

Table II. Structural Comparison of the $\text{Mo}_2\text{X}_8\text{H}^{3-}$ Ions with the $\text{Mo}_2\text{X}_9^{3-}$ Ions^a

Anion	Mo-Mo, Å	Mag moment	Angles at bridging X atoms, deg	Mo-X (term), Å	Mo-X (br), Å	Ref
$\text{Mo}_2\text{Cl}_9^{3-}$	2.665	~0	65.6	2.384	2.487	13
	(1)		(4)	(6)	(12)	
$\text{Mo}_2\text{Cl}_8\text{H}^{3-}$	2.380	0	56.8	2.380	2.500	1
	(10)		(9)	(10)	(20)	
$\text{Mo}_2\text{Br}_9^{3-}$	2.816	>0	64.9	2.544	2.624	13
	(9)		(4)	(3)	(5)	
$\text{Mo}_2\text{Br}_8\text{H}^{3-}$	2.439	0	54.3	2.554	2.672	2
	(7)		(2)	(3)	(5)	

^a Numbers in parentheses beneath each parameter are esd's occurring in the least significant digit.

the hydride-bridged dimers, characterized as $[\text{HTi}(\text{C}_5\text{H}_5)_2]_2$ and $[\text{HTi}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)]_2$, bands are observed at 1450 and 1230 cm^{-1} , respectively.¹² The dimeric chromium system $\text{H}_2\text{Cr}_2(\text{CO})_{10}^{2-}$ exhibits a Raman-active band at 1004 cm^{-1} which is shifted to 705 cm^{-1} upon deuteration.¹⁰ Thus, the bands we assign to bridging protium and deuterium atoms are within the proper range for μ -hydrido and -deuterio systems.

Now that the true identity of the $\text{Mo}_2\text{X}_8\text{H}^{3-}$ anions, with three bridging atoms including hydrogen, is known, a structural comparison of the pairs of $\text{Mo}_2\text{X}_9^{3-}$ - $\text{Mo}_2\text{X}_8\text{H}^{3-}$ anions (Table II) is of interest. The data for the $\text{Mo}_2\text{X}_9^{3-}$ ions are taken from the work of Saillant and Wentworth.¹³ It is evident that the replacement of one Cl or Br bridge by an H atom enormously increases the strength of the interaction between the metal atoms; in both the chloro and the bromo pairs, the hydrido-bridged species has an Mo-Mo distance some 0.3-0.4 Å shorter than in the species with three halogen bridges, and the angles at the bridging halogen atoms contract considerably (ca. 10°) to some of the lowest values ever recorded for bridging Cl and Br atoms. At the same time the Mo-Cl and Mo-Br distances to the bridging atoms lengthen slightly. The Mo-X distances to terminal X atoms are unchanged, however, in support of the assignment of the same oxidation number, +3, to the Mo atoms in both the $\text{Mo}_2\text{X}_9^{3-}$ and the $\text{Mo}_2\text{X}_8\text{H}^{3-}$ ions.

It seems reasonable to suppose¹³ that in the $\text{Mo}_2\text{X}_9^{3-}$ species

there exist Mo-Mo bonds, as in the analogous $\text{W}_2\text{Cl}_9^{3-}$ ion, since the central MX_3M bipyramid is significantly flattened relative to the shape expected for the ideal confacial biocahedron.¹⁴ The zero or near-zero magnetic moments are consistent with M-M bonding. Probably the factor which limits the closeness and strength of the Mo-Mo interaction in the $\text{Mo}_2\text{X}_9^{3-}$ species is the size of the bridging Cl or Br atoms, which impedes the approach of the Mo atoms to each other. When one of the three Cl or Br atoms is replaced by the bridging H atom, this steric factor is reduced and the Mo-Mo interaction can become appreciably closer and stronger.

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Registry No. $\text{Cs}_3\text{Mo}_2\text{Br}_8\text{H}$, 57719-38-7; $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$, 57719-39-8; $\text{Cs}_3\text{Mo}_2\text{Cl}_8\text{H}$, 57719-40-1.

References and Notes

- M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).
- F. A. Cotton, B. A. Frenz, and Z. C. Mester, *Acta Crystallogr., Sect. B*, **29**, 1515 (1973).
- These measurements were kindly carried out by Dr. Eric Pedersen, Technical University of Denmark, Copenhagen.
- This work was done by Dr. Z. C. Mester.
- J. V. Brencic, D. Dobcenik, and P. Segecin, *Monatsh. Chem.*, **105**, 944 (1974); *Chem. Abstr.*, **80**, 115441 (1974).
- J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 2698 (1969).
- J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 351 (1970).
- J. Knight and M. J. Mays, *J. Chem. Soc. A*, 711 (1970).
- B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 901 (1970).
- H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
- P. Dapporto, S. Midollini and L. Sacconi, *Inorg. Chem.*, **14**, 1643 (1975).
- J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, **91**, 7301 (1969); *ibid.*, **92**, 6182 (1970).
- R. Saillant, R. B. Jackson, W. E. Streib, K. Foltling, and R. A. D. Wentworth, *Inorg. Chem.*, **10**, 1453 (1971); R. Saillant and R. A. D. Wentworth, *ibid.*, **8**, 1226 (1969).
- F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972).
- We are unable to account with certainty for the earlier failure¹ to detect the infrared bands which we now find. Presumably the samples were not properly prepared or were too dilute.

