Journal of Organometallic Chemistry, 215 (1981) 41–48
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND STRUCTURE OF TETRAKIS[BIS-(TRIMETHYLSILYLMETHYL)TIN]

V.K. BELSKY *, N.N. ZEMLYANSKY, N.D. KOLOSOVA and I.V. BORISOVA
L.Ya. Karpov Physico-Chemical Institute, Moscow 107120 (U.S.S.R.)

(Received January 13th, 1981)

Summary

The synthesis of tetrakis[bis(trimethylsilylmethyl)tin] from the corresponding dihydride $[(CH_3)_3SiCH_2]_2SnH_2$ and the diethylamino derivative $[(CH_3)_3SiCH_2]_2Sn[(C_2H_5)_2]_2$ is described. The title compound has undergone full X-ray structure analysis. Crystals of $C_{32}H_{88}Si_8Sn_4$ are monoclinic, *a* 12.350, *b* 14.515, *c* 15.951 Å, γ 97.54°, $Z = 2$, space group $P2_1/n$. The molecule comprises a centrosymmetric square Sn_4 cluster, with Sn—Sn distances of 2.839 and 2.834 Å. The final *R* factor is 0.029.

Introduction

The compounds $(R_2Sn)_n$ which are usually cyclic substances with $n = 6–9$ [1] are obtained by the reactions:

$$R_2SnH_2 + R_2SnX_2 \rightarrow (R_2Sn)_n + 2\ HX \quad (1)$$

$$SnCl_2 + 2\ RM \rightarrow (R_2Sn)_n + 2\ MCl \quad (2)$$

where $X = NR_2$, OR, $N(C_6H_5)C(O)H$; M = Li, Na, MgX

It has often been mentioned in the literature that although the products of these reactions have the same elemental composition and similar molecular weights, their properties differ substantially. For instance, organotin substances synthesized by reaction 1 when halogenated give dialkyl(aryl)tin dihalides, but those synthesized by reaction 2 give a mixture of organotin halides R_nSnX_{4-n} of different composition. It has been proposed [2] that reaction 2 leads to products with branched chains of tin atoms.

The monomeric compounds R_2Sn have been generated from $(R_2Sn)_n$ by photochemical reactions [3]. Therefore, data on the synthesis and the properties of monomeric bivalent tin derivatives are of great interest, e.g. for bis[bis(trimethylsilyl)methyl]tin [4] and dicyclopentadienyltin [5]. These compounds were obtained as monomers by reaction 2. This assumption is based on the results of a

0022-328X/81/0000–0000/$02.50, © 1981, Elsevier Sequoia S.A.

gas electron diffraction study of $(C_5H_5)_2Sn$ [6], and this compound after halogenation gave $(C_5H_5)_2SnHal_2$ [7]. The properties given for the system in ref. 7 differ from those given in ref. 8.

It is known that $\{[(CH_3)_3Si]_2CH\}_2Sn$ [4] is a dimer in the solid state, according to X-ray analysis data, but a monomer in benzene and cyclohexane solutions. However, chlorination of this product leads [4] to a mixture of R_3SnCl, R_2SnCl_2 and $RSnCl_3$, which does not agree with its monomeric structure.

Experimental

Synthesis

All reactions were carried out in a dry argon atmosphere. Bis(trimethylsilylmethyl)tin dichloride was used as the starting material and was prepared as described in ref. 9. The compound is a liquid, b.p. 131—132°C/1 mmHg. Found: C, 26.53; H, 6.18; Cl, 19.74. $C_8H_{22}Cl_2Si_2Sn$ calcd.: C, 26.39; H, 6.10; Cl, 19.47%. In the air this compound turned into the crystallohydrate, m.p. 85—86°C, which had earlier been identified [9] as bis(trimethylsilylmethyl)tin dichloride.

Bis(trimethylsilylmethyl)tin dihydride

The compound was prepared according to the literature method [10] for dibutyltin dihydride. From bis(trimethylsilylmethyl)tin dichloride (18.72 g, 51.48 mmol) and $LiAlH_4$ (12.85 g, 338.2 mmol) in 250 ml of ether was obtained bis(trimethylsilylmethyl)tin dihydride (12.4 g, 83.6%), b.p. 80—81°C/5 mmHg. Found: C, 31.51; H, 8.11. $C_8H_{24}Si_2Sn$ calcd.: C, 32.58; H, 8.15%.

