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Ion Pairing in [Bis(trimethylsilyl)amido]potassium: X-ray Crystal Structure of Unsolvated $[KN(SiMe_3)_2]_2$

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The use of sterically bulky ligands to enforce low coordination numbers in metal complexes is well established.[1] A variety of [bis(trimethylsilyl)amido]metal complexes are known in which the metal center is two- and three-coordinate, and the electronic, spectroscopic, and structural properties of these species have been extensively studied.[2-15]

Such complexes are usually made by metathesis from the alkali-metal bis(trimethylsilyl)amides, which themselves possess unusual structures; the unsolvated Li derivative crystallizes as a cyclic trimer,[5] whereas the Na salt forms infinite chains of $[Na-N(SiMe_3)_2-]_n$ units.[9] The structure of the potassium salt has been determined as a dioxane-solvated derivative, in which it is found in monomeric units containing 5-coordinate potassium.[8]

Our interest in the chemistry of the heavy pretransition elements[16] induced us to determine the structure of the unsolvated K derivative, in order to determine whether it, like the Na species, would also form polymeric units in the crystalline state. As detailed below, we unexpectedly found that unsolvated $[KN(SiMe_3)_2]_2$ exists as a discrete *dimer* in the solid state, constructed around a nearly square $[K-N-]_2$ framework.

Experimental Section

All manipulations were performed with the rigid exclusion of air and moisture. [Bis(trimethylsilyl)amido]potassium was purchased as a 0.5 M solution in toluene from Aldrich. The solvent was removed under vacuum, and the residue was dissolved in hexane, from which colorless crystals were grown.

X-ray Crystallography of $[KN(SiMe_3)_2]_2$. General procedures for data collection and reduction have been described previously.[17] A colorless crystal measuring 0.25 × 0.25 × 0.25 mm was located and transferred by using standard inert-atmosphere techniques to a Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator. The crystal was cooled to −155 °C for characterization and data collection. Relevant crystal parameters for this study are given in Table I.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$ (alternate setting of $P2_1/c$, No. 14). Subsequent solution and refinement of the structure confirmed this choice.

Data collection was performed by using standard moving-crystal/moving-detector techniques with fixed backgrounds. No correction for absorption or decay was necessary. Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques, using locally modified versions of the Los Alamos Crystallographic Program Library. Neutral-atom scattering factors were used in refinement.[18] All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. A final difference Fourier synthesis was featureless, with the largest peak being 0.41 e/Å^3. Positional parameters are supplied in Table II; selected bond distances and angles are listed in Table III.

Discussion

Few better illustrations of the structural diversity that can accompany nominally "ionic" compounds can be found than among the bis(trimethylsilyl)amide derivatives of the alkali metals. Unsolvated [bis(trimethylsilyl)amido]lithium and -sodium are dimeric in hydrocarbon solutions, for example, and $Li[N(SiMe_3)_2]$ remains a dimer in the gas phase,[13] although the sodium derivative is primarily monomeric.[3d] In the solid state, the lithium derivative is found as a cyclic trimer[5] (although the diethyl etherate is a

Table I. Crystallographic Data for $[KN(SiMe_3)_2]_2$

chemical formula $C_{12}H_{36}K_2N_2Si_4$
fw 398.97
a = 12.644 (3) Å
b = 8.799 (2) Å
c = 10.430 (2) Å
β = 98.73 (1)°
V = 1146.9 Å^3
Z (dimers/cell) = 2
space group $P2_1/a$ (No. 14)
T = −155 °C
λ = 0.71069 Å
ρ_{calcd} = 1.155 g cm^{-3}
μ = 6.120 cm^{-1}
$R(F_o)$ = 0.038
$R_w(F_o)$ = 0.042

Table II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters (×10) for the Non-Hydrogen Atoms in $[KN(SiMe_3)_2]_2$

atom	x	y	z	B_{iso},[a] Å^2
K(1)	3763 (1)	4505 (1)	5732 (1)	17
Si(2)	6356 (1)	4399 (1)	7793 (1)	15
Si(3)	5550 (1)	7577 (1)	7045 (1)	14
N(4)	5727 (2)	5711 (3)	6786 (3)	16
C(5)	6938 (4)	5043 (6)	9476 (4)	29
C(6)	7509 (3)	3476 (5)	7119 (5)	22
C(7)	5447 (3)	2763 (5)	8040 (4)	20
C(8)	6756 (3)	8766 (5)	6803 (4)	20
C(9)	5186 (3)	8151 (5)	8660 (4)	21
C(10)	4417 (3)	8332 (5)	5827 (4)	19

[a] Isotropic values for those atoms refined anisotropically are calculated with the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610.

