

Crystal and Molecular Structure of *Tetrakis(trimethylsilylmethyl)bis- μ -trimethylsilylmethylidynediniobium(V)*

FAZLUL HUQ

*Discipline of Biomedical Science, Cumberland Campus, C42, The University of Sydney
East Street, P.O. Box 170, Lidcombe, NSW 1825, Australia
Fax: (61)(293)519520 Tel: (61)(293)519522; E-mail: f.huq@usyd.edu.au*

The crystal and molecular structure of *tetrakis(trimethylsilylmethyl)bis- μ -trimethylsilylmethylidynediniobium(V)*, $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$, were determined from three-dimensional X-ray diffraction data about 33 years ago using the facilities available at Imperial College, London, UK. The crystals are triclinic with unit-cell dimensions: $a = 19.540(3)$ Å, $b = 11.014(2)$ Å, $c = 12.155(2)$ Å, $\alpha = 115.91(1)^\circ$, $\beta = 110.14(2)^\circ$, $\gamma = 103.76(2)^\circ$, space group is $P\bar{1}$ and $Z = 2$. The structure was refined by least-squares methods to $R = 0.052$. The complex is dimeric and the two crystallographically independent dimers have the same structure. The dimers have $\bar{1}$ crystallographic symmetry and each niobium atom is joined to another niobium atom by two bridging CSiMe_3 groups. The distorted tetrahedral coordination around each metal atom is completed by two terminal CH_2SiMe_3 groups. The mean Nb-C(bridging) and Nb-CH₂ bond lengths are 1.974 and 2.160 Å, respectively. The compound has a quasi-aromatic ring of which the carbene bridges form a part. Although Nb...Nb distances are *ca.* 2.90 Å, the multiple bond character of the Nb-C(bridging) bonds and the distortion of the NbCCNb ring so as to reduce and Nb-Nb interaction suggest that the metal-metal bonding probably does not occur in this complex. The analogous tungsten complex is found to be isostructural.

Key Words: Niobium, Double bond, Silylmethyl, Triclinic.

INTRODUCTION

Among the compounds containing trimethylsilylmethyl ligands prepared by Mowat and Wilkinson¹ was one of niobium for which the analytical data suggested an empirical formula $\text{Nb}(\text{ligand})_3$, but for which the NMR spectrum was more complicated than that of the molybdenum complex². The interaction of niobium or tantalum pentachloride with the Grignard reagent gives distinct colour changes on the addition of successive equivalents of ligand. The final stage in the reaction is the formation of the dimeric species with a carbene bridge. The crystal structure of the

complex shows that the molecule contains not only trimethylsilylmethyl ligands but also bridging trimethylsilylmethylidyne ligands which along with niobium atoms form a novel quasi-aromatic NbCCNb ring.

This paper describes the solution of the structure of *tetrakis(trimethylsilylmethyl)bis- μ -trimethylsilylmethylidynediniobium(V)*, $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$ as it was carried out in Department of Chemistry, Imperial College, London in the year 1970³.

EXPERIMENTAL

Tetrakis(trimethylsilylmethyl)bis- μ -trimethylsilylmethylidynediniobium(V), $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$, crystallizes from light petroleum as reddish brown elongated plates. The crystals are air-sensitive and decompose in air within a few minutes. The compound was prepared by Mowat and Wilkinson¹ as follows. To a solution of trimethylsilylmethylmagnesium chloride (550 mmol) in diethyl ether (500 mL), was added NbCl_2 (37 g, 100 mmol) in diethyl ether (250 mL) at room temperature over 3 h. The dark red-brown solution was filtered and the solvent stripped. The residue was extracted with petroleum ether and the extracts filtered. After concentration *in vacuo* to 50 mL, cooling to -35°C for several hours and collection at that temperature the compound was recrystallized from petroleum ether (25 mL) at -40°C giving red-brown prisms (6 g, 20 %).

Crystal data: $\text{C}_{24}\text{H}_{62}\text{Si}_6\text{Nb}_2$, $M = 705.1 \text{ g mol}^{-1}$, Triclinic, space group, $P\bar{1}$, with unit-cell dimensions: $a = 19.540(3) \text{ \AA}$, $b = 11.014(2) \text{ \AA}$, $c = 12.155(2) \text{ \AA}$, $\alpha = 115.91(1)^\circ$, $\beta = 110.14(2)^\circ$, $\gamma = 103.76(2)^\circ$, $U = 1961.8 \text{ \AA}^3$, $Z = 2$, $d_c = 1.19 \text{ g cm}^{-3}$, $F(000) = 744$, $\mu(\text{Cu-K}\alpha) = 67.3 \text{ cm}^{-1}$. The structure of the compound was solved using the facilities at Imperial College, London. A Delauney reduction was carried out to check the unit cell. A crystal of approximate size $0.65 \text{ mm} \times 0.24 \text{ mm} \times 0.23 \text{ mm}$ was sealed under nitrogen in a Lindemann tube and intensity were measured on a Siemens off-line automatic diffractometer. Cu-K α radiation at a take-off angle of 4.5° , a Ni β filter and a Na(tl)I scintillation counter were used. The θ - 2θ scan technique was used, with a five-point measuring procedure⁴. A total of 3396 independent reflections were measured (to $\theta = 50^\circ$) of which 114 were judged to be unobserved. The 014 reflection was used as a reference every 25 reflections. The net count of this reflection dropped by about 8 % during the period of data collection (*ca.* 10 d).