Bis(diethylamino)bis(trimethylsilylmethyl)tin

The compound was prepared by the method described in ref. 11 for the synthesis of dimethylaminotrimethyltin. n-Butyllithium (460 ml 0.57 *N* solution, 262.2 mmol) in hexane, 100 ml ether and bis(trimethylsilylmethyl)tin dichloride (40.0 g, 110 mmol) gave bis(diethylamino)bis(trimethylsilylmethyl)tin, 36.23 g (75.4%), b.p. 115—116°C 0.1 mmHg. Found: C, 43.80; H, 9.72; N, 6.49. $C_{16}H_{42}N_2Si_2Sn$ calcd.: C, 43.96; H, 9.62; N, 6.41%.

Tetrakis[bis(trimethylsilylmethyl)tin]

The compound was prepared using the method described in ref. 12 for the synthesis of octadecaethylcyclononatin. Bis(diethylamino)bis(trimethylsilylmethyl)tin (10.506 g, 24.06 mmol) and bis(trimethylsilylmethyl)tin dihydride (7.09 g, 24.06 mmol) gave tetrakis[bis(trimethylsilylmethyl)tin], 5.53 g (78.3%), as a white crystalline powder which dissolved in organic solvents except for alcohols and ketones. Found: C, 32.63; H, 7.61. $C_{32}H_{88}Si_8Sn_4$ calcd.: C, 32.79; H, 7.57%. Molecular weight 1170, 1183 (by the Beckman method in benzene). On heating to 80—160°C the compound changes its colour from white to dark yellow, and a signal is seen in the ESR spectra of the coloured product. After cooling the compound becomes white again and is identical to its initial state. When titrated against Cl or Br in carbon tetrachloride at —40 to —50°C, bis(trimethylsilylmethyl)tin dichloride or dibromide is obtained, the purity of which was proved by GLC.

X-ray structure analysis

The single crystal chosen for X-ray analysis was covered by epoxy resin to avoid contact with air. The experiment was done using a syntex P$\bar{1}$ automatic four-circled diffractometer, employing Mo-K_α radiation and a graphite monochromator and $\theta/2\theta$ scanning up to $s_{max} = 0.54$ Å^{-1}. The crystals of $C_{32}H_{88}Si_8Sn_4$ are monoclinic, a 12.350(2), b 14.515(3), c 15.951(3) Å, γ 97.54° (1), V 2835 Å^3, D_c 1.37 g/cm^3, M.W. 1170, $Z = 2$, space group $P2_1/n$. The final number of reflections was 3146 with $I \geqslant 1.96\ \sigma\ (I)$. During the data collection three standard reflections were measured every 100 steps; their intensity remained stable during the whole time of experiment.

All the subsequent calculations were performed on a NOVA 3 computer using the complex of crystallographic programs XTL-F included in the Nicolet R3 system. The experimental intensities were corrected for polarization and Lorentz effects but not for absorption (μ(Mo) = 19.3 cm^{-1}).

The coordinates of the Sn atoms were found by a combination of heavy atom and direct methods (Patterson synthesis and MULTAN). The R factor at this stage was 0.36. After subsequent Fourier syntheses the coordinates of all non-hydrogen atoms were found. Those of the hydrogen atoms were localized from difference syntheses. The structure was refined using full-matrix (Sn, Si) and block-diagonal (C) least squares including H atoms. The former were refined anisotropically, the latter isotropically. The final R value is 0.029. The accuracy of interatomic distances is Sn—Sn ± 0.01, Sn—C ± 0.001, Si—C ± 0.012 Å; of bond angles is Sn—Sn—Sn ± 0.02, C—Sn—Sn ± 0.02, C—Sn—C ± 0.35, Sn—C—Si ±

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THEIR e.s.d.'s (in parentheses)

