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Preparation and Structural Characterization of Dioxane-Coordinated Alkali Metal Bis(trimethylsilyl)amides

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Unsolvated $RbN(SiMe_3)_2$ (**1**) and $CsN(SiMe_3)_2$ (**2**) have been prepared from rubidium and cesium metal respectively and excess hexamethyldisilazane. The molecular structures of the polymeric dioxane adducts $NaN(SiMe_3)_2 \cdot C_4H_8O_2$ (**3**) and $[MN(SiMe_3)_2 \cdot 1.5C_4H_8O_2] \cdot 0.5C_4H_8O_2$ (**4**, M = Rb; **5**, M = Cs) have been determined by low-temperature single-crystal X-ray diffraction.

Introduction

The bulky bis(trimethylsilyl)amido group, $-N(SiMe_3)_2$, plays an important role in the stabilization of low coordination numbers around main group and transition metal centers.[1-3] Dicoordination of the transition metals manganese, iron, cobalt, and nickel was observed for the first time in solution[4,5] and in the gas phase[6,7] in the compounds $M[N(SiMe_3)_2]_2$ (M = Mn, Fe, Co, Ni). The very unusual coordination number 3 for f-elements was realized in the lanthanide derivatives $Ln[N(SiMe_3)_2]_3$.[8-10] The preparation of these metal bis(trimethylsilyl)amides usually involves treatment of the appropriate metal halides with either $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$. The structural chemistry of the lighter alkali metal derivatives $MN(SiMe_3)_2$ (M = Li, Na, K) has already been studied in detail.[11-17] In all three cases the base-free silyl amides have been structurally characterized. In addition, for M = Li, K the molecular structures of several solvates containing diethyl ether, 12-crown-4, or dioxane have been investigated (Table I).

So far virtually nothing is known about bis(trimethylsilyl)amides containing the heavy alkali metals rubidium and cesium. We report here the synthesis of the hitherto unknown derivatives $RbN(SiMe_3)_2$ (**1**) and $CsN(SiMe_3)_2$ (**2**). Furthermore the molecular structures of three dioxane adducts, $NaN(SiMe_3)_2 \cdot 2C_4H_8O_2$ (**3**) and $[MN(SiMe_3)_2 \cdot 1.5C_4H_8O_2] \cdot 0.5C_4H_8O_2$ (**4**, M = Rb; **5**, M = Cs) have been determined by single-crystal X-ray diffraction. These results allow a comparison of a series of dioxane-coordinated bis(trimethylsilyl)amides $MN(SiMe_3)_2$ (M = Na, K, Rb, Cs).

Experimental Section

All operations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. All solvents were rigorously dried by standard methods and freshly distilled from Na/benzophenone prior to use. NMR spectra were recorded on a Bruker AM 250 spectrometer. $NaN(SiMe_3)_2$ was obtained by reacting $NaNH_2$ with $HN(SiMe_3)_2$ in toluene for 3 d.[18]

Synthesis of Rubidium Bis(trimethylsilyl)amide (1). A 1.0-g (12-mmol) sample of rubidium metal and an excess (10 mL, 47 mmol) of hexamethyldisilazane were stirred at reflux temperature for 3 d. During this time the alkali metal dissolved completely. The excess amine was removed in vacuo, and the residue was thoroughly dried to give 2.7 g (95%) of a white amorphous powder. ^1H NMR (C_6D_6): δ 0.15.

Synthesis of Cesium Bis(trimethylsilyl)amide (2). A 4.9-g (37-mmol) sample of cesium metal was suspended in a mixture of 100 mL of THF and 30 mL (142 mmol) of hexamethyldisilazane, and the mixture was refluxed for 60 h. During this time the metal dissolved completely. The solution was filtered through a thin layer of Celite, and the clear filtrate was evaporated to dryness. The residue was washed with hexane and dried under vacuum to give 10.5 g (98%) of microcrystalline material. ^1H NMR (C_6D_6): δ 0.19.