Table III. Bond Lengths (Å) and Angles (deg) in $[KN(SiMe_3)_2]_2$

Distances			
Si(2)–N(4)	1.678 (3)	Si(3)–C(8)	1.897 (4)
Si(2)–C(5)	1.885 (4)	Si(3)–C(9)	1.881 (4)
Si(2)–C(6)	1.894 (4)	Si(3)–C(10)	1.885 (4)
Si(2)–C(7)	1.884 (4)	K(1)–N(4)	2.770 (3)
Si(3)–N(4)	1.685 (3)	K(1)···N(4)′	2.803 (3)
Angles			
N(4)–Si(2)–C(5)	117.24 (19)	N(4)–Si(3)–C(10)	109.95 (17)
N(4)–Si(2)–C(6)	112.24 (18)	C(8)–Si(3)–C(9)	106.36 (20)
N(4)–Si(2)–C(7)	111.74 (18)	C(8)–Si(3)–C(10)	105.06 (19)
C(5)–Si(2)–C(6)	105.11 (22)	C(9)–Si(3)–C(10)	104.15 (20)
C(5)–Si(2)–C(7)	105.21 (23)	Si(2)–N(4)–Si(3)	129.18 (18)
C(6)–Si(2)–C(7)	104.05 (19)	N(4)···K(1)···N(4)′	94.47 (9)
N(4)–Si(3)–C(8)	112.76 (17)	K(1)···N(4)···K(1)′	85.53 (9)
N(4)–Si(3)–C(9)	117.53 (18)		

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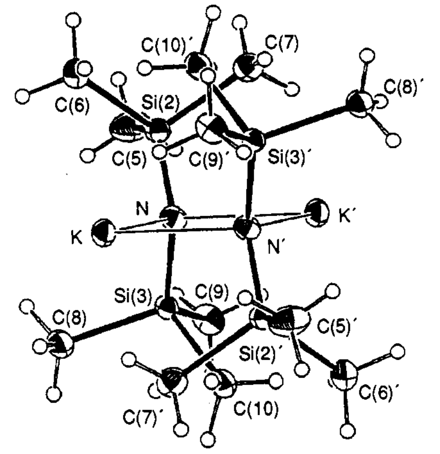

Figure 1. ORTEP view of $[KN(SiMe_3)_2]_2$, giving the numbering scheme used in the tables.

dimer[12]), and the sodium species is polymeric.[9]

Less is known about the properties of $K[N(SiMe_3)_2]$. As it contains a larger, more electropositive metal center, it might be expected to display more typically "saltlike" behavior than the Li or Na amides, although it also is soluble in aromatic solvents, in which it is found as a dimer.[19] Like its lighter congeners, $K[N(SiMe_3)_2]$ displays low electrical conductivity in solution and in the melt.[18] In the dioxane solvate $K[N(SiMe_3)_2]\cdot 2C_4H_8O_2$, however, the short Si–N distance of 1.64 (1) Å and the wide Si–N–Si angle of 136 (1)° have been taken as evidence for a larger degree of charge separation between K^+ and $N(SiMe_3)_2^-$ than is present with Li^+ or Na^+.[8]

Structure of $[KN(SiMe_3)_2]_2$. Since $\{Na[N(SiMe_3)_2]\}_n$ is polymeric in the solid state, it seemed reasonable that the potassium derivative, containing an even larger metal center,[20] should be similarly polymeric. As so few structures of heavy-alkali-metal (K–Cs) complexes containing amide or alkyl groups are known,[21] crystals of $[KN(SiMe_3)_2]_2$ grown from hexane were subjected to an X-ray structure determination. Unlike the lithium and sodium analogues, unsolvated $[KN(SiMe_3)_2]_2$ crystallizes as a dimeric ion pair, placing K in a two-coordinate environment within a $[K–N–]_2$ ring. The dimer contains a crystallographically imposed center of inversion, and the ring is necessarily planar. An ORTEP view of the complex is displayed in Figure 1.

