Inorg. Chem. **2004**, *43*, 4372–4382

Inorganic Chemistry

Article

# Six-Membered Metalla-coronands. Synthesis and Crystal Packing: Columns, Compartments, and 3D-Networks[†,‡]

**Rolf W. Saalfrank,*,§ Christian Deutscher,§ Stefan Sperner,§ Takayuki Nakajima,§ Ayuk M. Ako,§ Eveline Uller,§ Frank Hampel,§ and Frank W. Heinemann‖**

*Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42,*
*91054 Erlangen, Germany, and Institut für Anorganische Chemie der Universität*
*Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany*

Received February 16, 2004

Reaction of various *N*-substituted diethanolamines $H_2L^3$ (**4**) with calcium hydride and iron(III) chloride leads to the self-assembly of six-membered ferric wheels $[Fe_6X_6(L^3)_6]$ (**5**). Principally, all the iron coronands are isostructural; however, they differ fundamentally with respect to their crystal packing. Exemplarily, this is discussed for selected members of the space groups $R\bar{3}$, $P\bar{3}$, $P2_1/c$, $P2_1/n$, $C2/c$, and $P\bar{1}$. Depending on the nature of their sidearms, the ferric wheels create various substructures. For instance, the ferric wheels **5a**–**i** of space group $R\bar{3}$ or $P\bar{3}$ are piled in parallel in cylindrical columns, which are surrounded by six parallel columns alternately dislocated by $^1/_3c$ and $^2/_3c$ against the central one. Pronounced van der Waals interactions give rise to compartmentation and incarceration of guest molecules as seen for **5e**,**g**. However, in **5h** strong $\pi$–$\pi$ interactions create a three-dimensional scaffold. The most significant difference of the ferric wheels **5j**–**p** of space groups $P2_1/c$, $P2_1/n$, and $C2/c$ is that these ferric wheels are arranged in parallel in two orientations. They differ mainly only by the included angle of the two groups of parallel wheels. In the case of **5l**, molecular chains are formed in the crystal due to $\pi$–$\pi$ interactions. The ferric wheels **5q**–**y** of space group $P\bar{1}$ are packed in the crystal most simply, with all the ferric wheels piled in parallel.

## Introduction

Polyoxometalates have become the focus of intense research activities, because these compounds exhibit an enormous variety of structures as well as magnetic properties.[1] Over the past several years, considerable progress has been made toward the predictability of ordered supramolecular assemblies on the basis of coordinative metal/ligand bonds.[2] A particular symmetric class are the so-called ferric wheels with 6, 8, 10, 12, and even 18 iron(III) ions.[3] The magnetization of the ferric wheels exhibits steplike field dependencies at low temperatures and can be regarded as ideal model systems for so-called single molecule magnets (SMMs), the finite-size version of the linear Heisenberg chain.[4] Since SMMs are promising new materials, this class of molecules becomes more and more important.

We reported on the template-mediated self-assembly of six- and eight-membered iron-coronates $\{Na\subset[Fe_6(L^1)_6]\}^+$ (**1**) and $\{Cs\subset[Fe_8(L^1)_8]\}^+$ (**2**).[5] They were prepared from triethanolamine $H_3L^1$ with iron(III) chloride, sodium hydride, or cesium carbonate (Scheme 1). For instance, ferric wheel **1** allowed us to demonstrate the exciting effect of cooling by adiabatic magnetization.[6]

A common feature of complexes **1** and **2** is that the oxygen donors of one kind of ethanolate arm solely function as ligands for the coordinative saturation of the iron centers and for charge compensation, whereas the ethanolato $\mu_2$-O donors are structure determining. They are linkers, necessary for the ring formation. Consequently, reaction of *N*-methyldi-

---

* To whom correspondence should be addressed. E-mail: saalfrank@chemie.uni-erlangen.de. Fax: (+49)9131-852-1165.

[†] Dedicated to Professor Fritz Vögtle on the occasion of his 65th birthday.

[‡] Chelate complexes (metalla-coronands). 27. Part 26: see ref 9.

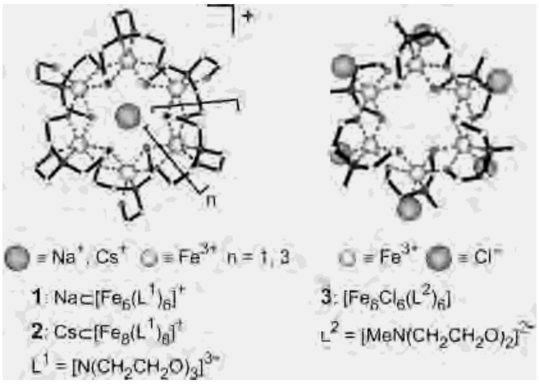
[§] Institut für Organische Chemie der Universität Erlangen-Nürnberg.

[‖] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg.

(1) Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, J.; Verdaguer, M. *Chem. Eur. J.* **2003**, *9*, 1677−1691. Sessoli, R.; Gatteschi, D. *Angew. Chem.* **2003**, *115*, 278−309; *Angew. Chem., Int. Ed.* **2003**, *42*, 268−297. Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054−1058. Koch, R.; Schromm, S.; Schülein, J.; Müller, P.; Bernt, I.; Saalfrank, R. W.; Hampel, F.; Balthes, E. *Inorg. Chem.* **2001**, *40*, 2986−2995. Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239−271. Gatteschi, D.; Caneschi, A.; Sessoli, R.; Cornia, A. *Chem. Soc. Rev.* **1996**, *25*, 101−107. Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* **1999**, *193*, 361−394.

10.1021/ic049799w CCC: $27.50

**Scheme 1.** Schematic Representation of the Metalla-Coronates **1** and **2** and Metalla-Coronand **3**



ethanolamine $H_2L^2$ with calcium hydride and iron(III) chloride yielded the unoccupied neutral iron-coronand $[Fe_6Cl_6(L^2)_6]$ (**3**).[7] Like in **1** and **2**, the $\mu_2$-O donors of the *N*-methyldiethanolamine ligands in **3** are structure determining. Completion of the octahedral coordination sphere at iron and charge compensation is achieved by the chloride coligands (Scheme 1). Consequently, this new synthesis for six-membered ferric wheels was applied for the convergent synthesis of metallo-dendrimers.[8] Variable temperature NMR spectroscopy, exemplarily carried out on a diamagnetic indium analogue, revealed that these species are not rigid and undergo nondissociative topomerization processes.[9]

A precondition for a crystal to behave like a ferromagnetic particle is the alignment of all magnetic moments and a minimum of intermolecular interactions. Therefore, it is decisive to control the crystal packing.[10]

An additional interesting feature of oligonuclear assemblies is their readiness to frame compartments and three-dimensional networks with discrete channels and pores.[10−12]

## Results and Discussion

Herein we report on the crystal packing of several six-membered ferric wheels $[Fe_6X_6(L^3)_6]$ (**5**), generated from various *N*-substituted diethanolamines $H_2L^3$ (**4**), calcium hydride, and iron(III) chloride (Scheme 2).

The focal point of the present manuscript is to gain insights to which extent the crystal packing of basically similar molecules can be controlled by variation of their periphery

---

(2) Recent reviews: Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem.* **2002**, *114*, 1556−1578; *Angew. Chem., Int. Ed.* **2002**, *41*, 1488−1508. Holliday, B. J.; Mirkin, C. A. *Angew. Chem.* **2001**, *113*, 2076−2097; *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972−983. Saalfrank, R. W.; Demleitner, B. In *Transition Metals in Supramolecular Chemistry*; Sauvage, J. P., Ed.; Wiley-VCH: Weinheim, 1999; pp 1−51. Uller, E.; Demleitner, B.; Bernt, I.; Saalfrank, R. W. In *Structure and Bonding*; Fujita, M., Ed.; Springer: Berlin, 2000; Vol. 96, pp 149−175. Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975−982. Atwood, J. L.; MacGillivray, L. R. *Angew. Chem.* **1999**, *111*, 1080−1096; *Angew. Chem., Int. Ed.* **1999**, *38*, 1018−1033. Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417−425. Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289−299. Philp, D.; Stoddart, J. F. *Angew. Chem.* **1996**, *108*, 1242−1286; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154−1196. Baxter, P. N. W. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon: Oxford, 1996; Vol. 9, pp 165−211. Constable, E. C. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon: Oxford, 1996; Vol. 9, pp 213−252. Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon: Oxford, 1996; Vol. 9, pp 43−83. Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005−2062. Saalfrank, R. W.; Demleitner, B.; Löw, N.; Trummer, S.; Kareth, S. *Mol. Cryst. Liq. Cryst.* **2001**, *356*, 71−90. Johnson, D. W.; Raymond, K. N. *Supramol. Chem.* **2001**, *13*, 639−659. Ziegler, M.; Brumaghim, J. L.; Raymond, K. N. *Angew. Chem.* **2000**, *112*, 4285−4287; *Angew. Chem., Int. Ed.* **2000**, *39*, 4119−4121. Swiegers, G. F.; Malefetse, T. J. *Coord. Chem. Rev.* **2002**, *225*, 91−121. Ward, M. D.; McCleverty, J. A.; Jeffery, J. C. *Coord. Chem. Rev.* **2001**, *222*, 251−272.

(3) Oshio, H.; Hoshino, N.; Ito, T.; Nakano, M.; Renz, F.; Gütlich, P. *Angew. Chem.* **2003**, *115*, 233−235; *Angew. Chem., Int. Ed.* **2003**, *42*, 223−225. Sydora, O. L.; Woleczanski, P. T.; Lobkovsky, E. B. *Angew. Chem.* **2003**, *115*, 2789−2791; *Angew. Chem., Int. Ed.*. **2003**, *42*, 2685−2687. Taft, K. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 9629−9630. Taft, L. K.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823−832. Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Malavasi, W.; Schenetti, L.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1997**, *36*, 6443−6446. Caneschi, A.; Cornia, A.; Lippard, S. J. *Angew. Chem.* **1995**, *107*, 511−513. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 467−469. Caneschi, A.; Cornia, A.; Fabretti, A. C.; Foner, S.; Gatteschi, D.; Grandi, R.; Schenetti, L. *Chem. Eur. J.* **1996**, *2*, 1379−1387. Pilawa, B.; Desquiotz, R.; Kelmen, M. T.; Weickmeier, M.; Geisselman, A. *J. Magn. Magn. Mater.* **1997**, *177−181*, 748−749. Benelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem.* **1996**, *108*, 1967−1970; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1825−1827. Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Angew. Chem.* **1999**, *111*, 1372−1374; *Angew. Chem., Int. Ed.* **1999**, *38*, 1295−1297. Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, J. S. *Angew. Chem.* **1997**, *109*, 2917−2919; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774−2776.

(4) Chiolero, A.; Loss, D. *Phys. Rev. Lett.* **1998**, *80*, 169−172. Gatteschi, D.; Sessoli, R.; Cornia, A. *Chem. Commun.* **2000**, 725−732. Barra, A. L.; Caneschi, A.; Cornia, A.; Fabrizi de Biani, F.; Gatteschi, D.; Sangregorio, C.; Sessoli, R.; Sorace, L. *J. Am. Chem. Soc.* **1999**, *121*, 5302−5310. Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491−2502. Saalfrank, R. W.; Trummer, S.; Reimann, U.; Chowdhry, M. M.; Hampel, F.; Waldmann, O. *Angew. Chem.* **2000**, *112*, 3634−3636; *Angew. Chem., Int. Ed.* **2000**, *39*, 3492−3494. Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C.-J.; Ensling, J.; Gütlich, P. *Chem. Eur. J.* **2000**, *6*, 552−563. Coronado, E.; Clemente-León, M.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Martínez-Ferrero, E. *J. Chem. Soc., Dalton Trans.* **2000**, 3955−3961. Waldmann, O.; Schülein, J.; Koch, R.; Müller, P.; Bernt, I.; Saalfrank, R. W.; Andres, H. P.; Güdel, H. U.; Allenspach, P. *Inorg. Chem.* **1999**, *38*, 5879−5886.

(5) Saalfrank, R. W.; Bernt, I.; Uller, E.; Hampel, F. *Angew. Chem.* **1997**, *109*, 2596−2599; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2482−2485. Saalfrank, R. W.; Bernt, I.; Hampel, F. *Angew. Chem.* **2001**, *113*, 1745−1748; *Angew. Chem., Int. Ed.* **2001**, *40*, 1700−1703. Saalfrank, R. W.; Bernt, I.; Hampel, F. *Chem. Eur. J.* **2001**, *7*, 2770−2774.

(6) Waldmann, O.; Koch, R.; Schromm, S.; Müller, P.; Bernt, I.; Saalfrank, R. W. *Phys. Rev. Lett.* **2002**, *89*, 246401-1-4.

(7) Saalfrank, R. W.; Bernt, I.; Chowdhry, M. M.; Hampel, F.; Vaughan, G. B. M. *Chem. Eur. J.* **2001**, 2765−2769.

(8) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286−296. Fréchet, J. M. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4782−4787.

