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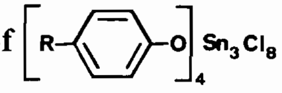
Novel Organotin Compounds from the Reactions of *p*-Alkylphenoxysilanes and Tin Tetrachloride.
Synthesis, Physical Properties and X-ray Crystal Structure of



($R = CH_3$)

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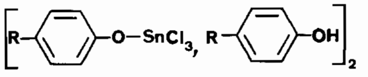
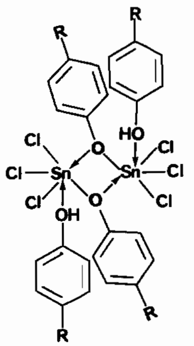
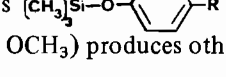
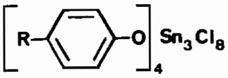
Abstract

Addition compounds of phenoxytin(IV) trichlorides with the formula



(where R = H, CH_3, $C(CH_3)_3$, OCH_3) were synthesised from $SnCl_4$ and the corresponding phenols. The tin atom is hexa-coordinated in a dimeric compound through oxygen bridging, as shown in the following structure:



The reaction of tin(IV) tetrachloride with phenoxytrimethylsilanes  (with R = H, CH_3, $C(CH_3)_3$ and OCH_3) produces other compounds with the general formula  . In the case where R = CH_3, the structure was determined by single crystal X-ray techniques. The space group is orthorhombic $P2_12_12$. The cell dimensions are a = 11.000(3), b = 21.600(8), c = 8.617(2) Å. Least-squares refinements of the structure led to a final R value of 0.0233 using 1552 observed intensities.

The molecule exhibits a two-fold axis with a tin atom lying on it. This tin atom is hexacoordinated in a distorted octahedral environment (four oxygen atoms and two chlorine atoms). The coordination polyhedra of the two other tin atoms are distorted trigonal bipyramids (with two chlorine and one oxygen atoms in the equatorial plane, and one chlorine and one oxygen atom at the apices).

Introduction

There is considerable difficulty in preparing alkoxychlorostannanes. Nevertheless, these compounds are of considerable practical interest since their structures resemble those of organotin compounds which are very effective as fungicides, bactericides, anthelmintics, stabilizers for polyvinylchloride, antioxydants for rubber, Ziegler-type catalysts and craze-prevention agents in polystyrene plastics [1, 2]. In recent years numerous studies were carried out on the reaction of methoxytrimethylsilane with tetrachlorides of silicon [3], titanium [4] and ger-

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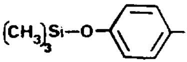
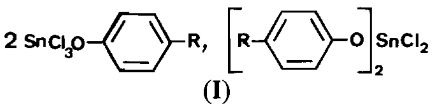
manium [5]. They have shown the exchange of a chlorine atom with the methoxy group on silicon atom.

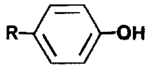
More recently it was established by NMR investigations (60 MHz) that the speed of the reactions between $SnCl_4$ and methoxytrimethylsilane [6] was dependent on the temperature. Studies of the NMR spectra of the liquid-phase reaction have shown the formation of soluble monochloromethoxystannanes and dichloromethoxystannanes, but no solid was isolated. Furthermore there appears to be little quantitative information concerning the reactions between tin tetrachloride and alkylphenols and the studies of $SnCl_4$–phenols systems in solution [7]. So the authors are inclined to think that the compound $SnCl_4,4C_6H_5OH$ was formed in the system. The formation of this compound was represented by the following equation:

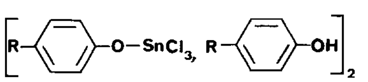
$$[SnCl_4(C_6H_5O)_2]H_2 + 2C_6H_5OH \longrightarrow [SnCl_4(C_6H_5O)_2]^{2-} + 2C_6H_5\overset{+}{O}H_2$$

In the present paper, the reaction of tin(IV) tetrachloride with phenoxytrimethylsilanes and *p*-alkylphenoxysilanes  (R = H, Me, OMe, $C(Me)_3$) is described. This synthesis is accompanied by the formation of solid phenoxychlorostannanes (I) of well-defined composition with the following stoichiometry:



(I)

The synthesis of (I), its crystal and molecular structure (R = CH_3) are reported and discussed. The vibrational and mass spectra are given and assigned in accordance with the structure. This study may be extended to include the reactions between tin(IV) tetrachloride and alkylphenols  (R = H, Me, OMe, $C(Me)_3$). This reaction yields solid compounds of dimeric structure:



(II)

The physical properties of these last compounds are also given.

Experimental

Starting Reactants

Extreme care was taken to exclude moisture from the reacting systems and products. $SnCl_4$ was distilled in an atmosphere of dried nitrogen and stored in a flask fitted with a special neck enabling quick withdrawal of known quantities. Phenols (99%, Gold Label) were used without further purification. Trimethylphenoxysilane, trimethyl *p*-tolyloxysilane, trimethyl(*p*-terbutylphenoxy)silane, trimethyl(*p*-methoxyphenoxysilane) were prepared by the method reported by Speier [8].

