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Bis(dioxane) Potassium Bis(trimethylsilyl)amide

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Abstract. $K(C_4H_8O_2)_2N[Si(CH_3)_3]_2$, tetragonal, $a=b=$ 11·46 (1), $c=17{\cdot}55$ (2) Å, $U=2305$ Å^3, $Z=4$, $D_x=$ 1·08 g cm^{-3}. The space group is $P4_12_12$ or its enantiomorph $P4_32_12$ from systematic absences; refinement of both absolute configurations confirmed $P4_32_12$ for the crystal studied. The structure is essentially ionic; the five-coordinated potassium ions are linked by disordered dioxane molecules. The very short Si–N bond [1·64 (1) Å] is consistent with delocalization of negative charge on nitrogen into *pπ–dπ* bonding orbitals. The refinement converged to $R=0{\cdot}109$ for 942 visually estimated unique reflexions.

Introduction. The structural anomalies of silicon–nitrogen compounds have provoked much discussion and a number of studies by X-ray and electron diffraction, and have been reviewed recently by Bürger (1973). Since the presence of a formal negative charge should certainly influence the Si–N bond, we have determined a structure which we thought might involve an effectively isolated $[(CH_3)_3Si]_2N^-$ anion.

Experimental. The compound was prepared by the reaction of a benzene solution of hexamethyldisilazane with liquid potassium in the presence of ammonia, as described by Wannagat & Niederprüm (1961). The resulting crystals of $[(CH_3)_3Si]_2NK$ were redissolved in ether, and the excess potassium filtered off under nitrogen. Addition of dioxane to the filtrate followed by evaporation of the ether gave highly moisture-sensitive colourless crystals, most of which were found to be twinned. The crystals were identified as $K(C_4H_8O_2)_2$-$N[Si(CH_3)_3]_2$ from infrared and n.m.r. spectra. Intensities were estimated visually from equi-inclination Weissenberg photographs (layers *h*0*l* to *h*9*l* inclusive) of a crystal of approximate dimensions 0·38 × 0·26 × 0·38 mm sealed in a Lindemann-glass capillary tube; Ni-filtered Cu *Kα* radiation ($\lambda=1{\cdot}5418$ Å) was used. Although the crystal gradually turned slightly yellow, the photographs did not indicate any decomposition in the X-ray beam. Lorentz, polarization and absorption corrections were applied [μ(Cu $K\alpha$) = 30·6 cm^{-1}], and data from different layers were placed on a self-consistent scale by a linear least-squares analysis of common reflexions. Unit-cell dimensions were obtained from a least-squares analysis of the positions of 46 reflexions on the *h*0*l* Weissenberg photograph.

The structure was solved by multisolution tangent refinement, the potassium, silicon and nitrogen atoms being identified in the best *E* map. The methyl carbon and dioxane oxygen atoms were located by difference syntheses, but these showed only diffuse maxima in the regions between the oxygen atoms of the same dioxane ring. After a large number of trials of structural models for the disorder of the dioxane carbon atoms, we chose a model involving 12 partial carbon atoms which were allowed to refine freely, but no chemical significance should be attached to the actual coordinates obtained in this way.

The structure was refined by full-matrix least-squares with complex neutral-atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) and the weighting scheme $w=(3{\cdot}45+|F_o|+0{\cdot}01224|F_o|^2)^{-1}$. The substitution of a K^+ scattering factor did not produce a significant improvement in the generalized index $R_g=(\sum w\Delta^2/\sum wF_o^2)^{1/2}$ $(\Delta=|F_o|-|F_c|)$. Refinements were performed for both enantiomorphs ($P4_12_12$ and $P4_32_12$), but the R_g ratio of 1·044 strongly indicated that the crystal actually studied possessed the space group $P4_32_12$, and all results quoted are for this structure. The final value of $R_w=\sum w\Delta/\sum wF_o$ was 0·133 for a total of 942 unique observed reflexions, with a corresponding unweighted *R* of 0·109. The secondary extinction coefficient (Larson, 1970) refined to the value $10^5Q_0r^*=13$ (5) cm^{-1}. A final difference synthesis did not reveal any pronounced features, the highest peak being 0·4 e Å^{-3}. Final coordinates are given in Table 1, temperature factors in Table 2, and interatomic distances and angles in Tables 3, 4 and 5.†

Table 1. *Fractional atomic coordinates* (× 10^4)

	x/a	*y/b*	*z/c*
K	8789 (2)	8789 (2)	5000
Si	8704 (4)	9635 (5)	9247 (3)
N	9546 (9)	9546 (9)	10000
C(1)	8825 (25)	8324 (24)	8587 (14)
C(2)	7056 (19)	9784 (23)	9450 (14)
C(3)	9050 (21)	10996 (22)	8714 (10)
O(1)	6933 (15)	8291 (18)	5866 (12)
O(2)	7179 (23)	10004 (14)	4207 (13)

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† Disordered atom parameters and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30239 (7 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic temperature factors* (Å$^2 \times 10^3$)