Solution and refinement of structure: The structure was solved and refined using the X-ray '63 system of programs⁵. The calculations were performed on the Imperial College IBM7094 computer. The interpretation of three-dimensional Patterson was relatively straight forward and three cycles of least-squares refinement of two independent niobium atoms gave $R = 0.40$. From a difference Fourier six silicon and six carbon atoms were

located to give $R = 0.19$. All other carbon atoms were then located and isotropic refinement reduced R to 0.090. All atoms were now allowed to refine anisotropically to give $R = 0.062$ and from a subsequent difference Fourier all 62 hydrogen atoms were located. These were included as a 'fixed contribution' with isotropic temperature factors of the parent carbon atoms, to give $R = 0.054$. Application of anomalous dispersion correction for niobium and silicon and the introduction of a weighting scheme lowered R to 0.052. The weighting scheme used was that due to Hughes⁶ where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 50$. Application of the weighting scheme reduced R fractionally and gave lower standard deviations. The scattering factors used were those tabulated by Cromer and Waber⁷ and the real and imaginary parts of the anomalous dispersion correction for molybdenum and silicon were those given by Cromer⁸. Crystallographic data for $C_{24}H_{62}Si_6Nb_2$ have been deposited with the Cambridge Crystallographic Data centre as Supplementary Publication no. CCDC 267160.

RESULTS AND DISCUSSION

The structure contains dimeric molecules which sit astride centres of symmetry. There are no significant differences between two crystallographically independent dimers and mean bond lengths and bond angles will be used throughout the discussion. Fig. 1 gives the structure of the molecule. More important bond lengths are in Table-1. The dimers have $\bar{1}$ crystallographic symmetry and each niobium atom is joined to another niobium atom by two bridging $CSiMe_3$ groups. The distorted tetrahedral coordination around each metal atom is completed by two terminal CH_2SiMe_3 groups. The central portion of the molecule is shown in Fig. 2. The Nb- CH_2 distances are 2.160 Å and this may be compared to Mo- CH_2 of 2.124 Å found⁹ in $Mo_2(CH_2SiMe_3)_6$, Cr- CH_3 of 2.199 Å found¹⁰ in $Li_4(Cr_2Me_8) \cdot 4C_4H_8O_8$. The mean value of the Nb-C(bridging) distance is 1.974 Å. However, because of symmetry at the bridging carbon where Nb-C-Si angles of 119.8° and 142.4° occur the two Nb-C(bridging) distances may not be strictly identical (Fig. 2 and Table-2).

There is some buckling at the bridging carbon atom such that these atoms are 0.20 Å above and below the plane defined by Nb, Si(n1), Nb'. The possibility that there is a hydrogen atom attached to these carbon atoms has to be considered. The reasons against are as follows: the Nb-C(bridging) bonds clearly have multiple bonding character *i.e.*, 1.5 bonds; NMR spectrum both in benzene and deuterobenzene is strictly consistent with present formulation and there is no peak for C(bridging)-H and no hydrogen could be found in the difference Fourier. The IR spectrum

TABLE-1
 Nb₂(CH₂SiMe₃)₄(CSiMe₃)₂ BOND LENGTHS (Å) WITH STANDARD
 DEVIATION IN PARENTHESES

Bond	Length	Bond	Length
Nb(1)-C(111)	1.965(9)	Nb(2)-C(211)‡	1.954(9)
Nb(1)-C(111)†	2.000(10)	Nb(2)-C(211)	1.989(9)
Mean Nb-C(bridging)		1.974	
Nb(1)-C(121)	2.157(10)	Nb(2)-C(221)	2.155(10)
Nb(1)-C(131)	2.159(7)	Nb(2)-C(231)	2.167(7)
Mean Nb-CH ₂		2.160	
Si(11)-C(111)	1.871(10)	Si(21)-C(211)	1.872(8)
Si(11)-C(112)	1.875(16)	Si(21)-C(212)	1.866(12)
Si(11)-C(113)	1.872(12)	Si(21)-C(213)	1.863(13)
Si(11)-C(114)	1.846(8)	Si(21)-C(214)	1.832(12)
Si(12)-C(121)	1.856(12)	Si(22)-C(221)	1.836(11)
Si(12)-C(122)	1.868(14)	Si(22)-C(222)	1.855(17)
Si(12)-C(123)	1.842(13)	Si(22)-C(223)	1.857(12)
Si(12)-C(124)	1.860(9)	Si(22)-C(224)	1.864(17)
Si(13)-C(131)	1.871(10)	Si(23)-C(231)	1.872(8)
Si(13)-C(132)	1.875(16)	Si(23)-C(232)	1.866(12)
Si(13)-C(133)	1.872(12)	Si(23)-C(233)	1.863(13)
Si(13)-C(134)	1.870(14)	Si(23)-C(234)	1.870(9)
Mean Si-C		1.860	