Atom	x	y	z
Sn(1)	9 147.2(5)	3756.6(4)	4767.1(4)
Sn(2)	9 401.1(5)	5508.6(4)	3955.6(4)
Si(11)	6 466(2)	3891(2)	5239(2)
Si(12)	9 158(3)	1559(2)	3832(2)
Si(21)	8 332(2)	7528(2)	3435(2)
Si(22)	9 500(3)	4981(2)	1831(2)
C(11)	7 561(8)	3152(7)	5262(6)
C(12)	9 854(8)	2766(6)	3953(7)
C(21)	8 034(7)	6248(6)	3610(6)
C(22)	10 287(8)	5328(6)	2792(6)
C(111)	5 211(9)	3293(9)	5780(8)
C(112)	6 920(9)	5004(8)	5798(7)
C(113)	6 090(9)	4088(8)	4120(7)
C(121)	10 113(11)	865(8)	3254(9)
C(122)	8 806(10)	970(8)	4863(8)
C(123)	7 864(11)	1566(9)	3208(9)
C(211)	9 775(10)	7888(7)	3064(8)
C(212)	8 046(10)	8148(8)	4420(8)
C(213)	7 403(10)	7890(9)	2613(8)
C(221)	8 294(10)	4092(8)	2044(8)
C(222)	10 425(11)	4476(9)	1074(8)
C(223)	8 979(11)	5987(9)	1320(8)

0.48, C—Si—C ± 0.53°. The geometric parameters with H atoms vary in the limits 0.80—1.10 Å (for C—H) and 105—116° (for C—C—H and H—C—H). The final coordinates of non-hydrogen atoms and their e.s.d.'s are given in Table 1 *.

Discussion

The tetrameric molecules with their own C_{2h} pseudosymmetry occupy the inversion centres; the Sn_4 cluster approximately represents a square plane. The whole conformation of the molecule is shown in Fig. 1. The interatomic distances and bond angles are given in Tables 2 and 3. The mean values of Sn—C and Si—C distances (2.191 and 1.869 Å) are in a good agreement with known data. Because of the formation of the rigid Sn_4 frame the coordination polyhedron of Sn differs greatly from an ideal tetrahedron (valence angles around Sn vary in the limits 90—124°). Some important geometric features of the molecule are presented in Tables 5—7 (mean planes and atomic deviations, interplanar angles, torsion angles).

The analysis of Sn—Sn distances in the cluster is of special interest. So far only few structures with Sn—Sn bonding are known [e.g. 13]. But if we take into consideration only alkyl derivatives of Sn, we can compare our results only with the structure of bis[bis(trimethylsilyl)methyl]tin [14]. The X-ray structure analysis of this compound revealed the presence of $\{[(CH_3)_3Si]_2CH\}_4Sn_2$ dimers. The Sn—Sn distance was found to be 2.764 Å which agrees with the triaryltin derivatives [13] and is a little bit less than the sum of the covalent radii [15]. In our case this distance is significantly longer (2.832 Å, and with the effect of rigid body libration 2.836 Å). However the lack of adequate information about the X-ray experiment, the higher value of the *R* factor and some doubts about the formulae of the substance investigated in ref. 14 do not allow thorough comparison of the above-mentioned results and ours. Considering our structure, the lengthening of the Sn—Sn distance compared with the sum of covalent radii may be explained by the formation of a rigid cluster which significantly diminishes the degree of freedom of the bulky substituent arrangement, and therefore steric factors causes the lengthening of the Sn—Sn bond. Moreover, the weakening of this bond may be the reason for the polymorphic transition at higher temperatures (see above), i.e. rupture of the bond becomes possible, and on heating —Sn—Sn—Sn—Sn— chains or dimers may arise, which at lower temperature again again form the energetically preferred tetramers.

The molecular packing in the (0.01) plane is shown in Fig. 2 (the terminal methyl atoms are not given for clarity). The packing is somewhat loose (all intermolecular contacts between terminal groups are more than the sum of Van der Waals radii), and agrees with the low density of the crystals. The shortest intermolecular contact between Sn atoms is 4.002 Å, which may make interactions during the polymorphic transition easier.

Hence, $[(CH_3)_3SiCH_2]_2Sn$ obtained by reaction 1, unlike $\{[(CH_3)_3Si]_2CH\}_2Sn$

---

* List of F_O and F_C, a table of H atoms coordinates and tables of anisotropic thermal parameters may be received upon request from the authors.