The anisotropic temperature factor exponent takes the form:

$$-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*).$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	96 (2)	96 (2)	115 (3)	1 (2)	− 1 (2)	−15 (2)
Si	111 (3)	170 (4)	132 (3)	−38 (3)	−19 (3)	−20 (3)
N	107 (6)	107 (6)	139 (11)	−10 (7)	10 (7)	− 8 (8)
C(1)	232 (23)	231 (24)	228 (21)	−114 (19)	−10 (20)	2 (22)
C(2)	140 (15)	240 (23)	222 (20)	−19 (20)	−32 (15)	−10 (17)
C(3)	228 (22)	228 (22)	129 (17)	24 (13)	−34 (14)	−32 (18)
O(1)	157 (12)	230 (19)	256 (18)	11 (15)	60 (12)	−30 (12)
O(2)	197 (17)	190 (15)	212 (17)	50 (14)	−64 (16)	15 (13)

Table 3. *Bond lengths* (Å)

Si–N	1·64 (1)	K–N	2·70 (2)
Si–C(1)	1·90 (2)	K–O(1)	2·67 (2)
Si–C(2)	1·93 (2)	K–O(2)	2·70 (2)
Si–C(3)	1·86 (2)		

Table 4. *Bond angles* (°)

Si—N–Si′	136·2 (1·2)	O(1)–K–O(2)	81·9 (1·0)
C(1)–Si–N	113·5 (1·2)	O(1)–K–O(2′)	88·4 (1·1)
C(2)–Si–N	115·7 (1·0)	O(1)–K–O(1′)	89·1 (1·0)
C(3)–Si–N	109·4 (1·1)	O(2)–K–O(2′)	116·4 (1·2)
C(1)–Si–C(2)	104·6 (1·3)	N—K–O(1)	135·5 (0·9)
C(2)–Si–C(3)	103·1 (1·3)	N—K–O(2)	96·8 (1·0)
C(3)–Si–C(1)	109·9 (1·3)		

Table 5. *Non-bonded distances less than* 4·0 Å

Si^{II}——Si	3·04	Si^{III} —K	3·64
Si^{II}——C(1)	3·94	K^{IV}—C(3)	3·36
Si^{II}——C(2)	3·94	N^{I}——C(1)	2·97
$C(3)^{V}$—O(1)	3·93	N^{I}——C(2)	3·03
$O(2)^{VI}$ –O(1)	2·71	N^{I}——C(3)	2·86
$O(1)^{I}$ —O(2)	3·52	$C(1)^{I}$ –C(2)	3·03
$O(2)^{VII}$–O(1)	3·75	$C(1)^{I}$ –C(3)	3·08
$O(1)^{VII}$–O(1)	3·75	$C(2)^{I}$ –C(3)	2·97
		$C(1)^{II}$–C(2)	3·90

Coordinate transformations

I	x	y	z
II	y	x	$2-z$
III	$2-x$	$2-y$	$z-0·5$
IV	$2-x$	$2-y$	$z+0·5$
V	$2-y$	$2-x$	$1·5-z$
VI	$y-0·5$	$1·5-x$	$z+0·25$
VII	y	x	$1-z$

Discussion. The coordination of the potassium ion and the anion geometry are illustrated in Fig. 1, and a projection of the structure is shown in Fig. 2. The potassium is coordinated by the nitrogen atom of the anion and by four oxygen atoms of different dioxane molecules, with a crystallographic diad axis through the nitrogen and potassium atoms; five-coordinated potassium is rather unusual. Disordered dioxane rings have also been reported in the adducts $N_2O_4.C_4H_8O_2$ (Groth & Hassel, 1965) and $Mg[Al(OCH_3)_2(CH_3)_2]_2.2C_4H_8O_2$ (Atwood & Stucky, 1968); as in the structure reported here, the oxygen-atom positions are well defined but the carbon atoms are disordered. The intramolecular distance between the two dioxane oxygen atoms in the potassium salt (2·71 Å) is similar to the distance in the free dioxane molecule.