After distillation, purity was controlled by gas chromatography. All solvents were distilled by standard techniques and thoroughly dried before use.

Physical Measurements

Infrared spectra were recorded using a Perkin-Elmer spectrophotometer from 200 to 4000 cm^{-1} (nujol mulls between caesium iodide windows).

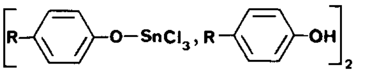
^1H NMR spectra were obtained on a Perkin-Elmer R 24 (60 MHz) using tetramethylsilane as an internal standard and d^6-acetone as the solvent.

Mass spectra were obtained on a VG 70-70 F mass spectrometer, and were measured at 70 eV.

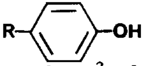
Elemental analyses were performed by the 'Service Central de Microanalyses du C.N.R.S., Echangeur de Solaize, B.P. 22, 69300 Vernaison, France.

All melting points, measured in sealed capillaries, were uncorrected.

Synthesis of the Compounds:



(R = H, Me, C(Me)₃, OMe)

The reactions were carried in an atmosphere of dried nitrogen. $SnCl_4$ (0.1 mol) was added to phenol  (0.2 mol) (R = H, Me, $C(Me)_3$, OMe) in 10 cm^3 of dry benzene. Instantly the solution turned a lemon colour (except in the case of C_6H_5OH itself).

After stirring and heating for 8 h at 333 K, a yellow powder appeared. After complete precipitation (30 h), the product was filtered in anhydrous conditions and the deposit was repeatedly washed with petroleum ether. The remaining solvent was evacuated under vacuum. The solid could be kept in sealed glass tubes.

R = Me

Mp 183–184 °C dec). *Anal.* Calcd.: C, 38.16; H, 3.40; Sn, 26.96; Cl, 24.19. Found: C, 37.72; H, 3.38; Sn, 26.38; Cl, 23.91%. *IR**: 3200br, 1890vw, 1600m, 1590m, 1500vs,br, 1450m, 1380s, 1350m,sh, 1255m, 1230vw, 1200w, 1180vs, 1170s, 1160vs,

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*IR abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder.

1120w, 1020m,sh, 940w, 840s, 820vs,sh, 750s, 740m,sh, 640w, 580s, 510s, 490m, 475s, 430m, 360s, 325s, 300vw. ^1H NMR*: 2.13, s, (CH_3); 6.70, m, p(-C_6H_4-), J = 9 H_z, A_2X_2: 7.80 bs (OH).

R = H

Mp 180–181 ℃ dec. *Anal.* Calcd.: C, 34.93; H, 2.67; Sn, 28.79; Cl, 25.83. Found: C, 34.68; H, 2.65; Sn, 28.34; Cl, 25.58%. *IR**: 3200br, 1610w, 1595m,sh, 1495m, 1480s, 1380s, 1340w, 1260m, 1190s,sh, 1165vs, 1080m, 1030m, 900w,sh, 835m, 815s,sh, 805s, 780s, 760vs,sh, 690vs, 585s,sh, 545w, 450s, 430m, 360s,sh, 325s,sh. ^1H NMR: 6.50–7.30, m (-C_6H_5); 8.20, bs (OH).

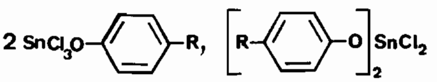
R = CH₃O

Mp 138–140 ℃ dec. *Anal.* Calcd.: C, 35.58; H, 3.17; Sn, 25.13; Cl, 22.55. Found: C, 34.59; H, 3.15; Sn, 25.05; Cl, 21.96%. *IR*: 3210br, 1610m, 1590m, 1500vs,sh, 1480m, 1440m, 1380s, 1350br, 1300 w, sh, 1255s, 1245s, 1175vs,sh, 1110m, 1030s, 1010w, 850w, 830vs,sh, 800vw, 755s, 730s,sh, 640vw, 585m, 500s, 460m, 410w, 360s,sh, 320s. ^1H NMR: 3.63, s (CH_3); 6.67, s (p-C_6H_4); 7.90, bs (OH).

R = C(CH₃)₃

Mp (195–197 ℃ dec. *Anal.* Calcd.: C, 45.78; H, 5.15; Sn, 22.64; Cl, 20.31. Found: C, 44.79; H, 5.00; Sn, 22.69; Cl, 20.21%. *IR*: 3180br, 1880vw, 1595m,sh, 1500vs,sh, 1480s, 1410w, 1395w, 1380s, 1340m, 1300w, 1270m,sh, 1200vs, 1165vs, 1115m, 1015s, 920w, 850s, 830vs,sh, 815vs,sh, 735m, 725m, 680s, 670w, 640vw, 590w, 560m, 530vs,sh, 480w, 430m, 410m, 370s, 360s, 320m,sh. ^1H NMR: 1.26, s, (($CH_3)_3C$); 1.30, s, (($CH_3)_3C$); 7.46–6.56, m, (p-C_6H_4-); 7.86, bs, (OH).

