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First row wheels, $\{(^t\mathrm{Bu_3SiS})\mathrm{MX}\}_{12}$ (M = Co, X = Cl; M = Ni, X = Br), are common amongst both simpler and more complex aggregates†

Orson L. Sydora,[a] Peter T. Wolczanski,*[a] Emil B. Lobkovsky,[a] Evan Rumberger[b] and David N. Hendrickson[b]

[a] *Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA. E-mail: ptw2@cornell.edu*

[b] *Department of Chemistry and Biochemistry, University of California, San Diego, San Diego, CA 92083, USA. E-mail: dhendrickson@ucsd.edu*

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$\{(^t\mathrm{Bu_3SiS})\mathrm{MX}\}_{12}$ are wheels for first row transition metals (M = Co, X = Cl; M = Ni, X = Br), but for nickel, simpler {*e.g.* $[(^t\mathrm{Bu_3SiS})\mathrm{Ni}]_2(\mu\text{-}\mathrm{SSi}^t\mathrm{Bu_3})_2$} and more complicated {*e.g.* $[(\mu\text{-}\mathrm{SSi}^t\mathrm{Bu_3})\mathrm{Ni}]_5(\mu_5\text{-S})$} structures are by-products.

While exploring the aggregation of $\{(^t\mathrm{Bu_3SiS})\mathrm{FeX}\}_n$, ferrous wheels (X = Cl, Br; $n = 12$) and an ellipse (X = I; $n = 14$) were discovered.[1] These compounds are among the first Fe(II) derivatives[2] to form cyclic structures based on an edge-shared tetrahedron connectivity. The ready formation of iron cyclics suggested an extension to other first row elements, since the metric parameters ascribed to late first row metal tetrahedral complexes are quite similar. Described herein are syntheses of Co(II)[3,4] and Ni(II)[4–6] wheels, and thiolate-based[7] by-products of the latter.

Treatment of $\mathrm{CoCl_2}$ with $\mathrm{NaSSi}^t\mathrm{Bu_3}$[8] in THF at 23 °C for 12 h led to a blue solid upon removal of the THF. Under the assumption that this was a simple coordination complex such as $(^t\mathrm{Bu_3SiS})\mathrm{CoCl(THF)_2}$ or $[(^t\mathrm{Bu_3SiS})\mathrm{CoCl(THF)}]_2$ (**1**), the solid was placed under dynamic vacuum at 81 °C for 90 min. The solid was then dissolved in benzene at 100 °C, filtered, and allowed to cool, to yield green blocks of $\{(^t\mathrm{Bu_3SiS})\mathrm{CoCl}\}_{12}\cdot(\mathrm{C_6H_6})_6$ (**2**) in 21% yield.‡ A protolytic quench of **2** with $\mathrm{D_2O}$–DCl in $\mathrm{D_3COD}$ suggested a thiolate to benzene ratio of approximately 2 : 1. Fig. 1 illustrates the molecular wheel structure of **2**,§ which is related to the previously reported ferrous chloride structure (tetragonal, $P\bar{4}2_1c$).[1] Core interatomic distances and angles reflect the slightly smaller Co(II) radius: $d(\mathrm{Co–Cl})_{\mathrm{av}} = 2.310(11)$, $d(\mathrm{Co–S})_{\mathrm{av}} = 2.305(9)$, $d(\mathrm{Cl\cdots Cl})_{\mathrm{av}} = 9.614(27)$, $d(\mathrm{Co\cdots Co})_{\mathrm{av}} = 3.115(40)$ Å; $\angle(\mathrm{Co–Cl–Co})_{\mathrm{av}} = 84.8(13)$, $\angle(\mathrm{Cl–Co–Cl})_{\mathrm{av}} = 107.8(13)$, $\angle(\mathrm{S–Co–S})_{\mathrm{av}} = 126.6(5)$, $\angle(\mathrm{Co–S–Co})_{\mathrm{av}} = 85.0(12)$, and $\angle(\mathrm{Cl–Co–S})_{\mathrm{av}} = 91.9(4), 119.7(12)°$. The cobaltous wheel was determined to be weakly antiferromagnetic, with $\mu_{\mathrm{eff}} \approx 15\ \mu_{\mathrm{B}}$ at 298 K, and the field dependence of its magnetism (Fig. 2) was basically linear to 5.5 T; no spin-crossover effects were discerned. Interest in antiferromagnetic wheels is due to the possibility of coherent quantum tunneling, which may render such species applicable for quantum computing.[5,9]