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Crystal and Molecular Structure of Hexadecamethylbicyclo[3.3.1]nonasilane¹

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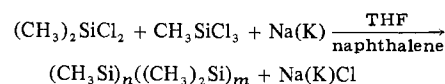
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The crystal structure of $\text{Si}_9(\text{CH}_3)_{16}$ was determined by the single-crystal x-ray diffraction technique using data collected from a fully automated diffractometer. The unit cell is monoclinic, space group $P2_1/c$, with $a = 25.952 \pm 0.007$ Å, $b = 10.398 \pm 0.005$ Å, $c = 28.146 \pm 0.009$ Å, and $\beta = 122.32 \pm 0.02^\circ$, and contains eight molecules. The structure was elucidated to determine which isomer of the polysilane backbone had been synthetically prepared. A trial structure was obtained by direct methods and Fourier techniques and refined by full-matrix least squares. The final value of the R index is 0.092. Each independent molecule contains a bicyclo[3.3.1] system, a six-membered polysilane ring in a classical chair conformation, a six-membered polysilane ring, five of whose atoms are roughly coplanar, and an Si-Si-Si bond angle of 120° . Methyl groups bonded to the five coplanar silicon atoms are eclipsed.

Introduction

The synthesis of permethylated, bicyclic, and cage polysilanes has been recently reported by West and Indriksons.² Their preparation was accomplished by the reaction



The product mixture was vacuum distilled and products in the

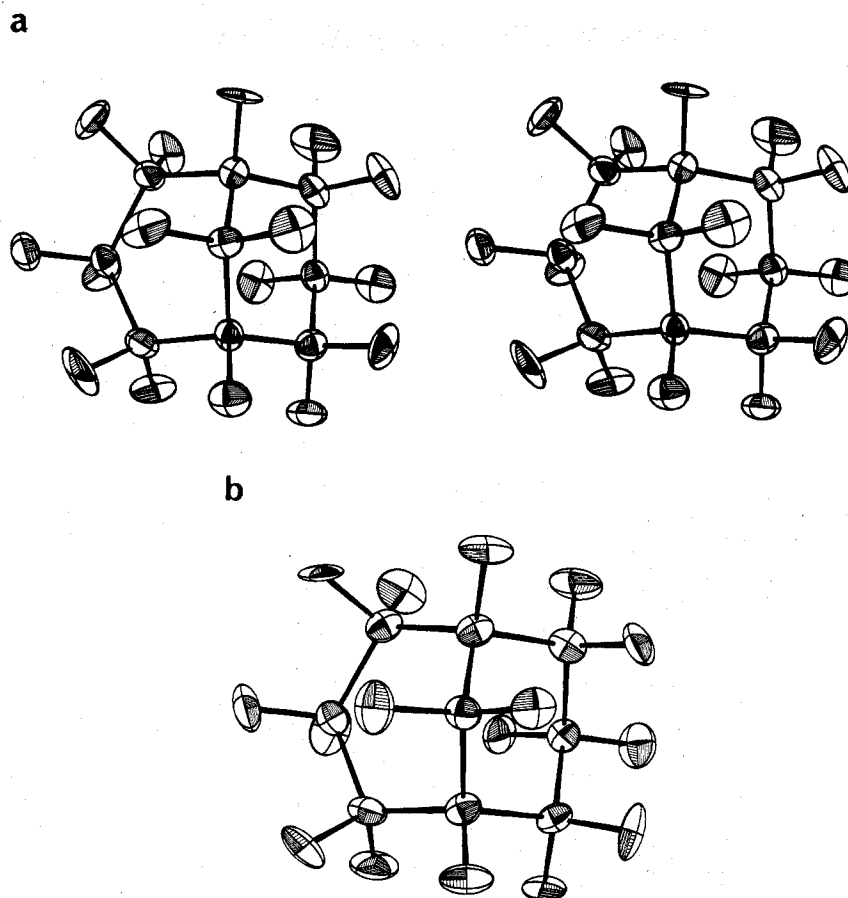
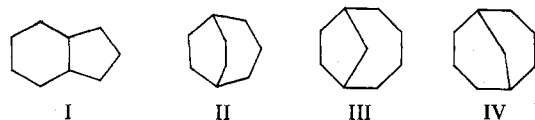


Figure 1. ORTEP drawings of $\text{Si}_9(\text{CH}_3)_{16}$: (a) stereoplot of molecule A; (b) plot of molecule B.

fractional distillates were separated by preparative gas chromatography. Compounds of the following empirical chemical composition were isolated: $\text{Si}_8(\text{CH}_3)_{14}$, $\text{Si}_9(\text{CH}_3)_{16}$, $\text{Si}_{10}(\text{CH}_3)_{16}$, $\text{Si}_{10}(\text{CH}_3)_{18}$, and $\text{Si}_{13}(\text{CH}_3)_{22}$; photolysis of $\text{Si}_8(\text{CH}_3)_{14}$ in cyclohexane yielded the product $\text{Si}_7(\text{CH}_3)_{12}$.

Proton nuclear magnetic resonance indicated that the $\text{Si}_8(\text{CH}_3)_{14}$ product had been prepared as the bicyclo[2.2.2] isomer and that the $\text{Si}_7(\text{CH}_3)_{12}$ product had been prepared as the bicyclo[2.2.1] isomer. Spectroscopy was not an adequate structure-giving tool in the case of $\text{Si}_9(\text{CH}_3)_{16}$, however, whose NMR spectrum contained only four peaks at +0.19, +0.175, +0.16 and +0.13 ppm (δ). Allowing for peak overlap, many isomers of the silicon backbone are possible; among the more likely are I-IV. In interpreting their NMR results, West



and Indriksons correctly but inconclusively pointed out the likelihood that IV or the bicyclo[3.3.1]nonasilane isomer was the structure in question. With regard to the remaining four compounds prepared, no definitive structural assignment has been made.

In this paper, we report the result of a single-crystal x-ray study of $\text{Si}_9(\text{CH}_3)_{16}$ in order to confirm the tentative isomeric assignment indicated by the spectroscopic results.

Experimental Section

Single crystals of the title compound were furnished by Professor R. West of the University of Wisconsin. They had been grown by vacuum sublimation as clear, colorless rods, growing along the b axis.

