the crystal is a racemic mixture of homoconfigurational $(\Delta,\Delta,\Delta,\Delta)$-*fac* and $(\Lambda,\Lambda,\Lambda,\Lambda)$-*fac* stereoisomers. There is no evidence that the small cavity of the tetrahedron contains a guest, as observed in some mixed-valent systems or in larger $[M_4L_6]$ tetrahedra.[5]

Contrary to di-*t*Bu malonate **5a** (R = *t*Bu), reaction of di-*p*Tol malonate **5b** (R = *p*Tol) with methyllithium/iron(II) dichloride and trichloride **4** at −78 °C in tetrahydrofuran and subsequent workup yielded the hexanuclear iron chelate complex $[Fe_6(L^5)_6]$ **7** instead of the tetranuclear iron chelate complex $[Fe_4(L^5)_4]$. To unequivocally establish the structure of $[Fe_6(L^5)_6]$ **7**, an X-ray crystallographic structure determination was carried out (Figure 3).[8] According to this analysis, **7** crystallizes as a neutral, hexanuclear iron(III) chelate complex in space group $P\bar{1}$ with two molecules per unit cell. While the molecule has no crystallographic symmetry it can be described as having idealized D_3 molecular symmetry. The iron centers define the apices of a distorted trigonal antiprism in which six tris-bidentate ligands $(L^5)^{3-}$ make up the equatorial faces leaving the top and the bottom triangles unoccupied. All six iron centers in **7** are identically octahedrally coordinated by six oxygen donors. The antiprism is compressed along the pseudo C_3 axis, with a mean Fe–Fe distance of 9.69 Å within the top and botton triangles, while the average Fe–Fe distance within the equatorial faces of the antiprism is 8.54 Å. Thus the vacant top and bottom triangles are larger than those occupied by the $(L^5)^{3-}$ ligands. The distances between the vacant and opposite occupied triangular faces amount to 6.53 and 7.77 Å. The average twist angle of the trigonal antiprism is 51°. In the crystal $[Fe_6(L^5)_6]$ **7** exists as a racemic mixture of homoconfigurational $(\Delta,\Delta,\Delta,\Delta,\Delta,\Delta)$-*fac* and $(\Lambda,\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)$-*fac* stereoisomers.

The UV/Vis spectrum of $[Fe_6(L^5)_6]$ **7** in dichloromethane exhibited a ligand-to-metal charge-transfer (LMCT) absorption band at $\lambda_{max} = 560$ nm.

Mössbauer spectroscopy: The all-iron(III) character of **6** and **7** was established unequivocally from their ^{57}Fe Mössbauer spectra. Measurements were performed at 4.2–77 K without and with a field (7 T) applied parallel to the γ beam. All zero-field spectra exhibit a broad and unresolved absorption pattern (Figure 4a,c) due to (temperature-independent) spin–spin relaxation. Application of a field of 7 T at 4.2 K results in well-resolved magnetic hyperfine patterns, which were analyzed with the spin-Hamiltonian formalism (Figure 4b,d).[9] The magnetic hyperfine patterns of **6** and **7** are practically the same; this is also reflected by the fact that both patterns have been successfully simulated by the same set of spin-Hamiltonian parameters (except small differences in the line width, see Table 1). From the isomer shift $\delta = 0.53$ and the quadrupole splittings $\Delta E_Q = 0$ we conclude that each individual iron ion in **6** and **7** is hexacoordinated by oxygen donors in a nearly perfect octahedral arrangement. The magnetic hyperfine patterns are successfully simulated by neglecting exchange interactions between the iron(III) sites. This result is plausible considering the relatively large Fe–Fe distances. Evidently, the nuclearity of the iron chelate complexes **6** and **7** has no substantial effect on the local electronic structure of each of the irons nor on the exchange interactions between them.