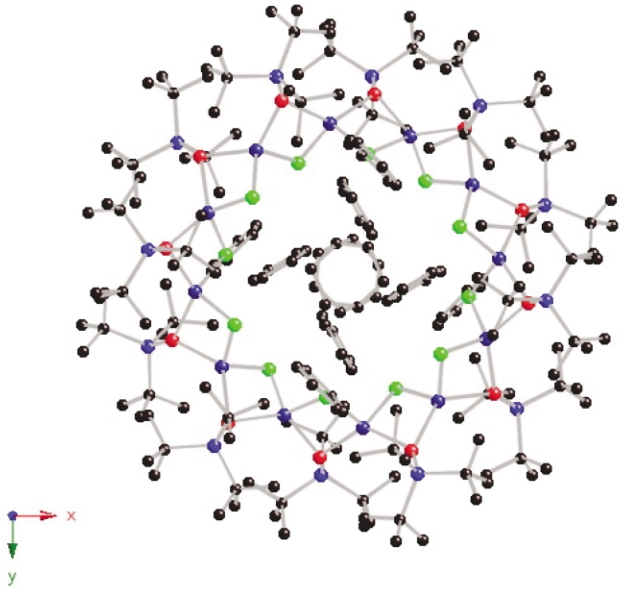

Fig. 1 Molecular view of the wheel $\{(^t\mathrm{Bu_3SiS})\mathrm{CoCl}\}_{12}\cdot(\mathrm{C_6H_6})_6$ [**2**, $d(\mathrm{Cl\cdots Cl}) = 9.584(2), 9.622(2), 9.636(2)$ Å], which is roughly D_{6d}; its asymmetric unit is 1/4 of the wheel. The structure of $\{(^t\mathrm{Bu_3SiS})\mathrm{NiBr}\}_{12}\cdot(\mathrm{C_6H_{14}})_n$ (**5**) is related to that of **2**, except that $d(\mathrm{Br\cdots Br}) = 9.583(8), 10.750(8)$ Å and it is approximately C_{6v}; its asymmetric unit is 1/6 of the wheel.

Isolation of the corresponding Ni wheel was somewhat more difficult. The reaction of 2 equiv. $\mathrm{NaSSi}^t\mathrm{Bu_3}$ and $\mathrm{NiBr_2(THF)_2}$ in THF (24 h, 23 °C) provided purple $[(^t\mathrm{Bu_3SiS})\mathrm{Ni}]_2(\mu\text{-}\mathrm{SSi}^t\mathrm{Bu_3})_2$ (**3**), a rare Ni(II) dithiolate dimer,[10] in 63% yield upon crystallization from diethyl ether. Its molecular weight indicated a dimeric formulation akin to $[(^t\mathrm{Bu_3SiS})\mathrm{Fe}]_2(\mu\text{-}\mathrm{SSi}^t\mathrm{Bu_3})_2$.[1] A 1 : 1 ratio of $\mathrm{NaSSi}^t\mathrm{Bu_3}$ and $\mathrm{NiBr_2(THF)_2}$ in THF kept at 23 °C for 16 h produced a green solid tentatively formulated as $[(^t\mathrm{Bu_3SiS})\mathrm{NiBr(THF)}]_2$ (**4**). Subsequent heating of solid **4** for 3 h at 88 °C afforded a red–purple solid that was washed with $\mathrm{Et_2O}$ to remove significant amounts of disproportionation product **3**. The resulting green solid was extracted into hexanes, and slow evaporation (12 h) produced red crystals of $\{(^t\mathrm{Bu_3SiS})\mathrm{NiBr}\}_{12}\cdot(\mathrm{C_6H_{14}})_n$ (**5**) in ~ 15% yield, although by-product contamination, presumably due to disproportionation, rendered elemental analysis and magnetic studies untenable. The nickel wheel crystallized in the hexagonal system ($P6_3mc$) with severely disordered ^{t}Bu groups and hexanes of crystallization. The core distances and angles of the

