[1] C. O. Pabo, R. T. Sauer, *Annu. Rev. Biochem.* **1992**, *61*, 1053–1095; D. Rhodes, J. W. R. Schwabe, L. Chapman, L. Fairall, *Phil. Trans. R. Soc. London B* **1996**, *351*, 501–509.
[2] P. E. Nielsen, *Chem. Eur. J.* **1997**, *3*, 505–508; H. E. Moser, P. B. Dervan, *Science* **1987**, *238*, 645–650; J. W. Trauger, E. E. Baird, P. B. Dervan, *Nature* **1986**, *382*, 559–561.
[3] S. Neidel, *Anti-Cancer Drug Des.* **1997**, *12*, 433–442; C. Giovannangeli, C. Hélène, *Antisense Nucleic Acid Drug Dev.* **1997**, *7*, 413–421; L. J. Maher, *Cancer Invest.* **1996**, *14*, 66–82.
[4] C. Escudé, J.-C. François, J.-S. Sun, G. Ott, M. Sprinzl, T. Garestier, C. Hélène, *Nucleic Acids Res.* **1993**, *21*, 5547–5553.
[5] W. T. Markiewicz, *J. Chem. Res. Synop.* **1979**, 24–25; M. Krecmerova, H. Hrebacebecky, A. Holly, *Collect. Czech. Chem. Commun.* **1990,** *55*, 2521–2536.
[6] The difference in melting temperature between the fully matched triplex and a complex containing one G:C mismatch in the double stranded DNA ds(GCTAA***G***AAGAGAGAGAGATCG) indicates a decrease of 9.9 °C for the 2′-aminoethoxy-modified oligonucleotide and a decrease of 2.4 °C for the unmodified DNA oligonucleotide control.
[7] C. J. Guinosso, G. D. Hoke, S. Frier, J. F. Martin, D. J. Ecker, C. K. Mirabelli, S. T. Crooke, P. D. Cook, *Nucl. Nucleotides* **1991**, *10*, 259–262.
[8] P. Martin, *Helv. Chim. Acta* **1995**, *78*, 486–504.
[9] A. Szabo, L. Stolz, R. Granzow, *Curr. Opin. Struct. Biol.* **1995**, *5*, 699–705.
[10] M. Rougée, B. Faucon, J.-L. Mergny, F. Barcelo, C. Giovannangeli, T. Garestier, C. Hélène, *Biochemistry* **1992**, *31*, 9269–9278; L. E. Xodo, *Eur. J. Biochem.* **1995**, *228*, 918–926.
[11] Upon binding of oligonucleotide **I** to its duplex DNA target, we observed by circular dichroism the appearance of two strong minima at 220 and 265 nm, indicative of the formation of a triple-strand complex: V. N. Soyfwer, V. N. Potaman, *Triple-Helical Nucleic Acids, 1st ed.*, Springer, New York, **1995**, pp. 54–55.
[12] R. H. Griffey, B. P. Monia, L. L. Cummins, S. Freier, M. J. Greig, C. J. Guinosso, E. Lesnik, S. M. Manalili, V. Mohan, S. Owens, B. R. Ross, H. Sasmor, E. Wancewicz, K. Weiler, P. D. Wheeler, P. D. Cook, *J. Med. Chem.* **1996**, *39*, 5100–5109.
[13] U. Pieles, W. Zürcher, M. Schär, H. E. Moser, *Nucleic Acids Res.* **1993**, *21*, 3191–3196.
[14] T. J. Povsic, P. B. Dervan, *J. Am. Chem. Soc.* **1989**, *111*, 3059–3061.
[15] V. Fritsch, R. Wolf, *J. Biomol. Struct. Dyn.* **1994**, *11*, 1161–1174.
[16] E. S. Priestley, P. B. Dervan, *J. Am. Chem. Soc.* **1995**, *117*, 4761–4765.