Crystal Growth and X-ray Structure Determinations. Suitable single crystals of **3**, **4**, and **5** were obtained by dissolving the base-free silylamides $MN(SiMe_3)_2$ (M = Na, Rb, Cs) in a small amount of hot dioxane and slowly cooling the solutions to room temperature. The crystals were oil-coated shock-cooled at the tip of a fiber. The data were collected on a Stoe Siemens AED four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The structure of **3** was solved by direct methods[20] while the structures of **4** and **5** were solved by the Patterson method[20] and refined by full-matrix least-squares techniques.[20] In the case of **4** and **5** a semiempirical absorption correction was applied. All nonhydrogen atoms were refined anisotropically; all hydrogen atoms were found by difference Fourier syntheses and refined isotropically employing a riding model.

Results and Discussion

Preparation. $NaN(SiMe_3)_2$ was prepared from $NaNH_2$ and $HN(SiMe_3)_2$ in toluene as previously described in the literature.[19] The hitherto unknown rubidium and cesium bis(trimethylsilyl)amides were synthesized by reacting the metal with excess hexamethyldisilazane:

$$M + HN(SiMe_3)_2 \rightarrow \underset{\substack{M = Rb\ (1)\\ M = Cs\ (2)}}{MN(SiMe_3)_2} + {}^1/_2\, H_2$$

The silylamides **1** and **2** are isolated in almost quantitative yields as white, moisture sensitive, microcrystalline solids. The diox-

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Table I. Selected Bond Lengths and Angles of Known Alkali Metal Bis(trimethylsilyl)amides

compound		Si–N (pm)	M–N (pm)	Si-N-Si (deg)	measurement temp (K)	ref
$[LiN(SiMe_3)_2]_3$	trimeric	172.0	200.0	118.0	295	11
$[LiN(SiMe_3)_2]_2$	dimeric	171.2	199.0	129.8	gas phase	12
$LiN(SiMe_3)_2{\cdot}Et_2O$	dimeric	170.5	205.5	121.2	295	13
$LiN(SiMe_3)_2{\cdot}$12-crown-4	monomeric	168.1	196.5	123.5	140	14
$NaN(SiMe_3)_2$	polymeric	169.4	235.2	125.6	295	15
		168.7	235.8			
$NaN(SiMe_3)_2{\cdot}2C_4H_8O_2$	polymeric (linked monomers)	167.2	238.0	139.8	153	this work
$[KN(SiMe_3)_2]_2$	dimeric	168.2	277.0	129.2	118	16
			280.3			
$KN(SiMe_3)_2{\cdot}2C_4H_8O_2$	polymeric (linked monomers)	164.0	270.0	136.2	295	17
$[RbN(SiMe_3)_2]_2{\cdot}3C_4H_8O_2$	polymeric (linked dimers)	165.2	294.6	129.5	193	this work
		167.7	314.1			
$[CsN(SiMe_3)_2]_2{\cdot}3C_4H_8O_2$	polymeric (linked dimers)	167.2	306.7	128.4	153	this work
		167.3	338.8			

Table II. Crystallographic Data of **3**, **4** and **5**

	3	**4**	**5**
data collcn at T (°C)	–120	–80	–120
cryst size (mm)	0.4 × 0.4 × 0.6	0.4 × 0.4 × 0.6	0.4 × 0.5 × 0.7
space group	$P4_12_12$	$P2_1/n$	$P2_1/n$
a (pm)	1149.9 (1)	1175.9 (1)	1259.7 (2)
b (pm)	1149.9 (2)	1123.3 (2)	1166.6 (3)
c (pm)	1579.5 (1)	1692.7 (2)	1520.0 (3)
α (deg):	90	90	90
β (deg):	90	93.91 (1)	98.40 (2)
γ (deg):	90	90	90
cell vol (nm^3):	2.089	2.230	2.208
units per cell Z:	4	4	4
calcd density D_c (Mg m^{-3})	1.144	1.257	1.412
abs coeff μ (mm^{-1}):	0.20	2.28	1.78
F(000)	784	888	960
2θ range (deg):	8–55	8–45	8–55
measd reflcns	1516	4629	7533
no. of unique reflcns	1438	2896	5053
no. of obsd reflcns	1223	2223	4710
p ($F > p\sigma(F)$)	3	3	3
R	0.0428	0.0703	0.0226
R_w	0.0442	0.0738	0.0265
weighting factor g ($w = 1/(\sigma^2(F) + gF^2)$	0.0005	0.0010	0.0005
no. of refined params	101	199	301
highest difference peak (e Å^{-3})	0.27	0.70	0.49