The four-membered ring is nearly square, with K–N distances of 2.770 (3) and 2.803 (3) Å. These distances are distinctly longer than the 2.70 (2) Å K–N length observed in $K[N(SiMe_3)_2]\cdot 2C_4H_8O_2$,[8] an unusual situation considering that the coordination number of the potassium ion is higher in the latter species, which should lead to longer metal–nitrogen distances. The K–N distance in $[KN(SiMe_3)_2]_2$ is 0.43 Å longer than the analogous Na–N length in $\{Na[N(SiMe_3)_2]\}_n$, a value consistent with the ~0.42 Å difference in radii (extrapolated for CN = 2) between these species.[19]

Table IV. Relationship between N–Si Distances and Si–N–Si Angles in Solid-State Homoleptic Bis(trimethylsilyl)amide Complexes and Adducts

complex	N–Si, Å	Si–N–Si′, deg	Si···Si′, Å	ref
$Al[N(SiMe_3)_2]_3$	1.75 (1)	118.0 (1.5)	3.00	4
$Co[N(SiMe_3)_2]_2\cdot P(C_6H_5)_3$	1.71 (3)	125 (1)	3.03	7
$Cr[N(SiMe_3)_2]_3$	1.740 (4)	122.0 (2)	3.04	2
$Eu[N(SiMe_3)_2]_3$	1.702 (3)	126.0 (6)	3.03	2
$Fe[N(SiMe_3)_2]_3$	1.731 (3)	121.2 (2)	3.01	2
$[KN(SiMe_3)_2]_2$	1.682 (4)	129.18 (18)	3.04	this work
$K[N(SiMe_3)_2]\cdot 2C_4H_8O_2$	1.64 (1)	136 (1)	3.04	8
$\{Li[N(SiMe_3)_2]\}_3$	1.729 (4)	118.6 (9)	2.97	5
$\{Li[N(SiMe3)_2]\cdot O(C_2H_5)_2]_2$	1.705 (2)	121.2 (2)	2.97	12b
$Li[N(SiMe_3)]_2\cdot$ 12-crown-4	1.681 (2)	123.5 (1)	2.96	12c
$\{Na[N(SiMe_3)_2]\}_n$	1.690 (5)	125.6 (1)	3.01	9
$Nd[N(SiMe_3)_2]_3$	1.70 (1)	126.4 (9)	3.04	10
$Ni[N(SiMe_3)_2]\cdot 2P(C_6H_5)_3$	1.70 (1)	126 (1)	3.03	7
$Pb[N(SiMe_3)_2]_2$	1.724	126	3.07	14
$Sc[N(SiMe_3)_2]_3$	1.751 (2)	121.6 (4)	3.06	2
$Sm[N(SiMe_3)_2]_2\cdot 2THF$	1.68 (2)	128.8 (8)	3.03	15
$Sn[N(SiMe_3)_2]_2$	1.742	123	3.06	14
$Ti[N(SiMe_3)_2]_3$	1.750 (3)	119.7 (2)	3.03	2
$Tl[N(SiMe_3)_2]_3$	1.738 (19)	122.6	3.05	11
$V[N(SiMe_3)_2]_3$	1.744 (4)	121.0 (2)	3.04	2
$Yb[N(SiMe_3)_2]_3$	1.720 (4)	122.1 (8)	3.01	2
			av 3.02 (3)	