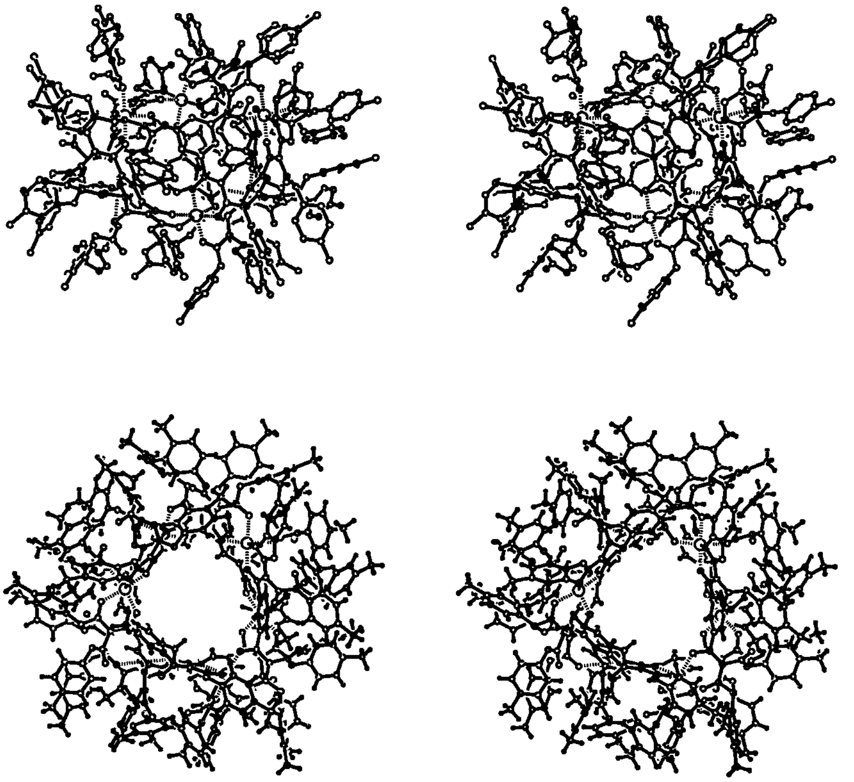

Figure 3. Stereo representation of $[Fe_6(L^5)_6]$ **7**. Top: side view, solvent molecules and H atoms are not depicted for clarity. Bottom: Top view, solvent molecules are not depicted for clarity.

The clusters $[Fe_4(L^4)_4]$ **6** and $[Fe_6(L^5)_6]$ **7** are relatively complicated metal–ligand systems and so it can be difficult to isolate what features make one structure favored over another. In this regard molecular modeling (CAChe, MM3 energy minimization)[10] of the four possible structures considered here ($[Fe_4(L^4)_4]$, $[Fe_4(L^5)_4]$, $[Fe_6(L^4)_6]$, and $[Fe_6(L^5)_6]$) proves to be very informative. When the calculated energies are normalized to account for metal–ligand

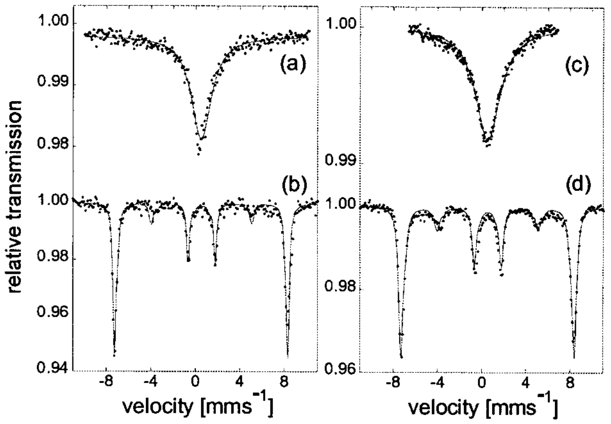

Figure 4. Experimental Mössbauer spectra of **6** (left) and **7** (right), recorded at a,c) 77 K; b,d) 4.2 K, 7 T parallel to the γ ray. Solid lines result from Lorentz fits (a,c) and a spin-Hamiltonian simulation (b,d) which used the parameters summarized in Table 1.

Table 1. Spin-Hamiltonian parameters of **6** and **7** which have been used for simulations of Mössbauer spectra at 4.2 K and a field of 7 T parallel to the γ beam.[a]

δ[b]	ΔE_Q[c]	D[d]	E/D[e]	$A_{xx}/g_n\mu_n$[f]	$A_{xx}/g_n\mu_n$	$A_{xx}/g_n\mu_n$	$g_{x,y,z}$[g]
0.53	0.0	– 1.3	0	– 22.2	– 22.2	– 22.2	2

