Intriguing Tetrasodium Dication Cluster Na_4^{2+} Stabilized between Two Silyl(fluorosilyl)phosphanide Shells

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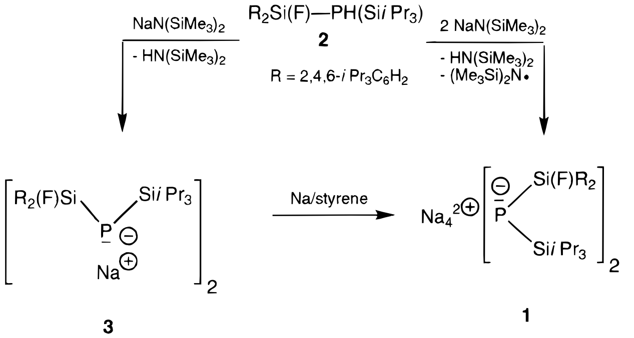
Clusters of the alkali metals are one of the fascinating ways to obtain a better understanding of structure−metallic property relationships when increasing the size of the aggregate. They possess intrinsical shallow potential surfaces and tend to form different isoenergetic topologies with increasing cluster size.[1] Recently, especially diamagnetic and paramagnetic alkali metal cluster cations of sodium, potassium, rubidium, and cesium are of considerable interest since it has been shown that they appear in zeolites which are differently loaded with alkali metals.[2] Thus, in the case of M_4^{n+} cations ($n = 2-4$), it has been demonstrated from extensive experimental and theoretical work that the topology of the M_4 cluster is dependent on electron delocalization (inorganic electrides) and the nature of the intrazeolite cavities.[3] To our knowledge, a *molecular* ion pair compound of an alkali metal cluster cation has not been obtained thus far. We report here on the synthesis of the unusual complex **1** bearing the tetrasodium dication which is coordinatively stabilized by two sterically congested silyl(fluorosilyl)phosphanide counterions. Compound **1** is furnished as an unexpected side-product by metalation of the corresponding secondary silyl(fluorosilyl)-phosphane **2** with $NaN(SiMe_3)_2$ in the molar ratio of 1:2 in hexane/toluene (5:1) at 60 °C (2 d). Previous investigations revealed that **2** can only be completely converted to the expected monosodium phosphanide **3** at room temperature if 2 molar equiv sodium amide is employed, due to the initial formation of heteroaggregate intermediates (Scheme 1).[4] Apparently, the latter incorporate two molecules of the sodium amide. Whereas the 1 m excess of $NaN(SiMe_3)_2$ may be recovered after the reaction at room temperature, we showed that the same reaction at 60 °C within 2 d leads additionally to the novel complex **1** and only 0.74 M excess of the amide can be recovered.

Scheme 1



Subsequent fractional crystallization of the reaction mixture in a small amount of hexane at 25 °C afforded bright yellow crystals of the sodium-rich phosphanide **1** in 8% yield, and further crystallization at 4 °C yielded colorless cubes of excess amide. Finally, the major product of the reaction is the expected monosodium phosphanide **3**, which crystallizes at −30 °C in the form of pale yellow plates in 59% yield. Compound **3**, which has been described previously, is a solvent-free dimeric sodium phosphanide with intramolecular Na−F bonds.[4] The mechanism of the formation of **1** is unknown. Evidently, the process involves a redox reaction in which the $N(SiMe_3)_2$ anion acts very likely as a base and reducing agent at the same time. Reducing properties of the $N(SiMe_3)_2$ anion, however, are already documented for its reactions with different cationic main groups and transition metal centers.[5] That **1** indeed represents a Na metal-containing sodium phosphanide, which accommodates two Na atoms and two Na^+ ions, is unequivocally proven by its independent synthesis through Na metal consumption of **3**. Thus, the reaction of powdered elemental Na with **3** in toluene in the presence of styrene as a catalyst at 40 °C within 2 d furnishes crystalline **1** in 24% yield. The integrity of the samples has been established by correct elemental analyses (C, H, P, F) and X-ray diffraction (see below). The characterization of **1** by means of different mass spectrometric techniques failed due to decomposition. EPR spectroscopic and magnetic susceptibility measurements (10−298 K) clearly showed that **1** is diamagnetic. In contrast to **3**, compound **1** cannot be dissolved in any common organic solvents without decomposition (^{31}P and ^{19}F NMR spectroscopy), and attempts to record a solid-state CP-MAS NMR spectrum (^{23}Na, ^{19}F, ^{31}P) failed due to the huge line-broadening by the ^{23}Na ions ($I = {}^3/_2$) and strong spin−spin coupling. However, the molecular structure has been unequivocally elaborated by single-crystal X-ray diffraction analysis (Figure 1).[6]