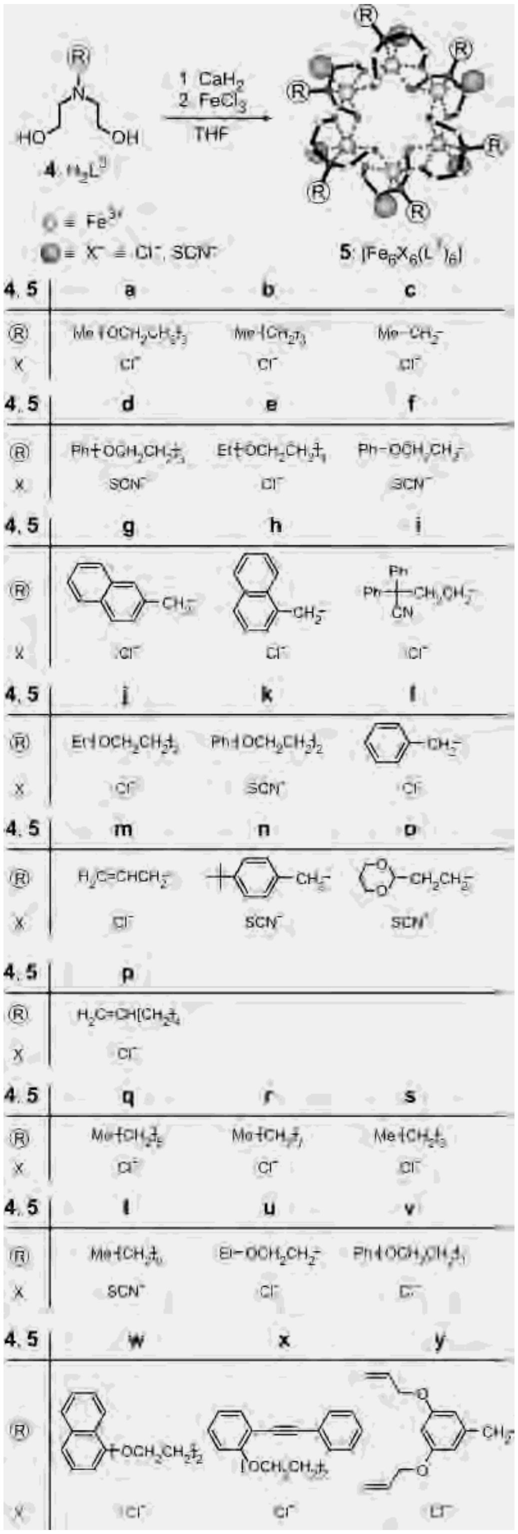
(9) Saalfrank, R. W.; Deutscher, C.; Maid, H.; Ako, A. M.; Sperner, S.; Nakajima, T.; Bauer, W.; Hampel, F.; Hess, B. A.; van Eikema Hommes, N. J. R.; Puchta, R.; Heinemann, F. W. *Chem. Eur. J.* **2004**, *10*, 1899−1905.

(10) Beatty, A. M.; Granger, K. E.; Simpson, A. E. *Chem. Eur. J.* **2002**, *8*, 3254−3259.

(11) Cf.: Su, C.-J.; Cai, Y.-P.; Chen, C.-L.; Smith, M. D.; Kaim, W.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2003**, *125*, 8595−8613.

(12) Stoddart, J. F.; Fyfe, M. C. T. *Acc. Chem. Res.* **1997**, *30*, 393−401. Janiak, C. J. *J. Chem. Soc., Dalton Trans.* **2000**, 3885−3896. Chang, C.-H.; Hwang, K. C.; Liu, C.-S.; Chi, Y.; Carty, A. J.; Scoles, L.; Peng, S.-M.; Lee, G.-H.; Reedijk, J. *Angew. Chem.* **2001**, *113*, 4787−4789; *Angew. Chem., Int. Ed.* **2001**, *40*, 4651−4653. Schmitt, W.; Baissa, E.; Mandel, A.; Anson, C. E.; Powell, A. K. *Angew. Chem.* **2001**, *113*, 3690−3693; *Angew. Chem., Int. Ed.* **2001**, *40*, 3578−3581. Xiong, R.-G.; You, X.-Z.; Abrahams, B. F.; Xue, Z.; Che, C.-M. *Angew. Chem.* **2001**, *113*, 4554−4557; *Angew. Chem., Int. Ed.* **2001**, *40*, 4422−4425. Ying, J. Y.; Melmert, C. P.; Wong, M. S. *Angew. Chem.* **1999**, *111*, 58−82; *Angew. Chem., Int. Ed.* **1999**, *38*, 56−77. Tsuzuki, S.; Honda, K.; Uchimura, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104−112.

**Scheme 2.** Synthesis of [$Fe_6X_6(L^3)_6$] (**5**)



by means of different substituents. In order to classify the numerous structures, space groups were applied.

For an unambiguous characterization, we carried out X-ray crystallographic structure analyses of **5** (Table 1).[13,14] Principally, all the six-membered ferric wheels [$Fe_6X_6(L^3)_6$] (**5**) are isostructural with iron-coronand [$Fe_6Cl_6(L^2)_6$] (**3**); however, there are fundamental differences concerning their crystal packing. Exemplarily, this will be discussed for selected members of the space groups $R\bar{3}$, $P\bar{3}$, $P2_1/c$, $P2_1/n$, $C2/c$, and $P\bar{1}$.

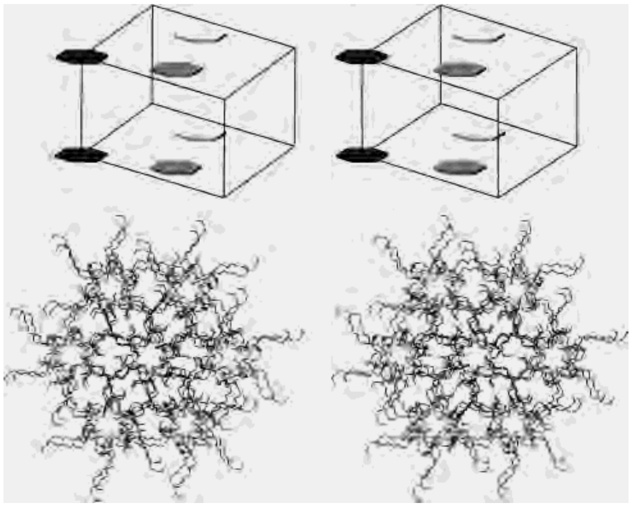


**Figure 1.** Top: stereo presentation of the crystal packing of **5a**−**h**. Bottom: stereoview of the crystal packing of the ferric wheel **5a**. View along the *c*-axis. Solvent molecules omitted for clarity.

**Crystal Packing of Ferric Wheels 5a−i of Space Group $R\bar{3}$ or $P\bar{3}$.** The ferric wheels [$Fe_6X_6(L^3)_6$] (**5a**−**i**) have idealized $S_6$ molecular symmetry and crystallize in the space group $R\bar{3}$ (**5a**−**f**,**h**,**i**) or $P\bar{3}$ (**5g**) (Table 1). The crystal packing of the ferric wheels **5a**−**h** is pretty much the same. For example, all the disklike clusters of **5a** are arranged in parallel and are piled in cylindrical columns, with all the iron centers superimposed. Each column is surrounded by six parallel columns which are alternately dislocated by $^1/_3c$ and $^2/_3c$ against the central one (Figure 1).

The most significant difference between **5b** and **5c** is the arrangement of the ferric wheels to one another. For instance, in **5b** the mean intra- and intercolumnar midpoint distances amount to 12.6 and 21.9 Å, and for **5c** to 23.6 and 15.1 Å, respectively. It is clearly seen that, for **5b** and **5c**, the relative arrangement of the ferric wheels is reciprocally proportional. That is to say, large intercolumnar distances correspond with small intracolumnar distances and vice versa (Figure 2).

An additional interesting feature of some ferric wheels is their readiness to create various substructures, depending on the nature of their sidearms. For instance, van der Waals interactions cause the sidearms of **5e** and **5g**[15] to interlock

---

(13) Sheldrick, G. M.; Krüger, C.; Goddard, P. *Crystallographic Computing 3*; Oxford University Press: Oxford, 1985; p 175. Sheldrick, G. M. *SHELXL-97, program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *SHELXTL NT 5.10*; Bruker AXS, Inc.: Madison WI, 1998.

(14) CCDC-231538 (**5a**), CCDC-230001 (**5b**), CCDC-231544 (**5c**), CCDC-231539 (**5d**), CCDC-231548 (**5e**), CCDC-231540 (**5f**), CCDC-231553 (**5g**), CCDC-211208 (**5h**), CCDC-230004 (**5i**), CCDC-231547 (**5j**), CCDC-231536 (**5k**), CCDC-231554 (**5l**), CCDC-231545 (**5m**), CCDC-231555 (**5n**), CCDC-231552 (**5o**), CCDC-231549 (**5p**), CCDC-230002 (**5q**), CCDC-230003 (**5r**), CCDC-231550 (**5s**), CCDC-231551 (**5t**), CCDC-231546 (**5u**), CCDC-231542 (**5v**), CCDC-231537 (**5w**), CCDC-231543 (**5x**), and CCDC-231541 (**5y**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, U.K.; fax (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(15) Compound **5g** belongs to space group $P\bar{3}$ but is best discussed here.

**Table 1.** X-ray Crystallographic Data and Structure Refinements for Compounds **5a−y**

| | **5a**[a] | **5b**[b] | **5c**[c] | **5d**[a] | **5e**[a] |
|---|---|---|---|---|---|
| empirical formula | $C_{66}H_{138}Cl_6Fe_6N_6O_{30}\cdot CHCl_3$ | $C_{48}H_{102}Cl_6Fe_6N_6O_{12}\cdot 0.75CHCl_3$ | $C_{36}H_{78}Cl_6Fe_6N_6O_{12}\cdot 2CHCl_3$ | $C_{102}H_{150}Fe_6N_{12}O_{30}S_6$ | $C_{72}H_{150}Cl_6Fe_6N_6O_{30}\cdot CHCl_3$ |
| $M_r$ [g mol$^{-1}$] | 2162.99 | 1592.68 | 1573.58 | 2551.80 | 2247.15 |
| cryst size [mm$^3$] | 0.35 × 0.35 × 0.30 | 0.45 × 0.40 × 0.28 | 0.35 × 0.30 × 0.30 | 0.35 × 0.30 × 0.20 | 0.40 × 0.30 × 0.20 |
| cryst syst | rhombohedral | rhombohedral | rhombohedral | rhombohedral | rhombohedral |
| space group | $R\bar{3}$ | $R\bar{3}$ | $R\bar{3}$ | $R\bar{3}$ | $R\bar{3}$ |
| $T$ [K] | 173(2) | 200(2) | 275(2) | 173(2) | 173(2) |
| $a$ [Å] | 26.161(4) | 21.919(2) | 15.095(2) | 25.0845(6) | 26.731(4) |
| $b$ [Å] | | | | | |
| $c$ [Å] | 12.283(3) | 12.603(2) | 23.647(3) | 16.0454(7) | 12.236(2) |
| $\alpha$ [deg] | | | | | |
| $\beta$ [deg] | | | | | |
| $\gamma$ [deg] | | | | | |
| $V$ [Å$^3$] | 7280(2) | 5243.8(11) | 4666.5(9) | 8743.6(5) | 7572(2) |
| $Z$ | 3 | 3 | 3 | 3 | 3 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.480 | 1.513 | 1.680 | 1.454 | 1.478 |
| $\theta$ range [deg] | 1.89−27.49 | 1.86−27.99 | 2.58−26.25 | 2.71−27.49 | 6.90−26.37 |
| reflns collected | 11425 | 3396 | 2352 | 9523 | 16083 |
| unique reflns | 3635 | 2741 | 2110 | 4168 | 3374 |
| [$R_{int}$] | 0.0437 | 0.0692 | 0.0608 | 0.0368 | 0.0270 |
| reflns obsd [$I > 2\sigma(I)$] | 3005 | 1924 | 1137 | 3316 | 3060 |
| params | 184 | 182 | 113 | 235 | 200 |
| abs corr method | empirical (Scalepack) | $\psi$-scans | $\psi$-scans | empirical (Scalepack) | empirical (Scalepack) |
| final $R1$ [$I > 2\sigma(I)$] | 0.0435 | 0.0558 | 0.0716 | 0.0389 | 0.0348 |
| $wR2$ (all data) | 0.1255 | 0.1461 | 0.2315 | 0.1138 | 0.0940 |
| largest residuals [e Å$^{-3}$] | 0.624/−0.632 | 0.523/−0.581 | 1.395/−1.092 | 0.615/−0.442 | 0.716/−0.469 |

