

$C_2$  symmetry, contains two parallel, distorted square planar  $[\text{NiS}_2\text{P}]$  units linked together by the arms of the ligands. Each nickel is coordinated by two sulfurs and a phosphorus from one ligand and a sulfur from the other ligand to form a distorted square planar  $[\text{NiS}_3\text{P}]$  array with the trans S1–Ni–S3 and P1–Ni1–S2 angles being  $156.0 (2)^\circ$  and  $171.8 (2)^\circ$ , respectively. The two  $[\text{NiS}_2\text{P}]$  units are aligned on top of one another in an eclipsed configuration in which the nickel atoms are separated by a Ni1–Ni1' distance of  $3.035 (4) \text{ \AA}$ .<sup>8</sup>

Electrochemical studies<sup>9</sup> indicate that  $[\text{Pr}_4\text{N}]_2[\text{Ni}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]$  (**1**) is oxidized by one electron to a  $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$  species at  $-0.57 \text{ V}$  and then to a  $[\text{Ni}(\text{III})\text{Ni}(\text{III})]$  species at  $-0.05 \text{ V}$  (vs SCE) (Figure 2). Controlled potential electrolysis studies show both the  $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$  and  $[\text{Ni}(\text{III})\text{Ni}(\text{III})]$  dimers to be thermally stable.  $[\text{Ni}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]^{2-}$  can be oxidized in situ or from isolated **1** by the addition of  $[\text{Cp}_2\text{Fe}]\text{BF}_4$  to yield the mixed-valence  $[\text{Ni}(\text{II})\text{Ni}(\text{III})]$  complex,  $[\text{Pr}_4\text{N}][\text{Ni}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]$  (**2**), in good yield.

The X-ray structure determination<sup>10</sup> of **2** (Figure 3) illustrates that the  $[\text{Ni}(\text{II})\text{Ni}(\text{II})]$  dimer has undergone a substantial structural change upon oxidation to the  $[\text{Ni}(\text{III})\text{Ni}(\text{II})]$  species. The  $[\text{Ni}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]^-$  anion has a crystallographically imposed  $C_2$  axis centered between the two  $[\text{NiS}_4\text{P}]$  square pyramidal units which are bridged by the S1 and S1' sulfur atoms. The structural transformation from **1** to **2** is accomplished by a twisting motion about the Ni–Ni axis with the two unique thiolates in **1** (S2 and S2') moving into the  $\mu_2$  bridging positions. Associated with this structural change is a  $0.53 \text{ \AA}$  shortening in the Ni–Ni distance to a value of  $2.501 (2) \text{ \AA}$ , which could be indicative of a substantial Ni–Ni interaction.<sup>8b</sup> The structural change must be rapid on the time scale of the electrochemical measurements; the cyclic voltammogram of isolated **2** in DMF is completely analogous to that of **1**.<sup>9,11</sup> The crystallographic symmetry that relates the two nickel centers in **2** rules out a type I (trapped-valence) electron configuration.<sup>12</sup>

In addition to the crystallographic evidence, the electronic spectrum of compound **2** suggests a delocalized mixed-valence state. Compound **2** absorbs more strongly in the visible region than does **1**, and it also exhibits two bands (lacking in **1**) of medium intensity in the near-IR region at 920 and 1325 nm.<sup>13</sup> If the 920 and 1325 nm bands are assigned as intervalence transitions (IT), their broad band widths of the order  $50\,000\text{--}30\,000 \text{ cm}^{-1}$  along with their solvent dependence<sup>14</sup> are suggestive of a class II mixed-valence species.<sup>12,15</sup> Compound **2** gives a rhombic EPR spectrum (DMF/ $\text{CH}_2\text{Cl}_2$  glass at 100 K) with  $g_x = 2.12$ ,  $g_y = 2.09$ , and  $g_z = 2.03$ .