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of **3**[a]

	x	y	z	U(eq)
Na(1)	6083 (1)	3917 (1)	2500	25 (1)
N(1)	4620 (2)	5380 (2)	2500	22 (1)
Si(1)	4799 (1)	6416 (1)	3232 (1)	25 (1)
C(11)	3714 (3)	6394 (3)	4122 (2)	44 (1)
C(12)	4757 (4)	7947 (3)	2813 (2)	48 (1)
C(13)	6252 (3)	6229 (3)	3753 (2)	43 (1)
O(1)	7838 (2)	3488 (2)	3282 (1)	28 (1)
C(1)	8656 (3)	4215 (3)	3707 (2)	32 (1)
C(2)	7820 (3)	2366 (3)	3681 (2)	26 (1)
O(2)	7557 (2)	5179 (2)	1630 (1)	29 (1)
C(3)	6827 (2)	5993 (3)	1187 (2)	26 (1)
C(4)	8671 (3)	5145 (3)	1228 (2)	33 (1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of **4**[a]

	x	y	z	U(eq)
Rb(1)	–1401 (1)	4811 (1)	5692 (1)	44 (1)
N(1)	657 (5)	6305 (5)	5894 (3)	47 (2)
Si(1)	1575 (2)	5739 (2)	6575 (1)	50 (1)
C(11)	1084 (9)	5773 (13)	7613 (5)	115 (6)
C(12)	3041 (7)	6443 (8)	6650 (6)	80 (4)
C(13)	1860 (9)	4124 (8)	6382 (6)	82 (4)
Si(2)	351 (2)	7734 (2)	5684 (1)	51 (1)
C(21)	–1225 (7)	7984 (8)	5435 (6)	76 (4)
C(22)	750 (8)	8851 (8)	6488 (6)	77 (4)
C(23)	1079 (11)	8288 (9)	4795 (6)	101 (5)
O(1)	–2607 (5)	6276 (5)	7078 (3)	65 (2)
O(2)	–1646 (6)	3226 (5)	7050 (4)	76 (3)
C(1)	–3669 (8)	6268 (8)	7406 (6)	70 (4)
C(2)	–858 (8)	2508 (8)	7536 (6)	76 (4)
C(3)	–2715 (8)	3237 (9)	7377 (7)	80 (4)
C(4)	–1824 (9)	6987 (9)	7555 (7)	89 (5)
O(3)	–3926 (5)	4860 (5)	5417 (4)	65 (2)
C(5)	–4827 (7)	4042 (8)	5514 (6)	65 (4)
C(6)	–4396 (7)	6017 (8)	5224 (6)	70 (4)
O(4)	906 (16)	5634 (19)	–167 (10)	245 (10)
C(7)	–11 (15)	6164 (11)	–4 (11)	156 (9)
C(8)	624 (17)	4370 (15)	–463 (10)	150 (9)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ane adducts **3**–**5** were obtained by dissolving the base-free derivatives $MN(SiMe_3)_2$ in a minimum amount of hot dioxane. Slow cooling of these solutions to room temperature yielded X-ray quality single crystals of the composition $NaN(SiMe_3)_2{\cdot}2C_4H_8O_2$ (**3**) (^1H NMR (C_6D_6) δ 0.24 ($Si(CH_3)_3$), 3.34 ($[O(CH_2)_2]_2$); ^{13}C NMR (C_6D_6) δ 6.74 ($Si(CH_3)_3$), 67.09 ($[O(CH_2)_2]_2$); ^{29}Si NMR δ –14.8), $[RbN(SiMe_3)_2{\cdot}1.5C_4H_8O_2]{\cdot}0.5C_4H_8O_2$ (**4**) (^1H NMR (C_7D_8) δ 0.15 ($Si(CH_3)_3$), 3.32 ($[O(CH_2)_2]_2$)), and $[CsN(SiMe_3)_2{\cdot}1.5C_4H_8O_2]{\cdot}0.5C_4H_8O_2$ (**5**) (^1H NMR (C_6D_6) δ 0.21 ($Si(CH_3)_3$), 3.35 ($[O(CH_2)_2]_2$); ^{13}C NMR (C_7D_8) δ 7.18 ($Si(CH_3)_3$), 67.13 ($[O(CH_2)_2]_2$); ^{133}Cs NMR (C_4D_8O) δ 138).