| | **5f**[a] | **5g**[a] | **5h**[a] | **5i**[a] | **5j**[c] |
|---|---|---|---|---|---|
| empirical formula | $C_{78}H_{102}Fe_6N_{12}O_{18}S_6\cdot CHCl_3\cdot 6CH_2Cl_2$ | $C_{90}H_{102}Cl_6Fe_6N_6O_{12}\cdot 13CHCl_3$ | $C_{90}H_{102}Cl_6Fe_6N_6O_{12}\cdot H_2O$ | $C_{120}H_{132}Cl_6Fe_6N_{12}O_{12}\cdot 6CHCl_3$ | $C_{60}H_{126}Cl_6Fe_6N_6O_{24}$ |
| $M_r$ [g mol$^{-1}$] | 2652.10 | 3559.47 | 2020.68 | 3198.38 | 1859.44 |
| cryst size [mm$^3$] | 0.35 × 0.20 × 0.20 | 0.30 × 0.20 × 0.20 | 0.40 × 0.30 × 0.30 | 0.39 × 0.23 × 0.21 | 0.30 × 0.20 × 0.20 |
| cryst syst | rhombohedral | hexagonal | rhombohedral | rhombohedral | monoclinic |
| space group | $R\bar{3}$ | $P\bar{3}$ | $R\bar{3}$ | $R\bar{3}$ | $P2_1/c$ |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 100(2) | 173(2) |
| $a$ [Å] | 29.0350(7) | 32.4052(2) | 30.060(3) | 41.114(2) | 17.101(3) |
| $b$ [Å] | | | | | 16.264(3) |
| $c$ [Å] | 11.8571(5) | 11.8909(2) | 12.127(2) | 21.987(1) | 15.114(3) |
| $\alpha$ [deg] | | | | | |
| $\beta$ [deg] | | | | | 96.74(3) |
| $\gamma$ [deg] | | | | | |
| $V$ [Å$^3$] | 8656.7(5) | 10813.7(3) | 9490(2) | 32187(3) | 4174.4(14) |
| $Z$ | 3 | 3 | 3 | 9 | 2 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.526 | 1.639 | 1.105 | 1.485 | 1.479 |
| $\theta$ range [deg] | 1.90−27.46 | 1.26−27.49 | 3.71−25.02 | 3.32−27.51 | 1.20−27.49 |
| reflns collected | 8460 | 24880 | 4585 | 120889 | 9558 |
| unique reflns | 3932 | 15649 | 1937 | 16363 | 9558 |
| [$R_{int}$] | 0.0402 | 0.0348 | 0.0712 | 0.0657 | 0.0000[d] |
| reflns obsd [$I > 2\sigma(I)$] | 3121 | 9064 | 1426 | 11050 | 8276 |
| params | 221 | 836 | 190 | 775 | 468 |
| abs corr method | empirical (Scalepack) | empirical (Scalepack) | empirical (Scalepack) | none | $\psi$-scans |
| final $R1$ [$I > 2\sigma(I)$] | 0.0817 | 0.0743 | 0.1001 | 0.0576 | 0.0406 |
| $wR2$ (all data) | 0.2556 | 0.2232 | 0.2760 | 0.1849 | 0.1589 |
| largest residuals [e Å$^{-3}$] | 1.641/−1.130 | 1.725/−0.861 | 0.851/−0.380 | 1.655/−2.632 | 0.868/−1.268 |

| | **5k**[a] | **5l**[a] | **5m**[c] | **5n**[a] | **5o**[a] |
|---|---|---|---|---|---|
| empirical formula | $C_{90}H_{126}Fe_6N_{12}O_{24}S_6\cdot 4CH_2Cl_2$ | $C_{66}H_{90}Cl_6Fe_6N_6O_{12}\cdot 2H_2O\cdot 4CHCl_3$ | $C_{42}H_{78}Cl_6Fe_6N_6O_{12}\cdot 2CHCl_3$ | $C_{96}H_{138}Fe_6N_{12}O_{12}S_6\cdot 4CHCl_3$ | $C_{66}H_{114}Fe_6N_{12}O_{24}S_6\cdot 8CHCl_3$ |
| $M_r$ [g mol$^{-1}$] | 2627.19 | 2220.74 | 1645.68 | 2657.12 | 2942.10 |
| cryst size [mm$^3$] | 0.35 × 0.30 × 0.30 | 0.20 × 0.20 × 0.20 | 0.60 × 0.30 × 0.20 | 0.20 × 0.20 × 0.10 | 0.20 × 0.20 × 0.20 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| $a$ [Å] | 17.30930(10) | 16.833(3) | 13.074(3) | 13.2578(4) | 13.5427(2) |
| $b$ [Å] | 20.8732(2) | 16.866(3) | 11.660(2) | 19.2200(3) | 21.8038(3) |
| $c$ [Å] | 16.27560(10) | 16.068(3) | 22.592(5) | 24.8933(8) | 20.6024(4) |
| $\alpha$ [deg] | | | | | |
| $\beta$ [deg] | 91.0410(10) | 106.81(3) | 105.51(3) | 96.6350(11) | 97.3160(10) |
| $\gamma$ [deg] | | | | | |
| $V$ [Å$^3$] | 5879.41(8) | 4367.2(15) | 3318.6(11) | 6300.7(3) | 6034.00(17) |
| $Z$ | 2 | 2 | 2 | 2 | 2 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.484 | 1.689 | 1.647 | 1.401 | 1.619 |
| $\theta$ range [deg] | 1.96−27.47 | 2.40−27.51 | 2.38−24.98 | 2.70−25.04 | 1.99−27.49 |
| reflns collected | 24701 | 18049 | 6092 | 21194 | 25527 |
| unique reflns | 13455 | 9951 | 5822 | 11015 | 13732 |
| [$R_{int}$] | 0.0196 | 0.0255 | 0.0366 | 0.0442 | 0.0329 |
| reflns obsd [$I > 2\sigma(I)$] | 10554 | 7731 | 4249 | 8204 | 9807 |
| params | 695 | 514 | 403 | 668 | 658 |
| abs corr method | empirical (Scalepack) | empirical (Scalepack) | $\psi$-scans | empirical (Scalepack) | empirical (Scalepack) |
| final $R1$ [$I > 2\sigma(I)$] | 0.0363 | 0.0712 | 0.0434 | 0.0781 | 0.0593 |
| $wR2$ (all data) | 0.1039 | 0.2344 | 0.1193 | 0.2334 | 0.1804 |
| largest residuals [e Å$^{-3}$] | 0.718/−0.669 | 2.009/−1.622 | 0.974/−0.591 | 1.057/−0.850 | 2.477/−1.407 |

**Table 1** (Continued)

| | **5p**[c] | **5q**[b] | **5r**[b] | **5s**[a] | **5t**[a] |
|---|---|---|---|---|---|
| empirical formula | $C_{60}H_{114}Cl_6Fe_6N_6O_{12}$ | $C_{60}H_{126}Cl_6Fe_6N_6O_{12}\cdot 2CHCl_3$ | $C_{72}H_{150}Cl_6Fe_6N_6O_{12}$ | $C_{84}H_{174}Cl_6Fe_6N_6O_{12}$ | $C_{90}H_{174}Fe_6N_{12}O_{12}S_6$ |
| $M_r$ [g mol$^{-1}$] | 1659.37 | 1910.20 | 1839.78 | 2008.09 | 2143.87 |
| cryst size [mm$^3$] | 0.30 × 0.30 × 0.30 | 0.65 × 0.45 × 0.22 | 0.38 × 0.26 × 0.20 | 0.35 × 0.35 × 0.30 | 0.35 × 0.30 × 0.30 |
| cryst syst | monoclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $T$ [K] | 173(2) | 200(2) | 200(2) | 173(2) | 173(2) |
| $a$ [Å] | 21.1158(4) | 11.306(2) | 12.056(1) | 13.0050(2) | 14.254(3) |
| $b$ [Å] | 16.4674(4) | 13.128(1) | 13.106(1) | 13.8403(2) | 15.202(3) |
| $c$ [Å] | 22.4019(5) | 15.502(1) | 15.006(2) | 16.4992(2) | 15.362(3) |
| α [deg] | | 110.07(1) | 76.53(1) | 65.7690(10) | 115.01(3) |
| $\beta$ [deg] | 97.2888(13) | 97.16(1) | 78.46(1) | 69.8380(10) | 92.71(3) |
| $\gamma$ [deg] | | 91.21(1) | 84.73(1) | 80.8020(10) | 111.09(3) |
| $V$ [Å$^3$] | 7726.7(3) | 2139.3(4) | 2256.7(4) | 2541.57(6) | 2735.0(10) |
| $Z$ | 4 | 1 | 1 | 1 | 1 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.426 | 1.483 | 1.354 | 1.312 | 1.302 |
| $\theta$ range [deg] | 1.57−27.47 | 1.76−27.00 | 1.89−27.00 | 1.42−27.50 | 1.51−27.51 |
| reflns collected | 16854 | 10530 | 11249 | 21970 | 23824 |
| unique reflns | 8821 | 9118 | 9816 | 11633 | 12547 |
| [$R_{int}$] | 0.0388 | 0.0233 | 0.0449 | 0.0199 | 0.0199 |
| reflns obsd [$I > 2\sigma(I)$] | 6065 | 7352 | 6063 | 9189 | 9807 |
| params | 410 | 635 | 460 | 514 | 568 |
| abs corr method | $\psi$-scans | $\psi$-scans | $\psi$-scans | empirical (Scalepack) | empirical (Scalepack) |
| final $R1$ [$I > 2\sigma(I)$] | 0.0385 | 0.0386 | 0.0618 | 0.0361 | 0.0439 |
| $wR2$ (all data) | 0.1014 | 0.1024 | 0.1481 | 0.1130 | 0.1423 |
| largest residuals [e Å$^{-3}$] | 0.613/−0.489 | 0.611/−0.474 | 1.374/−0.746 | 1.008/−0.730 | 1.345/−0.616 |

| | **5u**[c] | **5v**[a] | **5w**[a] | **5x**[a] | **5y**[a] |
|---|---|---|---|---|---|
| empirical formula | $C_{48}H_{102}Cl_6Fe_6N_6O_{18}\cdot 2CHCl_3$ | $C_{96}H_{150}Cl_6Fe_6N_6O_{30}$ | $C_{108}H_{138}Cl_6Fe_6N_6O_{24}$ | $C_{132}H_{150}Cl_6Fe_6N_6O_{24}\cdot 2C_5H1_2\cdot 2CH_2Cl_2$ | $C_{102}H_{138}Cl_6Fe_6N_6O_{24}\cdot Et_2O$ |
| $M_r$ [g mol$^{-1}$] | 1833.89 | 2416.02 | 2452.04 | 3066.52 | 2454.10 |
| cryst size [mm$^3$] | 0.30 × 0.30 × 0.30 | 0.20 × 0.20 × 0.15 | 0.40 × 0.30 × 0.25 | 0.20 × 0.20 × 0.20 | 0.20 × 0.20 × 0.10 |
| cryst syst | triclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $T$ [K] | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| $a$ [Å] | 12.420(3) | 11.9911(2) | 12.63210(10) | 15.3262(5) | 12.9941(2) |
| $b$ [Å] | 16.726(3) | 15.0678(4) | 15.0623(2) | 15.7033(4) | 14.8203(3) |
| $c$ [Å] | 18.384(4) | 15.7072(4) | 16.9855(2) | 16.1823(5) | 16.3250(3) |
| α [deg] | 89.95(3) | 87.4551(1) | 110.0940(10) | 79.255(2) | 74.1320(10) |
| $\beta$ [deg] | 82.56(3) | 80.3979(14) | 100.3340(10) | 76.0670(10) | 77.8580(10) |
| $\gamma$ [deg] | 89.73(3) | 75.6373(13) | 105.6920(10) | 76.438(2) | 80.4040(10) |
| $V$ [Å$^3$] | 3786.8(13) | 2710.74(11) | 2786.29(5) | 3639.61(19) | 2936.37(9) |
| $Z$ | 2 | 1 | 1 | 1 | 1 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.608 | 1.480 | 1.461 | 1.399 | 1.388 |
| $\theta$ range [deg] | 2.43−24.97 | 2.20−27.51 | 2.37−27.54 | 1.71−25.14 | 2.03−27.53 |
| reflns collected | 13984 | 23421 | 24235 | 24741 | 25519 |
| unique reflns | 13312 | 12433 | 12789 | 12930 | 13425 |
| [$R_{int}$] | 0.0682 | 0.0272 | 0.0232 | 0.0229 | 0.0485 |
| reflns obsd [$I > 2\sigma(I)$] | 5197 | 9362 | 9858 | 10112 | 8283 |
| params | 857 | 949 | 676 | 832 | 677 |
| abs corr method | $\psi$-scans | empirical (Scalepack) | empirical (Scalepack) | empirical (Scalepack) | empirical (Scalepack) |
| final $R1$ [$I > 2\sigma(I)$] | 0.0482 | 0.0332 | 0.0350 | 0.0800 | 0.0512 |
| $wR2$ (all data) | 0.1803 | 0.0837 | 0.1023 | 0.2549 | 0.1456 |
| largest residuals [e Å$^{-3}$] | 0.890/−1.243 | 0.700/−0.369 | 0.405/−0.432 | 1.656/−1.079 | 0.696/−0.697 |

[a] Nonius KappaCCD. [b] Siemens-P4. [c] Nonius MACH3. [d] The data have been collected on a four-circle diffractometer equipped with a scintillation counter. Only a set of symmetrically independent reflections has been collected.

and give rise to the formation of compartments occupied by chloroform. In contrast, the sidearms of **5d** give rise to a self-contained ball-shaped capsule, lacking further intermolecular interactions (Figure 3).