Preliminary precession and Weissenberg photographic investigations of the compound revealed the presence of only one mirror plane in the crystal structure, indicating, therefore, a monoclinic space group. The systematic absences of $0k0$, k odd, and $h0l$, l odd, uniquely determined the space group to be $P2_1/c$ with cell parameters of $a = 25.952 \pm 0.007$ Å, $b = 10.398 \pm 0.005$, $c = 28.146 \pm 0.009$, and $\beta = 122.32 \pm 0.02^\circ$. The density was measured quite crudely by flotation in water and found to be about 1 g cm^{-3} ; thus, there are eight molecules per unit cell or two independent molecules to be located. The calculated density, assuming $Z = 8$, is 1.016 g cm^{-3} .

One crystal of approximate dimensions $0.15 \times 0.15 \times 0.5$ mm was mounted parallel to the long or b direction and used for collecting intensity data. On this crystal, data were collected out to a maximum 2θ of 60° on a Picker four-circle automated diffractometer, using $\text{Cu K}\alpha$ radiation; the x-ray beam was monochromatized using a graphite crystal. Intensities were measured employing the θ - 2θ scan technique. During the data collection, a generally linear decay rate was observed by monitoring three standard reflections; by the end of the data collection, one of the standards had fallen by as much as 25% and the decay curves were exhibiting possible anisotropy. For this reason, data collection on this crystal was halted and continued on another of approximate dimensions $0.2 \times 0.2 \times 0.6$ mm; the mounting was in a similar orientation. On this crystal, data were collected from a 2θ of 60° to 2θ of 80° including roughly 2000 reflections. Again, during the data collection, a generally linear decay rate was observed; by the end of the data collection, one of the standards had fallen by as much as 50% and the decay curves were exhibiting possible anisotropy. For this reason, only the first 1000 reflections collected from the second crystal were included in the final data set which consisted of, then, 2641 nonequivalent reflections. The data were corrected for falloff in intensity due to decay with exposure time and for Lorentz and polarization factors. The two sets of data were then overlapped by comparing the ratios of the three standard reflections. No absorption corrections were applied ($\mu = 33.41 \text{ cm}^{-1}$). Of those reflections included in the final data set, 2347 were considered observable ($I/\sigma(I) > 2.33$ where $\sigma(F_o) = (F^2 + \sigma(I))^{1/2} - F_o$). The data were

placed on absolute scale³ and values of the normalized structure factor magnitudes $|E|$'s were calculated.

Structure Solution and Refinement

A trial structure was obtained by the direct-methods technique using the program MULTAN.⁴ An E map calculated with 274 reflections ($|E| \geq 1.60$) clearly revealed the positions of the 18 silicon atoms as the highest peaks in the map. The carbon atoms were cautiously located from three successive Fourier maps. At this point, three cycles of isotropic, full-matrix least squares and four cycles of anisotropic, full-matrix least squares resulted in a final R index, $\sum \|F_o\| - |F_c| / \sum \|F_o\|$, of 0.092; hydrogen atoms could not be located in a difference Fourier. Failure to locate the hydrogen atoms may result from rotation of the methyl groups; in the case of $\text{Si}_6(\text{CH}_3)_{12}$ ⁵ hydrogen atoms similarly could not be located, while artificial simulation of rotation, accomplished by half-weighting the hydrogen atoms in both eclipsed and staggered conformations at ideally calculated positions, improved the structure factor agreement to a surprising extent. We did not believe it worthwhile to use this procedure in the present case. All least-squares calculations were carried out using the program UCLALS⁶ which minimizes the function $\sum w [|F_o| - (1/k)|F_c|]^2$ where $w = \sigma(F)^{-2}$. Table I⁷ lists observed and calculated structure factors; those reflections distinguished by an asterisk were considered to be unobserved. Atomic scattering factors from ref 8 were used exclusively.

Results

The isomer prepared, then, was identified to be hexadecamethylbicyclo[3.3.1]nonasilane. Coordinates of the silicon and carbon atoms are given in Table II. Table III lists anisotropic thermal parameters of both types of atoms. The nomenclature is such that those atoms labeled A or B belong to molecule A or B, respectively; where appropriate carbon atoms preceded by the number 1 are methyl carbons which are exo to Si(9) while these preceded by a 2 are endo to Si(9). Methyl carbons 1C(9) and 2C(9) are cis to rings I and II, respectively; ring I contains Si(1), Si(2), Si(3), Si(4), Si(5), and Si(9), and ring II contains Si(5), Si(6), Si(7), Si(8), Si(1), and Si(9). The symbols in parentheses following each carbon atom designation indicate the silicon atom to which the methyl group is bonded. Figures 1a and 1b are ORTEP⁹ drawings of molecules A and B; Figure 1a is a stereopair of molecule A. Si(1) and Si(5) form the two bridgeheads while Si(9) is in the bridge; Si(1) appears below Si(5) in Figures 1a and 1b, the numbers increasing in clockwise fashion.

With regard to the size of the estimated standard deviations on the anisotropic temperature factors, the question of their real, physical significance must be raised. As an answer, the methyl ellipsoids should be carefully inspected. Though not so in every case, most of the methyl ellipsoids seem to be elongated in a direction which should suggest motion which is approximately perpendicular to the silicon backbone and through Si(9). Therefore, it is quite likely that the refined thermal parameters do indeed offer real physical information.

