Ferrous Complexes

Ferrous Wheels, Ellipse $[(t\mathrm{Bu}_3\mathrm{SiS})\mathrm{FeX}]_n$, and Cube $[(t\mathrm{Bu}_3\mathrm{SiS})\mathrm{Fe}(\mathrm{CCSi}t\mathrm{Bu}_3)]_4$**

Orson L. Sydora, Peter T. Wolczanski, and*
Emil B. Lobkovsky

Dedicated to Roald Hoffmann

The controlled aggregation of low-coordinate, transition-metal complexes can lead to the generation of unusual oligomers, polymers or clusters. Inspired by Hoffmann's treatise on tetrahedral units as building blocks,[1,2] we sought "XMY" species as potential monomers for $[\mathrm{M}(\mu\text{-X})(\mu\text{-Y})]_n$, an oligomer or polymer based on the *edge*-connectivity of tetrahedra. Literature precedent[3] suggested the use of bulky thiolate and halide ligands as the μ-X and μ-Y linkages.

Treatment of $[\{(\mathrm{Me_3Si})_2\mathrm{N}\}_2\mathrm{Fe}]_2$ with four equivalents $t\mathrm{Bu_3SiSH}$[4] afforded orange $[\{(t\mathrm{Bu_3SiS})\mathrm{Fe}\}_2(\mu\text{-SSi}t\mathrm{Bu_3})_2]$ (**1**, 86%) akin to trigonal-based dimers prepared by Holm et al.,[5,6] hence desymmetrization was viewed as one means toward oligomerization. $\mathrm{FeX_2(thf)_2}$ and one equivalent of $t\mathrm{Bu_3SiSNa(thf)}_x$ ($x = 1.4$–1.7) were stirred for 18–24 h to provide yellow $[(\mathrm{X_2Fe})(\mu\text{-SSi}t\mathrm{Bu_3})_2\{\mathrm{FeX(thf)}\}]\mathrm{Na(thf)_4}$ (**2a**, X = Cl, 74%; **2b**, X = Br, 86%) and *cis*-$[\{\mathrm{I(thf)Fe}\}_2(\mu\text{-SSi}t\mathrm{Bu_3})_2]$ (**3**, 75%) upon isolation. The structures of **1**, **2b** and **3** were determined by single-crystal X-ray crystallography, and quenching studies ($\mathrm{D_2O/DCl}$ in $\mathrm{D_3COD}$) suggested that **2a** has the same thiolate:THF ratio (1:3.9) as **2b**. Elemental analyses were indeterminate, probably because of variable desolvation. Each complex has a μ_{eff} consistent with an $S = 2$ ground state (Evans' method [7] in $[\mathrm{D_8}]$THF) and little orbital contribution: **2a**, 4.8 μ_B; **2b**, 4.5 μ_B; **3**, 4.8 μ_B.

If the solvent (THF) was removed after the above procedures, and the remaining solids were heated under vacuum (**2a**, 80°C, 1.5 h; **2b**, 79°C, 2 h); **3**, 117°C, 5 h) and extracted into benzene, then desolvation and aggregation occurred, but not to the expected polymers. Instead, ferrous wheels $[\mathrm{Fe}(\mu\text{-X})(\mu\text{-SSi}t\mathrm{Bu_3})]_n(\mathrm{C_6H_6})_m$ (X = Cl, $n = 12$, **4a**, 45%;[8] X = Br, $n = 12$, **4b**, 72%)[9] and the ferrous ellipse $[\mathrm{Fe}(\mu\text{-I})(\mu\text{-SSi}t\mathrm{Bu_3})]_{14}(\mathrm{C_6H_6})_m$ (**5**, 16%)[10] were isolated by crystallization. The structures of these complexes were determined by single-crystal X-ray crystallography,[11] but the benzene molecules of solvation, determined from quenching studies to be ~0.5–1.0 equivalent per Fe atom, exhibited significant disorder, and were removed from the refinement by using PLATON methods.