An especially interesting example of crystal packing leading to porous frameworks is caused by three-dimensional $\pi-\pi$ stacking of the naphthyl groups of the sidearms of ferric wheels **5h** (Figure 4). This leads to two different kinds of voids. Of the voids formed outside and between discrete wheels, only the outside voids host water molecules. Self-assembly by hydrogen bonding, van der Waals interaction, and $\pi-\pi$ stacking are widespread binding modes in supramolecular hybrid organic−inorganic 3D-networks.[9,10]

Unlike **5a**−**h**, the ferric wheels of **5i** are not arranged in parallel but are rather three-dimensionally perpendicular, a well-known construction for 3D coordination polymers.[16] In **5i**, the interpenetrating sidearms create large loose-fitting voids (Figure 5).

**Crystal Packing of Ferric Wheels 5j−l of Space Group *P*2₁/*c*.** The ferric wheels [$Fe_6X_6(L^3)_6$] (**5j**−**l**) have idealized $S_2$ (**5j**,**k**) and $S_6$ (**5l**) molecular symmetry and crystallize in the space group $P2_1/c$ (Table 1). The crystal packing of the ferric wheels **5j**−**l** is almost identical and differs only by the included angle of the two groups of parallel wheels (Figure 6, top). For example, all the disklike clusters of **5j** are arranged in parallel in two orientations (Figure 6, center) and are piled in cylindrical columns, with all the iron centers superimposed. Whereas the interpenetrating sidearms of the ferric wheels **5j**,**k** are subject to van der Waals interactions,

---

(16) Saalfrank, R. W.; Maid, H.; Hampel, F.; Peters, K. *Eur. J. Inorg. Chem.* **1999**, 1859−1876.

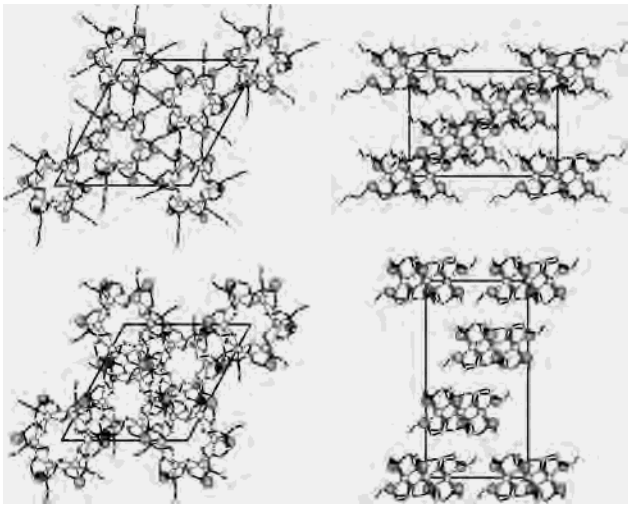


**Figure 2.** Presentation of the arrangement of the ferric wheels in **5b** (top) and **5c** (bottom). Left: view along the *c*-axis. Right: view along the *b*-axis.

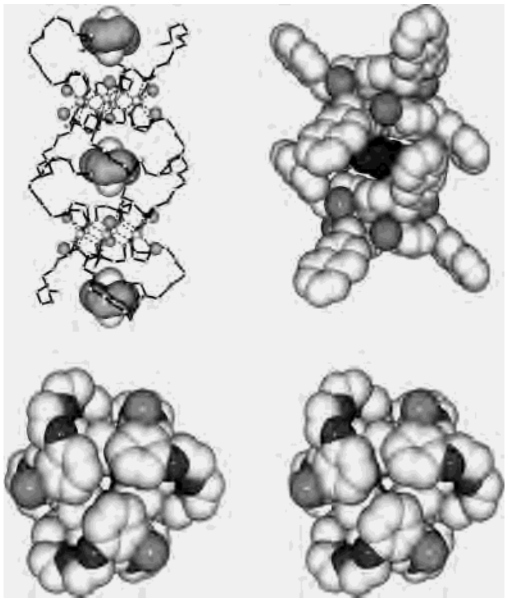


**Figure 3.** Top, left: presentation of the columnar crystal packing of **5e**, highlighting the compartments with encapsulated chloroform. Top, right: space-filling model, demonstrating the tight incarceration of chloroform by two interlocking entities of **5g**. Bottom: stereoview presentation of space-filling model of ball shaped **5d**.

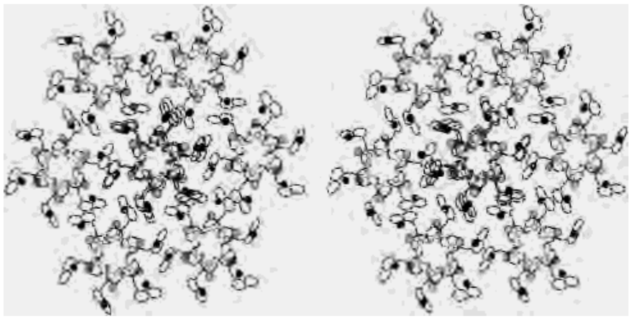


**Figure 4.** Stereoview of the crystal packing of **5h**, highlighting the $\pi-\pi$ interactions together with encapsulated water (black spheres) in the outside voids.

the packing of the ferric wheels of **5l** is governed by $\pi-\pi$ interactions (Figure 6, bottom).

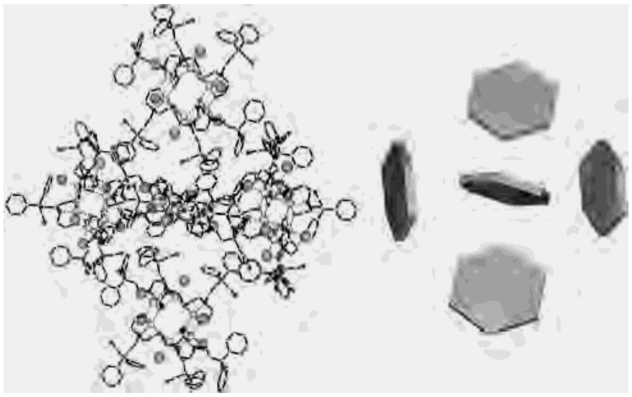


**Figure 5.** Left: crystal packing of **5i**. Right: graphical presentation, highlighting the three-dimensional perpendicular arrangement of the ferric wheels.

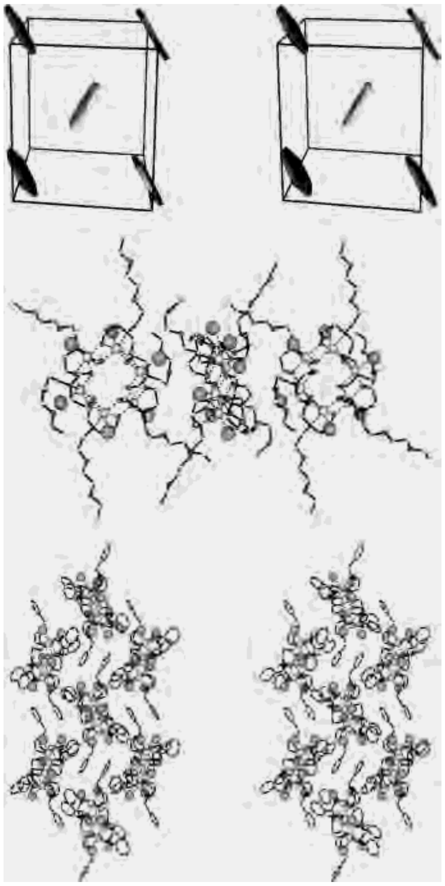


**Figure 6.** Top: schematic stereo presentation of the crystal packing of **5j**−**l**. Center: presentation of the two orientations of **5j**. Bottom: stereoview highlighting the one-dimensional $\pi-\pi$ interactions between parallel complexes of **5l**.

**Crystal Packing of Ferric Wheels 5m−o of Space Group $P2_1/n$ and 5p of Space Group $C2/c$.** Whereas the unit cells of **5j**−**l** of space group $P2_1/c$ are most simply depicted with five wheels (Figure 6, top), the crystal packings of **5m**−**o** of space group $P2_1/n$ and **5p** of space group $C2/c$ are more complex. The unit cells of **5m**−**o** are basically represented by six wheels (Figure 7, top), and that for **5p** is represented by 15 wheels (Figure 7, bottom).

**Crystal Packing of Ferric Wheels 5q−y of Space Group $P\bar{1}$.** The ferric wheels [$Fe_6X_6(L^3)_6$] (**5q**−**y**) have idealized

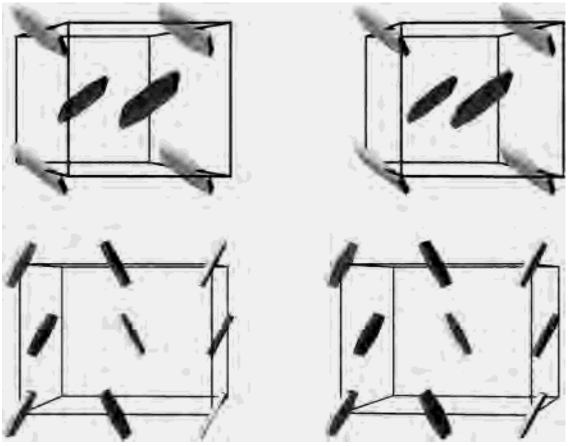


**Figure 7.** Schematic stereo presentation of the crystal packing of **5m**−**o** (top) and **5p** (bottom, for reasons of clarity only nine complexes are shown).

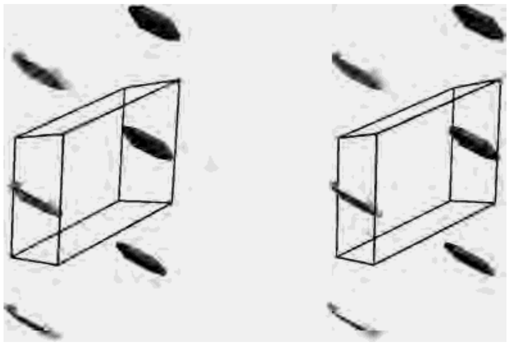


**Figure 8.** Schematic stereo presentation of the crystal packing of **5q**−**y**.

$S_2$ molecular symmetry and are packed in the crystal most simply, with all the ferric wheels piled in parallel (Figure 8).

## Conclusion

Earlier, we described an efficient, simple route for the template-mediated self-assembly of iron(III) ions and triethanolamine to give six-membered iron coronates. Careful analysis of the construction plan of these systems was the basis for the rational design of six-membered iron coronands, starting from *N*-substituted diethanolamines and iron(III) chloride. Although the structures of the iron coronands are almost identical and have idealized $S_6$ or $S_2$ molecular symmetry, their variable sidearms give rise to a whole variety of different crystal packing modes. Most interestingly, the iron coronands readily frame compartments and three-dimensional networks with discrete channels and pores, suitable for the encapsulation of guest molecules. Aiming at the use of oligonuclear clusters as single-molecule magnets (SMMs), efforts toward crystal engineering are indispensable.

## Experimental Section

**General Techniques.** All reactions were carried out under an atmosphere of dry nitrogen. All solvents used were purified and dried according to standard procedures. NMR spectra were recorded on JEOL EX 400 and JEOL GX 400 spectrometers. Solvent signals were employed as internal standards: $CDCl_3$ ($^1H$, 7.24 ppm; $^{13}C$, 77.0 ppm); $D_3CCOCD_3$ ($^1H$, 2.04 ppm; $^{13}C$, 29.30, 206.30 ppm).

**General Method for $H_2L^3$ (4a−y).** A suspension of the corresponding chloride, bromide, or toluenesulfonate (30 mmol), diethanolamine (1.1 equiv), and $Na_2CO_3$ (1.2 equivalents) in MeCN (125 mL) was heated at reflux for 48 h. The reaction mixture was then cooled, filtered to remove any residual salts, and concentrated under vacuum. The residue was taken up in $CHCl_3$ (100 mL) and washed with water (50 mL). The organic phase was dried over $Na_2SO_4$ and concentrated under vacuum to give the product.[17]

**4g**−**i**,**l**−**s.** The corresponding halides were commercially available.

**4a**,**e**,**j**,**u.** The corresponding halides were prepared according to a literature procedure.[18]

**4d**,**f**,**k**,**w**,**x.** The corresponding toluenesulfonate compounds were prepared according to a literature procedure.[19]

**4y.** 3,5-Bis(allyloxy)benzyl bromide was prepared according to a literature procedure.[20]

**$H_2L^3$ (4a).** Yield: 6.11 g (81%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3417, 2878, 1655, 1089 cm$^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.65−3.50 (m, 14H, 5 $CH_2$−O, 2 C$H_2$−OH), 3.34 (s, 3H, $CH_3$), 2.71 (t, 2H, $J$ = 5.0 Hz, $CH_2$−N), 2.66 (t, 4H, $J$ = 5.0 Hz, 2 N−$CH_2$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 71.84, 70.38 (two superimposed peaks), 70.17, 69.55 (5 $CH_2$−O), 59.71 (2 $CH_2$−OH), 58.92 ($CH_3$−O), 57.27 (2 N−$CH_2$), 54.02 ($CH_2$−N) ppm. FAB-MS (3-NBA): $m/z$ (%) = 252 (100) [M]$^+$, 220 (40) [M − $CH_2OH$]$^+$. Anal. Calcd (%) for $C_{11}H_{25}NO_5$ (251.32): C 52.57, H 10.03, N 5.57. Found: C 49.73, H 10.17, N 4.54.