Preparation and Study of the Compounds:



(I)

The reactions were performed under an atmosphere of dry nitrogen.

$SnCl_4$ (0.1 mol) in 10 cm^3 of dry benzene was added to 0.2 mol of the p-alkylphenoxysilane in the same solvent.

Again the solution turned instantly a lemon colour (except in the case of the trimethylsilylphenoxysilane) but no important exothermic effect was noticed. The mixture was stirred and progressively warmed to 373 K. A yellow crystalline precipitate appeared after two days. The supernatant liquid mixture was evaporated under vacuum. After complete precipitation, the product was filtered under dry nitrogen and the deposit repeatedly washed with C_6H_6.

The remaining solvent was evacuated under vacuum.

The compounds were stable in sealed tubes; they were further purified by recrystallization from $CHCl_3$ or CH_2Cl_2 and crystals of **I** (R = CH_3) suitable for X-ray diffraction were obtained.

R = H

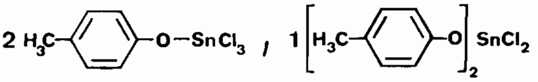
Mp 219 ℃ dec. *Anal.* Calcd.: C, 28.46; H, 1.97; Sn, 35.18; Cl, 28.06. Found: C, 28.35; H, 1.99; Sn, 35.01; Cl, 27.89%. *IR*: 1595m, 1590vs,sh, 1490vs, 1380s, 1250w, 1190s, 1180vs, 1160vs,sh, 1070s, 1030s, 1020m, 990w, 980w, 965w, 910vs, 890vw, 855w, 840m,sh, 810vs,sh, 770 vs,sh, 690vs, 620w, 610m, 600s, 580vs,sh, 470s, 450vs, 430vs, 420m, 395vs, 362vs, 350m. ^1H NMR: 6.67–7.60, m, (C_6H_5).

R = CH₃

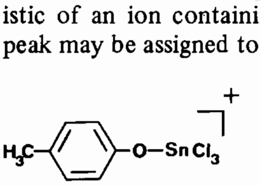
Mp 212–213 ℃ dec. *Anal.* Calcd.: C, 31.45; H, 2.62; Sn, 33.34; Cl, 26.59. Found: C, 31.31; H, 2.60; Sn, 33.04; Cl, 26.29%. *IR*: 1900w,sh, 1595w, 1590m, 1500vs, 1470s, 1380s, 1250vw, 1215vw, 1200s, 1180vs, 1160vs,sh, 1110m, 1020s, 945m, 840s, 830vs,sh, 755vs, 710vw, 640w, 600m, 590m, 580w, 510s, 480vs,sh, 440s, 430w, 390s,sh, 370s, 360s, 320m. ^1H NMR: 2.25, s, (CH_3); 2.16, s, (CH_3); 6.58–7.30, m, (p-C_6H_4).

R = CH₃

Crystallized with one CH_2Cl_2 molecule: mp 212–213 ℃ dec. *Anal.* Calcd.: C, 30.18; H, 2.60; Sn, 30.88; Cl, 30.78. Found: C, 30.08; H, 2.57; Sn, 30.39; Cl, 30.19%. *IR*: the infrared spectrum is the same as the previous one, with two additional bands due to CH_2Cl_2 molecule; 1265m,sh (CH_2 deformation) and 740s (C–Cl stretching). ^1H NMR: 2.25 s, (CH_3); 2.16, s, (CH_3); 5.46, s, (CH_2); 6.67–7.33, m, (p-C_6H_4). *MS*: The mass spectrum was recorded only for the compound:



The mass spectrum has a strong peak at m/e = 332 which exhibits the polyisotopic cluster characteristic of an ion containing a tin atom; this molecular peak may be assigned to the species



The molecular ions (m/e = 332) undergo mainly two schemes of fragmentation. The first scheme

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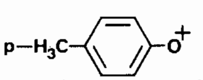
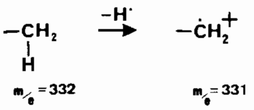
*^{1}H NMR data given as: δ (p.p.m/TMS), nature of the signal (assignment), coupling constant (Hz): s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet.

can be accounted for by the loss of  at m/e = 107. The second scheme can be accounted for by the loss of $SnCl_3^+$ (isotopic cluster centered at 225).

The ion m/e 107 is the peak of the basis of the spectrum (100%). The ion $SnCl_3^+$ is also very important (93%) m/e = 225. Otherwise, the molecular ion with its *p*-tolyl substituent has a tendency to undergo the homolytic scission, specific of methyl groups linked to aromatic rings.

The following scheme summarizes the scission in the present case:



Scheme 1

Afterwards the tropylium ion is separated from the $|M-H|^+$. A relatively important peak at m/e = 90 (14.1%) is observed but not interpreted unambiguously.