The results described above are consistent with the observation that thiolates can stabilize the Ni(III) oxidation level at biologically relevant redox potentials.<sup>1a</sup> Moreover, it is apparent that the chelating ability of the ligand has a marked effect upon the stability of the Ni(III)–thiolate center. We have synthesized and characterized a molecule that represents half the  $[\text{Ni}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]^{2-}$  dimer. That molecule which contains the  $[\text{Ni}^{\text{II}}\text{S}_3\text{P}]$  core,  $[\text{Et}_4\text{N}][\{(2\text{-PhC}_6\text{H}_4\text{S})\text{Ni}\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_2(\text{Ph})\}\}]$  (**3**),<sup>16</sup> cannot be

oxidized to a stable Ni(III)–thiolate species and in fact shows an irreversible CV wave at a potential of about  $-0.25 \text{ V}$  (vs SCE), a result that is consistent with the work reported by others.<sup>17</sup> These results can be extrapolated to indicate that the chelating nature of the hydrogenase proteins may be significant in stabilizing its  $[\text{Ni}^{\text{III}}\text{S-Cys}]$  center.

Compound **2** is unique because it is a crystallographically characterized mixed-valence nickel thiolate compound, as well as a robust Ni(III)–thiolate system.<sup>18</sup> Also, further work has shown that the properties of the  $[\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3]^{3-}$  ligand can be exploited to prepare other mixed-valence complexes of the type described above, including  $[\text{M}_2\{\text{P}(\text{o}-\text{C}_6\text{H}_4\text{S})_3\}_2]^-$  ( $\text{M} = \text{Co}$  and  $\text{Fe}$ ).<sup>19</sup>

**Acknowledgment.** This research was supported by a grant from the National Institutes of Health (GM 36308). We thank S. A. Koch for assistance with the X-ray structures and J. Lauher for use of his molecular graphics programs.

**Supplementary Material Available:** Tables of crystallographic parameters, atomic coordinates, thermal parameters, bond distances and angles, and ORTEP diagrams for **1–3** (35 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(16) Crystal data for  $3\text{-CH}_3\text{OH}$ :  $\text{NiS}_2\text{PNC}_6\text{H}_4\text{S}_3\text{OH}_{46}$ , monoclinic,  $P2_1$ ;  $a = 9.701 (4) \text{ \AA}$ ,  $b = 20.247 (6) \text{ \AA}$ ,  $c = 10.424 (4) \text{ \AA}$ ,  $\beta = 114.52 (3)^\circ$ ,  $V = 1863 (2) \text{ \AA}^3$ ,  $Z = 2$ . A total of 2616 reflections with  $I > 3\sigma(I)$  were refined to  $R (R_w) = 0.044 (0.058)$ . The methylene groups of the cation are disordered. Selected bond distances ( $\text{ \AA}$ ) and angles ( $\text{deg}$ ): Ni–S1 2.177 (2), Ni–S2 2.180 (2), Ni–S3 2.215 (2), Ni–P1 2.115 (2); S1–Ni–S2 166.1 (9), S1–Ni–S3 98.48 (9), S1–Ni–P1 87.65 (8), S2–Ni–S3 86.91 (9), S2–Ni–P1 87.65 (9), P1–Ni–S4 173.4 (1).

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## Vesicle of a Hybrid Bolaamphiphile: Flip-Flop Behavior of Spin Labels

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Received March 26, 1992

Vesicle monolayers formed by hydrocarbon bolaamphiphiles, single hydrophobic chains with two polar groups, one at each end, provide a lot more intriguing properties than the usual bilayer membranes.<sup>1–4</sup> Fluorocarbon amphiphiles possess many peculiar characteristics, such as limited miscibility with hydrocarbon amphiphiles.<sup>5–10</sup> In this communication, we report the synthesis of a single-chain hybrid bolaamphiphile with nearly equal lengths

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(9) Electrochemical studies: Solutions were 0.001 M in DMF with 0.1 M supporting electrolyte  $[\text{Bu}_4\text{N}][\text{BF}_4]$ ; scan rate was 200 mV/s, referenced to the saturated calomel electrode (SCE). Compound **1** (Pt electrode) shows two one-electron oxidations  $(E_{\text{pc}} + E_{\text{pa}})/2 = E_{1/2} (\Delta E_p, i_{\text{pa}}/i_{\text{pc}})$  at  $-0.57 \text{ V}$  (100 mV, 1.02) and  $-0.05 \text{ V}$  (60 mV, 0.98). Compound **2** (glassy carbon electrode) shows a one-electron reduction at  $-0.50 \text{ V}$  (130 mV, 0.92) and a one-electron oxidation at  $0.05 \text{ V}$  (90 mV, 0.94).