**$H_2L^3$ (4b,c).** Commercially available.

**$H_2L^3$ (4d).** Yield: 8.74 g (93%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3373, 2874, 1059, 757, 693 cm$^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.25−7.21 (m, 2H, 2 Ar−H), 6.92−6.88 (m, 3H, 3 Ar−H), 4.11 (t, 2H, $J$ = 4.9 Hz, $CH_2$−O), 3.81 (t, 2H, $J$ = 4.9 Hz, $CH_2$−O), 3.70−3.61 (m, 4H, 2 $CH_2$−O), 3.74−3.50 (m, 6H, $CH_2$−O, 2 C$H_2$−OH), 2.71 (t, 2H, $J$ = 5.2 Hz, $CH_2$−N), 2.66 (t, 4H, $J$ = 5.1 Hz, 2 N−$CH_2$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 158.47 (Ar−C), 129.21, 120.64, 114.47 (5 Ar−CH), 70.62, 70.16, 69.66, 69.63, 67.18 (5 $CH_2$−O), 59.71 (2 $CH_2$−OH), 57.09 (2 N−$CH_2$), 53.82 ($CH_2$−N) ppm. FAB-MS (3-NBA): $m/z$ (%) = 314 (100) [M]$^+$, 282 (45) [M − $CH_2OH$]$^+$. Anal. Calcd (%) for $C_{16}H_{27}NO_5$ (313.39): C 61.32, H 8.68, N 4.47. Found: C 57.98, H 7.94, N 4.14.

**$H_2L^3$ (4e).** Yield: 3.34 g (42%) colorless oil. IR (neat): $\tilde{\nu}$ = 3385, 2950, 2873, 1452, 1112 cm$^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.61−3.42 (m, 16H, 2 C$H_2$−OH, 6 $CH_2$−O), 3.42 (br s, 2H, 2 OH), 2.76 (t, 2H, $J$ = 5.1 Hz, $CH_2$−N), 2.72 (t, 4H, $J$ = 5.1 Hz, 2 N−$CH_2$), 1.21 (t, 3H, $J$ = 7.1 Hz, $CH_3$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 70.65, 70.49, 70.27, 69.81, 69.65, 66.63 (6 $CH_2$−O), 59.78 (2 $CH_2$−OH), 57.28 (2 N−$CH_2$), 54.04 ($CH_2$−N), 15.15 ($CH_3$) ppm. MS (EI, 70 eV): $m/z$ (%) = 265 (5) [M]$^+$, 234 (100) [M − $CH_2OH$]$^+$. Anal. Calcd (%) for $C_{12}H_{27}NO_2$ (265.35): C 54.32, H 10.26, N 5.28. Found: C 52.50, H 10.02, N 4.72.

**$H_2L^3$ (4f).** Yield: 6.42 g (95%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3359, 2949, 2879, 1037, 756, 693 cm$^{-1}$. $^1H$ NMR (400 MHz,

---

(17) Meadows, E. S.; De Wall, S. L.; Barbour, L. J.; Fronczek, F. R.; Kim, M.-S.; Gokel, G. W. *J. Am. Chem. Soc.* **2000**, *122*, 3325−3335. Schultz, R. N.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659−6668.

(18) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437−4447.

(19) Ashton, P. R.; Ballardini, R.; Balzani, V.; Constable, E. C.; Credi, A.; Kocian, O.; Langford, S. J.; Preece, J. A.; Prodi, L.; Schofield, E. R.; Spencer, N.; Stoddart, J. F.; Wenger, S. *Chem. Eur. J.* **1998**, *4*, 2413−2422.

(20) Yamakawa, Y.; Ueda, M.; Nagahata, R.; Takeuchi, K.; Asai, M. *J. Chem. Soc., Perkin Trans 1* **1998**, 4135−4139.

CDCl$_3$): $\delta$ = 7.30−7.23 (m, 2H, 2 Ar−H), 6.95−6.87 (m, 3H, 3 Ar−H), 4.02 (t, 2H, $J$ = 5.1 Hz, CH$_2$−O), 3.60 (t, 4H, $J$ = 5.2 Hz, 2 C$H_2$−OH), 2.94 (t, 2H, $J$ = 5.1 Hz, CH$_2$−N), 2.74 (t, 4H, $J$ = 5.2 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 158.34 (Ar−C), 129.50, 121.08, 114.46 (5 Ar−CH), 66.22 (O−CH$_2$), 59.68 (2 N−CH$_2$), 56.87 (2 CH$_2$−OH), 53.48 (CH$_2$−N) ppm. FAB-MS (3-NBA): $m/z$ (%) = 226 (100) [M]$^+$, 194 (50) [M − CH$_2$OH]$^+$. Anal. Calcd (%) for C$_{12}$H$_{19}$NO$_3$ (225.28): C 63.98, H 8.50, N 6.22. Found: C 60.96, H 8.68, N 5.81.

**H$_2$L$^3$ (4g).** Yield: 5.08 g (69%) thick pale yellow oil. IR (neat): $\tilde{\nu}$ = 3355, 3054, 1690, 1406, 1037 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.79−7.69 (m, 4H, 4 Naph-H), 7.47−7.45 (m, 1H, 1 Naph-H), 7.44−7.42 (m, 1H, 1 Naph-H), 7.24 (br s, 1H, 1 Naph-H), 3.79 (s, 2H, CH$_2$−N), 3.58 (t, 4H, $J$ = 5.4 Hz, 2 C$H_2$−OH), 3.57 (br s, 2H, 2 OH), 2.68 (t, 4H, $J$ = 5.4 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 136.36, 133.27, 132.27, 129.09, 128.45, 127.89, 127.37, 127.09, 126.05, 125.68 (3 Naph-C, 7 Naph-CH), 59.61 (2 CH$_2$−OH), 59.43 (CH$_2$−N), 55.98 (2 N−CH$_2$) ppm. MS (EI, 70 eV): $m/z$ (%) = 245 (10) [M]$^+$, 214 (20) [M − CH$_2$OH]$^+$, 141 (100) [M − N(CH$_2$CH$_2$OH)$_2$]$^+$. Anal. Calcd (%) for C$_{15}$H$_{19}$NO$_2$ (245.33): C 73.44, H 7.81, N 5.71. Found: C 73.59, H 7.93, N 5.67.

**H$_2$L$^3$ (4h).** Yield: 5.12 g (74%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3396, 2946, 2881, 1406, 1064 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.13−7.96 (m, 4H, 4 Naph-H), 7.81−7.79 (m, 1H, 1 Naph-H), 7.48−7.37 (m, 1H, 1 Naph-H), 7.18 (br s, 1H, 1 Naph-H), 4.09 (s, 2H, CH$_2$−N), 3.53 (t, 4H, $J$ = 5.3 Hz, 2 C$H_2$−OH), 3.14 (br s, 2H, 2 OH), 2.65 (t, 4H, $J$ = 5.3 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 134.44, 133.87, 133.27, 132.75, 132.21, 128.67, 127.64, 127.04, 125.16, 123.90 (3 Naph-C, 7 Naph-CH), 59.74 (2 CH$_2$−OH), 58.34 (CH$_2$−N), 56.12 (2 N−CH$_2$) ppm. MS (EI, 70 eV): $m/z$ (%) = 245 (10) [M]$^+$, 214 (20) [M − CH$_2$OH]$^+$, 142 (100) [M − N(CH$_2$CH$_2$OH)$_2$]$^+$. Anal. Calcd (%) for C$_{15}$H$_{19}$NO$_2$ (245.33): C 73.44, H 7.81, N 5.71. Found: C 73.51, H 7.79, N 5.68.

**H$_2$L$^3$ (4i).** Yield: 7.10 g (66%) colorless oil that solidifies on standing. IR (neat): $\tilde{\nu}$ = 3377, 3060, 2953, 2250, 1598, 1448, 1033 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.41−7.26 (m, 10H, 10 Ar−H), 3.64 (t, 4H, $J$ = 5.4 Hz, 2 C$H_2$−OH), 3.30 (t, 4H, $J$ = 5.3 Hz, 2 N−CH$_2$), 3.22 (br s, 2H, 2 OH), 2.90 (t, $J$ = 5.4 Hz, 2H, C$_q$−CH$_2$), 2.64 (t, 2H, $J$ = 5.4 Hz, CH$_2$−N), 2.55 (t, 2H, $J$ = 5.4 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 129.11, 128.92, 128.31, 128.28, 127.98, 127,76, 127.56, 126.95, 126.64, 126.54, 126.21, 126.04 (2 Ar−C, 10 Ar−CH), 119.16 (CN), 59.37 (2 CH$_2$−OH), 56.11 (2 N−CH$_2$), 53.10 (CH$_2$−N), 26.51 (C$_q$), 26.48 (C$_q$−C$H_2$) ppm. FAB-MS (3-NBA): $m/z$ (%) = 325 (100) [M]$^+$, 293 (20) [M − CH$_2$OH]$^+$. Anal. Calcd (%) for C$_{20}$H$_{24}$N$_2$O$_2$ (324.43): C 74.04, H 7.46, N 8.64. Found: C 74.17, H 7.39, N 8.66.

**H$_2$L$^3$ (4j).** Yield: 3.05 g (46%) colorless oil. IR (neat): $\tilde{\nu}$ = 3390, 2950, 2870, 1451, 1108 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.63 (t, 4H, $J$ = 4.2 Hz, 2 C$H_2$−OH), 3.56 (m, 8H, 4 CH$_2$−O), 3.38 (br s, 2H, 2 OH), 2.76 (t, 2H, $J$ = 5.1 Hz, CH$_2$−N), 2.72 (t, 4H, $J$ = 4.6 Hz, 2 N−CH$_2$), 1.22 (t, 3H, $J$ = 7.1 Hz, CH$_3$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 70.23, 69.61, 69.50, 66.78 (4 CH$_2$−O), 59.74 (2 CH$_2$−OH), 57.28 (2 N−CH$_2$), 53.82 (CH$_2$−N), 14.98 (CH$_3$) ppm. MS (EI, 70 eV): $m/z$ (%) = 221 (1) [M]$^+$, 190 (60) [M − CH$_2$OH]$^+$, 146 (19) [M − CH$_2$OH, − OC$_2$H$_5$]$^+$, 118 (100) [M − CH$_2$OH, − C$_2$H$_4$OC$_2$H$_5$]$^+$. Anal. Calcd (%) for C$_{10}$H$_{23}$NO$_2$ (221.30): C 54.28, H 10.48, N 6.33. Found: C 53.67, H 10.70, N 5.92.

**H$_2$L$^3$ (4k).** Yield: 7.43 g (92%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3371, 2945, 2875, 1043, 756, 693 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.27−7.23 (m, 2H, Ar−H), 6.94−6.89 (m, 3H, Ar−H), 4.09 (t, 2H, $J$ = 4.7 Hz, CH$_2$−O), 3.79 (t, 2H, $J$ = 4.7 Hz, CH$_2$−O), 3.59 (t, 2H, $J$ = 5.3 Hz, CH$_2$−O), 3.56 (t, 4H, $J$ = 5.2 Hz, 2 C$H_2$−OH), 3.30 (br s, 2H, 2 OH), 2.75 (t, 2H, $J$ = 5.3 Hz, CH$_2$−N), 2.68 (t, 4H, $J$ = 5.2 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 158.47 (Ar−C), 129.41, 120.97, 114.52 (5 Ar−CH), 69.76, 69.43, 66.96 (3 CH$_2$−O), 59.68 (2 CH$_2$−OH), 56.96 (2 N−CH$_2$), 53.72 (CH$_2$−N) ppm. FAB-MS (3-NBA): $m/z$ (%) = 270 (100) [M]$^+$, 238 (50) [M − CH$_2$OH]$^+$. Anal. Calcd (%) for C$_{14}$H$_{23}$NO$_4$ (269.34): C 62.43, H 8.61, N 5.20. Found: C 59.73, H 8.53, N 4.63.