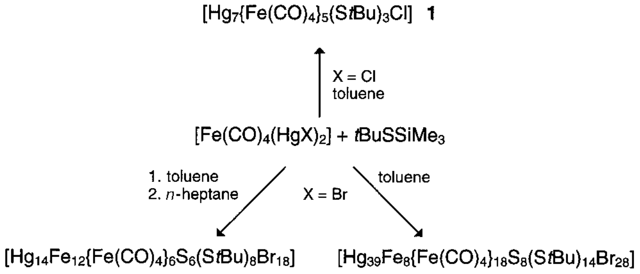
New Iron–Mercury Clusters: $[Hg_7\{Fe(CO)_4\}_5(S\mathit{t}Bu)_3Cl]$, $[Hg_{14}Fe_{12}\{Fe(CO)_4\}_6S_6(S\mathit{t}Bu)_8Br_{18}]$, and $[Hg_{39}Fe_8\{Fe(CO)_4\}_{18}S_8(S\mathit{t}Bu)_{14}Br_{28}]$**

Dieter Fenske* and Marco Bettenhausen

The reaction of coinage-metal salts with phosphanes and silylated chalcogen derivatives has already led to a great number of new compounds.[1] For example, the reaction of PR_3 complexes (R = organic group) of copper and silver halides with silylated derivatives of selenium and tellurium led to the isolation and characterization of many Cu–Se clusters such as $[Cu_{146}Se_{72}(PPh_3)_{30}]$,[2] and a large number of Ag–Te clusters such as $[Ag_{48}(\mathit{n}BuTe)_{24}Te_{12}(PEt_3)_{14}]$.[3] This method was applied recently for the synthesis and subsequent structure determination of $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$ and $[Hg_{32}Se_{14}(SePh)_{36}]$.[4] These compounds have similar structures to the previously described $[Cd_{32}Se_{14}(SR)_{36}(L)_4]$ clusters (R = organic group; L = H_2O, DMF).[5] The compound $[Hg_{32}Se_{14}(SePh)_{36}]$ can be formed by the treatment of $[Fe(CO)_4(HgCl)_2]$ with $PhSeSiMe_3$. The synthesis of $[Fe(CO)_4(HgCl)_2]$ was described in 1928 by Hock and Stuhlmann.[6] Recently the phosphane-bridged mercury cluster $[\{(HgP\mathit{t}Bu)_4\}_3]$ was synthesized by the treatment of $[Fe(CO)_4(HgOAc)_2]$ with $\mathit{t}BuP(SiMe_3)_2$;[7] this cluster is not accessible from the reaction of $HgCl_2$ with silylated phosphanes.

In this work we present the reactions of $[Fe(CO)_4(HgX)_2]$ (X = Cl, Br) with the silylated sulfur derivative $\mathit{t}BuSSiMe_3$. Only a few examples of metal-rich chalcogen-bridged mercury complexes, such as the adamantane-like compounds $[Hg_4(SPh)_6(PPh_3)_4](ClO_4)_2$, $[Hg_4(SPh)_5(\mu_2\text{-}Br)Br_4](PPh_4)_2$,[8] and the complex $[Hg_4(\mathit{t}BuS)_4(\mu_2\text{-}Cl)_2(Cl)_2(py)_2]$[9] have been reported. Clegg and Sola et al.[10] have isolated the compound $[Hg_7(SC_6H_{11})_{12}Br_2]$, and characterized it by X-ray crystallography.

Treatment of a suspension of $[Fe(CO)_4(HgX)_2]$ (X = Cl, Br) in toluene with $\mathit{t}BuSSiMe_3$ affords a yellow-red solution within a few days. Crystals of the iron–mercury clusters **1**–**3**, which were characterized by X-ray crystallography, were grown directly from this solution or by layering with *n*-heptane (Scheme 1).[11]



2 **3**

Scheme 1. Synthesis of the iron–mercury clusters **1**–**3**.