Crystal Structures of 3, 4, and 5. The molecular structure of dioxane-solvated $KN(SiMe_3)_2$ has been known since 1973.[17] In order to compare the structures of a whole series of dioxane-coordinated alkali metal bis(trimethylsilyl)amides, the crystal structures of **3**–**5** have been determined by single-crystal X-ray diffraction. The crystallographic data for **3**–**5** are given in Table II, atomic coordinates and equivalent isotropic displacement parameters in Tables III–V. Table VI contains selected bond lengths and bond angles.

Polymeric $NaN(SiMe_3)_2{\cdot}2C_4H_8O_2$ (**3**) (Figure 1) is isostructural with the corresponding potassium derivative. The central sodium atom is coordinated by the nitrogen atom of the $N(SiMe_3)_2$ ligand and four oxygen atoms, resulting in a distorted trigonal-bipyramidal coordination geometry. The nitrogen and two oxygen atoms are in the equatorial plane, while two oxygen atoms occupy the axial positions. The Si–N bond length (average 167.8 pm) is longer and the Si–N–Si angle (130.6°) is smaller than in the corresponding potassium derivative $KN(SiMe_3)_2{\cdot}2C_4H_8O_2$ (164.0 pm and 136.3° respectively).[17] This may be attributed to a lesser degree of ionic character in the sodium compound. In the unsolvated $NaN(SiMe_3)_2$ the average Si–N distance is 169.0 pm and the Si–N–Si angle is 125.6°.[15] As with most compounds in which more than one silyl group is attached to nitrogen, the nitrogen atom adopts a planar geometry. The monomeric units are linked via 1,4-dioxane bridges to give an overall polymeric structure.

$[RbN(SiMe_3)_2]_2{\cdot}3C_4H_8O_2$ (**4**) and $[CsN(SiMe_3)_2]_2{\cdot}3C_4H_8O_2$

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of **5**[a]

	x	*y*	*z*	*U*(eq)
Cs(1)	−1367 (1)	4839 (1)	5644 (1)	25 (1)
N(1)	508 (1)	6519 (1)	6091 (1)	24 (1)
Si(1)	1428 (1)	6088 (1)	6932 (1)	24 (1)
C(11)	1392 (2)	6793 (2)	8043 (2)	40 (1)
C(12)	2862 (2)	6283 (2)	6737 (2)	42 (1)
C(13)	1276 (2)	4503 (2)	7134 (2)	44 (1)
Si(2)	270 (1)	7847 (1)	5695 (1)	26 (1)
C(21)	−1108 (2)	7948 (2)	5024 (2)	50 (1)
C(22)	338 (2)	9030 (2)	6547 (2)	42 (1)
C(23)	1241 (3)	8334 (2)	4932 (2)	57 (1)
O(1)	−2522 (1)	6242 (1)	7012 (1)	36 (1)
O(2)	−1659 (1)	3174 (1)	7174 (1)	41 (1)
C(1)	−3525 (2)	6200 (2)	7344 (2)	34 (1)
C(2)	−967 (2)	2367 (2)	7687 (2)	41 (1)
C(3)	−2668 (2)	3210 (2)	7499 (2)	41 (1)
C(4)	−1824 (2)	7041 (2)	7522 (2)	39 (1)
O(3)	−3900 (1)	4822 (1)	5307 (1)	39 (1)
C(5)	−4610 (2)	3879 (2)	5082 (2)	38 (1)
C(6)	−4264 (2)	5801 (2)	4787 (2)	42 (1)
O(4)	−291 (2)	3843 (1)	9837 (1)	50 (1)
C(7)	−1067 (2)	4713 (3)	9796 (2)	56 (1)
C(8)	676 (3)	4314 (3)	9607 (3)	63 (1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Lengths (pm) and Bond Angles (deg) for **3**, **4**, and **5**

