°C, almost 5 orders slower than that of fatty acids in hydrocarbon vesicles.[17] 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.

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(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

$$dN_i/dt = k_iN_o - k_oN_i \qquad (1)$$

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

$$dN_i/dt = -k_oN_i \qquad (2)$$

and

$$\ln N_i = -k_ot + C \qquad (3)$$

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

(17) Sanson, A.; Egret-Charlier, M.; Bouloussa, O.; Maget-Dona, R.; Charles, M.; Ptak, M. *Proceedings of the 5th International Symposium on Surfactants in Solution*; Mittal, K. L., Bothorel, P., Eds.; Plenum Press: New York, 1987.

Synthesis and Crystallographic Characterization of $[CsHN(SiMe_3)]_4$, a Cesium-Based Heterocubane

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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,[1] whereas the sodium salt exists as chains of $[NaN(SiMe_3)_2]_n$ units.[2] Rather than forming an analogous nonmolecular substance, the potassium amide crystallizes as a discrete dimer with a nearly square $K-N(SiMe_3)_2-K'-N(SiMe_3)_2'$ ring.[3,4] 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 in compounds of the heavy s-block metals,[5-7] and we report here the unusual result obtained from attempts to generate [bis(trimethylsilyl)amido]cesium.[8]

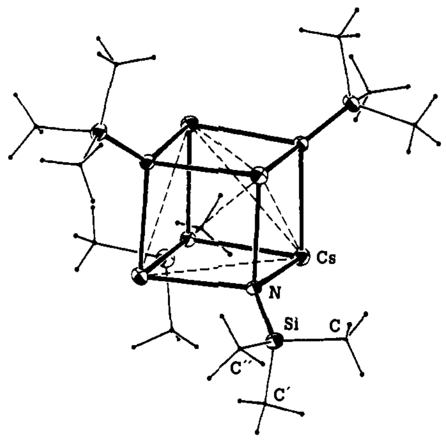

Figure 1. ORTEP view of $[CsHN(SiMe_3)]_4$, with thermal ellipsoids drawn at the 50% probability level. The dashed lines between the cesium atoms illustrate the alternate description of the compound as a Cs_4 tetrahedron capped on each face with μ_3-amido groups. For clarity, the methyl groups of the $SiMe_3$ units are rendered as lines.

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.[9] Its EI mass spectrum contains a weak signal for the parent ion at m/z 884, consistent with the $C_{12}H_{40}Cs_4N_4Si_4^+$ ion. The base peak (m/z 797) represents the loss of a single $N(SiMe_3)$ group from the parent ion, i.e., $\{Cs_4H[HN(SiMe_3)]_3\}^+$. Strong signals corresponding to the Cs^+, Cs_2^+, and Cs_3^+ ions are also observed. The IR spectrum of the material (KBr pellet) reveals a broad ν(NH) centered at 3150 cm^{-1}.[10] These results suggest that the compound should be formulated as the mono(trimethylsilyl)amido species, $[CsHN(SiMe_3)]_4$.[11] The fragmentation pattern in the mass spectrum is reminiscent of the behavior of various alkyllithium tetramers $[LiR]_4$ (R = Et, CH_2SiMe_2, t-Bu), whose parent ions are weak or nonexistent but which display strong signals for $[Li_4R_3]^+$ fragments.[12-14]

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(1) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229-237.

(2) Grüning, R.; Atwood, J. L. *J. Organomet. Chem.* **1977**, *137*, 101-111.

(3) Tesh, K. F.; Hanusa, T. P.; Huffman, J. C. *Inorg. Chem.* **1990**, *29*, 1584-1586.

(4) After our publication of the structure of unsolvated $[KN(SiMe_3)_2]_2$, we became aware of an earlier report of $[KN(SiMe_3)_2]_2\cdot$(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.

(5) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121-125.

(6) Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96-101.

(7) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 127-140.

(8) The synthesis of $CsN(SiMe_3)_2$ from $CsNH_2$ or Cs metal and $HN(SiMe_3)_2$ in liquid ammonia has been reported without details (Wannagat, U. *Pure Appl. Chem.* **1969**, *19*, 329-342). It is not certain in what respects that synthesis differs from the present one.

(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 $Fe(NO_3)_3\cdot 9H_2O$. 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 ^1H NMR spectrum at 20 °C contains the singlet expected for the $SiMe_3$ groups at δ 0.21 (C_6D_6). 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 $HN(SiMe_3)_2$ 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.

(12) Berkowitz, J.; Bafus, D. A.; Brown, T. L. *J. Phys. Chem.* **1961**, *65*, 1380-1383.