Discussion

Bond lengths and their standard deviations are listed in Table IV; the values of the Si-C bond lengths, corrected for riding motion,¹⁰ are also included. The average Si-Si bond distance is 2.343 ± 0.02 Å; a bond length of 2.34 Å is predicted by the single-bond covalent radius.¹¹ The value 2.338 ± 0.004 Å was reported for $\text{Si}_6(\text{CH}_3)_{12}$.⁵ Donohue¹² has compiled an average value of the silicon-silicon bond length as determined from 14 independent x-ray studies of elemental silicon; this value is 2.3515 ± 0.0001 Å. Our average value, as well as that reported for $\text{Si}_6(\text{CH}_3)_{12}$ is, then, about 0.01 Å shorter. The average Si-C bond length is 1.935 ± 0.035 Å after correction has been made for riding motion (this value, without correction, is 1.909 ± 0.025 Å). These differences are not significant¹³ because of the large root-mean-square deviations. Averaging here will be taken over both independent molecules as there are no significant differences between them. The

Table II. Refined Positional Parameters for $\text{Si}_6(\text{CH}_3)_{16}$ ^a

Atom	x	y	z
Si(1A)	0.4020 (2)	0.4427 (4)	0.3023 (2)
Si(2A)	0.3396 (2)	0.4891 (5)	0.3380 (3)
Si(3A)	0.2873 (2)	0.3130 (5)	0.3465 (2)
Si(4A)	0.2983 (2)	0.1067 (5)	0.3198 (3)
Si(5A)	0.3623 (2)	0.0869 (4)	0.2843 (2)
Si(6A)	0.4627 (2)	0.0394 (5)	0.3526 (3)
Si(7A)	0.5102 (2)	0.2037 (5)	0.4170 (2)
Si(8A)	0.5036 (2)	0.3947 (5)	0.3714 (3)
Si(9A)	0.3553 (2)	0.2774 (4)	0.2377 (2)
Si(1B)	0.8771 (2)	0.0743 (4)	0.0736 (2)
Si(2B)	0.8126 (2)	0.0974 (5)	-0.0248 (3)
Si(3B)	0.7871 (2)	0.3083 (5)	-0.0598 (2)
Si(4B)	0.8196 (2)	0.4836 (5)	0.0028 (3)
Si(5B)	0.8793 (2)	0.4333 (5)	0.0990 (2)
Si(6B)	0.9848 (2)	0.4354 (5)	0.1369 (3)
Si(7B)	1.0122 (2)	0.2799 (4)	0.0951 (2)
Si(8B)	0.9821 (2)	0.0789 (4)	0.1078 (2)
Si(9B)	0.8494 (2)	0.2325 (4)	0.1145 (2)
C(1A)	0.4023 (8)	0.593 (2)	0.2621 (8)
1C(2A)	0.2788 (9)	0.599 (2)	0.2862 (11)
2C(2A)	0.3828 (9)	0.566 (2)	0.4082 (9)
1C(3A)	0.2018 (7)	0.355 (2)	0.2999 (9)
2C(3A)	0.3052 (8)	0.308 (2)	0.4212 (8)
1C(4A)	0.2188 (8)	0.048 (2)	0.2599 (10)
2C(4A)	0.3250 (9)	-0.006 (2)	0.3830 (10)
C(5A)	0.3320 (8)	-0.046 (2)	0.2321 (8)
1C(6A)	0.5057 (9)	0.001 (2)	0.3161 (9)
2C(6A)	0.4682 (11)	-0.113 (2)	0.3927 (11)
1C(7A)	0.5935 (8)	0.161 (2)	0.4700 (9)
2C(7A)	0.4702 (10)	0.227 (2)	0.4570 (9)
1C(8A)	0.5508 (9)	0.379 (2)	0.3341 (9)
2C(8A)	0.5377 (8)	0.537 (2)	0.4231 (9)
1C(9A)	0.2724 (8)	0.314 (2)	0.1864 (9)
2C(9A)	0.3894 (9)	0.252 (2)	0.1907 (9)
C(1B)	0.8642 (8)	-0.084 (2)	0.0951 (9)
1C(2B)	0.7411 (9)	0.004 (2)	-0.0425 (11)
2C(2B)	0.8439 (11)	0.010 (2)	-0.0624 (10)
1C(3B)	0.7005 (8)	0.315 (2)	-0.1039 (9)
2C(3B)	0.8120 (9)	0.330 (2)	-0.1116 (9)
1C(4B)	0.7459 (9)	0.563 (2)	-0.0114 (9)
2C(4B)	0.8575 (10)	0.605 (2)	-0.0184 (10)
C(5B)	0.8646 (9)	0.558 (2)	0.1412 (8)
1C(6B)	1.0231 (9)	0.401 (2)	0.2139 (9)
2C(6B)	1.0093 (9)	0.598 (2)	0.1287 (10)
1C(7B)	1.1020 (8)	0.279 (2)	0.1301 (9)
2C(7B)	0.9756 (8)	0.316 (2)	0.0173 (8)
1C(8B)	1.0286 (7)	0.027 (2)	0.1861 (8)
2C(8B)	0.9977 (8)	-0.050 (2)	0.0680 (8)
1C(9B)	0.7614 (7)	0.223 (2)	0.0771 (10)
2C(9B)	0.8829 (9)	0.205 (2)	0.1922 (8)

^a The estimated standard deviation in the least significant figure of a parameter is given parentheses.

corrected values agrees well with the 1.94-Å bond length predicted by the sum of the single-bond covalent radii.¹¹ Carrell and Donohue⁵ reported an average value of 1.924 ± 0.012 Å for this quantity in the $\text{Si}_6(\text{CH}_3)_{12}$ study.

Bond angles are given Figure 2a and 2b. In general, these valence angles are close to tetrahedral, indicative of the expected sp^3 bonding scheme. The average Si-Si-Si angle is $112.4 \pm 3.7^\circ$ comparing with $111.9 \pm 0.4^\circ$ reported for $\text{Si}_6(\text{CH}_3)_{12}$. One anomaly is the Si(2)-Si(3)-Si(4) angle of 120° found in both independent molecules. Some rationalization for this phenomenon will be offered. The average Si-Si-C angle is $108.8 \pm 2.1^\circ$ while the average C-Si-C angle is $106.4 \pm 1.6^\circ$; these values compare, respectively, with 109.2 ± 1.2 and $108.1 \pm 0.5^\circ$, reported for $\text{Si}_6(\text{CH}_3)_{12}$.⁵ Average standard deviations on these angles are given respectively as 0.25, 0.65, and 0.80° .