The reaction of $[Fe(CO)_4(HgCl)_2]$ with $\mathit{t}BuSSiMe_3$ leads to a yellow solution from which orange needles of **1** (Figure 1) crystallize. Compound **1** consists of an Hg_3Fe_2 (Hg5-Fe4-Hg6-Fe5-Hg7) and an Hg_4Fe_3 fragment (Hg1-Fe1-Hg2-Fe2-Hg3-Fe3-Hg4). These Hg–Fe chains are linked together by three sulfur atoms from the *t*BuS groups and a chlorine atom. The chlorine atom is in the center of the molecule with Hg–Cl bond lengths of 298.2(7)–359.6(7) pm. These values lie significantly above the sum of the ionic radii of Hg^{2+} and Cl^-(Cl–Hg1 302.5(7), Cl–Hg5 303.5(7), Cl–Hg7 298.2(7) pm) or in the range of the van der Waals radii (Cl–Hg2 3596(7), Cl–Hg3 330.4(7), Cl–Hg4 337.0(7), Cl–Hg6: 348.7(7) pm). Thus, the Hg–Cl bonds are very weak. In

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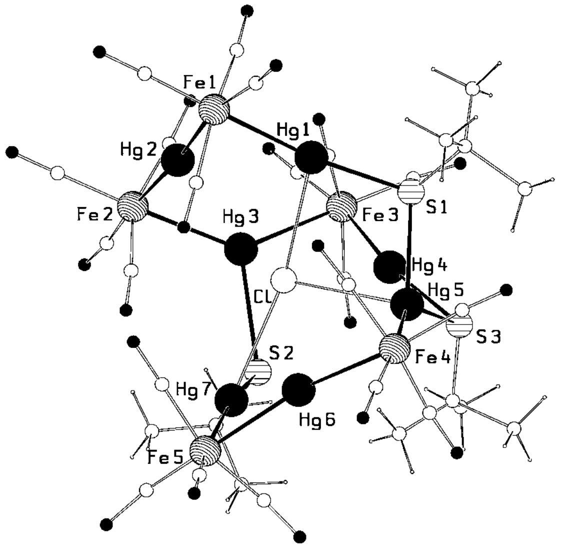

Figure 1. The molecular structure of **1** in the crystal. Hg–Cl bonds are shown up to 330 pm. Selected bond lengths [pm] and angles [°]: Hg···Hg 329.4(2)–373.1(2); Hg-Fe-Hg 80.21(10)–88.65(11); Cl–Hg1 302.5(7), Cl–Hg5 303.5(7), Cl–Hg7 298.2(7); Hg with coordination number 3 (Hg3, Hg5): Hg–Fe 254.1(4)–267.2(4), Hg–S 254.9(8)–281.9(7), sum of the angles 355.3–359.6; Hg with coordination number 2 (Hg1, Hg2, Hg4, Hg6, Hg7): Hg–Fe 250.5(4)–257.6(4), Hg–S 241.3(8)–245.0(8); Fe-Hg-Fe and Fe-Hg-S 167.5(2)–175.3(2).