	Compound **3**		
Na(1)–N(1)	238.0 (1)	Si(1)–N(1)–Si(1a)	139.8 (1)
Na(1)–O(1)	241.7 (2)	Si(1)–N(1)–Na(1)	114.6 (1)
Na(1)–O(2)	262.1 (2)		
Si(1)–N(1)	167.3 (2)		
	Compound **4**		
Rb(1)–N(1)	294.6 (6)	Si(1)–N(1)–Si(2)	129.5 (4)
Rb(1)–N(1a)	314.1 (6)	N(1)–Rb(1)–N(1a)	93.0 (2)
Rb(1)–O(1)	326.6 (6)	Rb(1)–N(1)–Rb(1a)	87.0 (2)
Rb(1)–O(2)	293.4 (6)		
Rb(1)–O(3)	297.4 (6)		
Si(1)–N(1)	165.2 (6)		
Si(2)–N(1)	167.7 (6)		
Rb(1)···Rb(1a)	419.4 (2)		
	Compound **5**		
Cs(1)–N(1)	306.7 (1)	Si(1)–N(1)–Si(2)	128.4 (1)
Cs(1)–N(1a)	338.8 (2)	N(1)–Cs(1)–N(1a)	98.5 (1)
Cs(1)–O(1)	316.1 (2)	Cs(19)–N(1)–Cs(1a)	81.5 (1)
Cs(1)–O(2)	309.3 (2)		
Cs(1)–O(3)	315.3 (1)		
Si(1)–N(1)	167.2 (2)		
Si(2)–N(1)	167.3 (2)		
Cs(1)···Cs(1a)	421.9 (1)		

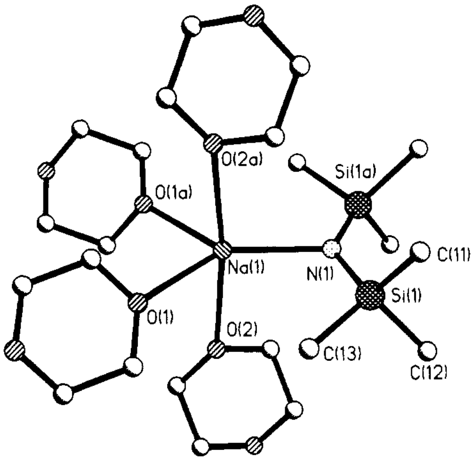

Figure 1. Structure of NaN$(SiMe_3)_2$·$2C_4H_8O_2$ (**3**) in the solid state.

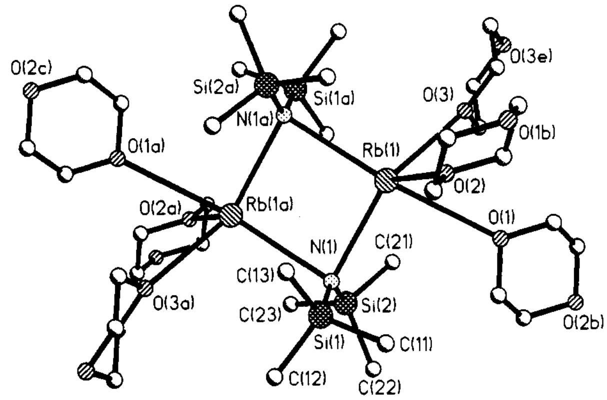

Figure 2. Structure of RbN$(SiMe_3)_2$·$1.5C_4H_8O_2$ (**4**) in the solid state. The uncoordinated lattice solvent dioxane is omitted.

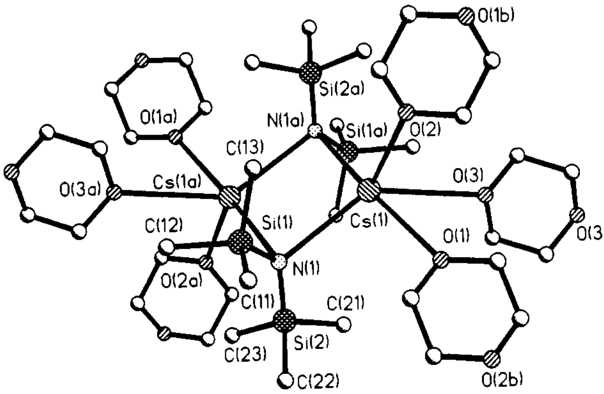

Figure 3. Structure of CsN$(SiMe_3)_2$·$1.5C_4H_8O_2$ (**5**) in the solid state. The uncoordinated lattice solvent dioxane is omitted.