(13) Hartwell, G. E.; Brown, T. L. *Inorg. Chem.* **1966**, *5*, 1257-1259.

(14) Darensbourg, M. Y.; Kimura, B. Y.; Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 1236-1242.

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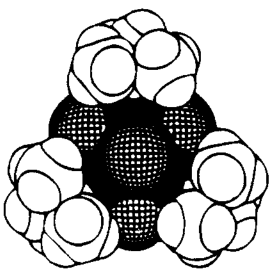

Figure 2. Space-filling drawing of $[CsHN(SiMe_3)]_4$, indicating the exposure of the cesium atoms (cross-hatched spheres). The adjacent nitrogen atoms are black.

To characterize the compound further, a single-crystal structure determination was completed at −174 °C.[15] Consistent with its mass spectrum, the compound crystallizes as a tetramer with a slightly distorted $[CsN]_4$ heterocubane core or, equivalently, a Cs_4 tetrahedron with a μ_3-amido group over each face (see Figure 1). This represents the first structurally characterized heterocubane containing cesium; the coordination number of three for cesium is unprecedented in a molecular complex.[16] The N–Cs–N′ angle of 87.8 (3)° and the Cs–N–Cs′ angle of 93.1 (3)° are unexceptional deviations from the ideal 90°; both greater and lesser deviations are known in main-group cages.[19] The amido hydrogens were not located in the crystal structure, and the thermal ellipsoids of the carbon atoms were considerably elongated, suggestive of high thermal motion of the $SiMe_3$ groups.[20]

Several unusual structural features are present in the structure, including the fact that the Cs, N, and Si atoms lie on crystallographically imposed C_3 axes. The N—Si distance of 1.59 (1) Å is strikingly short for a (trimethylsilyl)amido complex and lies in the range previously identified with N=Si double bonds.[21] N—Si single bond lengths are known to be as short as 1.634 (4) (in the $[Ph_3SiNSiPh_3]^-$ ion[25]) and 1.64 (1) Å (in $KN(SiMe_3)_2$-(dioxane)$_2$[26]), but they are often 1.70 Å in length or greater.[27] The shortening of the N—Si distance suggests that the bonding in the cubane could be described as $[Cs^+H^+(NSiMe_3)^{2-}]_4$, with the protons disordered over the cube faces.[28] Donation from the electron-rich nitrogen to the silicon could lead to bond shortening.[29]

An equally unanticipated structural feature is the Cs–N length of 2.915 (5) Å, which is only 0.13 Å longer than the average K–N distance of 2.79 Å in $[KN(SiMe_3)_2]_2$.[3] Considering that the difference between K^+ and Cs^+ radii for the same coordination number is normally 0.22–0.29 Å[33] and that the coordination number is larger in the cesium complex, this represents an unexpectedly small increase in the M–N distance.

It is notoriously difficult to infer the significance of metal–metal interactions in main-group compounds by distance criteria alone;[34] nevertheless, the Cs···Cs′ distance of 4.234 (1) Å can be compared to the benchmark values of 5.309 (Cs–Cs distance in the metal)[35] and 4.56 Å (distance in the Cs_2 dimer).[36] The $Cs^+\cdots Cs^+$ separation is 4.55 Å in the cesium carbazide dimer;[18] the change in metal coordination number (3 in the heterocubane vs 8 and 9 in the dimer) certainly accounts for some of the difference in metal–metal distances. A further comparison can be made with the deeply colored, conducting suboxides of cesium (e.g., $Cs_{11}O_3$, Cs_4O, Cs_7O) that have been described as ionic clusters embedded in a matrix of electrons (e.g., $(Cs_{11}O_3)^{5+}(e^-)_5$).[37] These have intracluster Cs–Cs distances of up to 4.31 Å with undoubtedly some M–M bonding. Unlike the cesium suboxides, however, the individual cubes of $[CsHN(SiMe_3)]_4$ are well separated in the solid state; the closest intermolecular $CH_3\cdots CH_3'$ contacts are over 4.2 Å. As indicated by a space-filling drawing (Figure 2), the cesium atoms are exposed to external molecules and are largely unshielded by the trimethylsilyl groups. This makes the hydrocarbon solubility of the complex all the more unusual.

The sum of the spectroscopic, structural, and solubility data argues for at least extremely tight ion pairing, if not some degree of covalency, between the cesium and amido groups. The isolation of this heterocubane suggests that the molecular chemistry of the heaviest alkali metals may be considerably more diverse than previously expected.