(10) Crystal data for  $2\text{-2CH}_3\text{OH}$ :  $\text{Ni}_2\text{S}_6\text{P}_2\text{O}_7\text{NC}_{50}\text{H}_{60}$ , monoclinic,  $C2/c$ ;  $a = 13.843 (1) \text{ \AA}$ ,  $b = 17.487 (2) \text{ \AA}$ ,  $c = 21.224 (3) \text{ \AA}$ ,  $\beta = 94.26 (1)^\circ$ ,  $V = 5124 (2) \text{ \AA}^3$ ,  $Z = 4$ . A total of 2549 unique reflections with  $I > 3\sigma(I)$  were refined to  $R = 0.052$  and  $R_w = 0.069$ . The cation is disordered.

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°C, almost 5 orders slower than that of fatty acids in hydrocarbon vesicles.<sup>17</sup> The limited miscibility between hydrocarbon and fluorocarbon compounds results in an unfavorable solubilization of hydrocarbon spin label, H-Tempo, in the fluorocarbon phase, which causes a slow flip-flop rate of H-Tempo in the vesicle monolayer of **1**.

This study established the vesicle monolayer of **1** as the simplest system with well-defined hydro- and fluorocarbon domains. Consequently, it can be used in the study of interactions such as charge and energy transfer between hydro- and fluorocarbon molecules. Such a study is the object of our current attention.

**Registry No.** **1**, 142319-50-4; **3**, 68136-90-3; **4**, 142319-51-5; **5**, 142319-52-6; 10-undecenoic acid, 112-38-9.

(16) If every inward or outward translocation of a paramagnetic molecule is an independent event, then the time rate of change of the internal spin label paramagnetism is given by

$$dN_i/dt = k_i N_o - k_o N_i \quad (1)$$

Since the reduction of spin label by sodium ascorbate is much faster than the inward translocation process of spin-label molecules on outer semi-monolayer, then

$$dN_i/dt = -k_o N_i \quad (2)$$

and

$$\ln N_i = -k_o t + C \quad (3)$$

where  $C$  is a constant and  $k_o$  is the rate constant of the outward translocation process.

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## Synthesis and Crystallographic Characterization of [CsHN(SiMe<sub>3</sub>)<sub>4</sub>], a Cesium-Based Heterocubane

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Received February 12, 1992

The unsolvated bis(trimethylsilyl)amido complexes of the alkali metals display a remarkable progression of structures as the metallic radii increase. In the solid state, the lithium compound is a cyclic trimer,<sup>1</sup> whereas the sodium salt exists as chains of [NaN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>n</sub> units.<sup>2</sup> Rather than forming an analogous nonmolecular substance, the potassium amide crystallizes as a discrete dimer with a nearly square K-N(SiMe<sub>3</sub>)<sub>2</sub>-K'-N(SiMe<sub>3</sub>)<sub>2</sub>' ring.<sup>3,4</sup> The factors that induce the sodium complex to form a polymeric material when the lithium and potassium counterparts do not are unknown. We are interested in the ability of the (trimethylsilyl)amido group to support low coordination numbers

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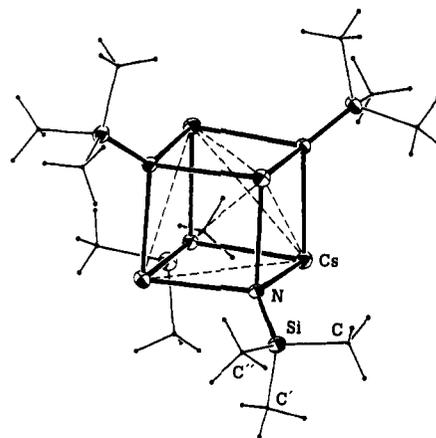
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(4) After our publication of the structure of unsolvated [KN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, we became aware of an earlier report of [KN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(toluene), in which the toluene is present as lattice solvent (Williard, P. G. *Acta Crystallogr.* **1988**, *C44*, 270-272). The geometry of the potassium amide itself appears to be essentially identical in the two structures.