The geometry of the silicon backbone is of interest. Ring II is in a chair conformation; the average absolute Si-Si-Si-Si torsion angle about this ring is $56.5 \pm 0.5^\circ$, comparing closely with $53.5 \pm 0.3^\circ$ for $\text{Si}_6(\text{CH}_3)_{12}$ and $54.5 \pm 0.8^\circ$ for the

Table III. Refined Thermal Parameters for the Silicon Atoms (Values $\times 10^5$) and the Carbon Atoms (Values $\times 10^4$) in $\text{Si}_6(\text{CH}_3)_{16}$ ^a

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1A)	171 (14)	812 (67)	165 (19)	119 (44)	185 (31)	164 (50)
Si(2A)	276 (16)	757 (70)	243 (22)	65 (51)	342 (35)	8 (56)
Si(3A)	226 (14)	1063 (75)	217 (20)	141 (49)	297 (32)	6 (55)
Si(4A)	255 (15)	708 (68)	306 (22)	-30 (48)	395 (35)	38 (55)
Si(5A)	169 (14)	891 (70)	123 (18)	-5 (44)	143 (30)	43 (49)
Si(6A)	259 (16)	950 (71)	212 (20)	300 (48)	287 (33)	121 (54)
Si(7A)	210 (14)	1002 (72)	181 (20)	172 (45)	211 (32)	123 (51)
Si(8A)	232 (16)	997 (73)	205 (20)	-33 (51)	255 (33)	64 (58)
Si(9A)	191 (14)	784 (67)	137 (19)	-30 (43)	126 (31)	69 (49)
Si(1B)	189 (14)	826 (70)	207 (19)	62 (45)	259 (30)	63 (50)
Si(2B)	259 (15)	693 (69)	232 (20)	-153 (49)	272 (33)	-184 (55)
Si(3B)	228 (16)	1084 (77)	159 (20)	-48 (49)	160 (34)	-109 (57)
Si(4B)	254 (15)	872 (76)	209 (20)	169 (52)	238 (32)	173 (56)
Si(5B)	227 (15)	924 (73)	183 (19)	118 (47)	291 (32)	23 (52)
Si(6B)	249 (16)	1042 (75)	199 (22)	-128 (50)	298 (35)	-99 (53)
Si(7B)	162 (14)	1028 (70)	195 (21)	-9 (44)	245 (32)	20 (50)
Si(8B)	202 (15)	804 (71)	213 (21)	198 (47)	260 (32)	102 (53)
Si(9B)	174 (15)	846 (70)	200 (21)	-99 (44)	232 (33)	-60 (50)
C(1A)	28 (5)	99 (26)	19 (7)	8 (18)	17 (11)	20 (19)
1C(2A)	42 (7)	131 (31)	49 (9)	119 (24)	54 (15)	101 (26)
2C(2A)	51 (7)	123 (27)	23 (7)	-68 (21)	56 (13)	-70 (20)
1C(3A)	22 (5)	111 (26)	31 (7)	27 (18)	32 (11)	23 (21)
2C(3A)	32 (6)	174 (30)	17 (6)	-50 (20)	31 (11)	-25 (21)
1C(4A)	15 (5)	200 (33)	34 (8)	-55 (18)	21 (12)	-58 (24)
2C(4A)	44 (7)	92 (27)	51 (9)	66 (20)	68 (15)	119 (24)
C(5A)	39 (6)	44 (21)	20 (6)	-36 (16)	33 (11)	-48 (17)
1C(6A)	36 (7)	162 (33)	33 (7)	85 (22)	40 (13)	9 (23)
2C(6A)	54 (8)	97 (31)	34 (9)	53 (26)	28 (16)	56 (26)
1C(7A)	23 (5)	151 (32)	19 (7)	42 (21)	-9 (11)	28 (24)
2C(7A)	43 (7)	240 (35)	22 (7)	-4 (23)	50 (13)	-12 (23)
1C(8A)	31 (6)	233 (34)	35 (8)	-37 (22)	57 (13)	-24 (25)
2C(8A)	28 (6)	71 (25)	27 (7)	-9 (18)	15 (12)	-4 (22)
1C(9A)	20 (5)	112 (29)	20 (7)	-4 (19)	-16 (12)	48 (23)
2C(9A)	41 (7)	175 (31)	20 (7)	-13 (22)	43 (12)	0 (22)
C(1B)	44 (6)	55 (23)	34 (7)	-13 (18)	56 (13)	15 (18)
1C(2B)	30 (6)	131 (33)	46 (9)	-91 (23)	23 (14)	-56 (27)
2C(2B)	60 (9)	100 (31)	24 (7)	24 (21)	33 (15)	-41 (23)
1C(3B)	21 (5)	186 (35)	22 (7)	-31 (21)	-2 (12)	-19 (25)
2C(3B)	40 (7)	23 (39)	21 (7)	29 (25)	35 (13)	70 (26)
1C(4B)	39 (6)	63 (23)	27 (7)	45 (19)	34 (12)	-29 (19)
2C(4B)	54 (8)	175 (35)	26 (7)	-30 (25)	50 (14)	1 (24)
1C(5B)	51 (7)	92 (25)	24 (7)	9 (19)	62 (13)	-20 (18)
1C(6B)	31 (6)	144 (30)	12 (7)	-25 (21)	4 (12)	-25 (22)
2C(6B)	42 (6)	77 (25)	51 (9)	-51 (20)	64 (14)	-36 (23)
1C(7B)	21 (5)	201 (32)	31 (8)	1 (20)	29 (12)	0 (23)
2C(7B)	32 (6)	147 (29)	13 (6)	24 (20)	16 (11)	17 (21)
1C(8B)	20 (5)	260 (35)	7 (6)	49 (21)	13 (10)	68 (22)
2C(8B)	32 (5)	75 (22)	31 (7)	14 (16)	48 (11)	-31 (18)
1C(9B)	13 (5)	218 (37)	48 (10)	-15 (20)	24 (13)	-24 (27)
2C(9B)	44 (6)	118 (25)	9 (6)	23 (19)	30 (11)	27 (18)