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Supplementary Material Available: Summary of data collection, tables of fractional coordinates, bond distances and angles, and anisotropic thermal parameters, and an ORTEP view with all thermal ellipsoids (4 pages); table of observed and calculated structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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(15) Crystals of $[CsHN(SiMe_3)]_4$ are cubic, space group $P23$, with a = 9.201 (1) Å, and $D_{calcd} = 1.89$ g cm^{-3} for $Z = 1$ (tetramer). Data were collected on a Picker four-circle goniostat at −174 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Continuous θ–2θ scans with fixed backgrounds were used to collect a total of 2553 intensities (448 unique) in the range $6° < 2\theta < 45°$, of which 415 had $F > 2.33\sigma(F)$. No decay was observed during the collection. Data were corrected for absorption and reduced to a unique set of intensities and associated σ in the usual manner. The previously located Cs, N, and Si atoms[20] were introduced, and difference Fourier transform located the unique carbon atom. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated using idealized geometries and d(C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. A final difference Fourier had as its largest peak a possible alternate location for the carbon (1.4 e/A^3), but attempts to use two half-weight carbon atoms led to less satisfactory results. The final $R(F)$ value was 0.032 ($R_w(F)$ = 0.034); GOF = 0.83.

(16) The synthesis of a $(Me_3SiNCs)_2SiMe_2$ amide has been described, but its structure is unknown.[17] The only molecular cesium amide that has been structurally characterized is the dimeric PMDTA derivative of cesium carbazide.[18] In the latter, the cesiums are eight- and nine-coordinate.

(17) Brauer, D. J.; Bürger, H.; Liewald, G. R. *J. Organomet. Chem.* **1983**, *248*, 1–15.

(18) Gregory, K.; Bremer, M.; vonRaguē Schleyer, P.; Klusener, A. A.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224–1225.

(19) Veith, M. *Chem. Rev.* **1990**, *90*, 3–16.

(20) At 20 °C, the unit cell volume is approximately 2% larger (a = 9.271 (2) Å). A room-temperature data set collected at Vanderbilt University readily revealed the Cs, N, and Si atoms (using SHELXS-86), but no evidence for the carbon atom could be found in difference maps. This leads us to believe that, despite the low temperature, the smearing of the methyl group ellipsoids at −174 °C represents kinetic rather than static disorder.

(21) Crystallographically established N=Si values include the following: 1.568 (3) Å in $(t\text{-Bu})_2Si{=}NSi(t\text{-Bu})_3$;[22] 1.574 (10) and 1.588 (9) Å in $(THF)(Me)_2Si{=}NSi(t\text{-Bu})_3$;[22] 1.596 (2) Å in $(THF)(Me)_2Si{=}NSi(Me)(t\text{-Bu})_2$;[23] 1.619 (5) Å in $(THF)_3LiF(i\text{-Pr})_2Si{=}NC_6H_2(t\text{-Bu})_3$.[24]

(22) Wiberg, N.; Schurz, K.; Reber, G.; Mueller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591–592.

(23) Walter, S.; Klingebiel, U.; Schmidt, B. D. *J. Organomet. Chem.* **1991**, *412*, 319–26.

(24) Boese, R.; Klingebiel, U. *J. Organomet. Chem.* **1986**, *315*, C17–C21.

(25) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 6509–6510.

(26) Domingos, A. M.; Sheldrick, G. M. *Acta Crystallogr.* **1974**, *B30*, 517–719.

(27) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z.; John Wiley: Chichester, England, 1989; Chapter 3, p 254.

(28) We are grateful to a reviewer for this suggestion.

(29) It may be significant that the ^{29}Si NMR shift of δ 83.1 (toluene, ext. TMS) lies in a range associated with multiply bonded silicon species; for example: δ 78.3 in $(t\text{-Bu})_2Si{=}NSi(t\text{-Bu})_3$;[22] δ 60.3 in $(i\text{-Pr})_2Si{=}N(2,4,6\text{-}(t\text{-Bu})_3C_6H_2)$;[30] δ 63.1 in $(t\text{-Bu})_2Si{=}N(2,4,6\text{-}(t\text{-Bu})_3C_6H_2)$.[31] Disilenes have ^{29}Si shifts in the range δ 49–95.[32]

(30) Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649–650.

(31) Stalke, D.; Keweloh, N.; Klingebiel, U.; Noltemeyer, M.; Sheldrick, G. M. *Z. Naturforsch., B* **1987**, *42*, 1237–1244.

(32) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902–930.

(33) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(34) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924–5946.

(35) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 67th ed.; Chemical Rubber Company: Cleveland, 1986; p F-159.

(36) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169–278.

(37) Simon, A. In *Structure and Bonding*; J. D. Dunitz, Ed.; Springer-Verlag: Berlin, 1979; Vol. 36, pp 81–127.