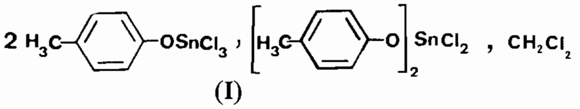
R = OCH₃

Mp 210–212 °C dec. *Anal.* Calcd: C, 29.67; H, 2.47; Sn, 31.45; Cl, 25.08. Found:C, 29.15; H, 2.28; Sn, 30.78; Cl, 24.91%. *IR*: 1600m,sh, 1590m, 1500vs,sh, 1470s, 1380s, 1300m, 1250s, 1180vs, 1160s,sh, 1110m, 1030s, 1010m, 940w, 840vs, 830vs, 750vs,sh, 640w, 600w, 590m, 550vw, 505s, 460m,sh, 420w, 395s, 362s, 340s. *^1H NMR*: 3.73, s, (CH_3); 3.63, s, (CH_3); 6.70, s, (p-C_6H_4).

R = C(Me)₃

Mp 225 °C dec. *Anal.* Calcd: C, 38.83; H, 4.21; Sn, 28.80; Cl, 22.97. Found: C, 38.51; H, 4.07; Sn, 28.83; Cl, 22.50%. *IR*: 1905vw, 1890w, 1595m,sh, 1500vs,sh, 1470s. 1400m,sh, 1395m, 1380m, 1365s, 1270s, 1240w, 1200s,sh, 1160vs,sh, 1110 m,sh, 1015vs,sh, 965w, 955w, 945w, 850vs,sh, 840vs, 810vs, 740m,sh, 680vs, 600m, 590m, 530 vs,br, 475m, 410s,sh, 385vs, 370vs, 355vs, 320m. ^1H NMR: 1.30, s, $(C(Me)_3)$; 1.26, s, $(C(Me)_3)$; 6.53–7.50, m (p-C_6H_4).

Structure of:



(I)

Crystal Data

$C_{28}H_{28}O_4Sn_3Cl_8 \cdot CH_2Cl_2$. The compound is orthorhombic, space group $P2_12_12$ a = 11.000(3), b = 21.600(8), c = 8.617(2) Å, V = 2047.0 (Å)^3, Z = 2, M = 1153.1, D_{calc} = 1.93 g/cm^3, D_{obs} = 2 g/cm^3.

X-ray Structure Determination

A yellow crystal of approximate dimensions 0.25 × 0.25 × 0.25 mm was sealed in a Lindemann tube, and used for inspection by the Weissenberg and Buerger methods.

The lattice parameters and intensities of reflections were recorded at 290 K on a CAD-4 diffractometer using the MoK_α radiation (λ = 0.7107 Å) monochromated with a flat graphite crystal. 4407 independent reflections were collected for the following values of θ and h, k, l:

$$1^\circ \leqslant \theta \leqslant 34^\circ \quad 0 \leqslant h \leqslant 14 \quad 0 \leqslant k \leqslant 33 \quad 0 \leqslant l \leqslant 13$$

A total of 1552 reflections with $F/\sigma(F) > 5$ were used in the F-refinements.

Determination of the Structure

After the specific gravity measurement had shown that the unit cell contained six tin atoms, it appeared that the more likely combination of Wyckoff positions for the tin atoms was one four-fold Sn(1) general position and one two-fold special Sn(2) position. So two tin atoms should be located in the asymmetric unit.

These positions were determined by the heavy atoms method and also by the Multan method [9] with the Sn(2) atom on a two-fold axis. Successive Fourier-difference syntheses enabled us to locate the atoms surrounding the Sn(2) atom two times O(1), O(2) and Cl(1), and three atoms surrounding the Sn(1) atom O(1), O(2), Cl(4). O(1) and O(2) appeared as bridges between the Sn(1) and Sn(2) atoms. The aromatic substituted cycle C(11) to C(17) was difficult to locate due to its rather weak influence on Fourier maps. It appeared that the solvent molecule CH_2Cl_2 was located on another two-fold axis parallel to Oz. Refinements were made with the SHELX program [10] considering anisotropic temperature factors for the tin, oxygen and chlorine atoms (except those of the CH_2Cl_2 molecule).

The hydrogen atoms of the four aromatic rings were fixed by the program at a distance C–H = 1 Å and the same isotropic thermal factor was attributed to them.

Similarly, two methyl groups C(17) and C(27) were considered as rigid with C–H distances = 1 Å and H–C–H angles equal to the perfect tetrahedral value.

Setting-up a constraint tetrahedral environment of Cl and H atoms in the CH_2Cl_2 molecule was slightly more complicated since that molecule is in a special position. The difficulty was solved by introducing two symmetrical chlorine atoms with an occupancy factor of 1/2.