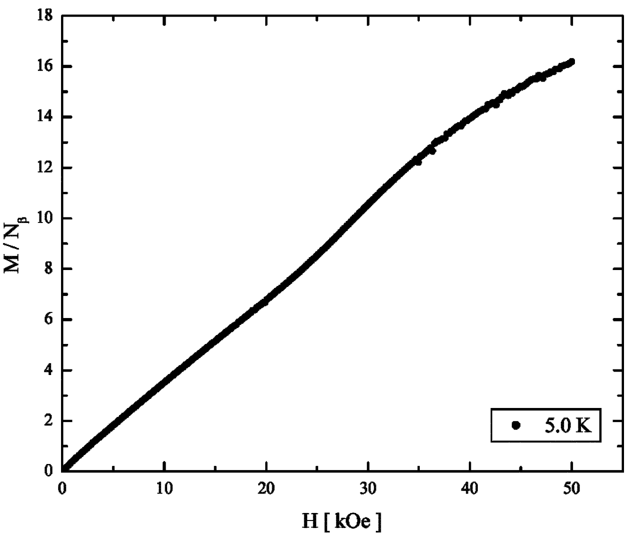

Fig. 2 Field dependence of weakly antiferromagnetic $\{(^t\mathrm{Bu_3SiS})\mathrm{CoCl}\}_{12}\cdot(\mathrm{C_6H_6})_6$ (**2**).

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† Electronic supplementary information (ESI) available: molecular view of the wheel $\{(^t\mathrm{Bu_3SiS})\mathrm{NiBr}\}_{12}\cdot(\mathrm{C_6H_{14}})_6$ (**5**). See http://www.rsc.org/suppdata/cc/b3/b311212h/

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$\{(^t\mathrm{Bu_3SiS})\mathrm{NiBr}\}_2$ asymmetric unit, and those pertaining to the $\mathrm{Ni_{12}}$ wheel are related to those of $\{(^t\mathrm{Bu_3SiS})\mathrm{FeBr}\}_{12}$,[1] yet reflecting the slightly smaller size of Ni(II) compared to Fe(II): $d(\text{Ni–Br})_\text{av}$ = 2.440(9), $d(\text{Ni–S})_\text{av}$ = 2.276(53), $d(\text{Br}\cdots\text{Br})$ = 9.583(8), 10.750(8), $d(\text{Ni}\cdots\text{Ni})_\text{av}$ = 3.314(41) Å, $\angle(\text{Ni–Br–Ni})_\text{av}$ = 85.5(15), $\angle(\text{Br–Ni–Br})_\text{av}$ = 103.33(11), $\angle(\text{S–Ni–S})_\text{av}$ = 137.0(26), $\angle(\text{Ni–S–Ni})_\text{av}$ = 93.9(11), and $\angle(\text{Br–Ni–S})_\text{av}$ = 88.8(17), 118.4(21)°. Six bromides are inclined slightly below the $\mathrm{Ni_{12}}$ plane and the remainder are substantially above it, whereas the halides in the ferrous and cobaltous wheels are essentially equidistant across the ring. Cavities in the crystal are rife with disordered hexane molecules that were removed *via* the SQUEEZE procedure of the PLATON program;[11] the final model consisted of only the ordered part. Apparently, the solvent type has no template effect or influence on wheel formation or size.