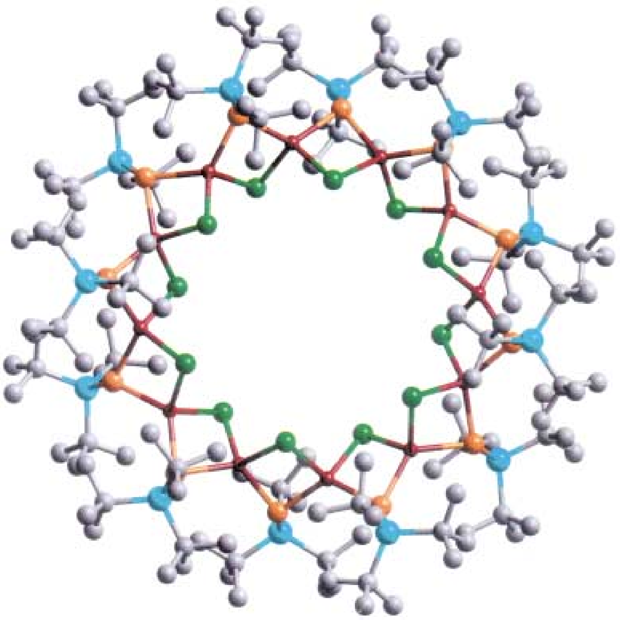

Figure 1. Molecular view of $[\mathrm{Fe}(\mu\text{-Cl})(\mu\text{-SSi}t\mathrm{Bu_3})]_{12}$ (**4a**) Fe = red, Cl = green, S = orange, Si = blue, C = gray; pertinent interatomic distances (Å) and angles (°): $d(\mathrm{FeS})_{\mathrm{av}} = 2.340\ (9)$; transannular $d(\mathrm{Cl\cdots Cl})_{\mathrm{av}} = 9.484\ (29)$; $d(\mathrm{FeCl})_{\mathrm{av}} = 2.339\ (9)$; $d(\mathrm{Fe\cdots Fe})_{\mathrm{av}} = 3.127\ (44)$; $(\mathrm{Cl\text{-}Fe\text{-}Cl})_{\mathrm{av}} = 103.5\ (13)$; $(\mathrm{S\text{-}Fe\text{-}S})_{\mathrm{av}} = 124.8\ (6)$; $(\mathrm{Fe\text{-}S\text{-}Fe})_{\mathrm{av}} = 83.9\ (14)$; $(\mathrm{Fe\text{-}Cl\text{-}Fe})_{\mathrm{av}} = 83.9\ (15)$; $(\mathrm{Cl\text{-}Fe\text{-}S})_{\mathrm{av}} = 93.3\ (5)$, 121.0 (14). $[\mathrm{Fe}(\mu\text{-Br})(\mu\text{-SSi}t\mathrm{Bu_3})]_{12}$ (**4b**) is isomorphous: $d(\mathrm{FeS})_{\mathrm{av}} = 2.339\ (6)$; transannular $d(\mathrm{Br\cdots Br})_{\mathrm{av}} = 9.483\ (22)$; $d(\mathrm{FeBr})_{\mathrm{av}} = 2.474\ (9)$; $d(\mathrm{Fe\cdots Fe})_{\mathrm{av}}$ of 3.171 (51); $(\mathrm{Br\text{-}Fe\text{-}Br})_{\mathrm{av}} = 103.6\ (15)$; $(\mathrm{S\text{-}Fe\text{-}S})_{\mathrm{av}} = 127.4\ (8)$; $(\mathrm{Fe\text{-}S\text{-}Fe})_{\mathrm{av}} = 85.4\ (18)$; $(\mathrm{Fe\text{-}Br\text{-}Fe})_{\mathrm{av}} = 79.7\ (17)$; $(\mathrm{Br\text{-}Fe\text{-}S})_{\mathrm{av}} = 94.7\ (7)$, 117.7 (13).

The chloride ferrous wheel, **4a** (Figure 1), packs in a tetragonal array of columns; the bromide derivative, **4b**, is isomorphous. The wheels consist of edge-shared tetrahedra, with the inner diameter comprises μ-X ligands, and the periphery composed of $\mu\text{-SSi}t\mathrm{Bu_3}$ linkages. The orientation of each shared tetrahedral edge alternates relative to the ring plane such that the three different transannular X···X separations are basically the same (**4a**, 9.484 (29) Å av; **4b**, 9.483 (22) Å av) Because of the greater size of Br ion, the iron atoms in **4b** are slightly displaced towards the outside of the wheel relative to **4a.**