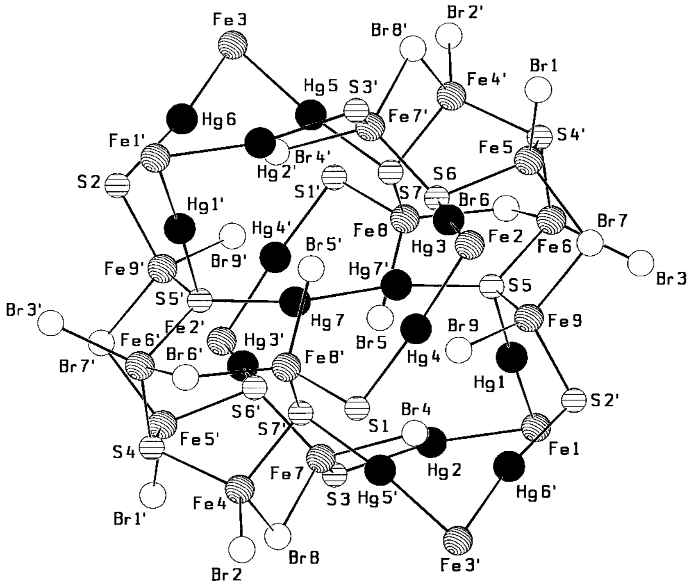

Figure 2. The molecular structure of **2** in the crystal (without C, H, and O atoms). There are four CO groups coordinated to each of the iron atoms Fe1–Fe3 and Fe1'–Fe3' and a *t*Bu group to the sulfur atoms S1–S4 and S1'–S4'. Selected bond lengths [pm] and angles [°]: Hg^I–Hg^I 245.6(10)–254.6(8), Hg^I–S 237.1(6)–250.2(8), $Hg^{II}\cdots Hg^{II}$ 318.2(2)–322.5(1); Hg-Fe-Hg 77.96(9)–79.62(9); Hg^{II}–S 240.2(5)–242.4(5), Hg–Fe 251.0(3)–253.6(3), Fe–S 233.4(5)–240.3(6), Fe–(μ_2-Br) 246.0(3)–251.3(4), Fe–$Br_{terminal}$ 234.3(4)–236.4(4).

agreement with this the estimated values for v_{ij}, calculated from the equation developed by Brese and O'Keeffe, are in the range 0.3–0.14.[12] If the chlorine atom is not considered because of the long Hg–Cl bond lengths, the mercury atoms have either a distorted trigonal planar (Hg3 and Hg5) or almost linear coordination environment (Hg1, Hg2, Hg4, Hg6, and Hg7). All the iron atoms (as in the reactant) are in distorted octahedral environments, coordinated by four CO ligands and two *cis*-positioned Hg atoms (Hg-Fe-Hg angle: 80.21(10)–88.65(11)°). In $[Fe(CO)_4(HgCl)_2]$ the average Hg-Fe-Hg angle is 80.9°.[13] Because of the large Hg–Hg distances (329.4(2)–373.1(2) pm) one can assume that only very weak interactions between the Hg atoms exist, which are clearly weaker than in $[\{(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg\}_4]$ in which the Hg–Hg bond lengths were found to be 289 pm.[14] Similar bonding relationships are found in $[\{(HgP\mathit{t}Bu)_4\}_3]$ (Hg–Hg: 333.0(1)–356.4(1) pm).[7]

Reaction of $[Fe(CO)_4(HgBr)_2]$ with *t*BuSSiMe$_3$ in toluene leads to **2** and **3**. Compound **2** is formed by layering the reaction mixture with *n*-heptane, and crystallizes in the form of small orange crystals after two weeks. Figure 2 shows the molecular structure of the $Hg_{14}Fe_{12}$ cluster **2**; the CO ligands attached to the Fe atoms and the *t*Bu groups attached to the S atoms have been omitted for the sake of clarity. An inversion center is located in the center of the cluster. As in **1** the periphery contains six $FeHg_2$ units (Hg1-Fe-Hg2, Hg3-Fe2-Hg4, Hg5-Fe3-Hg6, and their symmetry equivalents), which are also present in the reactant. The iron atoms Fe1, Fe2, Fe3, Fe1', Fe2', and Fe3' are coordinated in a distorted octahedral fashion by four CO ligands and two *cis*-positioned Hg atoms (Hg-Fe-Hg angle: 77.96–79.62(9)°). The shortest Hg–Hg bond length is 318.2 pm and is thus about 12 pm shorter than those in **1**.

The iron atoms Fe4–Fe9 (and their symmetry equivalents) have distorted tetrahedral environments, coordinated by Br^-, *t*BuS$^-$, and S^{2-} ligands. The core of the cluster contains six μ_3-bridging S^{2-} ligands (S5, S6, S7, S5', S6', and S7') that form a trigonal antiprism. Within this antiprism there is a threefold disordered mercury "dumbbell" (Hg7 and Hg7'); each possible position is found between opposite pairs of sulfur atoms with Hg–Hg bond lengths of 245.6(10)–254.6(8) pm and Hg–S bond lengths of 237.1(6)–250.2(8) pm.