**H$_2$L$^3$ (4l).** Yield: 5.27 g (90%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3353, 2947, 2880, 2826, 1039, 734, 700 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.24−7.16 (m, 5H, 5 Ar−H), 3.61 (s, 2H, CH$_2$−N), 3.52 (t, 4H, $J$ = 5.3 Hz, 2 C$H_2$−OH), 3.19 (br s, 2H, 2 OH), 2.61 (t, 4H, $J$ = 5.3 Hz, 2 N−CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 139.07 (Ar−C), 129.39, 128.84, 127.90 (5 Ar−CH), 59.97 (2 CH$_2$−OH), 59.59 (CH$_2$−N), 56.14 (2 N−CH$_2$) ppm. FAB-MS (3-NBA): $m/z$ (%) = 196 (100) [M]$^+$, 164 (70) [M − CH$_2$-OH]$^+$. Anal. Calcd (%) for C$_{11}$H$_{17}$NO$_2$ (195.26): C 67.66, H 8.78, N 7.17. Found: C 65.65, H 8.95, N 6.88.

**H$_2$L$^3$ (4m).** Yield: 2.61 g (60%) yellow oil. IR (neat): $\tilde{\nu}$ = 3347, 3077, 2955, 2882, 2823, 1643, 1077, 921 cm$^{-1}$. $^1$H NMR (400 MHz, CD$_3$COCD$_3$): $\delta$ = 5.87 (m, 1H, CH$_2$=C$H$), 5.14 (m, 2H, C$H_2$=CH), 3.62 (br s, 2H, 2 OH), 3.55 (t, 4H, $J$ = 5.6 Hz, 2 C$H_2$−OH), 3.20 (d, 2H, $J$ = 6.4 Hz, CH$_2$−N), 2.63 (t, 4H, $J$ = 5.6 Hz, 2 N−CH$_2$). $^{13}$C NMR (100.5 MHz, CD$_3$COCD$_3$): $\delta$ = 137.04 (CH$_2$=$C$H), 117.26 ($C$H$_2$=CH), 60.27 (2 CH$_2$−OH), 58.59 (CH$_2$−N), 57.06 (2 N−CH$_2$) ppm. MS (EI, 70 eV): $m/z$ (%) = 145 (4) [M]$^+$, 114 (100) [M − CH$_2$OH]$^+$. Anal. Calcd (%) for C$_7$H$_{15}$NO$_2$ (145.20): C 57.90, H 10.41, N 9.65. Found: C 54.41, H 9.11, N 9.83.

**H$_2$L$^3$ (4n).** Yield: 7.16 g (95%) colorless oil. IR (neat): $\tilde{\nu}$ = 3356, 2961, 2875, 1364, 1038 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.32 (d, 2H, $J$ = 8.3 Hz, 2 Ar−H), 7.21 (d, 2H, $J$ = 8.8 Hz, 2 Ar−H), 3.65 (s, 2H, CH$_2$−N), 3.60 (t, 4H, $J$ = 5.5 Hz, 2 C$H_2$−OH), 2.78 (br s, 2H, 2 OH), 2.69 (t, 4H, $J$ = 5.5 Hz, 2 N−CH$_2$), 1.29 (s, 9H, 3 CH$_3$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 150.15, 135.49 (2 Ar−C), 128.56, 125.32 (4 Ar−CH), 59.56 (2 CH$_2$−OH), 58.78 (CH$_2$−N), 55.64 (2 N−CH$_2$), 34.42 ($t$Bu-$C_q$), 31.33 ppm (3 CH$_3$). FAB-MS (3-NBA): $m/z$ (%) = 252 (75) [M]$^+$, 220 (45) [M − CH$_2$OH]$^+$, 147 (100) [M − N(CH$_2$CH$_2$OH)$_2$]$^+$. Anal. Calcd (%) for C$_{15}$H$_{25}$NO$_2$ (251.37): C 71.67, H 10.03, N 5.57. Found: C 70.28, H 10.15, N 5.20.

**H$_2$L$^3$ (4o).** Yield: 5.70 g (81%) thick pink oil. IR (neat): $\tilde{\nu}$ = 3422, 2964, 2797, 1610, 1045 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 4.62 (t, 1H, $J$ = 5.4 Hz, CH−O), 3.98 (m, 2H, C$H_2$−CH−O), 3.46 (t, 4H, $J$ = 5.4 Hz, 2 CH$_2$−O), 3.30 (t, 4H, $J$ = 5.4 Hz, 2 C$H_2$−OH), 3.22 (br s, 2H, 2 OH), 2.61 (t, 2H, $J$ = 5.4 Hz, CH$_2$−N), 2.58 (t, 4H, $J$ = 5.4 Hz, 2 N−CH$_2$), 1.59 (m, 2H, C$H_2$−CH$_2$−O) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$): $\delta$ = 101.35 (CH−O), 67.21 (2 CH$_2$−O), 60.48 (2 CH$_2$−OH), 55.84 (2 N−CH$_2$), 48.44 (CH$_2$−N), 32.32 ($C$H$_2$−CH−O), 25.44 ($C$H$_2$−CH$_2$−O) ppm. MS (EI, 70 eV): $m/z$ (%) = 219 (5) [M]$^+$, 188 (10) [M − CH$_2$OH]$^+$, 130 (10) [M − NCH$_2$CH$_2$OH]$^+$, 83 (100) [M − CH$_2$ − N(CH$_2$-CH$_2$OH)$_2$]$^+$. Anal. Calcd (%) for C$_{10}$H$_{21}$NO$_4$ (219.29): C 54.77, H 9.65, N 6.39. Found: C 53.96, H 9.41, N 6.28.

**H$_2$L$^3$ (4p).** Yield: 3.20 g (57%) yellow oil. IR (neat): $\tilde{\nu}$ = 3354, 3079, 2946, 2881, 2827, 1639, 1047, 910 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.80 (m, 1H, CH$_2$=C$H$), 5.10 (m, 2H, C$H_2$=CH), 3.61 (t, 4H, $J$ = 5.6 Hz, 2 C$H_2$−OH), 3.25 (br s, 2H, 2 OH), 2.65 (t, 4H, $J$ = 5.6 Hz, 2 N−CH$_2$), 2.64 (t, 2H, $J$ = 7.1 Hz, CH$_2$−N), 2.30 (m, 6H, 3 CH$_2$) ppm. $^{13}$C NMR (100.5 MHz, CDCl$_3$):

$\delta$ = 136.40 ($CH_2{=}CH$), 116.12 ($CH_2{=}CH$), 69.42 (2 $CH_2{-}OH$), 55.85 ($CH_2{-}N$), 53.65 (2 $N{-}CH_2$), 32.12, 31.68, 31.44 (3 $CH_2$) ppm. MS (EI, 70 eV): *m/z* (%) = 187 (8) $[M]^+$, 156 (100) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{10}H_{21}NO_2$ (187.28): C 64.13, H 11.30, N 7.48. Found: C 63.74, H 11.28, N 7.32.

**$H_2L^3$ (4q).** Yield: 2.73 g (48%) colorless oil. IR (neat): $\tilde{\nu}$ = 3346, 2929, 2858, 1466, 1047 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.61 (t, 4H, $J$ = 5.4 Hz, 2 $CH_2{-}OH$), 3.18 (br s, 2H, 2 OH), 2.65 (t, 4H, $J$ = 5.4 Hz, 2 $N{-}CH_2$), 2.52 (t, 2H, $J$ = 7.6 Hz, $CH_2{-}N$), 1.44 (m, 2H, $CH_2{-}CH_3$), 1.28 (m, 6H, 3 $CH_2$) 0.89 (t, 3H, $J$ = 7.1 Hz, $CH_3$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 59.63 (2 $CH_2{-}OH$), 56.06 ($CH_2{-}N$), 54.80 (2 $N{-}CH_2$), 31.71, 27.00, 26.96, 22.59 (4 $CH_2$), 13.99 ($CH_3$) ppm. MS (EI, 70 eV): *m/z* (%) = 189 (6) $[M]^+$, 158 (100) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{10}H_{23}NO_2$ (189.31): C 63.45, H 12.25, N 7.40. Found: C 60.77, H 11.99, N 6.91.

**$H_2L^3$ (4r).** Yield: 2.93 g (45%) colorless oil. IR (neat): $\tilde{\nu}$ = 3355, 2925, 2855, 1465, 1043 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.61 (t, 4H, $J$ = 5.4 Hz, 2 $CH_2{-}OH$), 3.15 (br s, 2H, 2 OH), 2.65 (t, 4H, $J$ = 5.4 Hz, 2 $N{-}CH_2$), 2.53 (t, 2H, $J$ = 7.6 Hz, $CH_2{-}N$), 1.46 (m, 2H, $CH_2{-}CH_3$), 1.27 (m, 10H, 5 $CH_2$), 0.88 (t, 3H, $J$ = 6.6 Hz, $CH_3$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 59.63 (2 $CH_2{-}OH$), 56.13 ($CH_2{-}N$), 54.86 (2 $N{-}CH_2$), 31.86, 29.54, 29.31, 27.42, 26.97, 22.66 (6 $CH_2$), 14.10 ($CH_3$) ppm. MS (EI, 70 eV): *m/z* (%) = 217 (4) $[M]^+$, 186 (100) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{12}H_{27}NO_2$ (217.35): C 66.31, H 12.52, N 6.44. Found: C 65.95, H 12.74, N 6.41.

**$H_2L^3$ (4s).** Yield: 3.90 g (73%) yellow oil. IR (neat): $\tilde{\nu}$ = 3370, 2980, 2881, 1466, 1068, 766 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.62 (t, 4H, $J$ = 5.4 Hz, 2 $CH_2{-}OH$), 3.21 (br s, 2H, 2 OH), 2.72 (t, 4H, $J$ = 5.4 Hz, 2 $N{-}CH_2$), 1.64 (m, 18H, 9 $CH_2$), 0.96 (t, 3H, $CH_3$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 61.42 (2 $CH_2{-}OH$), 55.95 (2 $N{-}CH_2$), 55.85 ($CH_2{-}N$), 33.24, 32.19, 31.89, 28.74, 28.15, 27.36, 26.93, 26.17, 22.66 (9 $CH_2$), 19.33 ($CH_3$) ppm. MS (EI, 70 eV): *m/z* (%) = 245 (10) $[M]^+$, 214 (100) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{14}H_{31}NO_2$ (245.41): C 68.52, H 12.73, N 5.71. Found: C 67.16, H 12.96, N 5.49.

**$H_2L^3$ (4t).** Same as **4s**.

**$H_2L^3$ (4u).** Yield: 2.55 g (48%) colorless oil. IR (neat): $\tilde{\nu}$ = 3373, 2949, 2869, 1447, 1114 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.57 (br s, 2H, 2 OH), 3.52 (t, 4H, $J$ = 5.4 Hz, 2 $CH_2{-}OH$), 3.47 (m, 4H, 2 $CH_2{-}O$), 2.75 (t, 2H, $J$ = 5.9 Hz, $CH_2{-}N$), 2.69 (t, 4H, $J$ = 5.4 Hz, 2 $N{-}CH_2$), 1.13 (t, 3H, $J$ = 7.0 Hz, $CH_3$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 69.88, 66.65 (2 $CH_2{-}O$), 60.48 (2 $CH_2{-}OH$), 58.06 (2 $N{-}CH_2$), 53.82 ($CH_2{-}N$), 15.68 ($CH_3$) ppm. MS (EI, 70 eV): *m/z* (%) = 177 (6) $[M]^+$, 146 (61) $[M - CH_2OH]^+$, 118 (100) $[M - CH_2OH, - CH_2OC_2H_5]^+$. Anal. Calcd (%) for $C_8H_{19}NO_2$ (177.24): C 54.21, H 10.81, N 7.90. Found: C 53.27, H 10.96, N 7.96.

**$H_2L^3$ (4v).** Same as **4d**.

**$H_2L^3$ (4w).** Yield: 8.62 g (90%) pale red oil. IR (neat): $\tilde{\nu}$ = 3371, 2942, 2875, 1047, 757, 692 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.28−8.26 (m, 1H, Naph-H), 7.78−7.76 (m, 1H, Naph-H), 7.47−7.32 (m, 4H, 4 Naph-H), 6.81−6.79 (m, 1H, Naph-H), 4.28 (t, 2H, $J$ = 4.8 Hz, $CH_2{-}O$), 3.95 (t, 2H, $J$ = 4.8 Hz, $CH_2{-}O$), 3.67 (t, 2H, $J$ = 5.2 Hz, $CH_2{-}O$), 3.56 (t, 4H, $J$ = 5.2 Hz, 2 $CH_2{-}OH$), 2.79 (t, 2H, $J$ = 5.2 Hz, $CH_2{-}N$), 2.70 (t, 4H, $J$ = 5.2 Hz, 2 $N{-}CH_2$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 154.41, 134.49, 127.39, 126.38, 125.75, 125.64, 125.20, 122.01, 120.58, 104.99 (3 Naph-C, 7 Naph-CH), 70.10, 69.61, 67.67 (3 $CH_2{-}O$), 59.78 (2 $CH_2{-}OH$), 56.95 (2 $N{-}CH_2$), 53.92 ($CH_2{-}N$) ppm. FAB-MS (3-NBA): *m/z* (%) = 320 (100) $[M]^+$, 288 (80) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{18}H_{25}NO_4$ (319.40): C 67.69, H 7.89, N 4.39. Found: C 64.67, H 7.72, N 4.08.