^a The anisotropic temperature factor expression is $T = \exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$. The estimated standard deviation for each parameter is given in parentheses.

average absolute C-C-C torsion angle reported for the cyclohexyl ring in $(\text{PC}_6\text{H}_{11})_4$.¹⁴ Ring I assumes neither a chair nor a boat conformation to avoid steric repulsion between methyl groups. Were ring I to force itself into a chair conformation, the endo methyl groups of Si(3) and Si(7) would approach too closely. Were ring I to force itself into a boat conformation, the exo methyl groups of Si(3) and 1C(9) would approach too closely. In the refined structure, the distances between these methyl carbon atoms are 3.83 and 3.93 Å and 4.47 and 4.75 Å for molecules A and B, respectively. As a result of steric hindrance, ring I adopts a compromised conformation; absolute Si-Si-Si-Si torsion angles about this ring are listed in Table V; that ring I is neither a chair nor a boat conformer is, at once, outstanding. A best plane in the least-squares sense, calculated through Si(1), Si(2), Si(3), Si(4), and Si(5), revealed that the average deviation from planarity of these atoms is 0.026 ± 0.013 Å for molecule A and 0.006 ± 0.003 Å for molecule B. Atoms Si(9) deviate from the best planes by 1.2 Å.

Around ring II, the chair conformer, the average absolute

Si-Si-Si-C (axial) torsion angle is $65.4 \pm 2.8^\circ$; the average absolute Si-Si-Si-C (equatorial) torsion angle about this ring is $175.8 \pm 2.0^\circ$. For the case of $\text{Si}(\text{CH}_3)_{12}$ ⁵ the comparable values are 68.2 ± 1.2 and $173.5 \pm 0.3^\circ$, respectively. Three types of C-Si-Si-C torsion angles exist about the chair conformer, depending upon the steric disposition of the methyl substituents involved. When both carbon atoms are of equatorial methyl groups, the average value is $64.0 \pm 3.8^\circ$; when both carbon atoms are of axial methyl groups, the average value is $174.7 \pm 3.2^\circ$; when the carbon atoms are mixed, the average value is $53.8 \pm 4.1^\circ$. The corresponding values for $\text{Si}_6(\text{CH}_3)_{12}$ ⁵ are 66.7 ± 0.8 , 169.3 ± 1.5 , and $51.3 \pm 1.3^\circ$. Examination of the listing of interatomic distances between methyl groups not bonded to the same silicon atom reveals that, in general, the geometry of the molecule is determined by a maintenance of twice the van der Waals radius,⁸ 2.0 Å,¹¹ as the distance of closest intramolecular contact between methyl groups not bonded to the same silicon atom. The generality is violated, to some degree, around ring I. Inasmuch as five of the silicon atoms are planar with a 120°

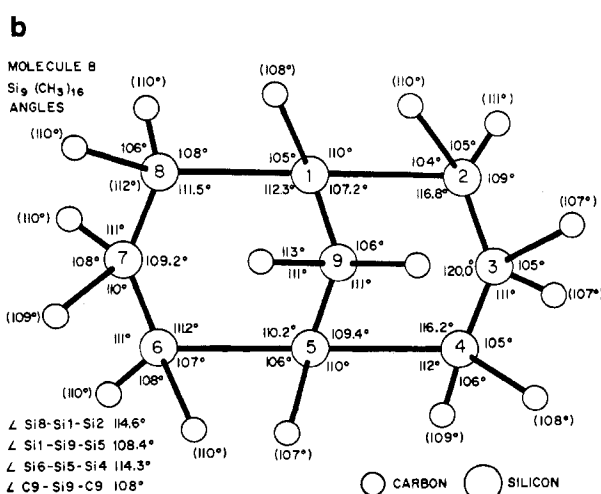
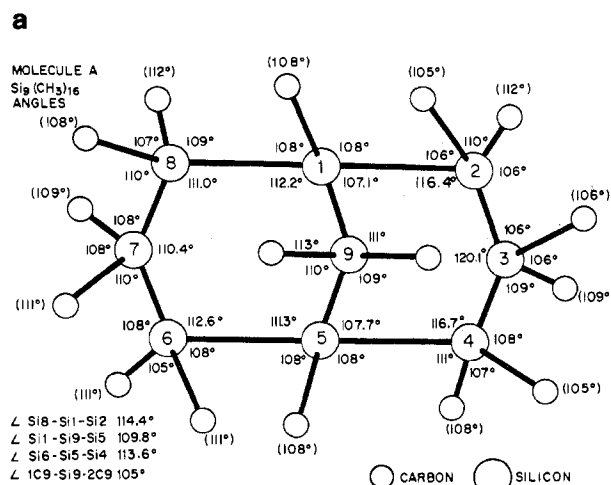


Figure 2. Bond angles in Si₉(CH₃)₁₆: (a) molecule A; (b) molecule B.

valence angle formed by Si(2)-Si(3)-Si(4), the methyl groups bonded to these coplanar silicon atoms are generally eclipsed; pertinent absolute torsion angles of the type C-Si-Si-C where