There are several facts that support the existence of an Hg_2^{2+} dumbbell. On the one hand a short Hg–Hg distance is also observed in the compounds $[Hg_2(p\text{-}SC_6H_4NO_2)]NO_3$ (254.8 pm)[15] and $[Hg_2S_2C_4H_4](NO_3)_2$ (252.7 pm).[16] The Hg–S bond lengths in **2** are, however, 10 pm shorter than those reported in the literature. On the other hand the estimation of the valence sum according to Brese and O'Keeffe[12] for Hg7 is 1.2 and for the rest of the mercury atoms in the Hg_2Fe fragments 2.0.[17] Furthermore the overall charge of the cluster with the Hg_2^{2+} dumbbell is balanced.

If we assume that *t*BuS$^-$, S^{2-}, Br^-, and $(Fe(CO)_4)^{2-}$ ligands are present, then we arrive at a formal charge of +50 for the $Hg_{14}Fe_{12}$ cluster. Following the above assumption that the central Hg_2 dumbbell has a charge of +2 and the rest of the mercury atoms (Hg1–Hg6 and their symmetry equivalents) have a formal oxidation state of +2, then the tetrahedrally coordinated Fe atoms (Fe4–Fe9 and symmetry equivalents) must have a formal oxidation state of +2. This is supported by the fact that the valance sum of the Fe atoms Fe4–Fe9 lies between 2.3 and 2.4.

Orange needles of **3** crystallize within a few weeks directly from the mother liquor. The crystal structure of **3** (Figure 3)