**$H_2L^3$ (4x).** Yield: 9.20 g (83%) pale red oil. IR (neat): $\tilde{\nu}$ = 3386, 2942, 2875, 1047, 757, 692 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.52−7.46 (m, 3H, 3 Ar−H), 7.34−7.25 (m, 4H, 4 Ar−H), 6.95−6.89 (m, 2H, 2 Ar−H), 4.21 (t, 2H, $J$ = 4.7 Hz, $CH_2{-}O$), 3.90 (t, 2H, $J$ = 4.7 Hz, $CH_2{-}O$), 3.72 (t, 2H, $J$ = 5.2 Hz, $CH_2{-}O$), 3.52 (t, 4H, $J$ = 5.2 Hz, 2 $CH_2{-}OH$), 2.72 (t, 2H, $J$ = 5.2 Hz, $CH_2{-}N$), 2.65 (t, 4H, $J$ = 5.2 Hz, 2 $N{-}CH_2$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ = 159.23 (Ar−C), 133.42, 131.48, 129.74, 128.28, 128.10 (5 Ar−CH), 123.66 (Ar−C), 121.01 (Ar−CH), 113.09 (Ar−C), 112.60 (Ar−CH), 93.35, 85.91 (2 C≡), 70.43, 69.52, 68.85 (3 $CH_2{-}O$), 59.77 (2 $CH_2{-}OH$), 56.85 (2 $N{-}CH_2$), 53.94 ($CH_2{-}N$) ppm. FAB-MS (3-NBA): *m/z* (%) = 370 (100) $[M]^+$, 338 (40) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{22}H_{27}NO_4$ (369.45): C 71.52, H 7.37, N 3.79. Found: C 69.40, H 7.30, N 3.32.

**$H_2L^3$ (4y).** Yield: 7.38 g (80%) pale yellow oil. IR (neat): $\tilde{\nu}$ = 3371, 2946, 2874, 1053, 995 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 6.48−6.47 (m, 2H, 2 Ar−H), 6.37−6.36 (m, 1H, 1 Ar−H), 6.05−5.96 (m, 2H, 2 $CH{=}CH_2$), 5.37 (dd, 2H, $J$ = 17.0 Hz, 1.6 Hz; 2 $CH{=}CH_2$ cis), 5.25 (d, 2H, $J$ = 9.9 Hz, 2 $CH{=}CH_2$ trans), 4.47 (d, 4H, $J$ = 5.5 Hz, 2 $O{-}CH_2$), 3.59 (s, 2H, $CH_2{-}N$), 3.58 (t, 4H, $J$ = 5.2 Hz, 2 $CH_2{-}OH$), 2.67 (t, 4H, $J$ = 5.2 Hz, 2 $N{-}CH_2$) ppm. $^{13}C$ NMR (100.5 MHz, $CDCl_3$): $\delta$ =159.71 (2 Ar−C), 141.27 (Ar−C), 133.13 (2 $CH{=}CH_2$), 117.70 (2 $CH{=}CH_2$), 107.62 (2 Ar−CH), 100.42 (Ar−CH), 68.77 ($O{-}CH_2$), 59.59 (2 $CH_2{-}OH$), 59.36 ($CH_2{-}N$), 55.87 (2 $N{-}CH_2$) ppm. FAB-MS (3-NBA): *m/z* (%) = 308 (100) $[M]^+$, 276 (80) $[M - CH_2OH]^+$. Anal. Calcd (%) for $C_{17}H_{25}NO_4$ (307.38): C 66.43, H 8.20, N 4.56. Found: C 63.44, H 8.17, N 4.20.

**General Method for $[Fe_6Cl_6(L^3)_6]$ (5a−c,e,g−j,l,m,p−s,u−y).** To a suspension of calcium hydride (189 mg, 4.5 mmol) in anhydrous THF (75 mL) was added $H_2L^3$ (**4a−y**) (3.0 mmol). After the suspension was stirred for 1 h at 20 °C, a solution of iron(III) chloride (487 mg, 3.0 mmol) in anhydrous THF (25 mL) was added. The reaction mixture was stirred at 20 °C for 72 h, and then, the solvent was removed under vacuum. The precipitate was dissolved in $CH_2Cl_2$ (50 mL), and the remaining residue was filtered off. After evaporation of the solvent, a yellow powder was obtained.

**General Method for $[Fe_6(SCN)_6(L^3)_6]$ (5d,f,k,n,o,t).** In order to prepare the rhodanide complexes, 3.0 mmol of the corresponding chloride complexes $[Fe_6Cl_6(L^3)_6]$, vide supra, were dissolved in $CHCl_3$ (50 mL), and a solution of KSCN (1.46 g, 15 mmol) in anhydrous MeOH (50 mL) was added. The reaction mixture was refluxed for 1 h (in the case of **5n**, the suspension was stirred at 20 °C for 24 h), and then, the solvent was removed under vacuum. The precipitate was dissolved in $CH_2Cl_2$ (50 mL), and the remaining residue was filtered off. After evaporation of the solvent, a red powder was obtained.

**$[Fe_6Cl_6(L^3)_6]$ (5a).** Educt: **4a** (754 mg). Yield: 296 mg (29%) yellow rhombic crystals from chloroform/*n*-pentane. Mp 99 °C.[21] IR (KBr): $\tilde{\nu}$ = 2869, 1460, 1089 $cm^{-1}$. FAB-MS (3-NBA): *m/z* (%) = 2043 (1) $[Fe_6Cl_6(L^3)_6]^+$, 2007 (10) $[Fe_6Cl_5(L^3)_6]^+$, 1325 (20) $[Fe_4Cl_3(L^3)_4]^+$, 701 (80) $[Fe_3Cl(L^3)_2]^+$, 645 (100) $[Fe_2Cl(L^3)_2]^+$. Anal. Calcd (%) for $C_{66}H_{138}Cl_6Fe_6N_6O_{30}$ (2043.61): C 38.79, H 6.82, N 3.68. Found: C 37.38, H 7.24, N 3.68.

**$[Fe_6Cl_6(L^3)_6]$ (5b).** Educt: **4b** (484 mg). Yield: 188 mg (25%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2958, 2929, 2865, 1457, 1089 $cm^{-1}$. FAB-

---

(21) The low melting points of **5a**,**k**,**v**,**x** (99, 117, 118, 100 °C) are noteworthy.

MS (3-NBA): $m/z$ (%) = 1502 (52) $[Fe_6Cl_6(L^3)_6]^+$, 1469 (100) $[Fe_6Cl_5(L^3)_6]^+$, 1399 (88) $[Fe_6Cl_3(L^3)_6]^+$. Anal. Calcd (%) for $C_{48}H_{102}Cl_6Fe_6N_6O_{12}$ (1503.17): C 38.35, H 6.84, N 5.59. Found: C 34.88, H 6.10, N 4.65.

**$[Fe_6Cl_6(L^3)_6]$ (5c).** Educt: **4c** (400 mg). Yield: 167 mg (25%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2970, 2934, 2903, 2858, 1473, 1447, 1077 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1334 (11) $[Fe_6Cl_6(L^3)_6]^+$, 1299 (15) $[Fe_6Cl_5(L^3)_6]^+$, 759 (100) $[Fe_4Cl_4(L^3)_3]^+$. Anal. Calcd (%) for $C_{36}H_{78}Cl_6Fe_6N_6O_{12}$ (1334.36): C 32.39, H 5.89, N 6.30. Found: C 29.47, H 5.36, N 5.30.

**$[Fe_6(SCN)_6(L^3)_6]$ (5d).** Educt: **4d** (940 mg). Yield: 434 mg (34%) brown rhombic crystals from dichlorometane/*n*-pentane. Mp >165 °C (dec). IR (KBr): $\tilde{\nu}$ = 2915, 2876, 2050, 1249, 1080 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2492 (5) $[Fe_6(SCN)_5(L^3)_6]^+$, 1642 (10) $[Fe_4(SCN)_3(L^3)_4]^+$, 1159 (15) $[Fe_3(SCN)(L^3)_3]^+$, 849 (50) $[Fe_5(SCN)(L^3)_3]^+$, 792 (50) $[Fe_4(SCN)(L^3)_3]^+$, 734 (100) $[Fe_2(L^3)_2]^+$. Anal. Calcd (%) for $C_{102}H_{150}Fe_6N_{12}O_{30}S_6$ (2551.80): C 48.00, H 5.93, N 6.59. Found: C 47.24, H 5.73, N 6.45.

**$[Fe_6Cl_6(L^3)_6]$ (5e).** Educt: **4e** (796 mg). Yield: 223 mg (21%) light yellow crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2974, 2904, 2868, 1458, 1441, 1142, 1089 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2127 (15) $[Fe_6Cl_6(L^3)_6]^+$, 2091 (100) $[Fe_6Cl_5(L^3)_6]^+$, 1863 (45) $[Fe_6Cl_6(L^3)_5]^+$. Anal. Calcd (%) for $C_{72}H_{150}Cl_6Fe_6N_6O_{30}$ (2127.80): C 40.64, H 7.11, N 3.95. Found: C 39.22, H 7.20, N 3.51.

**$[Fe_6(SCN)_6(L^3)_6]$ (5f).** Educt: **4f** (676 mg). Yield: 233 mg (23%) brown rhombic crystals from dichloromethane/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2922, 2871, 2040, 1240, 1081 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1045 (100) $[Fe_5Cl_3(L^3)_3]^+$. Anal. Calcd (%) for $C_{78}H_{102}Fe_6N_{12}O_{18}S_6$ (2023.18): C 46.31, H 5.08, N 8.31. Found: C 45.19, H 5.22, N 8.37.

**$[Fe_6Cl_6(L^3)_6]$ (5g).** Educt: **4g** (736 mg). Yield: 412 g (41%) yellow hexagonal crystals from chloroform/diethyl ether. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3024, 2866, 2250, 1081, 756 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2007 (55) $[Fe_6Cl_6(L^3)_6]^+$, 1972 (90) $[Fe_6Cl_5(L^3)_6]^+$, 1303 (25) $[Fe_4Cl_3(L^3)_4]^+$. Anal. Calcd (%) for $C_{90}H_{102}Cl_6Fe_6N_6O_{12}$ (2007.67): C 53.84, H 5.12, N 4.19. Found: C 53.63, H 5.19, N 4.26.

**$[Fe_6Cl_6(L^3)_6]$ (5h).** Educt: **4h** (736 mg). Yield: 446 mg (39%) yellow crystals from chloroform/diethyl ether. Mp >240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3021, 2863, 2256, 1083, 758 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2008 (25) $[Fe_6Cl_6(L^3)_6]^+$, 1971 (40) $[Fe_6Cl_5(L^3)_6]^+$, 1303 (100) $[Fe_4Cl_3(L^3)_4]^+$. Anal. Calcd (%) for $C_{90}H_{102}Cl_6Fe_6N_6O_{12}$ (2007.67): C 53.84, H 5.12, N 4.19. Found: C 53.45, H 5.09, N 4.19.

**$[Fe_6Cl_6(L^3)_6]$ (5i).** Educt: **4i** (973 mg). Yield: 760 mg (41%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >200 °C (dec). IR (KBr): $\tilde{\nu}$ = 3443, 2906, 2865, 1493, 1086, 754, 698 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2483 (15) $[Fe_6Cl_6(L^3)_6]^+$, 2444 (20) $[Fe_6Cl_5(L^3)_6]^+$, 2160 (100) $[Fe_6Cl_6(L^3)_5]^+$, 1619 (40) $[Fe_4Cl_3(L^3)_4]^+$. Anal. Calcd (%) for $C_{120}H_{132}Cl_6Fe_6N_6O_{12}$ (2482.30): C 58.06, H 5.36, N 6.77. Found: C 58.33, H 5.28, N 6.89.

**$[Fe_6Cl_6(L^3)_6]$ (5j).** Educt: **4j** (664 mg). Yield: 205 mg (22%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2974, 2905, 2867, 1458, 1440, 1143, 1088 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1863 (12) $[Fe_6Cl_6(L^3)_6]^+$, 1827 (100) $[Fe_6Cl_5(L^3)_6]^+$, 1792 (6) $[Fe_6Cl_4(L^3)_6]^+$. Anal. Calcd (%) for $C_{60}H_{138}Cl_6Fe_6N_6O_{24}$ (1863.49): C 38.67, H 6.49, N 5.24. Found: C 46.20, H 8.42, N 5.24.

**$[Fe_6(SCN)_6(L^3)_6]$ (5k).** Educt: **4k** (808 mg). Yield: 332 mg (29%) brown rhombic crystals from dichloromethane/*n*-pentane. Mp 117 °C.[21] IR (KBr): $\tilde{\nu}$ = 2930, 2870, 2046, 1248, 1082 cm$^{-1}$; FAB-MS (3-NBA): $m/z$ (%) = 1467 (20) $[Fe_4(SCN)_3(L^3)_4]^+$, 1408 (35) $[Fe_4(SCN)_2(L^3)_4]^+$, 1027 (100) $[Fe_4(SCN)(L^3)_3]^+$; elemental analysis calcd (%) for $C_{90}H_{126}Fe_6N_{12}O_{24}S_6$ (2287.50): C 47.25, H 5.56, N 7.35; found: C 47.23, H 5.74, N 6.91.