(**5**) also form a pair of isostructural compounds. Figures 2 and 3 show the structures of the dimeric subunits MN$(SiMe_3)_2$·$3C_4H_8O_2$. The metal cations are coordinated by two nitrogen and three oxygen atoms. This results in a distorted tetragonal-pyramidal coordination geometry around the metal centers. A center of inversion lies in the middle of the central four-membered M_2N_2 ring. The metal–nitrogen bonds within the four-membered ring are not equivalent. The difference in the Rb–N bond lengths in **4** (Rb(1)–N(1) = 294.6 (6) pm; Rb(1)–N(1a) = 314.1 (6) pm) is 19.5 pm; that of the Cs–N distances in **5** (Cs(1)–N(1) = 306.7 (1) pm; Cs(1)–N(1a) = 338.8 pm) (2) is even larger (32.1 pm). In **4** the N(1) is as much as 32.3 pm above the Si(1), Si(2), Rb(1) plane. The Rb(1)–N(1) vector forms an angle of 123.4° with the Si(1), Si(2), N(1) plane. This means the plane of the ligand almost bisects the Rb(1)–N(1)–Rb(1a) bond angle. In **5** the N(1) atom is only 19.5 pm above the Si(1), Si(2), Cs(1) plane, indicating nearly planar environment of the nitrogen atom. The Cs(1)–N(1) vector forms an angle of 160.6° with the –N$(SiMe_3)_2$ ligand plane. That means despite the steric hinderence the ligand is almost entirely bended toward the symmetry-related metal atom Cs(1a). This geometrical arrangement together with the asymmetric bridging and the planar environment of N(1) indicates that the nitrogen atom is not sp^3 hybridized. We suggest that the nitrogen atom in **5** is sp^2 hybridized and the lone pair is located in an unhybridized p atom orbital. This orbital is perpendicular to the Si(1), Si(2), N(1), Cs(1) plane and directed toward the second metal Cs(1a), forming the longer distance of 338.8 (2) pm, whereas the shorter bond is realized by the sp^2-orbital directed toward Cs(1) (Figure 4).

On the other hand we think that the bonding situation in the Rb–N four-membered ring is described more adequately by a sp^3-hybridized nitrogen atom. The Rb–N distances differ only by 19.5 pm and the –N$(SiMe_3)_2$ ligand plane bisects the Rb(1)–N–Rb(1a) angle (Figure 4). However, both descriptions may be too simple minded, and the truth is probably somewhere in between.

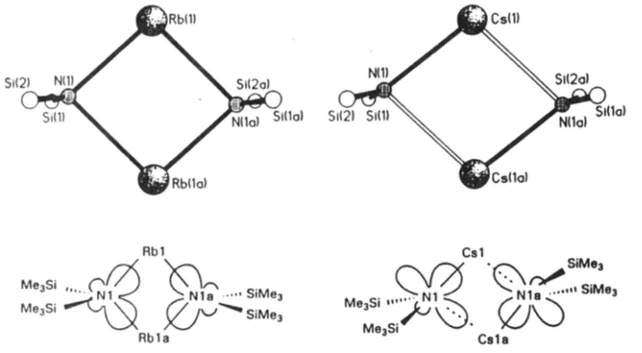

Figure 4. Bonding situation in the Rb_2N_2 and the Cs_2N_2 four-membered ring. The nitrogen atom in the first ring is sp^3 hybridized and is sp^2 hybridized in the latter.

The Rb-N and Cs-N bond lengths in **4** and **5** are in good agreement with the distances in the central N_2M_2-ring of $[PhS(NSiMe_3)_2Rb\cdot THF]_2$[18] and $[PhS(NSiMe_3)_2Cs\cdot THF]_2$.[18] Furthermore, each coordinated dioxane ligand bridges two metal centers, thus connecting the dimers to give an overall polymeric structure.

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Supplementary Material Available: Listings of crystal and diffractometer data, atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients (18 pages). Ordering information is given on any current masthead page.