Nonbonded methyl–methyl repulsions from the $SiMe_3$ groups may exert some influence on the geometry of the complex. The Si–N–Si′ plane is nearly perpendicular (87.3°) to the $[K–N–]_2$ ring, which is the sterically optimum arrangement, and the $SiMe_3$ groups above and below the plane are rotated by 38°, determined as the average angle between the CH_3–Si–Si′ and Si–Si′–CH_3′ planes. Two of these interplanar angles are nearly identical (35.6 and 35.1°); that involving the CH_3 groups closest to the potassium (C(7) and C(10)) is 44.1°, perhaps an indication of $K(\delta+)\cdots C(\delta-)$ interaction (see below). This amount of staggering may be influenced by $CH_3\cdots CH_3$′ contacts across the ring, the shortest of which is between C(5) and C(9) at a distance of 3.54 Å. This distance is appreciably shorter than the sum of van der Waals radii (4.0 Å).[22] The longer K–N length in the dimer may thus reflect the existence of steric interactions between the $SiMe_3$ groups. No appreciable interaction is expected between methyl groups on the same face of the $[K–N–]_2$ plane, however, whose closest approach is 3.95 Å (C(6)–C(10)′).

As has been observed in various bis(trimethylsilyl)amide structures of the lanthanides, a number of close contacts are evident between the metal and several of the methyl groups, a situation indicative of $K(\delta+)\cdots C(\delta-)$ interaction.[15,23] The closest contacts involve C(7) and C(10), which are at distances of 3.34 and 3.47 Å, respectively, from the potassium; the sum of van der Waals radius of CH_3 and the covalent radius of K is 3.94 Å.[25] Associated with these contacts are N–Si–C angles of 111.7 (2)°

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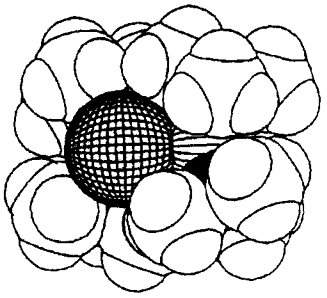

Figure 2. Space-filling drawing of $[KN(SiMe_3)_2]_2$, indicating the exposure of the potassium ion (crosshatched sphere). The adjacent nitrogen atom is banded, and the silicon is solid black.

(N-Si-C(7)) and 110.0 (2)° (N-Si-C(10)), which are the smallest such angles on their respective trimethylsilyl groups. The closest $K-H_3(C)$ contacts are 2.96 and 3.16 Å; as these are roughly equal to the sum of the van der Waals radius for hydrogen and the covalent radius of K (3.1 Å), and as the hydrogens are not oriented toward the metal for optimum interaction, it would appear that any direct K···H···C involvement is slight.

Of additional interest are the Si-N distances, which average 1.682 (4) Å, and the Si-N-Si′ angle of 129.18 (18)°. These parameters are similar to those found in the polymeric sodium structure (Si-N = 1.690 (5) Å; Si-N-Si′ = 125.6 (1)°),[9] but are appreciably longer and narrower, respectively, than the 1.64 (1) Å Si-N distance and 136.2 (1.2)° Si-N-Si′ angle observed in $K[N(SiMe_3)_2]\cdot 2C_4H_8O_2$.[8] These structural trends (short Si-N distances coupled with wide Si-N-Si angles and vice versa) follow a well-established pattern in bis(trimethylsilyl)amide complexes.[2]

The correlation between the Si-N distance and the Si-N-Si′ angle in silylamides has been the subject of considerable discussion.[3c,9,24] Partial multiple bonding between Si and N, in which the lone-pair electrons on nitrogen are delocalized onto silicon, has been invoked as an explanation for the Si-N distance/Si-N-Si′ angle relationships, but steric interactions may also play a critical role in determining the geometries.[2c,9,12] The latter effects are difficult to quantify, since both the relative steric bulk and the orientation of various alkyl and aryl groups must be taken into account. One way this problem might be assessed in silylamides with the same substituents is by measuring the separation of the silicon centers; the Si···Si′ distance should be relatively constant if the bond length and angles are linearly related to each other. This separation is calculated in Table IV for a variety of transition-metal, main-group, and f-element bis(trimethylsilyl)amide complexes and is found to have the nearly constant value of 3.02 (3) Å. The persistence of this number over a wide range of metals suggests that it probably is of steric origin, i.e., that ~3.0 Å represents the limit imposed by interligand repulsions on the close approach of two $SiMe_3$ groups. Hence, bis(trimethylsilyl)amide complexes containing short Si-N bonds must necessarily possess relatively large Si-N-Si′ angles to avoid violating the minimum $SiMe_3\cdots SiMe_3'$ separation. It should be stressed that the 3.0 Å Si···Si′ distance applies only to (trimethylsilyl)amides; different substituents on the nitrogen will affect this value. Both $HN(SiPh_3)_2$ and the $[Ph_3SiNSiPH_3]^-$ ion, for example, have Si···Si′ separations of 3.19 Å.[23b]