Due to the lack of improper elements of symmetry in the $P2_12_12$ space group, it was advisable to inves-

TABLE I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (A^2 $\times$ 10^4).[a]

	x	y	z	U_{eq} (A^2 $\times$ 10^4)
Sn(1)	−1273(1)	−1159(1)	−455(1)	363(3)
Sn(2)	0	0	1733(1)	286(4)
Cl(1)	−1586(2)	31(1)	3497(2)	510(12)
Cl(2)	−1902(3)	−992(1)	−2970(3)	699(17)
Cl(3)	−271(3)	−2078(1)	−946(3)	751(17)
Cl(4)	−2936(3)	−1410(1)	979(4)	704(17)
O(1)	38(6)	−946(2)	1252(6)	321(27)
O(2)	−1206(6)	−204(2)	−129(6)	349(28)
C(11)	479(7)	−1391(3)	2300(9)	295(17)
C(12)	1598(8)	−1659(4)	2048(11)	467(23)
C(13)	2016(9)	−2092(4)	3118(11)	495(24)
C(14)	1341(8)	−2241(3)	4406(10)	419(18)
C(15)	236(7)	−1957(3)	4625(10)	390(18)
C(16)	−205(7)	−1534(3)	3580(8)	346(18)
C(17)	1796(9)	−2720(4)	5534(12)	570(25)
C(21)	−2017(7)	230(3)	−765(9)	349(18)
C(22)	−3122(8)	320(4)	−73(10)	461(23)
C(23)	−3892(10)	781(4)	−672(12)	600(26)
C(24)	−3557(9)	1121(4)	−1945(11)	550(23)
C(25)	−2460(8)	1003(4)	−2638(11)	507(23)
C(26)	−1670(8)	558(4)	−2056(10)	411(21)
C(27)	−4401(11)	1619(5)	−2573(14)	872(39)
Cl(51)	5(6)	−4359(2)	−3891(6)	1724(20)
C(5)	0	−1/2	−5068(29)	1572(91)

Equations of the mean planes through groups of atoms and deviations of atoms from the planes (A)

Plane 1
O(1), O(1P), O(2), O(2P)
equation of the plane:
0.00000x + 0.00000y − 1.00000z − 0.4839 = 0
O(1), 0.595; O(1P), 0.595; O(2), −0.595; O(2P), −0.595

Plane 2
Sn(1), Sn(2), O(1), O(2)
equation of the plane:
0.7220x + 0.1086y − 0.6833z − 0.9722 = 0
Sn(1), 0.043; Sn(2), 0.043; O(1), −0.043; O(2), −0.043

Plane 3
C(11), C(12), C(13), C(14), C(15), C(16)
equation of the plane:
−0.4451x − 0.7334y − 0.5138z + 0.9439 = 0
C(11), −0.006; C(12), 0.0079; C(13), −0.0033; C(14), −0.0034, C(15), 0.0055; C(16), −0.0008

Plane 4
C(21), C(22), C(23), C(24), C(25), C(26)
equation of the plane:
−0.4242x − 0.6856y − 0.5916z + 1.0022 = 0
C(21), 0.0130; C(22), −0.0174; C(23), 0.0085; C(24), 0.0048; C(25), −0.0096; C(26), 0.0007

Plane 5
Sn(1), Sn(2), Cl(4), Cl(1)
equation of the plane
−0.5130x + 0.6580y − 0.5513z − 0.7664 = 0
Sn(1), −0.0537; Cl(4), 0.0455; Cl(1), −0.0437; Sn(2), 0.0520

Plane 6
C(11), C(12), C(13), C(14), C(15), C(16), C(21), C(22), C(23), C(24), C(25), C(26)
equation of the plane:
−0.4226x − 0.7274y − 0.5406z + 0.8716 = 0
C(11), −0.019; C(12), −0.035; C(13), −0.026; C(14), 0.0218; C(15), 0.0596; C(16) 0.0346; C(21), −0.0602; C(22), −0.1105; C(23), −0.0156 C(24), 0.0663; C(25), 0.0702; C(26), 0.0137

(continued overleaf)

TABLE I. *(continued)*

Angle between Plane 1 and Plane 2 = 46.89°
Angle between Plane 2 and Plane 3 = 92.86°
Angle between Plane 2 and Plane 4 = 88.65°
Angle between Plane 3 and Plane 4 = 5.36°
Angle between Plane 6 and Plane 2 = 90.84°
Angle between Plane 2 and Plane 5 = 85.54°

[a] For Sn, Cl and O atoms, $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. For the other atoms, $U_{eq} = U_{isotropic}$.

TABLE II. Observed Bond Distances (Å) with Estimated Standard Deviations.