The iodide ellipse, **5** (Figure 2) is constructed of tetrahedra linked on the perimeter by $\mu\text{-SSi}t\mathrm{Bu_3}$ ligands, and internally by bridging iodides. Ellipse **5** also packs in columnar fashion, and has transannular $d(\mathrm{I\cdots I})$ of 11.101 (2), 11.499 (2), 12.402 (2) and 13.469 (2) Å. The tetrahedra form a ring with the iodides inside, despite the $d(\mathrm{FeI})_{\mathrm{av}} = 2.672$ (11) Å that is substantially longer than $d(\mathrm{FeS})_{\mathrm{av}} = 2.342$ (7) Å. Now the iron atoms are even further apart than in **4a** and **4b**, and those tetrahedra nearest the foci exhibit metric parameters consistent with slightly greater strain. The wheels and ellipse are unusual examples of ferrous-based rings with a tetrahedral motif, of which $[\mathrm{Fe_{12}(SePh)_{24}}]$ of Fenske and Fischer is the first documented example.[12] The sulfide cluster $[\mathrm{Na_2Fe^{III}_{14}Fe^{II}_4S_{30}}]^{8-}$ contains tetrahedral $\mathrm{FeS_4}$ units, but it is a mixed valence compound,[13] as is $[\mathrm{Fe_6S_6I_6}]^{2-}$.[14] An eight-

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[*] Prof. P. T. Wolczanski, O. L. Sydora, E. B. Lobkovsky
Department of Chemistry & Chemical Biology
Baker Laboratory
Cornell University
Ithaca, New York 14853 (USA)
Fax: (+1) 607-255-4137
E-mail: ptw2@cornell.edu

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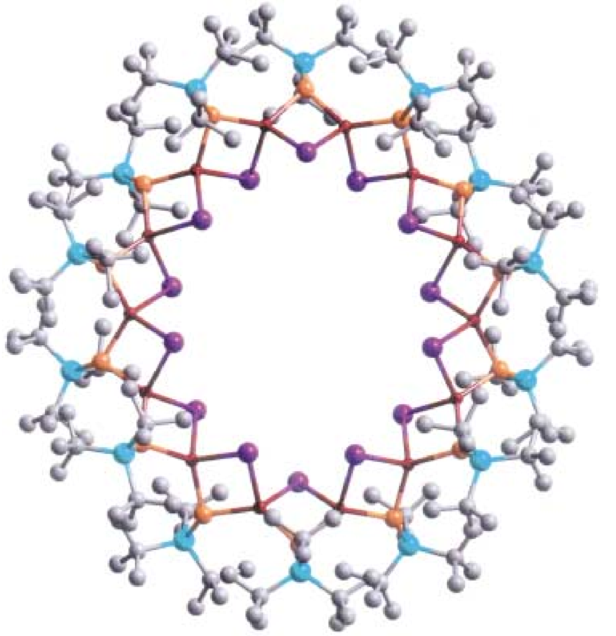

Figure 2. Molecular view of $[Fe(\mu\text{-}I)(\mu\text{-}SSi\,tBu_3)]_{14}$ (**5**) Fe = red, I = purple, S = orange, Si = blue, C = gray; pertinent interatomic distances (Å) and angles (°): $d(FeS)_{av} = 2.342$ (7); transannular $d(I\cdots I) = 11.101$ (2), 11.499 (2), 12.402 (2), 13.469 (2); $d(FeI)_{av} = 2.672$ (11); $d(Fe\cdots Fe)_{av} = 3.238$ (46); $(I\text{-}Fe\text{-}I)_{av} = 101.6$ (7); near foci (Fe-I-Fe) = 72.98 (10), other $(Fe\text{-}I\text{-}Fe)_{av}$ of 75.1 (9); near foci (S-Fe-S) = 132.13 (17), other $(S\text{-}Fe\text{-}S)_{av}$ of 125.0 (9); near foci (I-Fe-S) = 112.85 (12) and 115.35 (16), other $(I\text{-}Fe\text{-}S)_{av}$ of 117.0 (6).

membered Fe^{II} wheel of sulfide cubes, $[\{(Cy_3P)FeS\}_2Fe_2S_2]_4$ has been prepared,[15] but all remaining iron wheels are based on octahedral Fe^{III}.[16–21]