[a] For **6** an intrinsic line width of $\Gamma = 0.30$ mms^{-1} and for **7** $\Gamma = 0.45$ mms^{-1} was used. The 77 K spectra were fitted with Lorentzian lineshape yielding $\Gamma = 2.2$ mms^{-1} for **6** and $\Gamma = 2.7$ mms^{-1} for **7** and the same isomer shift $\delta = 0.53$ mms^{-1} and quadrupole splitting $\Delta E_Q = 0$ for both **6** and **7**. [b] Isomeric shift relative to α-Fe at room temperature (mm s^{-1}). [c] Quadrupole splitting (mm s^{-1}). [d] Zero-field splitting parameter (cm^{-1}). [e] Rhombicity parameter. [f] Magnetic hyperfine coupling tensor components (T). [g] g-tensor components.

stoichiometry, the minimized $[Fe_6(L^5)_6]$ structure is favored over the minimized $[Fe_4(L^5)_4]$ structure, with the difference largely due to angle strain energies. In the $[Fe_6(L^5)_6]$ structure, π-stacking interactions between the *p*-tolyl groups are apparent; whereas, parallel arrangement of these rings in the tetramer is more difficult to achieve and creates greater angle strain throughout the structure. Conversely, energy minimization of $[Fe_4(L^4)_4]$ and $[Fe_6(L^4)_6]$ predicts the tetramer to be the lower energy form. Angle strain is generated in the $[Fe_6(L^4)_6]$ hexamer due to steric crowding of the *tert*-butyl groups. These substituents are more evenly distributed over the surface of the tetramer.

In summary, $[Fe_4(L^4)_4]$ **6** and $[Fe_6(L^5)_6]$ **7** are two classic examples of the generation of three-dimensional clusters of high symmetry by spontaneous self-assembly. Again, the symmetry-based rational design concept proved to be applicable to the formation of clusters of different size, shape, and stoichiometry. However, as metal–ligand systems become larger and more complex, more subtle intramolecular interactions may be significant in structure determination. Here, molecular modeling can be a valuable tool in supramolecular structural evaluation, as demonstrated for $[Fe_4(L^4)_4]$ **6** and $[Fe_6(L^5)_6]$ **7**. Ultimately, greater understanding and control of these secondary interactions will enhance supramolecular design and synthesis.

Experimental Section

Compound 6: A methyllithium solution (18.75 mL, 1.6 M in diethyl ether, 30 mmol) diluted with dry THF (10 mL) was added dropwise to a solution of di-*tert*-butyl malonate (6.49 g, 30 mmol) in dry THF (50 mL)(N_2, – 78 °C) over 30 min. After the mixture had been stirred for 1 h, $FeCl_2 \cdot 4H_2O$ (0.99 g, 5.0 mmol) was added and 1 h later a solution of benzene-1,3,5-tricarboxylic acid trichloride (1.33 g, 5.0 mmol) in dry THF (20 mL) was added dropwise to the suspension over 2 h. The reaction mixture was kept at – 78 °C for another 10 h and then allowed to warm to 20 °C. On treatment with 10% aqueous potassium chloride (100 mL) in the presence of atmospheric oxygen, the mixture turned deep red. The organic solution was separated, washed twice with water (70 mL), dried over potassium sulfate, and concentrated. The residue was purified by preparative thin-layer chromatography (SiO_2: pentane/ethyl acetate, 10:11, $R_F = 0.95$) to give **6**. Bordeaux crystals from acetone. Yield: 1.72 g (40%); m. p. 198 °C (decomp); IR (KBr): $\tilde{\nu} = 1710$ cm^{-1} (C=O); FAB-MS (3-nitrobenzyl alcohol matrix): *m/z*: 3564 $[Fe_4(L^4)_4+Cs]$; $C_{168}H_{228}O_{60}Fe_4$ (3431.03): calcd: C 58.81, H 6.70; found: C 58.69, H 6.70.