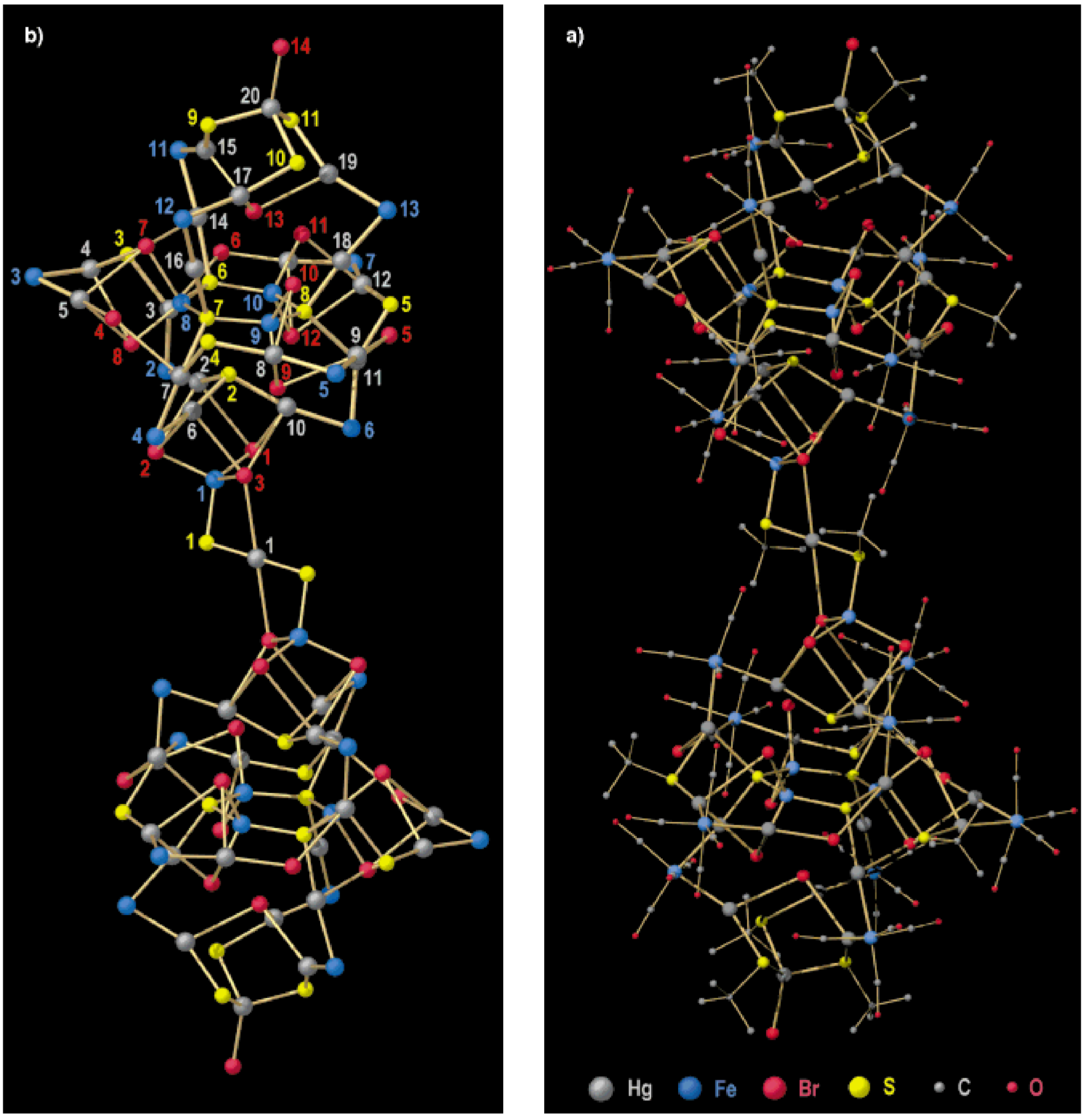

Figure 3. Two views of the molecular structure of **3**. a) With all heavy atoms. b) Without the C, H, and O atoms. The Hg–Br bonds are shown up to 334 pm. Selected bond lengths [pm] and angles [°]: Hg⋯Hg 306.4(2)–336.5(2); Hg-Fe-Hg 74.04(11)–83.71(11); Hg–Fe 251(2)–256.3(4), Hg1–S1 235.7(9), Hg–(μ_2-S) 237.8(13)–259.2(8), Hg–(μ_3-S2) 244.5(6)–245.0(6), Hg–(μ_4-S) 239.7(7)–280.3(7), Fe–S 230.3(9)–236.8(9), Hg–Br14 246.0(5), Hg–Br 250.3(3)–252.7(13), and 292.3(4)–333.4(7).

shows that it is built up from two $Hg_{19}Fe_{13}$ clusters that are linked together by a bridging central Hg atom (Hg1), which is situated on an inversion center. The CO and *t*Bu groups are omitted from Figure 3b for the sake of clarity. Hg1 is linearly coordinated by two S atoms from *t*BuS groups if one ignores the Br3 center that lies within the coordination sphere of Hg1 at a distance of 315.3 pm. The $FeHg_2$ units, which are present in the reactant, are also found again in this cluster (Fe2–Fe7, Fe11–Fe13, and their symmetry equivalents). However, there are also Hg (Hg1, Hg20) and Fe atoms (Fe1, and Fe8–Fe10) that have no Hg–Fe bonds. A characteristic of this cluster is an almost planar Fe_3S_3 six-membered ring (S7, Fe8, S6, Fe10, S8, Fe9) in the center of the $Hg_{19}Fe_{13}$ fragment. The largest deviation of any atom out of the plane of this six-membered ring is about 13 pm. Holm et al.[18] have reported an iron thiolate compound $[Fe_3(SR)_3X_6]^{3-}$ (R = organic group, X = Cl, Br) in which the $Fe_3(SR)_3$ structure corresponds to that found in the center of the $Hg_{19}Fe_{13}$ fragment.

If the $Hg_{19}Fe_{13}$ cluster is described starting from the six-membered ring, then three S-Hg-Fe-Hg-S-Hg chains (e.g., S6-Hg14-Fe11-Hg15-S9-Hg20) connect one sulfur atom from the six-membered ring to a terminal Hg atom (Hg20) and likewise three S-Hg-Fe-Hg-Br-Fe-S-Hg chains (e.g., S6-Hg3-Fe2-Hg2-Br2-Fe1-S1-Hg1) link the Fe_3S_3 ring to the bridging Hg atom (Hg1). The first mercury atom (Hg3) is linked through a bridging sulfur atom (S3) to a further H_2Fe unit (Hg4-Fe3-Hg5) that lies in the plane of the six-membered ring. As in **1**, the Hg atoms in **3** have the formal charge of +2 (d^{10} configuration). Correspondingly one observes only very long Hg–Hg contacts of the order of 306.4(2) pm.