What is the aggregation state if only one ligand can bridge? The treatment of **4b** with one equivalent of LiCC-SitBu$_3$ per mole of Fe (chosen in part for size compatibility) afforded the ferrous cube $[\{(tBu_3SiCC)Fe(\mu\text{-}SSi\text{-}tBu_3)\}_4(C_6H_6)_3]$ (**6** (67%)).[11,22] The cube is nearly perfect (Figure 3), with $S\text{-}Fe\text{-}S_{av} = 90.6$ (8)° and $Fe\text{-}S\text{-}Fe_{av} = 89.4$ (8)°. Thiolate-containing cubes with a ferrous-only core are rarely observed,[15–21,23] although a ferrous acetylide phosphaneimide derivative is known.[24]

The magnetic properties of **4a**, **4b**, **5** and **6** were briefly examined. When a Heisenberg $S = 2$ quantum infinite chain model[25] is applied (10 K to 290 K), chloride wheel **4a** is essentially a simple paramagnet, with $J = 0.0$ at both 0.5 and 2.0 T. When a similar approach was used with the bromide wheel, the fits at 1.0 ($R^2 = 97.6$) and 4.0 T ($R^2 = 98.0$) were not as satisfactory, especially below 100 K, but J remained weakly antiferromagnetic (−0.7 and −1.0 cm^{-1} respectively). The temperature dependence of χ_{mol}/Fe for **5** was not properly fit by any model, and $\mu_{eff} = 3.6$ (1.0, 4.0 T) at 23 °C. Thiolate acetylide cube **6** was fit to a tetrahedral array of iron(II) centers according to the Kambe method,[26] and it exhibited no significant interactions (0.5, 2.0 T; $J = 0.1$, 0.3 cm^{-1}; $\mu_{eff}(295\ K) = 5.7$, 5.4 μ_B). Most wheels based on octahedral Fe^{III} motifs have modest antiferromagnetic behavior,[16–21] although certain Mn^{III} (O_h),[27] Cr^{III} (O_h),[28] and Ni^{II}[29] wheels have manifested ferromagnetic properties.

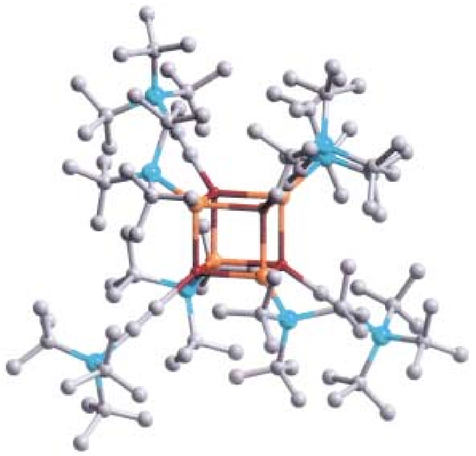

Figure 3. Molecular view of $[(tBu_3SiCC)Fe(\mu\text{-}SSitBu_3)]_4$ (**6**), Fe = red, Si = blue, C = gray; pertinent interatomic distances (Å) and angles (°): $d(FeC)_{av} = 1.996$ (12); $d(FeS)_{av} = 2.460$ (3); $(S\text{-}Fe\text{-}S)_{av} = 90.6$ (8); $(Fe\text{-}S\text{-}Fe)_{av} = 89.4$ (8); $(S\text{-}Fe\text{-}C)_{av} = 124.9$ (8).

Use of the extremely bulky tBu_3SiS ligand has enabled the synthesis of rare ferrous wheels, a unique ellipse, and an uncommon ferrous cube based on tetrahedral coordination. Extensions to other first-row elements and further scrutiny of the magnetic properties of these compounds is underway.[30]