Sn(1)–Sn(2)	3.432(1)
Sn(1)–Cl(2)	2.304(3)
Sn(1)–Cl(3)	2.309(3)
Sn(1)–Cl(4)	2.273(3)
Sn(1)–O(1)	2.110(6)
Sn(1)–O(2)	2.083(5)
Sn(2)–Cl(1)	2.314(2)
Sn(2)–O(1)	2.086(5)
Sn(2)–O(2)	2.128(6)
C(21)–O(2)	1.405(7)
C(11)–O(1)	1.405(7)
C(12)–C(11)	1.377(11)
C(16)–C(11)	1.371(10)
C(13)–C(12)	1.392(13)
C(14)–C(13)	1.373(13)
C(15)–C(14)	1.374(11)
C(17)–C(14)	1.505(13)
C(16)–C(15)	1.371(10)
C(21)–O(2)	1.405(7)
C(26)–C(21)	1.372(11)
C(21)–C(22)	1.368(12)
C(23)–C(22)	1.406(13)
C(24)–C(23)	1.370(14)
C(25)–C(24)	1.370(13)
C(27)–C(24)	1.521(15)
C(26)–C(25)	1.389(12)
C(5)–Cl(51)	1.716(16)

tigate the absolute configuration of that structure. Therefore all coordinates were changed into their inverse values, and the reliability factor dropped from 0.025 to 0.023.

The difference may be significant and the coordinates appearing in Table I correspond to the last configuration.

Description of the Structure

Distances and angles are given in Tables II and III.

The crystal contains two types of molecules: the $C_{28}H_{28}O_4Sn_3Cl_8$ molecule (**A**) and the CH_2Cl_2 molecule (**B**). Both lie on C_2 axes.

(**A**) contains three tin atoms: one Sn(2) atom which is on a symmetry axis and two Sn(1) atoms.

TABLE III. Observed Bond Angles (°), with Estimated Standard Deviations.

Cl(2)–Sn(1)–Sn(2)	121.7(1)
Cl(3)–Sn(1)–Sn(2)	122.2(1)
Cl(3)–Sn(1)–Cl(2)	96.1(1)
Cl(4)–Sn(1)–Cl(2)	107.9(1)
Cl(4)–Sn(1)–Sn(2)	101.8(1)
Cl(4)–Sn(1)–Cl(3)	106.2(1)
O(1)–Sn(1)–Sn(2)	34.9(1)
O(1)–Sn(1)–Cl(2)	145.8(2)
O(1)–Sn(1)–Cl(3)	89.3(2)
O(1)–Sn(1)–Cl(4)	102.9(2)
O(2)–Sn(1)–Sn(2)	35.9(2)
O(2)–Sn(1)–Cl(2)	89.0(2)
O(2)–Sn(1)–Cl(3)	149.2(2)
O(2)–Sn(1)–Cl(4)	101.0(2)
O(2)–Sn(1)–O(1)	70.5(2)
Cl(1)–Sn(2)–Sn(1)	94.3(1)
O(1)–Sn(2)–Sn(1)	35.3(2)
O(1)–Sn(2)–Cl(1)	100.0(2)
O(2)–Sn(2)–Sn(1)	35.0(1)
O(2)–Sn(2)–Cl(1)	91.8(2)
O(2)–Sn(2)–O(1)	70.1(2)
Sn(2)–O(1)–Sn(1)	109.8(2)
C(11)–O(1)–Sn(1)	122.4(3)
C(11)–O(1)–Sn(2)	123.3(3)
Sn(2)–O(2)–Sn(1)	109.2(2)
C(21)–O(2)–Sn(1)	125.9(3)
C(21)–O(2)–Sn(2)	123.5(3)
C(12)–C(11)–O(1)	119.7(6)
C(16)–C(11)–O(1)	118.8(6)
C(16)–C(11)–C(12)	121.5(7)
C(13)–C(12)–C(11)	118.3(8)
C(14)–C(13)–C(12)	120.9(9)
C(17)–C(14)–C(13)	120.1(8)
C(17)–C(14)–C(15)	120.8(8)
C(16)–C(15)–C(14)	121.3(8)
C(15)–C(16)–C(11)	119.0(7)
C(22)–C(21)–O(2)	119.2(6)
C(26)–C(21)–O(2)	118.9(7)
C(26)–C(21)–C(22)	121.9(7)
C(23)–C(22)–C(21)	118.4(8)
C(24)–C(23)–C(22)	120.7(9)
C(25)–C(24)–C(23)	119.1(9)
C(26)–C(25)–C(24)	121.4(8)
C(25)–C(26)–C(21)	118.4(8)
C(15)–C(14)–C(13)	119.1(8)
C(27)–C(24)–C(23)	119.9(9)
C(27)–C(24)–C(25)	120.9(9)
Cl(52)–C(5)–Cl(51)	107.6(1.4)