1 crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell, whereas **3** is triclinic. The centrosymmetric molecule consists of a rhomboidally distorted planar Na_4 ring as the most interesting part of the aggregate. The distinctly different Na−Na distances of 3.076(3) (Na1−Na2) and 3.202(3) Å (Na1−Na1′) reflect attractive Na−Na interactions (3.82 Å in elemental Na), whereas the Na1−Na2′ distance of 3.530(3) Å is longer than that value in **3** (3.509(5) Å), indicating less attractive interactions between Na1−Na2′. Since the compound is intensely yellow and not red or blue as observed for Na-loaded zeolites (e.g., Na_4^{3+} and related clusters), the residual metal electrons are

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[6] Crystal data of **1**: $C_{39}H_{67}FNa_2PSi_2$, MW = 688.06, $a = 10.919(6)$ Å, $b = 26.140(14)$ Å, $c = 15.057(8)$ Å, $\beta = 102.78(4)°$, $V = 4191(4)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 4$, final R1 = 0.0625, wR2 = 0.1849 (all data) for 4131 [$I > 2\sigma(I)$] observed reflections, GOF (on F^2) = 1.029.

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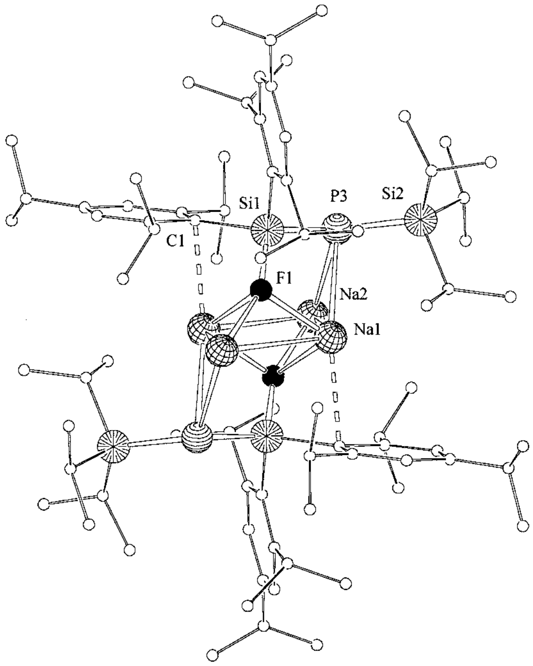
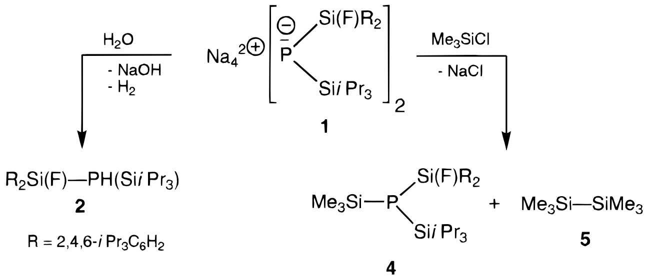