Experimental Section

All manipulations were performed by using either a glovebox (N_2) or high vacuum techniques (Ar), and dried deoxygenated solvents. **1**: A 50 mL flask was charged with $[\{(Me_3Si)_2N\}_2Fe]_2$ (1.099 g, 2.918 mmol), tBu_3SiSH (1.357 g, 5.836 mmol and benzene (25 mL) at 23 °C. The reaction mixture was stirred for 30 min, after which the volatiles removed, and the resulting brown solid was subjected to dynamic vacuum for 3 h. This material was dissolved in pentane, filtered and cooled to −78 °C to provide orange **1** (1.308 g, 86%). ^{1}H NMR (400 MHz, C_6D_6, 23 °C, TMS): $\delta = 1.91$ ($\tilde{\nu}_{1/2} = 200$ Hz), 3.63 ($\tilde{\nu}_{1/2} = 200$ Hz). Elemental analysis calcd (%) for $C_{24}H_{54}Si_2S_2Fe$: C 55.56, H 10.49; found: C 55.3, H 10.6.
2a: A 50 mL flask was charged with $NaSSitBu_3(thf)_{1.48}$ (0.250 g, 0.692 mmol), $FeCl_2(thf)_2$ (0.188 g, 0.694 mmol) and THF (20 mL). The pale yellow solution was stirred for 18 h, filtered and allowed to evaporate to give **2a** (0.271 g, 74%). ^{1}H NMR (400 MHz, [D$_8$]THF, 23 °C, TMS): $\delta = 9.11$ ($\tilde{\nu}_{1/2} = 940$ Hz). Elemental analysis calcd (%) for $[\{Cl_2Fe\}(\mu\text{-}SSitBu_3)_2\{FeCl(thf)\}]Na$ (desolvated), $C_{28}H_{62}Cl_3Si_2S_2Fe_2Na$: C 43.32, H 8.07, Cl 13.70; found: C 42.5, H 8.2, Cl 13.4.
2b: A 50 mL flask was charged with $NaSSitBu_3(thf)_{1.68}$ (0.325 g, 0.865 mmol), $FeBr_2(thf)_2$ (0.311 g, 0.864 mmol) and THF (20 mL). The pale yellow solution was stirred for 18 h, filtered and the solvent allowed to evaporate to give 0.446 g **2b** (86%). ^{1}H NMR (400 MHz, [D$_8$]THF, 23 °C, TMS): $\delta = 12.46$ ($\tilde{\nu}_{1/2} = 280$ Hz). Elemental analysis calcd (%) for $[(Cl_2Fe)(\mu\text{-}SSitBu_3)_2\{FeCl(thf)\}]Na(thf)$ (desolvated), $C_{32}H_{70}Br_3Si_2S_2Fe_2Na$: C 42.67, H 7.87, Br 21.29; found: C 42.3, H 7.9, Br 21.8.
3: A 50 mL flask was charged with (0.504 g, 1.34 mmol) $NaSSi\text{-}tBu_3(thf)_{1.68}$, (0.608 g, 1.34 mmol) $FeI_2(thf)_2$ and THF (25 mL). The yellow solution was stirred for 24 h, filtered and the solvent was removed. The yellow solid was heated under vacuum at 98 °C for 2 h, extracted into benzene (40 mL) and filtered. Slow evaporation of the solvent afforded **3** (0.485 g, 75%) after 5 days. ^{1}H NMR (400 MHz, [D$_8$]THF, 23 °C, TMS): $\delta = 6.82$ ($\tilde{\nu}_{1/2} = 140$ Hz). Elemental analysis calcd (%) for $[(IFe)_2(\mu\text{-}SSitBu_3)]_2$ (desolvated), $C_{12}H_{27}SiSIFe$: C,