**$[Fe_6Cl_6(L^3)_6]$ (5l).** Educt: **4l** (586 mg). Yield: 324 mg (38%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3062, 3030, 2909, 2865, 1496 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1707 (10) $[Fe_6Cl_6(L^3)_6]^+$, 1671 (25) $[Fe_6Cl_5(L^3)_6]^+$, 1513 (15) $[Fe_6Cl_6(L^3)_5]^+$, 1229 (15) $[Fe_5Cl_5(L^3)_4]^+$, 1101 (100) $[Fe_4Cl_3(L^3)_4]^+$, 1066 (40) $[Fe_4Cl_2(L^3)_4]^+$, 945 (70) $[Fe_4Cl_4(L^3)_3]^+$, 873 (35) $[Fe_4Cl_2(L^3)_3]^+$, 838 (25) $[Fe_4Cl(L^3)_3]^+$, 817 (95) $[Fe_3Cl_2(L^3)_3]^+$, 782 (100) $[Fe_3Cl(L^3)_3]^+$, 749 (75) $[Fe_3(L^3)_3]^+$. Anal. Calcd (%) for $C_{66}H_{90}Cl_6Fe_6N_6O_{12}$ (1707.24): C 46.43, H 5.31, N 4.92. Found: C 46.11, H 5.25, N 4.70.

**$[Fe_6Cl_6(L^3)_6]$ (5m).** Educt: **4m** (436 mg). Yield: 197 mg (28%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3074, 3000, 2907, 2865, 1638, 1085, 929 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1406 (100) $[Fe_6Cl_6(L^3)_6]^+$. Anal. Calcd (%) for $C_{42}H_{78}Cl_6Fe_6N_6O_{12}$ (1406.92): C 35.86, H 5.59, N 5.97. Found: C 32.45, H 4.93, N 4.81.

**$[Fe_6(SCN)_6(L^3)_6]$ (5n).** Educt: **4n** (754 mg). Yield: 606 mg (55%) red rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2963, 2928, 2869, 2032, 1460, 1264, 1081 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2179 (1) $[Fe_6(SCN)_6(L^3)_6]^+$, 2121 (4) $[Fe_6(SCN)_5(L^3)_6]^+$, 1336 (35) $[Fe_4(SCN)_2(L^3)_4]^+$, 1087 (30) $[Fe_4(SCN)_2(L^3)_3]^+$, 973 (52) $[Fe_3(SCN)(L^3)_3]^+$, 724 (100) $[Fe_3(SCN)(L^3)_2]^+$. Anal. Calcd (%) for $C_{96}H_{138}Fe_6N_{12}O_{24}S_6$ (2179.73): C 52.90, H 6.38, N 7.71. Found: C 52.59, H 6.21, N 7.56.

**$[Fe_6(SCN)_6(L^3)_6]$ (5o).** Educt: **4o** (658 mg). Yield: 210 mg (35%) pink crystals from chloroform/*n*-pentane. Mp >240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3490, 2864, 2250, 2190, 1250, 1088 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1987 (10) $[Fe_6(SCN)_6(L^3)_6]^+$, 1928 (100) $[Fe_6(SCN)_5(L^3)_6]^+$, 1266 (100) $[Fe_4(SCN)_3(L^3)_4]^+$. Anal. Calcd (%) for $C_{66}H_{114}Fe_6N_{12}O_{24}S_6$ (1987.22): C 39.89, H 5.78, N 8.46. Found: C 39.58, H 5.82, N 7.58.

**$[Fe_6Cl_6(L^3)_6]$ (5p).** Educt: **4p** (562 mg). Yield: 66 mg (8%) light green rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3098, 3072, 2909, 2870, 1638, 1081, 925 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1659 (100) $[Fe_6Cl_6(L^3)_6]^+$. Anal. calcd (%) for $C_{60}H_{114}Cl_6Fe_6N_6O_{12}$ (1659.40): C 43.43, H 6.92, N 5.06. Found: C 42.34, H 7.05, N 4.87.

**$[Fe_6Cl_6(L^3)_6]$ (5q).** Educt: **4q** (568 mg). Yield: 176 mg (21%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2956, 2927, 2859, 1458, 1089 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1671 (29) $[Fe_6Cl_6(L^3)_6]^+$, 1636 (94) $[Fe_6Cl_5(L^3)_6]^+$, 1483 (100) $[Fe_6Cl_6(L^3)_5]^+$. Anal. Calcd (%) for $C_{60}H_{126}Cl_6Fe_6N_6O_{12}$ (1671.50): C 43.12, H 7.60, N 5.03. Found: C 43.46, H 7.66, N 5.06.

**$[Fe_6Cl_6(L^3)_6]$ (5r).** Educt: **4r** (652 mg). Yield: 166 mg (18%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 3005, 2924, 2855, 1468, 1089 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 1837 (64) $[Fe_6Cl_6(L^3)_6]^+$, 1802 (100) $[Fe_6Cl_5(L^3)_6]^+$. Anal. Calcd (%) for $C_{72}H_{150}Cl_6Fe_6N_6O_{12}$ (1839.82): C 47.00, H 8.22, N 4.57. Found: C 45.71, H 8.12, N 4.37.

**$[Fe_6Cl_6(L^3)_6]$ (5s).** Educt: **4s** (736 mg). Yield: 440 mg (36%) yellow crystals from dichloromethane/*n*-pentane. Mp >240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3354, 2926, 2854, 1469, 1082 cm$^{-1}$. FAB-MS (3-NBA): $m/z$ (%) = 2091 (50) $[Fe_6Cl_6(L^3)_6]^+$, 2055 (85) $[Fe_6Cl_5(L^3)_6]^+$, 1833 (80) $[Fe_6Cl_6(L^3)_5]^+$, 1485 (100) $[Fe_3Cl_3(L^3)_4]^+$. Anal. Calcd (%) for $C_{84}H_{174}Cl_6Fe_6N_6O_{12}$ (2008.18): C 50.24, H 8.73, N 4.19. Found: C 51.59, H 8.88, N 4.16.

**[$Fe_6(SCN)_6(L^3)_6$] (5t).** Educt: **4t** (736 mg). Yield: 160 mg (30%) pink crystals from dichloromethane/*n*-pentane. Mp >240 °C (dec). IR (KBr): $\tilde{\nu}$ = 3440, 2925, 2855, 2247, 1084, 609 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 2141 (10) [$Fe_6(SCN)_6(L^3)_6$]$^+$, 2085 (55) [$Fe_6(SCN)_5(L^3)_6$]$^+$, 1427 (80) [$Fe_4(SCN)_4(L^3)_4$]$^+$, 1370 (65) [$Fe_4(SCN)_3(L^3)_4$]$^+$, 1312 (70) [$Fe_4(SCN)_2(L^3)_4$]$^+$. Anal. Calcd (%) for $C_{90}H_{174}Fe_6N_{12}O_{12}S_6$ (2143.60): C 50.43, H 8.18, N 7.84, S 8.96. Found: C 50.68, H 8.19, N 7.93, S 9.04.

**[$Fe_6Cl_6(L^3)_6$] (5u).** Educt: **4u** (532 mg). Yield: 144 mg (18%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >220 °C (dec). IR (KBr): $\tilde{\nu}$ = 2971, 2928, 2904, 2865, 1485, 1442, 1104, 1087 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 1599 (26) [$Fe_6Cl_6(L^3)_6$]$^+$, 1563 (100) [$Fe_6Cl_5(L^3)_6$]$^+$, 1422 (24) [$Fe_6Cl_6(L^3)_5$]$^+$. Anal. Calcd (%) for $C_{48}H_{102}Cl_6Fe_6N_6O_{12}$ (1599.55): C 36.04, H 7.18, N 5.25. Found: C 32.60, H 5.86, N 4.42.

**[$Fe_6Cl_6(L^3)_6$] (5v).** Educt: **4v** (940 mg). Yield: 519 mg (43%) yellow rhombic crystals from chloroform/diethyl ether. Mp 118 °C.[21] IR (KBr): $\tilde{\nu}$ = 2910, 2870, 1598, 1493, 1248, 1087 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 2416 (1) [$Fe_6Cl_6(L^3)_6$]$^+$, 2379 (5) [$Fe_6Cl_5(L^3)_6$]$^+$, 1575 (10) [$Fe_4Cl_3(L^3)_4$]$^+$, 825 (45) [$Fe_3Cl(L^3)_2$]$^+$, 769 (100) [$Fe_2Cl(L^3)_2$]$^+$. Anal. Calcd (%) for $C_{96}H_{150}Cl_6Fe_6N_6O_{30}$ (2416.02): C 47.72, H 6.62, N 3.48. Found: C 47.34, H 6.49, N 3.48.

**[$Fe_6Cl_6(L^3)_6$] (5w).** Educt: **4w** (958 mg). Yield: 1.02 g (80%) yellow rhombic crystals from chloroform/*n*-pentane. Mp >195 °C (dec). IR (KBr): $\tilde{\nu}$ = 2932, 2863, 1102, 1088 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 1266 (100) [$Fe_3Cl_3(L^3)_3$]$^+$. Anal. Calcd (%) for $C_{108}H_{138}Cl_6Fe_6N_6O_{24}$ (2452.04): C 52.90, H 5.67, N 3.43. Found: C 51.72, H 5.20, N 3.18.

**[$Fe_6Cl_6(L^3)_6$] (5x).** Educt: **4x** (1.11 g). Yield: 317 mg (23%) yellow rhombic crystals from dichloromethane/diethyl ether. Mp 100 °C.[21] IR (KBr): $\tilde{\nu}$ = 2914, 2867, 1088 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 2717 (2) [$Fe_6Cl_5(L^3)_6$]$^+$, 1800 (5) [$Fe_4Cl_3(L^3)_4$]$^+$, 1467 (5) [$Fe_4Cl_4(L^3)_3$]$^+$, 1339 (5) [$Fe_3Cl_2(L^3)_3$]$^+$, 972 (15) [$Fe_3Cl(L^3)_2$]$^+$, 937 (40) [$Fe_3(L^3)_2$]$^+$, 881 (100) [$Fe_2(L^3)_2$]$^+$. Anal. Calcd (%) for $C_{132}H_{150}Cl_6Fe_6N_6O_{24}$ (2752.42): C 57.60, H 5.49, N 3.05. Found: C 57.21, H 5.51, N 3.05.

**[$Fe_6Cl_6(L^3)_6$] (5y).** Educt: **4y** (922 mg). Yield 619 mg (52%) yellow rhombic crystals from dichloromethane/*n*-pentane. Mp >255 °C (dec). IR (KBr): $\tilde{\nu}$ = 2910, 2865, 1596, 1167, 1086 cm$^{-1}$. FAB-MS (3-NBA): *m*/*z* (%) = 2380 (3) [$Fe_6Cl_6(L^3)_6$]$^+$, 2343 (3) [$Fe_6Cl_5(L^3)_6$]$^+$, 2073 (3) [$Fe_6Cl_6(L^3)_5$]$^+$, 1551 (35) [$Fe_4Cl_3(L^3)_4$]$^+$, 1281 (30) [$Fe_4Cl_4(L^3)_3$]$^+$, 1154 (55) [$Fe_3Cl_2(L^3)_3$]$^+$, 1118 (55) [$Fe_3Cl(L^3)_3$]$^+$, 848 (60) [$Fe_3Cl_2(L^3)_3$]$^+$, 813 (90) [$Fe_3Cl(L^3)_3$]$^+$, 757 (100) [$Fe_2Cl(L^3)_2$]$^+$, 722 (60) [$Fe_2(L^3)_2$]$^+$. Anal. Calcd (%) for $C_{102}H_{138}Cl_6Fe_6N_6O_{24}$ (2380.00): C 51.47, H 5.84, N 3.53. Found: C 49.75, H 5.67, N 3.33.

**Single-Crystal X-ray Structure Analyses.** Final crystallographic data and *R*1 and *wR*2 values are listed in Table 1. X-ray data for all complexes were collected at low temperatures with a Nonius KappaCCD area detector, a Siemens-P4 diffractometer, or a Nonius MACH3 diffractometer using graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). The structures were solved by direct methods using SHELXS-86 or SHELXS-97, and the structure refinements were carried out using full-matrix least-squares (SHELXL-93, SHELXL-97, or SHELXTL NT 5.10[13,14]). All non-hydrogen atoms were refined anisotropically.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft (Sa 276/25-1, SFB 583, GK 312, SPP 1137), the Bayerisches Langzeitprogrammm *Neue Werkstoffe*, and the Fonds der Chemischen Industrie. T.N. thanks the Alexander von Humboldt-Stiftung for a postdoctoral fellowship. The generous allocation of X-ray facilities by Professor D. Sellmann, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, is also gratefully acknowledged.

**Supporting Information Available:** X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049799W