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): Na1−Na2 3.076(3), Na1−Na1′ 3.202(3), Na1−Na2′ 3.530(3), Na1−F1 2.284(3), Na1−F1′ 2.395(3), Na2−F1′ 2.209(3), Na1−P3 2.911(2), Na2−P3 2.905(3), P3−Si2 2.233(2), P3−Si1 2.254(2), Si1−F1 1.618(3), Na1−C1′ 2.712(4), Na2−Na1−Na1′ 68.39(7), Na1−Na2−Na1′ 57.50(6), Na2−P3−Na1 63.87(6), Si2−P3−Si1 117.07(7), Si1−P3−Na2 104.36(7), Si1−P3−Na1 71.97(6), Na1−F1−Na1′ 86.35(10), Na2′−F1−Na1′ 83.75(11).

probably much less delocalized. The Na_4^{2+} cluster is embedded between the two silyl(fluorosilyl)phosphanide counterions. The latter impose that each P atom is μ_2-bonded to a Na_2 edge and each F atom coordinates to three Na centers. The Na−P distances of 2.911(2) and 2.905(3) Å are in the typical range of values of other sodium phosphanides.[7] The three different Na−F distances (2.284(3), 2.395(3), 2.210(3) Å) reflect steric restrictions but resemble those values observed for other sodium fluorosilylphosphanides (2.26−2.38 Å).[8] Interestingly, the Si−F distance of 1.618(3) Å is shorter than that in **3** (1.673(3) Å), although the F atoms in the latter are only two-coordinate, but this can be explained by a higher polarity of the Si−F bond in **1**. The different Si−P distances (2.253(2), 2.232(2) Å) are unremarkable and resemble those of other metalated silylphosphanes.[7] The Na1 center benefits additionally from an attractive interaction with the *ipso*-C atom of a aryl ring (Na1−C1′ 2.712(4) Å), while Na2 is weakly coordinated by C−H bonds of a Si*i*Pr_3 group close by (Na2−C15′ 3.012(6) Å). While calculations showed that the naked Na_4^{2+} cluster, stabilized by four-center two-electron delocalization, prefers the tetrahedral arrangement (the only Na_4^{2+} minimum!), which is 7.3 kcal mol^{-1} more stable than the rhomboid form (D_{2h}),[9] apparently, the coordination of the Na centers in **1** through the counterions and the steric congestion of the substituents favor the D_{2h} form of the cationic Na_4-core. Since **1** contains 2 equiv Na metal, which could serve for reduction processes, we investigated its reactivity toward 4 molar equiv Me_3SiCl in boiling diethyl ether (Scheme 2).

Scheme 2



The reaction is complete after 4 h, affording a pale yellow solution and solid NaCl. Interestingly, while the phosphanide anions of **1** are silylated to give the corresponding disilyl(fluorosilyl)phosphane **4** (δ (^{31}P) = −243, δ (^{19}F) = −122.3)[10] in quantitative yield, the only other molecular product, detectable by means of GC/MS analysis and ^{29}Si NMR spectroscopy, is the disilane $Me_3Si-SiMe_3$ **5**, which has been isolated by fractional condensation in 68% yield. Furthermore, hydrolysis of **1** in diethyl ether leads, under evolution of H_2, to the starting silyl(fluorosilyl)phosphane **2** (^{31}P, ^{19}F NMR) in quantitative yield.

In summary, we have succeeded in the synthesis of the first Na-cluster cation. Its existence suggests a terra incognita of other novel and exciting types of molecular alkali metal cluster compounds.

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Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **1** (7 pages, print/PDF). The crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering information and Web access instructions.

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(10) **4**: colorless oil; ^{31}P NMR (C_6D_6) δ −243.0 (s); ^{19}F NMR (C_6D_6, $CFCl_3$ ext. standard) δ −122.3; ^{29}Si NMR (C_6D_6) δ −2.81 (dd, SiF, ^1J (Si, F) 303 Hz, ^1J (Si, P) 48 Hz), 18.30 (dd, $SiMe_3$, ^1J (Si, P) 37 Hz, ^3J (Si, F) 8.8 Hz), 28.81 (d, Si*i*Pr_3, ^1J (Si, P) = 39 Hz). HRMS Calcd for $C_{42}H_{76}FPSi_3$ M^+ 716.296. Found M^+ 716.291.