When the solid formulated as $[(^t\mathrm{Bu_3SiS})\mathrm{NiBr(THF)}]_2$ (**4**) was heated for 22 h at 130 °C, the residue dissolved in hexane, and the resulting solution filtered, red rods corresponding to the 'hubcap' complex $[(\mu\text{-SSi}^t\mathrm{Bu_3})\mathrm{Ni}]_5(\mu_5\text{-S})$ (**6**) were isolated upon crystallization in ~75% yield. This mixed valence $\mathrm{Ni^{II}}_2\mathrm{Ni^{I}}_3$ complex is reminiscent of $[\{\mathrm{Ni^{II}Ni^{I}}_4(\mu\text{-S}^t\mathrm{Bu})_5\}(\mu_5\text{-S})]^-$, which was synthesized from $\mathrm{NaS}^t\mathrm{Bu}$ and $\mathrm{NiCl_2}$ over a lengthy period.[12–14] 'Hubcap' complex **6** appears to be derived from a reproducible thermal breakdown of **4** or wheel **5**, as proposed in eqn. 1.

$$48\ \text{‘}(^t\mathrm{Bu_3SiS})\mathrm{NiBr}\text{’} \longrightarrow 22\ \mathrm{NiBr_2} + 6\ ^t\mathrm{Bu_3SiSSSi}^t\mathrm{Bu_3} + 4\ ^t\mathrm{Bu_3SiBr} + 4\ [(\mu\text{-SSi}^t\mathrm{Bu_3})\mathrm{Ni}]_5(\mu_5\text{-S})\ (\mathbf{6}) + 3\ [(^t\mathrm{Bu_3SiS})\mathrm{Ni}]_2(\mu\text{-SSi}^t\mathrm{Bu_3})_2\ (\mathbf{3}) \quad (1)$$

Fig. 3. illustrates the 'hubcap', which is actually a symmetric star whose points are $\mu\text{-SSi}^t\mathrm{Bu_3}$ groups distributed about a pentagon of nickels capped by the μ_5-sulfide. A non-crystallographic mirror plane splits the star such that $^t\mathrm{Bu_3Si}$ groups are 'up' toward the μ_5-S at S1, S2, and S4, and 'down' at the remaining points. The Ni–Ni distances average 2.475(22) Å, and the Ni–μ-S [2.191(10) Å (av)] and Ni–μ_5-S [2.181(5) Å (av)] distances are virtually identical. Despite the steric interactions of the silyl groups, each μ-S–$\mathrm{Ni_2}$–μ_5-S diamond is relatively flat, with Ni–μ-S–Ni angles of 68.8(5)° (av), within error of the average Ni–μ_5-S–Ni angles of 69.1(7)°; the μ_5-S–Ni–μ-S angles [109.5(11)° (av)] are very close to the sum of the μ_5-S–Ni–Ni [55.4(4)° (av)] and μ-S–Ni–Ni [55.6(4)° (av)] angles. Subtle creasing about each Ni–Ni bond in the pentagon [$\angle$(Ni–Ni–Ni) = 107.3(26) (av), $\angle$(Ni–μ_5-S–Ni) = 132.2(46)° (av)] allows some relief from inter-$^t\mathrm{Bu_3SiS}$ repulsions [$\angle$(μ-S–Ni–μ-S) = 140.3(6)° (av)]. Calculations predict that **6** should have one unpaired electron,[13] but impurities such as $\mathrm{NiBr_2}$ in bulk samples have thus far hampered magnetic investigations.