Table IV. Bond Distances (Å) in Si₉(CH₃)₁₆^a

Atoms	Dist in molecule A	Dist in molecule B
Si(1)-Si(2)	2.367 (4)	2.362 (8)
Si(1)-Si(9)	2.317 (7)	2.330 (6)
Si(2)-Si(3)	2.367 (6)	2.349 (7)
Si(3)-Si(4)	2.339 (7)	2.356 (8)
Si(4)-Si(5)	2.360 (4)	2.348 (8)
Si(5)-Si(6)	2.317 (6)	2.347 (4)
Si(5)-Si(9)	2.327 (7)	2.349 (6)
Si(6)-Si(7)	2.308 (8)	2.323 (6)
Si(8)-Si(9)	2.321 (7)	2.323 (6)
Si(8)-Si(11)	2.345 (6)	2.356 (4)

Atoms	Dist in molecule A		Dist in molecule B	
	Uncor	Cor	Uncor	Cor
Si(1)-C(1)	1.93 (2)	1.94	1.84 (2)	1.86
Si(2)-C(2)	1.86 (2)	1.91	1.91 (2)	1.95
Si(2)-C(2)	1.85 (2)	1.87	1.88 (2)	1.91
Si(3)-C(3)	1.93 (2)	1.94	1.90 (2)	1.93
Si(3)-C(3)	1.90 (2)	1.92	1.90 (2)	1.93
Si(4)-C(4)	1.94 (2)	1.97	1.92 (2)	1.93
Si(4)-C(4)	1.92 (2)	1.96	1.88 (2)	1.91
Si(5)-C(5)	1.87 (2)	1.89	1.93 (2)	1.95
Si(6)-C(6)	1.92 (2)	1.94	1.87 (2)	1.89
Si(6)-C(6)	1.91 (2)	1.94	1.86 (2)	1.89
Si(7)-C(7)	1.91 (2)	1.94	1.99 (2)	2.01
Si(7)-C(7)	1.91 (2)	1.94	1.90 (2)	1.93
Si(8)-C(8)	2.00 (2)	2.03	1.94 (2)	1.97
Si(8)-C(8)	1.93 (2)	1.95	1.92 (2)	1.93
Si(9)-C(9)	1.88 (2)	1.91	1.94 (2)	1.98
Si(9)-C(9)	1.97 (2)	2.00	1.89 (2)	1.92

^a When a value has not been corrected for thermal riding motion, the estimated standard deviation in the least significant figure is given in parentheses.

the methyl groups are either both endo or both exo substituents are listed in Table VI. Distances, which are significantly less than twice the methyl group van der Waals radius, between methyl groups which are not bonded to the same silicon atom are listed in Table VII. Hence, in adjusting its conformation to a shape corresponding to a minimum in potential energy, the molecule must still accept some strain which manifests itself in the form of interpenetration of the electron clouds between these methyl groups.

The packing of the molecule is illustrated in Figure 3 which is a simple *b* axis projection of the structure. The packing of

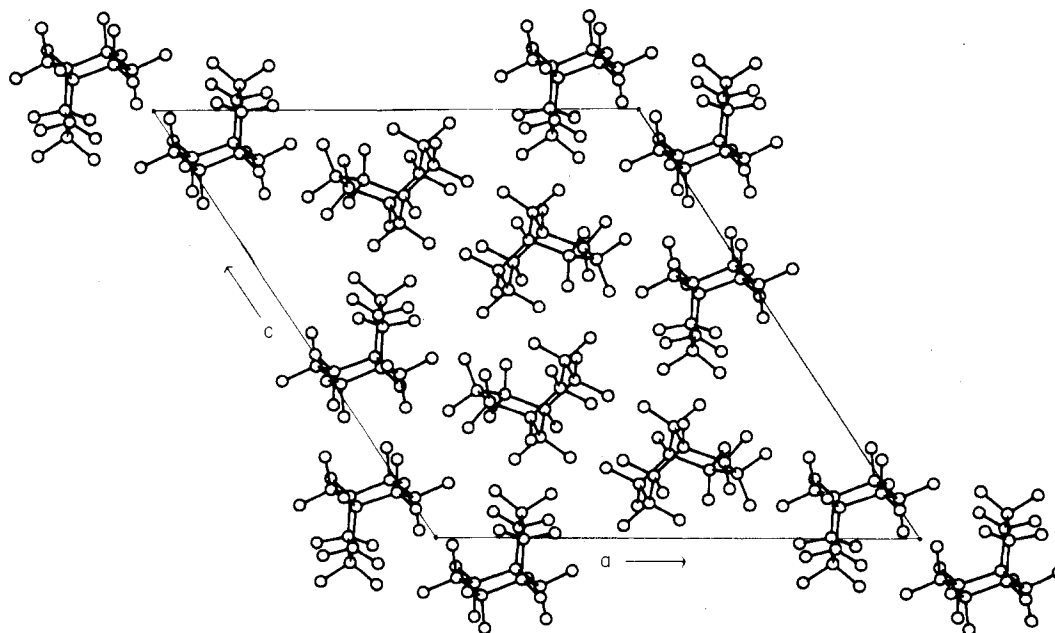


Figure 3. A view of the packing in Si₉(CH₃)₁₆ as projected down the *b* axis.