1433-7851/98/3709-1293 $ 17.50+.50/0

Experimental Section

1: tBuSSiMe$_3$ (0.53 mL, 2.7 mmol) was added to a suspension of [Fe(CO)$_4$(HgCl)$_2$] (0.43 g, 0.67 mmol) in toluene (20 mL) at room temperature. A yellow powder precipitated immediately, and the solution turned yellow within two days. After three days orange needles of **1** were formed in the solution (yield 45%).

2: tBuSSiMe$_3$ (0.18 mL, 0.9 mmol) was added to a suspension of [Fe(CO)$_4$(HgBr)$_2$] (0.34 g, 0.47 mmol) in toluene (20 mL) at room temperature. The brown solution was layered with *n*-heptane and after two weeks small orange crystals of **2** were formed together with a black-brown precipitate (yield 15%).

3 tBuSSiMe$_3$ (0.27 mL, 1.4 mmol) was added to a suspension of [Fe(CO)$_4$(HgBr)$_2$] (0.50 g, 0.7 mmol) in toluene (20 mL) at room temperature. Within a few weeks, a light brown precipitate and orange crystals of **3** were formed from the yellow-brown solution (yield 30%). Satisfactory elemental analyses (Hg, Fe, C, and H) were obtained for **1**–**3**.

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[1] I. Dance, K. Fischer, *Prog. Inorg. Chem.* **1994**, *41*, 637.

[2] H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, *105*, 1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1303.

[3] J. F. Corrigan, D. Fenske, *Chem. Commun.* **1996**, 943; J. F. Corrigan, D. Fenske, W. P. Power, *Angew. Chem.* **1997**, *109*, 1224; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1176.

[4] S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde, U. Woggon, *Angew. Chem.* **1996**, *108*, 2360; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2215.

[5] N. Herron, J. C. Calabrese, W. E. Farneth, Y. Wang, *Science* **1993**, *259*, 1426; T. Vossmeier, G. Reck, B.Schulz, L. Katsikas, H. Weller, *J. Am. Chem. Soc.* **1995**, *117*, 12881.

[6] H. Hock, H. Stuhlmann, *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2097; *Ber. Dtsch. Chem. Ges. B* **1929**, *62*, 431.

[7] R. Ahlrichs, M. von Arnim, J. Eisenmann, D. Fenske, *Angew. Chem.* **1997**, *109*, 243; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 233.

[8] J. J. Vittal, P. A. W. Dean, N. C. Payne, *Can. J. Chem.* **1993**, *71*, 2043; P. A. W. Dean, J. J. Vittal, Y. Wu, *Inorg. Chem.* **1994**, *33*, 2180.

[9] A. J. Canty, C. L. Raston, A. H. White, *Aust. J. Chem.* **1978**, *31*, 677.

[10] T. Alsina, W. Clegg, K. A. Fraser, J. Sola, *J. Chem. Soc. Chem. Commun.* **1992**, 1010.