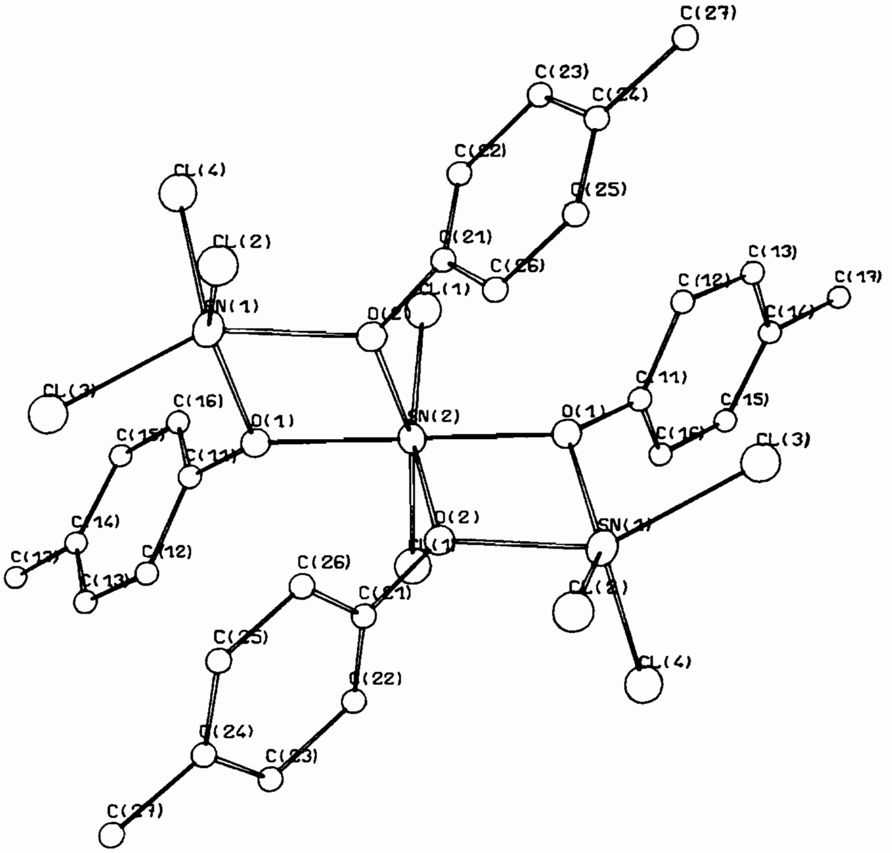


Fig. 1. ORTEP projection of an isolated molecule along the z axis (two fold axis passing through Sn(2).

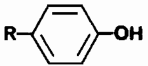
The two Sn(1) atoms are five-coordinated in a rather distorted trigonal-bipyramidal coordination geometry, with O(2) and Cl(3) as apices and Cl(2), Cl(4) and O(1) as equatorial atoms.

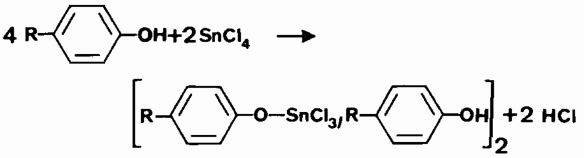
Two Sn(1)–O(2)–Sn(2)–O(1) rings are present in **A**; they are both planar and are linked to the central Sn(2) atom.

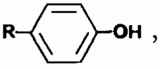
Sn–O distances between 2.08 and 2.11 Å compare well with those found by Graziani and coworkers [11] in $\{[(n\text{-}C_4H_9)_2SnO_2C_2Cl_3]_2O\}_2$, which range from 2.03 to 2.12 Å, and those found by Chow [12] in $\{[(CH_3)_2SnNCS]_2O\}_2$, which range from 2.04 to 2.10 Å.

A good agreement was also observed for the internal angles of the Sn_2O_2 ring: 70.5(2) and 109.8(2)° in this work; 75.0(1) and 105.0(1) in the above-mentioned compound, and 69.2 and 110.8° in the dimeric, centrosymmetric structure of $[Cl_3SnOH{\cdot}H_2O]_2{\cdot}3C_4H_8O_2$ [13]. The two bridging phenoxy groups are linked to the Sn(2) atom. This is six-coordinated in an approximatively octahedral arrangement. The Sn(2)–Sn(1) distance of 3.432 Å in the present compound may be compared with the Ti–Ti distance (3.30 Å) in $TiCl_2(OEt)_2$ and the obtuse angle Sn(2)–O(2)–Sn(1) of 109.2° confirms the view that metal–metal bonding is negligible in these structures.

Discussion

In the present work the reaction of tin tetrachloride with phenols  has been investigated. $SnCl_4$ reacts with phenols (R = H, Me, OMe, $C(Me)_3$) in C_6H_6 to yield solid compounds of dimeric structure according to the following reaction:



This reaction, easy in the case of alcohols [20, 21] and leading to the corresponding trichloroalcoxytin(IV) alcoholates dimers, is more difficult with phenols. The common feature of those compounds with monodentate bridging ligands , is