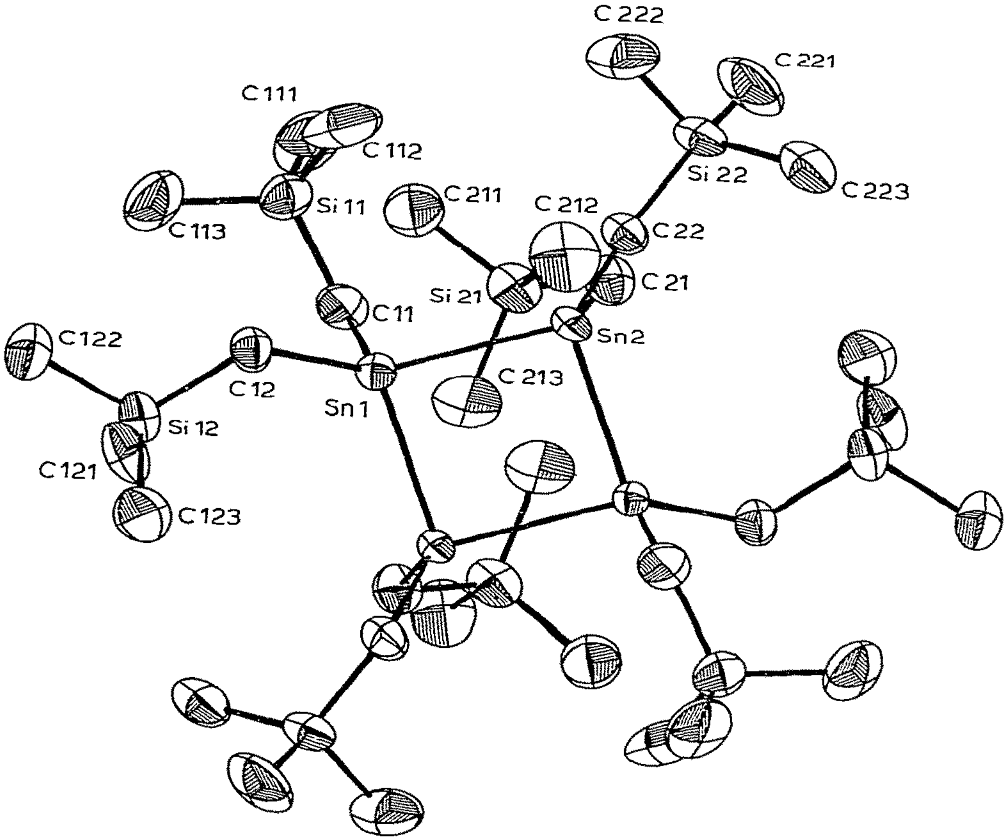

Fig. 1. The conformation of tetrakis[bis(trimethylsilylmethyl)tin] (Thermal ellipsoids are shown with 50% probability).

TABLE 2

INTERATOMIC DISTANCES (in Å) AND THEIR e.s.d.'s (in parentheses)

Bond	Distance	Distance, corrected for thermal vibration
Sn(1)—Sn(2)	2.834(1)	2.838
Sn(1)—Sn(2′)	2.829(1)	2.833
Sn(1)—C(11)	2.186(10)	2.191
Sn(1)—C(12)	2.202(10)	2.206
Sn(2)—C(21)	2.187(9)	2.191
Sn(2)—C(22)	2.189(9)	2.193
C(11)—Si(11)	1.832(9)	
C(12)—Si(12)	1.856(9)	
C(21)—Si(21)	1.866(9)	
C(22)—Si(22)	1.848(10)	
Si(12)—C(121)	1.889(14)	
Si(12)—C(122)	1.879(13)	
Si(12)—C(123)	1.883(14)	
Si(11)—C(111)	1.883(13)	
Si(11)—C(112)	1.867(12)	
Si(11)—C(113)	1.875(12)	
Si(21)—C(211)	1.885(12)	
Si(21)—C(212)	1.867(13)	
Si(21)—C(213)	1.864(12)	
Si(22)—C(221)	1.868(13)	
Si(22)—C(222)	1.877(14)	
Si(22)—C(223)	1.860(13)	

TABLE 3

VALENCE ANGLES (in deg.) AND THEIR e.s.d.'s (in parentheses)