Table V. Absolute Torsion Angles (deg) around the Silicon Backbone in $\text{Si}_9(\text{CH}_3)_{16}$

Atoms	Torsion angle	
	In molecule A	In molecule B
In Ring I		
Si(9)-Si(1)-Si(2)-Si(3)	33.5	37.4
Si(4)-Si(3)-Si(2)-Si(1)	0.3	4.3
Si(5)-Si(4)-Si(3)-Si(2)	0.6	1.5
Si(9)-Si(5)-Si(4)-Si(3)	32.0	32.0
Si(4)-Si(5)-Si(9)-Si(1)	69.9	68.4
Si(5)-Si(9)-Si(1)-Si(2)	70.5	70.4
In Ring II		
The average absolute torsion angle is $56.5 \pm 0.5^\circ$.		
Between Both Rings		
Si(8)-Si(1)-Si(2)-Si(3)	91.4	87.9
Si(7)-Si(8)-Si(1)-Si(2)	66.2	66.4
Si(6)-Si(5)-Si(4)-Si(3)	91.8	92.1
Si(7)-Si(6)-Si(5)-Si(4)	65.6	63.0

Table VI. Absolute Torsion Angles (deg) Involving Eclipsed Methyl Groups in $\text{Si}_9(\text{CH}_3)_{16}$

Atoms	Torsion angle	
	In molecule A	In molecule B
C(1)-Si(1)-Si(2)-1C(2)	33.0	32.4
1C(2)-Si(2)-Si(3)-1C(3)	7.2	3.3
2C(2)-Si(2)-Si(3)-2C(3)	4.5	0.7
1C(3)-Si(3)-Si(4)-1C(4)	3.0	0.6
2C(3)-Si(3)-Si(4)-2C(4)	3.9	1.9
1C(4)-Si(4)-Si(5)-C(5)	31.3	28.0

Table VII. Distances (Å) between Methyl Carbon Atoms around Ring I Which Are Less Than 4.0 Å

Atoms	Dist in molecule A	Dist in molecule B
C(1)-1C(2)	3.61 (2)	3.58 (4)
1C(2)-1C(3)	3.38 (3)	3.55 (4)
2C(2)-2C(3)	3.49 (3)	3.52 (3)
1C(3)-1C(4)	3.50 (3)	3.39 (3)
2C(3)-2C(4)	3.56 (3)	3.63 (4)
1C(4)-C(5)	3.57 (2)	3.71 (3)

molecules occupying positions $A(x, y, z)$, $B(x, y, z)$, $A(x, 1/2 - y, 1/2 + z)$, and $B(x, 1/2 - y, 1/2 + z)$ may be thought of as chains of molecules whose centers all have a y coordinate of approximately $1/4$. The centrosymmetric mates of the molecules produce a similar array; the centers of these molecules all lie on an approximate plane at $y = 3/4$. Hence, Figure 3 is a composite of these two planes. The closest contact between neighboring molecules is 3.83 Å and occurs between 2C(6)A and 2C(7)A and again between 1C(9)A and 1C(7)B, indicative of the fact that the crystal is held together almost exclusively by van der Waals forces. The closest approach between methyl groups of neighboring molecules in $\text{Si}_6(\text{C}-\text{H}_3)_{12}^4$ has been reported as 3.98 Å.

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Registry No. $\text{Si}_9(\text{CH}_3)_{16}$, 37249-25-5.

Supplementary Material Available: Table I, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Supported by the National Science Foundation, DMR-72.
- (2) R. West and A. Indriksons, *J. Am. Chem. Soc.*, **94**, 6110 (1972).
- (3) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).
- (4) P. Main, M. M. Woolfson, and G. Germain, "MULTAN, A Computer Programme for the Automatic Solution of Crystal Structures", Centre Europeen de Calcul Atomique et Moleculaire, Orsay, France, 1971.
- (5) H. L. Carrell and J. Donohue, *Acta Crystallogr., Sect. B*, **28**, 1566 (1972).
- (6) P. K. Gantzel, R. A. Sparks, R. E. Long, and K. N. Trueblood, unpublished work, 1964.
- (7) Supplementary material.
- (8) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, 1968, pp 202-209.
- (9) C. K. Johnson, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
- (10) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FEE. A Fortran Crystallographic Function and Error Program", Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
- (11) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960.
- (12) J. Donohue, "The Structures of the Elements", Wiley, New York, N.Y., 1974.
- (13) D. W. J. Cruickshank, *Acta Crystallogr.*, **2**, 65 (1949).
- (14) J. C. J. Bart, *Acta Crystallogr., Sect. B*, **25**, 762 (1969).

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Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Acetate Dihydrate, $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3](\text{O}_2\text{C}_2\text{H}_3)_2 \cdot 2\text{H}_2\text{O}$

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The crystal structure of $[\text{Ni}(\text{en})_3](\text{O}_2\text{C}_2\text{H}_3)_2 \cdot 2\text{H}_2\text{O}$ has been determined by single-crystal x-ray diffraction techniques. After least-squares refinement using anisotropic thermal parameters for the nonhydrogen atoms and isotropic ones for hydrogens, the conventional R index converged at 0.033. The purple crystals form in the monoclinic space group $P2_1/c$ with $a = 10.936$ (1) Å, $b = 13.132$ (3) Å, $c = 15.151$ (3) Å, $\beta = 116.16$ (1)°, and $Z = 4$. The divalent nickel is hexacoordinated and exhibits the usual distortion from octahedral symmetry found in tris(ethylenediamine) complexes. A twist angle of $50.4 \pm 1.0^\circ$ exists between trigonal planes formed by the coordinating nitrogen atoms. The centric cell contains complex cations in both the $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$ configurations. Disorder about the metal center is attributed to a superposition of $\Delta\lambda\lambda\lambda$ over $\Lambda\delta\delta\delta$ and is estimated to occur about 14% of the time. An extensive network of hydrogen bonding is described between the cation and anion, the anion with H_2O , and the cation with H_2O . The effect of hydrogen bonding on the observed structure is discussed and a new parameter which considers anion size is postulated as influencing the occurrence of λ rings in tris(ethylenediamine) complexes.

Introduction

We have been interested in studying the ring conformations of ethylenediamine (en) chelates in solution and in a recent paper¹ we examined the effect of various anions on ring conformational equilibria. From the temperature dependence

of the NMR contact shifts of $[\text{Ni}(\text{en})_3]^{2+}$ in the presence of nitrate, acetate, and benzoate we argued that the formation at low temperature of multiple hydrogen bonds between cation and anion would favor the $\Lambda\delta\delta\lambda$ conformation for the complex. At higher temperatures each of these three systems yielded