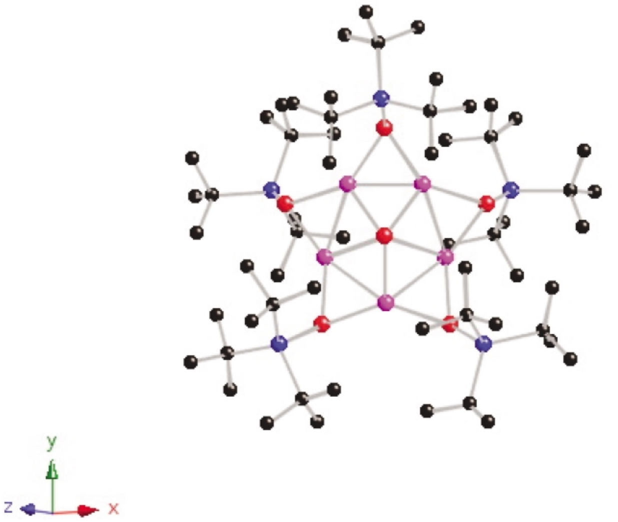

Fig. 3 Molecular structure of the 'hubcap' complex $[(\mu\text{-SSi}^t\mathrm{Bu_3})\mathrm{Ni}]_5(\mu_5\text{-S})$ (**6**).

In summary, while the wheel is apparently a common motif for the secondary structure of first row '$(^t\mathrm{Bu_3SiS})\mathrm{MX}$' species, redox or disproportion reactions replete with bond-breaking events may lead to additional structural complexity in the formation of unusual aggregates.[15]

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Notes and references

‡ *Selected characterization data* for **2**: (^{1}H NMR, $\mathrm{C_6D_6}$, 400 MHz) δ 3.60 ($\nu_{1/2} \approx$ 50 Hz); anal. calcd. for $\mathrm{C_{12}H_{27}SiSClCo}$ C, 44.2; H, 8.37; Cl, 10.9; found C, 44.2; H, 8.4; Cl, 10.9%. For **3**: (^{1}H NMR, $\mathrm{C_6D_6}$, 400 MHz) δ 1.31 (s), 1.35 (s); (^{13}C NMR, $\mathrm{C_6D_6}$) δ 25.84, 26.41 (SiC), 31.97, 32.25 ($\mathrm{CH_3}$); anal. calcd. for $\mathrm{C_{24}H_{54}Si_2S_2Ni}$ C, 55.2; H, 10.5; found C, 54.9; H, 10.9%. M_w (Signer) calcd. 1044, found 1030(60). For **6**: (^{1}H NMR, $\mathrm{C_6D_6}$, 400 MHz) δ 1.73 ($\nu_{1/2} \approx$ 130 Hz) tentative assignment.

§ *Crystal data* for **2**: $\mathrm{C_{45}H_{90}Cl_3S_3Si_3Co_3}$, M = 1094.81, tetragonal, a = 23.287(3), c = 24.155(4) Å, U = 13098(3) Å^3, T = 173(2) K, $P\bar{4}2_1c$, Z = 8 (1/4 wheels), $\mu(\text{Mo-K}_\alpha)$ = 1.048 mm^{-1}, 8000 (R_int = 0.1040) independent reflections, R_1 (2σ) = 0.0533. For **5**: $\mathrm{C_{24}H_{54}Br_2S_2Si_2Ni_2}$, M = 740.20, hexagonal, a = 26.128(16), c = 24.69(2) Å, U = 14597(18) Å^3, T = 173(2) K, $P6_3mc$, Z = 12 (1/6 wheels), $\mu(\text{Mo-K}_\alpha)$ = 1.010 mm^{-1}, 3730 (R_int = 0.1259) independent reflections, R_1 (2σ) = 0.1491. For **6**·$\mathrm{C_6H_{14}}$: $\mathrm{C_{66}H_{149}S_6Si_5Ni_5}$, M = 1569.21, monoclinic, a = 14.193(8), b = 16.493(10), c = 36.54(2) Å, β = 98.564(11)°, U = 8459(9) Å^3, T = 293(2) K, $P2_1/n$, Z = 4, $\mu(\text{Mo-K}_\alpha)$ = 1.231 mm^{-1}, 11776 (R_int = 0.1174) independent reflections, R_1 (2σ) = 0.1105. CCDC 220005–220007. See http://www.rsc.org/suppdata/cc/b3/b311212h/ for crystallographic data in CIF or other electronic format.

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