[11] X-ray structure analysis: Stoe-IPDS (Mo$_{K\alpha}$ radiation); data collection and refinement (SHELXS-86, SHELXL-93).
1: monoclinc, space group $P2_1/n$ (no. 14), $Z=4$, $T=200$ K, $a=1106.4(2)$, $b=4379.6(9)$, $c=1208.7(2)$ pm, $\beta=107.69(3)^\circ$, $V=5580(2)\times10^6$ pm^3, $\mu(\mathrm{Mo}_{K\alpha})=206.57$ cm^{-1}, $2\Theta_{\max}=48^\circ$, 17550 reflections (empirical absorption correction), 7529 independent reflections ($R_{\mathrm{int}}=0.1259$) and 6014 observed with $I>2\sigma(I)$, 622 parameters (Hg, Fe, Cl, S, O, and C anisotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 3.868 e Å^{-3}, $R1=0.0758$, $wR2=0.2407$. **2** $\cdot$ 2 C$_7$H$_8$: monoclinic, space group $C2/c$ (no. 15), $Z=4$, $T=200$ K, $a=3061.7(8)$, $b=1651.2(6)$, $c=3244.9(10)$ pm, $\beta=110.97(2)^\circ$, $V=15318(8)\times10^6$ pm^3, $\mu(\mathrm{Mo}_{K\alpha})=205.43$ cm^{-1}, $2\Theta_{\max}=45^\circ$, 36397 reflections (empirical absorption correction), 9740 independent reflections ($R_{\mathrm{int}}=0.0874$) and 6748 observed with $I>2\sigma(I)$, 695 parameters (Hg, Fe, Br, S, O, and C anisotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 2.394 e Å^{-3}, $R1=0.0501$, $wR2=0.1333$. With the disordered Hg7 atom an occupation of 1/3 was assumed for the threefold disordered position. **3** $\cdot$ 5 C$_7$H$_8$: monoclinic, space group $I2/a$ (no. 15), $Z=4$, $T=190$ K, $a=3145.9(6)$, $b=3205.8(6)$, $c=3380.2(7)$ pm, $\beta=101.62(3)^\circ$, $V=33391(12)\times10^6$ pm^3, $\mu(\mathrm{Mo}_{K\alpha})=224.80$ cm^{-1}, $2\Theta_{\max}=45^\circ$, 59953 reflections (empirical absorption correction), 21145 independent reflections ($R_{\mathrm{int}}=0.1009$) and 14405 observed with $I>2\sigma(I)$, 1099 parameters (Hg, Br, Fe, and S anisotropic; O and C isotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 2.775 e Å^{-3}, $R1=0.0628$, $wR2=0.1718$. The heavy-metal skeleton of **3** is partly disordered (Hg12–Hg15, Fe7, Fe11, Br6, Br7, Br11, and S9). An indication of a possible superstructure could not be found. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), (fax: (+49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-408008, CSD-408009, and CSD-408010.

[12] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192.

[13] C. L. Raston, A. H. White, S. B. Wild, *Aust. J. Chem.* **1976**, *29*, 1905.

[14] W. Gäde, E. Weiss, *Angew. Chem.* **1981**, *93*, 796; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 803.

[15] K. Brodersen, A. Knörr, *Z. Naturforsch. B* **1990**, *45*, 1193.

[16] K. Brodersen, G. Liehr, W. Rölz, *Z. Anorg. Allg. Chem.* **1977**, *428*, 166.

[17] For the estimation of the valence sum according to Brese and O'Keeffe,[12] the bonding-valence parameters were taken from their publication. A value of 2.47 was assumed for Hg–Fe(CO)$_4$ (not given in ref. [12]).

[18] M. A. Witener, J. K. Baschkin, K. S. Hagen, J.-J. Girerd, E. Gamp, N. Edelstein, R. H. Holm, *J. Am. Chem Soc.* **1986**, *108*, 5607.

Supramolecular Daisy Chains[**]

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The appeal that interlocked molecular assemblies and intertwined superarchitectures holds for chemists is reflected in the extensive literature[1] devoted to the construction and characterization of such systems. A natural development is the fabrication of interwoven[2] supermolecules and supramolecular arrays by the noncovalent oligomerization/polymerization[3] of self-complementary (plerotopic[4]) monomeric species. An approach that offers much potential involves[5] a plerotopic macrocyclic monomer that can oligomerize or polymerize through noncovalent bonds. However, this monomer must be designed in such a way that its two complementary sites are compelled to recognize each other in an intermolecular,[6] rather than an intramolecular,[7] sense; that is, the plerotopic monomer must be prevented from "biting its own tail" and encouraged to form a "daisy chain"[8] instead (Figure 1).

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