Sn(2)—Sn(1)—Sn(2')	89.96(2)	C(11)—Si(11)—C(111)	110.3(5)
Sn(1)—Sn(2)—Sn(1')	90.04(2)	C(11)—Si(11)—C(112)	109.6(5)
		C(11)—Si(11)—C(113)	109.0(5)
C(11)—Sn(1)—Sn(2)	120.8(3)	C(111)—Si(11)—C(112)	108.4(6)
C(11)—Sn(1)—Sn(2')	112.4(2)	C(111)—Si(11)—C(113)	107.5(5)
C(12)—Sn(1)—Sn(2)	108.1(3)	C(112)—Si(11)—C(113)	112.0(5)
C(12)—Sn(1)—Sn(2')	112.7(3)	C(12)—Si(12)—C(121)	108.1(5)
		C(12)—Si(12)—C(122)	112.9(5)
C(11)—Sn(1)—C(12)	111.2(4)	C(12)—Si(12)—C(123)	109.7(5)
C(21)—Sn(2)—Sn(1)	123.6(2)	C(121)—Si(12)—C(122)	107.9(6)
C(21)—Sn(2)—Sn(1')	119.3(2)	C(121)—Si(12)—C(123)	109.6(6)
C(22)—Sn(2)—Sn(1)	106.1(2)	C(122)—Si(12)—C(123)	108.6(6)
C(22)—Sn(2)—Sn(1')	110.8(2)	C(21)—Si(21)—C(211)	112.3(5)
C(21)—Sn(2)—C(22)	106.0(3)	C(21)—Si(21)—C(212)	109.2(5)
		C(21)—Si(21)—C(213)	109.7(5)
Sn(1)—C(11)—Si(11)	116.7(5)	C(211)—Si(21)—C(212)	111.2(5)
Sn(1)—C(12)—Si(12)	120.2(5)	C(211)—Si(21)—C(213)	107.2(5)
Sn(2)—C(21)—Si(21)	117.5(5)	C(212)—Si(21)—C(213)	107.1(6)
Sn(2)—C(22)—Si(22)	118.8(5)	C(22)—Si(22)—C(221)	112.4(5)
Average	118.3	C(22)—Si(22)—C(222)	108.3(5)
		C(22)—Si(22)—C(223)	111.9(5)
		C(221)—Si(22)—C(222)	108.5(6)
		C(221)—Si(22)—C(223)	107.2(6)
		C(222)—Si(22)—C(223)	108.4(6)
		Average	109.5

TABLE 4

TENSORS OF THERMAL VIBRATIONS

L (rad^2)	0.0014	0.0001	0.0006
		0.0022	−0.0004
			0.0018
T (Å^2)	0.0324	0.0009	0.0066
		0.0265	0.0004
			0.0323

TABLE 5

SOME TORSION ANGLES (in deg.) AND THEIR e.s.d.'s (A—bond—B)

Bond	A	B	
Sn(1)—Sn(2)	C(11)	C(21)	9.5(3)
	C(11)	C(22)	48.0(5)
	C(12)	C(21)	59.3(5)
	C(12)	C(22)	2.3(2)
Sn(1)—Sn(2')	C(11)	C(21')	42.5(5)
	C(11)	C(22')	16.4(3)
	C(12)	C(21')	10.8(3)
	C(12)	C(22')	36.9(4)

TABLE 6

ATOMIC DEVIATIONS FROM THE PLANE OF THE Sn_4-SQUARE (Å)

C(11)	−1.68	C(12)	1.91	C(21)	−1.48	C(22)	1.95

TABLE 7

ANGLES BETWEEN SOME PLANES (deg.)

Plane 1	Plane 2	Angle
Sn(1)—Sn(2)—Sn(2')—Sn(1')	C(11)—Sn(1)—C(12)	94.9
Sn(1)—Sn(2)—Sn(2')—Sn(1')	C(21)—Sn(2)—C(22)	93.6
C(11)—Sn(1)—C(12)	C(21)—Sn(2)—C(22)	87.0