Subscripts refer to atoms in the following positions: †1-x, -y, -z; ‡-x, -y, -z.

TABLE-2
 Nb₂(CH₂SiMe₃)₄(CSiMe₃)₂ BOND ANGLES (°) WITH STANDARD
 DEVIATION IN PARENTHESES

C(111)-Nb(1)-C(111)†	86.0(4)	C(211)-Nb(2)-C(211)‡	85.3(4)
C(111)-Nb(1)-C(121)	113.5(4)	C(211)-Nb(2)-C(221)	115.1(4)
C(111)-Nb(1)-C(131)	113.7(3)	C(211)-Nb(2)-C(231)	112.6(3)
C(121)-Nb(1)-C(131)	113.3(4)	C(221)-Nb(2)-C(231)	113.3(3)
C(111)†-Nb(1)-C(121)	115.7(3)	C(211)‡-Nb(2)-C(231)	115.7(4)
C(111)†-Nb(1)-C(131)	112.0(4)	C(211)‡-Nb(2)-C(221)	112.1(4)
Nb(1)-C(111)-Nb(1)†	94.0(4)	Nb(2)-C(211)-Nb(2)‡	94.7(4)
Nb(1)-C(111)-Si(11)	143.6(6)	Nb(2)‡-C(211)-Si(21)	141.1(5)
Nb(1)†-C(111)-Si(11)	118.7(5)	Nb(2)-C(211)-Si(21)	120.9(4)
Nb(1)-C(121)-Si(12)	130.6(6)	Nb(2)-C(221)-Si(22)	130.3(3)
Nb(1)-C(131)-Si(13)	121.4(5)	Nb(2)-C(231)-Si(23)	123.4(4)
Mean C-Si-CH ₃		110.6(5)	
Mean CH ₂ -Si-CH ₃		110.1(5)	
Mean CH ₃ -Si-CH ₃		108.6(6)	

Subscripts refer to atoms in the following positions: †1-x, -y, -z; ‡-x, -y, -z.

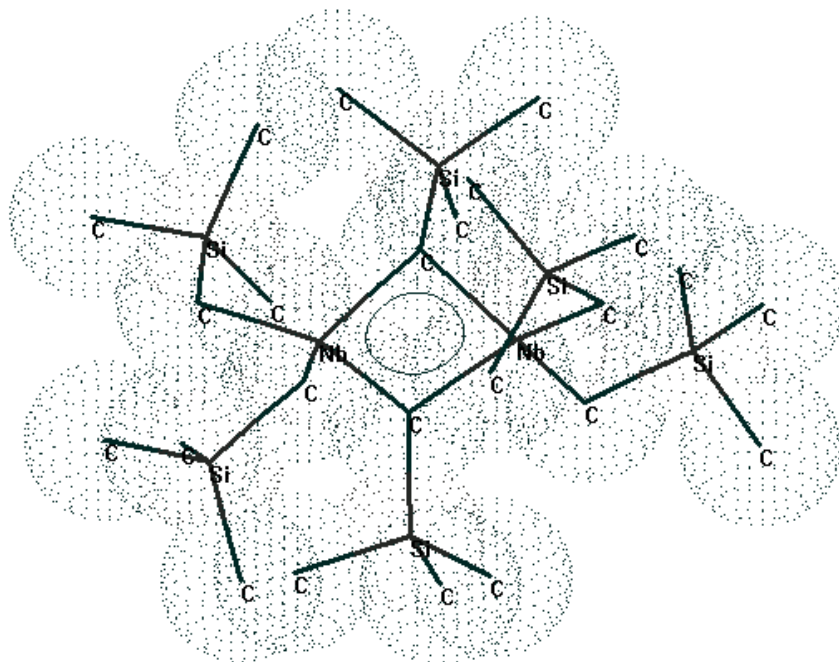


Fig. 1. Structure of $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$ - hydrogen atoms not shown