Compound 7: A methyllithium solution (18.75 mL, 1.6 M in diethyl ether, 30 mmol) diluted with dry THF (10 mL) was added dropwise to a solution of di-*para*-tolyl malonate (8.53 g, 30 mmol) in dry THF (50 mL)(N_2, – 78 °C) over 30 min. After the mixture had been stirred for 1 h, $FeCl_2 \cdot 4H_2O$ (0.99 g, 5.0 mmol) was added and 1 h later a solution of benzene-1,3,5-tricarboxylic acid trichloride (1.33 g, 5.0 mmol) in dry THF (20 mL) was added dropwise to the suspension over 2 h. The reaction mixture was kept for another 10 h at – 78 °C and allowed to warm to 20 °C. The solvent was removed in vacuo, the residue diluted in dichloromethane (150 mL) and oxidized by athmospheric oxygen for 2 h. The solution was dried over anhydrous sodium sulfate. The residue was purified twice by preparative thin-layer chromatography (SiO_2: ethyl acetate, $R_F = 0.90$) to give compound **7**. Bordeaux crystals from acetonitrile. Yield: 1.91 g (36%); m. p. 186 °C (decomp); IR (KBr): $\tilde{\nu} = 1750$ cm^{-1} (C=O); FAB-MS (3-nitrobenzyl alcohol matrix): *m/z*: 6394 $[Fe_6(L^5)_6+Na]$; $C_{360}H_{270}O_{90}Fe_6$ (6371.18): calcd: C 67.87, H 4.27; found: C 67.39 H 4.43.

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[8] Crystal data for $[Fe_4(L^4)_4]$ **6**: $C_{168}H_{228}O_{60}Fe_4 \cdot 2Me_2CO$, $M_r = 3547.07$; crystal dimensions $0.40 \times 0.40 \times 0.30$ mm; monoclinic, space group $C2/c$, $a = 2508.6(5)$, $b = 3114.6(6)$, $c = 2864.8(6)$ pm, $\beta = 91.38(3)^\circ$, $V = 22377(8)$ Å^3; $Z = 4$; $F(000) = 7536$, $\rho_{calcd} = 1.053$ g cm^{-3}. Diffractometer: Nonius Kappa CCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 198(2)$ K; graphite monochromator; θ range [°] $2.92^\circ < \theta < 26.49$; section of the reciprocal lattice: $-31 \leq h \leq 31$, $-38 \leq k \leq 34$, $-35 \leq l \leq 35$; of 42123 measured reflections, 22843 were independent and 13462 with $I > 2\sigma(I)$; linear absorption coefficient 0.324 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement with all data (1081 parameters) by full-matrix least-squares on F^2 using SHELXL97;[11] all non-hydrogen atoms were refined anisotropically; $R1 = 0.0914$ for $I > 2\sigma(I)$ and $wR2 = 0.2849$ (all data); largest peak (1.778 e Å^{-3}) and hole (-0.469 e Å^{-3}). Crystal data for $[Fe_6(L^5)_6]$ **7**: $M_r = 3547.07$; crystal dimensions $0.05 \times 0.03 \times 0.02$ mm; triclinic, space group $P\bar{1}$, $a = 2464.5(5)$, $b = 2528.2(9)$, $c = 3690.0(13)$ pm, $\alpha = 76.007(8)$, $\beta = 76.080(17)$, $\gamma = 79.636(17)^\circ$, $V = 21472(11)$ Å^3; $Z = 2$; $F(000) = 6696$, $\rho_{calcd} = 0.998$ g cm^{-3}. Diffractometer: Bruker Smart CCD, Synchrotron radiation ($\lambda = 0.42753$ Å); $T = 120(2)$ K; Si(111) monochromator; θ range [°] $4.91 < \theta < 12.34$; section of the reciprocal lattice: $-24 \leq h \leq 24$, $-25 \leq k \leq 25$, $-36 \leq l \leq 36$; of 133788 measured reflections, 41432 were independent and 22884 with $I > 2\sigma(I)$; linear absorption coeficient 0.143 mm^{-1}. All of the tested crystals were twinned; the structure was solved and refined on data collected from one domain of such a crystal; highly redundant data were taken and corrupted reflections were rejected based on bunch statistics. Thirty-one independent intercalated acetonitrile molecules were located in the asymmetric unit, presumably accounting for both the volatility of the crystals and the low crystallographic symmetry with respect to the ideal molecular symmetry. The structure was solved by direct methods using SHELXS-97 and refinement with all data (4943 parameters) by blocked full-matrix least-squares on F^2 using SHELXL97;[11] all non-hydrogen atoms were refined anisotropically; constraints were placed on all anisotropic thermal factors and on the geometry of the 31 intercalated acetonitrile molecules; $R1 = 0.1282$ for $I > 2\sigma(I)$ and $wR2 = 0.3752$ (all data) with $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = \Sigma w|(F_o^2 - F_c^2)^2|/\Sigma w(F_o^2)^2)^{0.5}$; largest peak (0.944 e Å^{-3}) and hole (-1.037 e Å^{-3}). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160023 (**6**) and CCDC-164710 (**7**). 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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