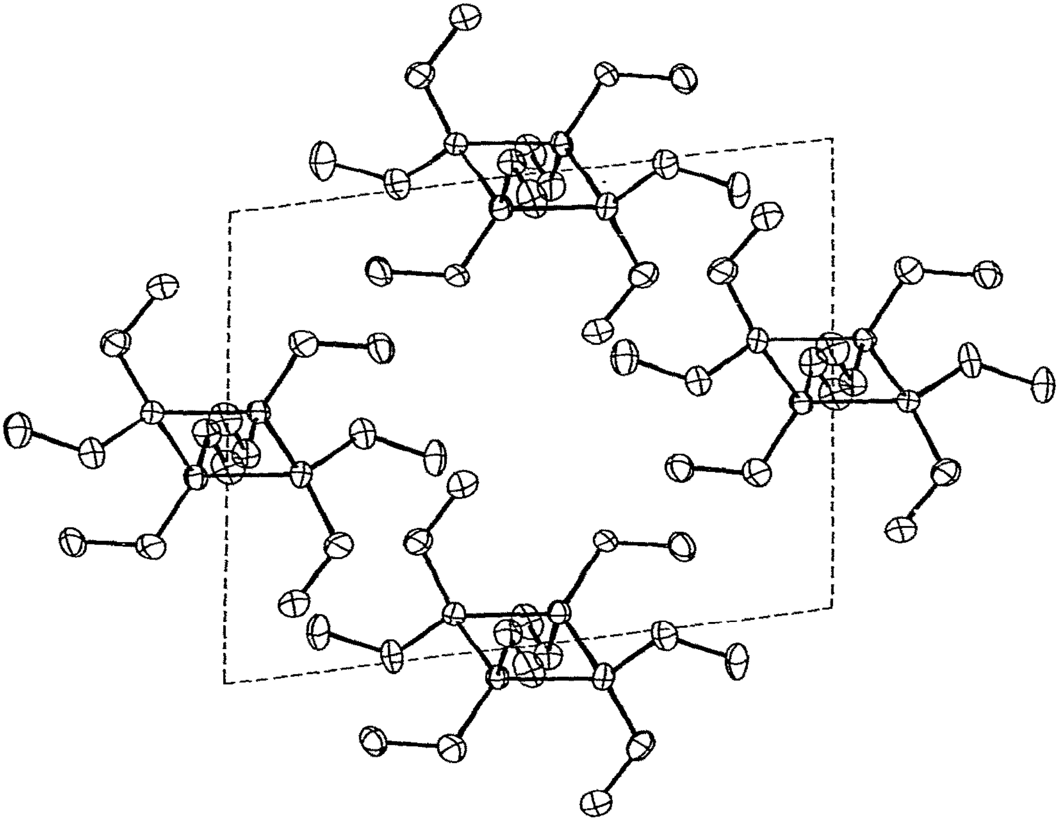

Fig. 2. Molecular packing on the (001) plane.

obtained by reaction 2, is tetrameric and under halogenation gives only one product. The structure investigated is the first example known of the formation of tetrameric organotin compounds with Sn—Sn bonds.

References

1 V.I. Shiryaev, V.F. Mironov and V.P. Kochergin. Bivalent tin compounds in the synthesis of organotin substances, Moscow, NIITEKHIM, 1977 (in Russian).

2 W.P. Neuman. The Organic chemistry of tin, J. Wiley & Sons, London, New York, Toronto, 1970.

3 W.P. Neuman and A. Schwarz. Angew. Chem., 87 (1975) 844.

4 P.J. Davidson, D.H. Harris and M.F. Lappert. J. Chem. Soc., Dalton Trans. (1976) 2268, 2275, 2286.

5 P.G. Harrison and J.J. Zuckerman. J. Amer. Chem. Soc., 91 (1969) 6885.
6 A.A. Almenningen, A. Haaland and T. Motzfeldt. J. Organometal. Chem., 7 (1967) 97.
7 U. Schröder, H.J. Albert and W.P. Neumann, J. Organometal. Chem., 102 (1975) 291.
8 N.D. Kolosova, N.N. Zemlyansky and Yu.A. Ustynyuk. Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 625.
9 V.F. Mironov, E.M. Stepina and V.I. Shiryaev. Zh. Obshch. Khim., 42 (1972) 631.
10 G.J.M. van der Kerk, J.G. Noltes and J.G.A. Luijten. J. Appl. Chem., 7 (1957) 366.
11 K. Jones and M.F. Lappert. J. Chem. Soc., (1965) 1944.
12 W.P. Neumann, B. Schneider and R. Sommer. Ann., 692 (1966) 1.
13 H. Freut, H.J. Haupt and F. Huber. Z. Anorg. Allg. Chem., 396 (1973) 81.
14 D.E. Goldberg. D.H. Harris, M.F. Lappert and K.M. Thomas. J. Chem. Soc., Chem. Commun., (1976) 261.
15 Tables of Interatomic Distances and Configuration in Molecules, L. Sutton (Eds.), The Chemical Society, London, 1965.