Alkane Solubility of $[KN(SiMe_3)_2]_2$. The solubility of [bis(trimethylsilyl)amido]potassium in hexane, already somewhat unusual if the compound is regarded as a "salt" (i.e., $\{K^+[N(SiMe_3)_2]^-\})_2$), becomes even more remarkable in light of the present structure. Although hydrocarbon solubility of potassium "salts" of transition-metal species has previously been described (e.g., in $[KOsH_3(PMe_2Ph)_3]_2$[25] and $K\{H_3Rh_3(\mu\text{-}Cl)[\mu\text{-}OP(O\text{-}i\text{-}C_3H_7)_2]_2[P(O\text{-}i\text{-}C_3H_7)_3]_3\}$[26]), these compounds owe their solubility to the virtual encapsulation of the K^+ by the surrounding ligands, so that a hydrocarbon shell is displayed toward the solvent. As indicated in a space-filling drawing of $[KN(SiMe_3)_2]_2$ (Figure 2), however, the potassium atoms are exposed to external molecules and are not appreciably shielded by the trimethylsilyl group of the amide. The only adequate explanation of the alkane solubility would seem to be an unusually strong ion-pairing interaction between the K^+ and $N(SiMe_3)_2^-$, so that the term "salt" is not a meaningful description of the nature of the compound. Such pairing would also account for the low electrical conductivity of molten $K[N(SiMe_3)_2]$.[16]

Conclusion

The determination of the solid-state dimeric configuration of $[KN(SiMe_3)_2]_2$ establishes a third structural type for unsolvated bis(trimethylsilyl)amides of the alkali metals. Even though a polymeric geometry is observed in $\{Na[N(SiMe_3)_2]\}_n$, the fact that the bis(trimethylsilyl)amide group supports a two-coordinate environment for the much larger potassium ion suggests that the interplay of the factors controlling the structures of these complexes (e.g., crystal-packing effects, entropic forces, etc.) are more subtle than previously expected.[9] Their influence on the structures of other heavy-pretransition-metal bis(trimethylsilyl)amides and related complexes remains to be determined.

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Supplementary Material Available: Tables of crystal and data collection parameters, hydrogen atom fractional coordinates, bond distances and angles involving hydrogen atoms, and anisotropic thermal parameters (4 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Dipartimento di Chimica,
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Formation and Structure of the Tris(catecholato)vanadate(IV) Complex in Aqueous Solution

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The coordination chemistry of simple catechols continues to be the object of extensive interest because of this ligand's involvement at the active sites of biological chelators, e.g. siderophores.[2-11] Catechols have a pronounced affinity for ions in high oxidation states or with high charge-to-radius ratios. Low molecular weight pigments known as tunichromes serve as complexing agents in the accumulation and storage of vanadium in some marine organisms. The catechol derivative, tunichrome b_1, has been isolated from the blood of *Ascidia nigra* and is suggested to be such a vanadium complexing agent.[12-14]

Over the years much effort has been devoted to characterizing vanadium-catechol complexes. Beginning with the pioneering work of Rosenheim,[15] the nature of the blue species formed by the interaction of V(IV) or V(V) with catechol has been studied extensively.[21-27] For some time it was unclear if, in addition to the mono- and bis(catecholato)oxovanadium(IV) complexes, the tris(catecholato)vanadate(IV) species also was formed in the catechol-$V^{IV}O$ system. Indeed, in spite of the isolation of the thallium(I) salt of the $[V(cat)_3]^{2-}$ complex,[21] which exhibited properties suggestive of a tris octahedral structure at the V(IV) atom, several potentiometric studies failed to provide evidence for the existence of such a species in solution.[18-20,22] The rather contradictory literature in this field was reconciled by Cooper,

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