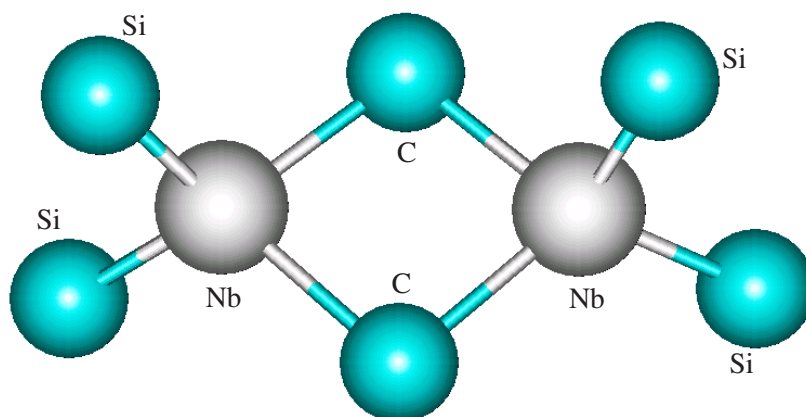


Fig. 2. A schematic view of the central portion of $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$

shows no metal-hydride band and the diamagnetic nature of the complex is consistent with its Nb(V) oxidation state. The distortions at the bridging carbon atoms and the relatively large Nb-CH₂-Nb angles, therefore, may well be the product of mutual repulsion between the bulky ligand groups.

Although the Nb..Nb distance *ca.* 2.90 Å it seems unlikely that metal-metal bonding occurs in this complex. This length is comparable to Nb-Nb distance of 2.9015(4) Å found in the structure of a 1,3-dimetallacyclobutadiene derivative of niobium supported by carbazole ligation¹¹. The NbCCNb is distorted in such a way as to minimise and Nb-Nb interaction and given the multiple-bond character of the Nb-C(bridging) bonds and the short distances involved. It is difficult to see how the niobium atoms could move further apart. The angle between the planes Nb, C, C' and Nb, CH₂, CH₂' is *ca.* 88°, very close to that expected for a tetrahedral coordination at the niobium atom.

The structure is not very tightly packed, in line with the fact that the molecules have only methyl groups pointing outwards. There are no unusually short intermolecular distances.

Semi-empirical calculations using the routine ZINDO/1 were carried out on model compound $\text{Nb}_2(\text{CH}_2)_2(\text{CH}_3)_6$ in which the methyl group replaces the trimethylsilylmethyl group of the compound in present study using the program¹² HyperChem 7.0. The 2D contour plot of the electrostatic potential in the model compound (Fig. 3) illustrates the symmetry in the electrostatic potential.

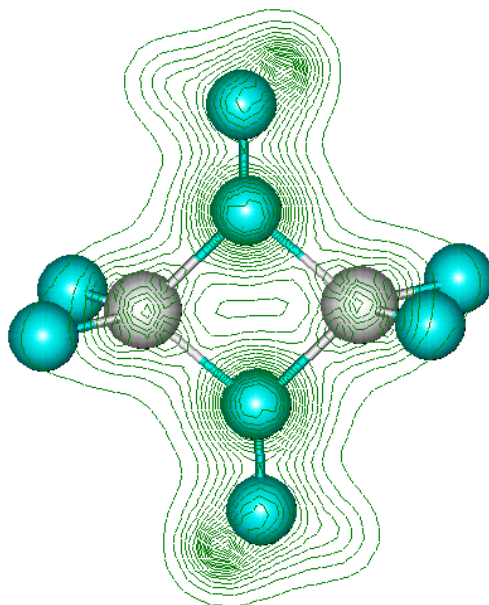


Fig. 3. 2D Contour plots of electrostatic potential around $\text{Nb}_2(\text{CH}_2)_2(\text{CH}_3)_2$ in which the methyl group replaces the trimethylsilylmethyl group of the compound

Conclusion

The crystal and molecular structure of *tetrakis*(trimethylsilylmethyl)*bis*- μ -trimethylsilylmethylidynediniobium(V), $\text{Nb}_2(\text{CH}_2\text{SiMe}_3)_4(\text{CSiMe}_3)_2$ that contains a quasi-aromatic ring, were determined from three-dimensional X-ray diffraction data over 33 years ago. The crystals are triclinic with unit-cell dimensions: triclinic, space group, P1, with unit-cell dimensions: $a = 19.540(3) \text{ \AA}$, $b = 11.014(2) \text{ \AA}$, $c = 12.155(2) \text{ \AA}$, $\alpha = 115.91(1)^\circ$, $\beta = 110.14(2)^\circ$, $\gamma = 103.76(2)^\circ$, space group is $P\bar{1}$ and $Z = 2$. The structure was refined by least-squares methods to $R = 0.052$. The compound has a quasi-aromatic ring of which the carbene bridges form a part. Although Nb...Nb distances are *ca.* 2.90 \AA , the multiple bond character of the Nb-C(bridging) bonds and the distortion of the NbCCNb ring so as to reduce and Nb-Nb interaction suggest the metal-metal bonding probably does not occur in this complex.

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