**Figure 1.** ORTEP view of [CsHN(SiMe<sub>3</sub>)<sub>4</sub>]<sub>4</sub>, with thermal ellipsoids drawn at the 50% probability level. The dashed lines between the cesium atoms illustrate the alternate description of the compound as a Cs<sub>4</sub> tetrahedron capped on each face with μ<sub>3</sub>-amido groups. For clarity, the methyl groups of the SiMe<sub>3</sub> units are rendered as lines.

in compounds of the heavy s-block metals,<sup>5-7</sup> and we report here the unusual result obtained from attempts to generate [bis(trimethylsilyl)amido]cesium.<sup>8</sup>

Addition of a few crystals of iron(III) nitrate to a deep blue solution of cesium in liquid ammonia followed by a slight molar excess of hexamethyldisilazane in hexane causes a slow discharge of the blue color. Upon evaporation of the ammonia, a tan residue is left that has modest solubility in aromatics; cubes of a cream-colored solid can be grown from hexane.<sup>9</sup> Its EI mass spectrum contains a weak signal for the parent ion at  $m/z$  884, consistent with the C<sub>12</sub>H<sub>40</sub>Cs<sub>4</sub>N<sub>4</sub>Si<sub>4</sub><sup>+</sup> ion. The base peak ( $m/z$  797) represents the loss of a single N(SiMe<sub>3</sub>) group from the parent ion, i.e., {Cs<sub>4</sub>H[HN(SiMe<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. Strong signals corresponding to the Cs<sup>+</sup>, Cs<sub>2</sub><sup>+</sup>, and Cs<sub>3</sub><sup>+</sup> ions are also observed. The IR spectrum of the material (KBr pellet) reveals a broad ν(NH) centered at 3150 cm<sup>-1</sup>.<sup>10</sup> These results suggest that the compound should be formulated as the mono(trimethylsilyl)amido species, [CsHN(SiMe<sub>3</sub>)<sub>4</sub>].<sup>11</sup> The fragmentation pattern in the mass spectrum is reminiscent of the behavior of various alkyl lithium tetramers [LiR]<sub>4</sub> (R = Et, CH<sub>2</sub>SiMe<sub>2</sub>, *t*-Bu), whose parent ions are weak or nonexistent but which display strong signals for [Li<sub>4</sub>R<sub>3</sub>]<sup>+</sup> fragments.<sup>12-14</sup>

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(9) In a typical preparation, Cs metal (0.80 g, 6.0 mmol) was loaded in a flask and transferred to an argon-equipped Schlenk line. Ammonia was condensed into the flask at -78 °C (ca. 200 mL), followed by countercurrent addition of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. Hexamethyldisilazane (1.15 g, 7.1 mmol) in hexane (15 mL) was dripped into the mixture, and the reaction was allowed to come to room temperature. Evaporation of the residual hexane left the crude product in quantitative yield. Although it has only trace solubility in alkanes, addition of hexane to the crude material, followed by slow evaporation and periodic replacement of the lost hexane, will generate crystalline material; this process requires more than 30 days.

(10) The <sup>1</sup>H NMR spectrum at 20 °C contains the singlet expected for the SiMe<sub>3</sub> groups at δ 0.21 (C<sub>6</sub>D<sub>6</sub>). The resonance for the amido hydrogens was not observed.

(11) An N-Si bond of the hexamethyldisilazane must be cleaved in the synthesis; although the mechanism is unknown, the presence of ammonia appears to be important. If elemental Cs and HN(SiMe<sub>3</sub>)<sub>2</sub> are allowed to react in refluxing hexane (3 days), an unidentified brown precipitate forms, and only a small amount of the monosilylamide can be isolated.

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