34.79; H, 6.58; I, 30.63. Found: C, 33.4; H, 6.4; I, 27.7.
4a: A 50 mL flask was charged with **2a** (0.271 g, 0.255 mmol) and heated under vacuum at 80 °C for 1.5 h. The product was extracted with benzene and filtered, and yellow crystalline **4a** (0.082 g, 45 %) deposited after slow evaporation of the solvent (6 days). Elemental analysis calcd (%) for $[\mathrm{Fe}(\mu\text{-Cl})(\mu\text{-SSi}t\mathrm{Bu}_3)]_{12}$(desolvated), $C_{12}H_{27}ClSiSFe$: C 44.64, H 8.45, Cl 10.98; found: C 43.9, H 8.4, Cl, 9.9.
4b: A 100 mL flask was charged with $\mathrm{NaSSi}t\mathrm{Bu}_3(\mathrm{thf})_{1.40}$ (0.801 g, 2.25 mmol), $\mathrm{FeBr}_2(\mathrm{thf})_2$ (0.736 g, 2.28 mmol), and THF (50 mL). The mixture was stirred at 23 °C for 24 h, and the solvent was removed to yield a yellow solid. The solid was heated at 79 °C under vacuum for 2 h, then extracted into benzene and filtered. After slow evaporation of the solvent (5 days), yellow crystals of the product formed (0.739 g, 72 %). Elemental analysis calcd (%) for $[\mathrm{Fe}(\mu\text{-Br})(\mu\text{-SSi}t\mathrm{Bu}_3)]_{12}$-(desolvated), $C_{12}H_{27}BrSiSFe$: C 39.24, H 7.42, Br 21.75; found: C 39.7, H 7.3, Br 21.8.
5: A 50 mL flask was charged with $\mathrm{NaSSi}t\mathrm{Bu}_3(\mathrm{thf})_{1.56}$ (0.301 g, 0.820 mmol), $\mathrm{FeI}_2(\mathrm{thf})_2$ (0.371 g, 0.817 mmol), and THF (20 mL). The mixture was stirred at 23 °C for 24 h, and the solvent was removed to yield a yellow solid. The solid was heated at 117 °C under vacuum for 5 h, then extracted into benzene and filtered. After slow evaporation of the solvent (7 days), dark yellow crystals formed (0.064 g, 16 %). Suitable elemental analyses could not be obtained.
6: A 12 mL darkened vial was charged with **4a** (0.099 g, 0.222 mmol), $\mathrm{LiCCSSi}t\mathrm{Bu}_3(\mathrm{OEt}_2)_{0.28}$ (0.059 g, 0.235 mmol), and benzene (8 mL). The solution was stirred for 10 h, filtered, and the solvent slowly evaporated over 4 days to provide dark yellow crystalline **6** (0.079 g 67 %).

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Keywords: cluster compounds · iron · magnetic properties · S ligands

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[8] **4a**: tetragonal; $P\bar{4}2_1c$; $a = 23.3716$ (7), $c = 24.0912$ (11) Å; $V = 13\,159.4$ (8) Å^3; $Z = 8$; $C_{36}H_{81}Cl_3S_3Si_3Fe_3$ (benzenes removed); $T = 173$ (2) K; $\lambda = 0.71073$; 46 598 reflections, 9453 independent ($R_{\mathrm{int}} = 0.0726$); $R1 = 0.0506$ ($I > 2\sigma(I)$), $wR2 = 0.1445$; $\mu = 0.951$ mm^{-1} (SADABS); full-matrix, least squares on F^2.
[9] **4b**: tetragonal; $P\bar{4}2_1c$; $a = 23.542$ (5), $c = 24.086$ (8) Å; $V = 13\,349$ (6)) Å^3; $Z = 8$; $C_{36}H_{81}Br_3S_3Si_3Fe_3$ (benzenes removed); $T = 173$ (2) K; $\lambda = 0.71073$; 17 324 reflections, 5190 independent ($R_{\mathrm{int}} = 0.0976$); $R1 = 0.0615$ ($I > 2\sigma(I)$), $wR2 = 0.1414$; $\mu = 2.605$ mm^{-1}; full-matrix, least squares on F^2.
[10] **5**: orthorhombic; *Cmca*; $a = 38.173$ (6), $b = 24.296$ (4), $c = 35.977$ (5) Å; $V = 33\,367$ (9)) Å^3; $Z = 16$; $C_{44}H_{93.5}I_{3.5}S_{3.5}Si_{3.5}Fe_{3.5}$ (benzenes removed); $T = 173$ (2) K; $\lambda = 0.71073$; 104 844 reflections, 10 375 independent ($R_{\mathrm{int}} = 0.0961$); $R1 = 0.0762$ ($I > 2\sigma(I)$), $wR2 = 0.1952$; $\mu = 2.055$ mm^{-1}; full-matrix, least squares on F^2.
[11] CCDC-203239 (**4a**), CCDC-203238 (**4b**), CCDC-203240 (**5**) and CCDC-203237 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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[22] **6**: cubic; $P2_13$; $a = 23.8617$ (17) Å; $V = 13\,586.4$ (17)) Å^3; $Z = 12$; $C_{40.67}H_{72}S_{1.33}Si_{2.66}Fe_{1.33}$; $T = 173$ (2) K; $\lambda = 0.71073$; 49 628 reflections, 6526 independent ($R_{\mathrm{int}} = 0.1949$); $R1 = 0.0685$ ($I > 2\sigma(I)$), $wR2 = 0.1379$; $\mu = 0.664$ mm^{-1}; full-matrix, least squares on F^2.
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