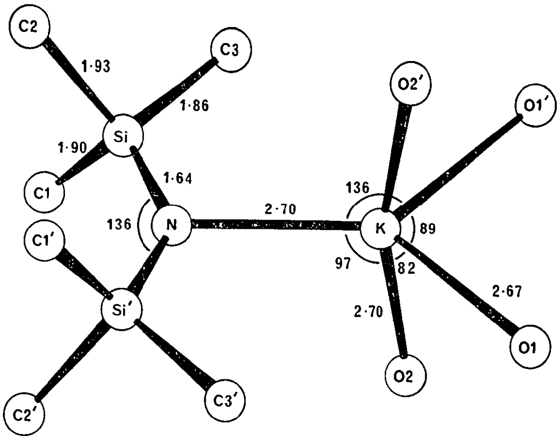

Fig. 1. Anion geometry and coordination of potassium

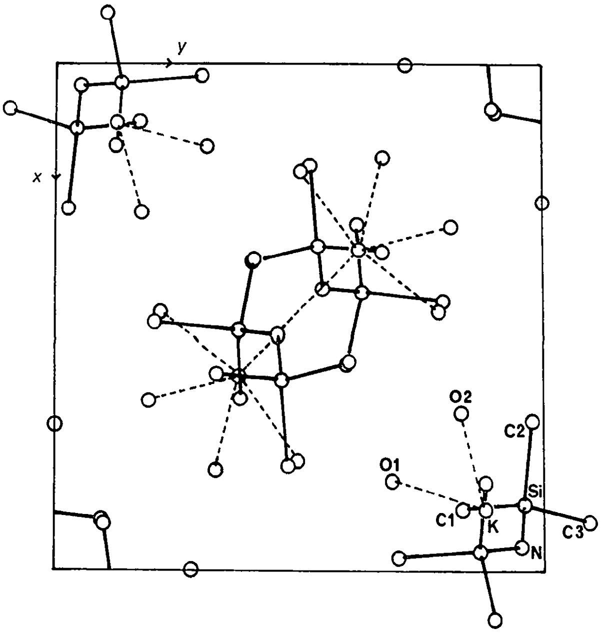

Fig. 2. Projection of the structure perpendicular to [001].

The Si–N bond length of 1·64 (1) Å is significantly shorter than the 'short' Si–N distances in the range 1·72–1·74 Å found in $(H_3Si)_2N$– and $[(CH_3)_3Si]_2N$– derivatives, and appears to be the shortest Si–N bond length reported for a stable compound [very similar anion dimensions have recently been found in $Eu\{N[Si(CH_3)_3]_2\}_3$, which can also be considered to be essentially ionic (Hursthouse, 1973)]. The formal negative charge on nitrogen should favour delocalization of its lone pairs; it appears that this delocalization has taken place into bonding orbital(s), which is certainly consistent with some degree of $p\pi$–$d\pi$ bonding in the Si–N bonds. The Si–N–Si angle of 136·3 (1·2)° is greater than those found in other disilazanes (range 118 to 129°), consistent with spectroscopic predictions (Bürger, 1973). However, the angle may also be influenced by steric factors, and it is possible that the total covalent bonding energy of the isolated molecule is relatively insensitive to the Si–N–Si angle. The mean Si–C(H_3) bond length has the typical value of 1·90 (2) Å, suggesting that there is little librational shortening of this distance, and therefore that the short Si–N bond cannot be accounted for by libration.

The calculations were performed on the Cambridge University Titan and IBM 370/165 computers with programs written by G.M.S.

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Trimethyltin Methoxide

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Abstract. $(CH_3)_3SnOCH_3$, orthorhombic, $P2_12_12_1$, $a=6·61$ (1), $b=8·10$ (5), $c=12·61$ (2) Å, $U=675$ Å^3, $Z=4$, $D_x=1·92$ g cm^{-3} at −55 °C. Approximately planar trimethyltin groups are linked by methoxide units to form infinite zigzag -O–Sn–O–Sn– chains along the y (needle) axis, with trigonal bipyramidal coordination of tin. Mean bond lengths and angles are: Sn–C 2·14 (2); Sn–O 2·23 (3); O–C 1·43 (3) Å; O–Sn–O′ 172·4 (7); Sn–O–Sn′ 131·2 (12)°. The structure was refined to an R of 0·057 for 1106 unique observed reflexions obtained at about −55 °C with a two-circle diffractometer.

Introduction. X-ray crystallographic studies have established the presence of approximately symmetrical hydroxide bridging in a number of organotin compounds. This results in dimeric molecules in dimethyltin hydroxide nitrate (Domingos & Sheldrick, 1974*a*), and in polymeric structures in $(CH_3)_3SnOH$ (Kasai, Yasuda & Okawara, 1965), $(CH_3)_3SnNCO.(CH_3)_3SnOH$ (Hall & Britton, 1972) and $[(CH_3)_3Sn]_3(OH)CrO_4$ (Domingos & Sheldrick, 1974*b*). Chapman, Davies, Harrison & McFarlane (1970) have proposed a methoxide-bridged dimeric structure for dimethyltin methoxide chloride on the basis of infrared, Mössbauer, n.m.r. and molecular-weight measurements. We report here the determination of the structure of a crystal which we obtained from a preparation of dimethyltin dimethoxide, although the structure determination shows unambiguously that it was trimethyltin methoxide. The crystals were found to sublime rapidly out of the X-ray beam at room temperature, so the intensities were collected at about −55 °C on a Stoe computer-controlled two-circle diffractometer modified for low-temperature operation.

Experimental. Dimethyltin dimethoxide was prepared by the reaction of dimethyltin dichloride with sodium methoxide in dry methanol at 0 °C (Davies & Harrison, 1967), and identified by its infrared spectrum. Since it is sensitive to hydrolysis, we removed the solvent under vacuum and attempted to grow crystals by vacuum sublimation. The temperature was progressively increased to about 120 °C, when a few needle-shaped crystals formed on the cold finger; these were sealed into Lindemann-glass capillary tubes. A suitable crystal for X-ray diffraction, of approximate dimensions 0·12 × 0·88 × 0·11 mm, was obtained by melting one of

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