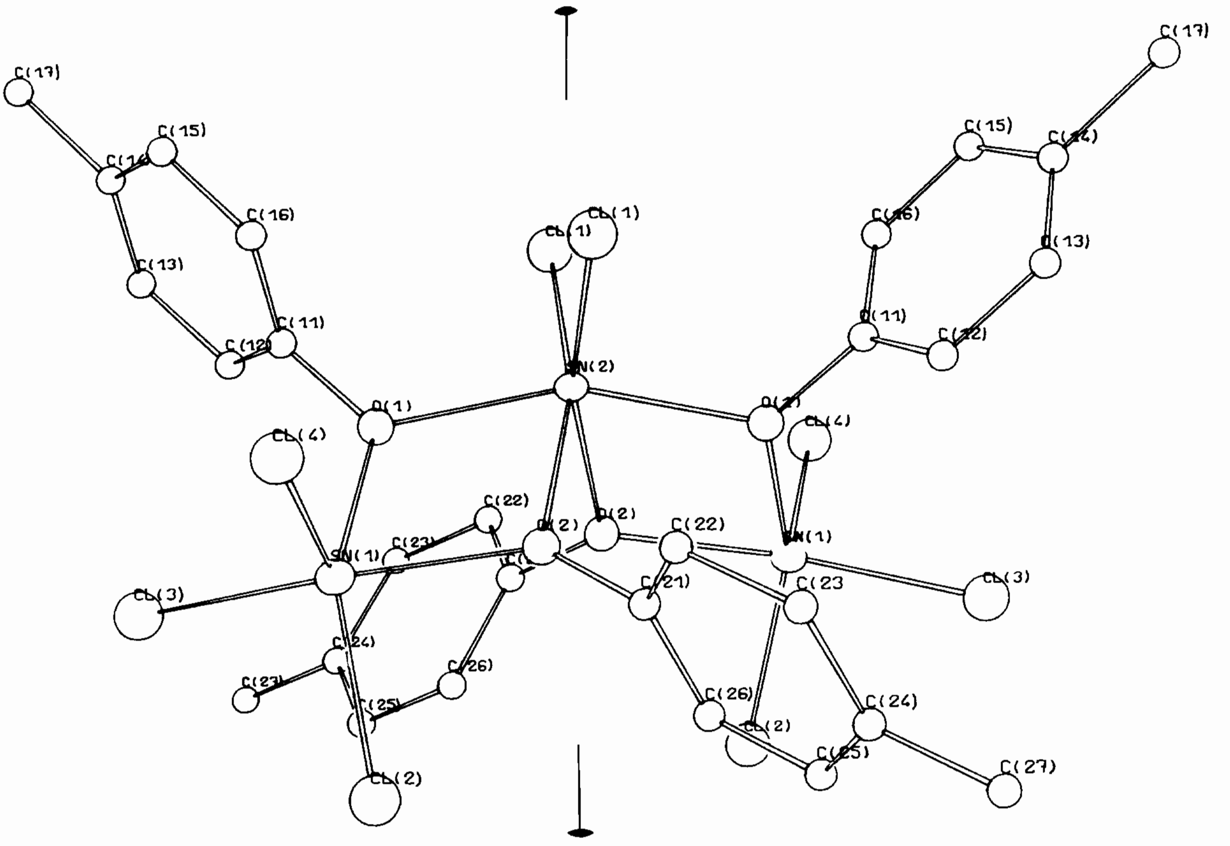
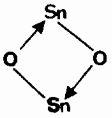
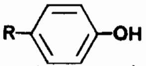
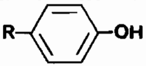
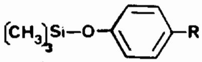
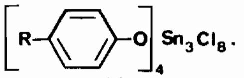
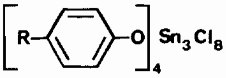


Fig. 2. Drawing of an isolated molecule with its two fold axis lying in the plane of projection.

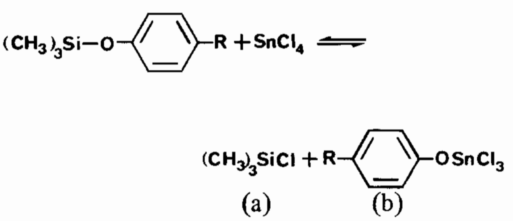
a dimeric structure through tin–oxygen bridges in the solid state:



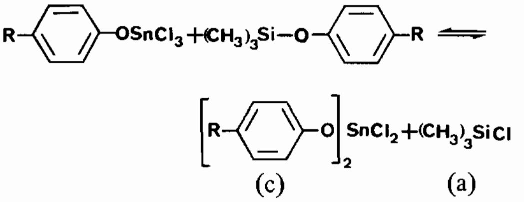
This Sn_2O_2 ring is present in the adduct obtained after the exchange of the ligand  by CH_3CN (adduct which has 1:1 stoichiometry), but this Sn_2O_2 ring is absent in the adduct after the exchange of the ligand  by pyridine, since this last compound has 1:2 stoichiometry (see note about IR spectra).

The reaction of $SnCl_4$ with phenoxytrimethylsilanes  (R = H, Me, $C(Me)_3$, OMe) has also been studied. It leads to the formation of solid compounds of well-defined composition  (I). The compound  $\cdot CH_2Cl_2$ has been structurally characterized in the present work.

The synthesis of **(I)** can be easily explained by the following reactions:



(1)



(2)

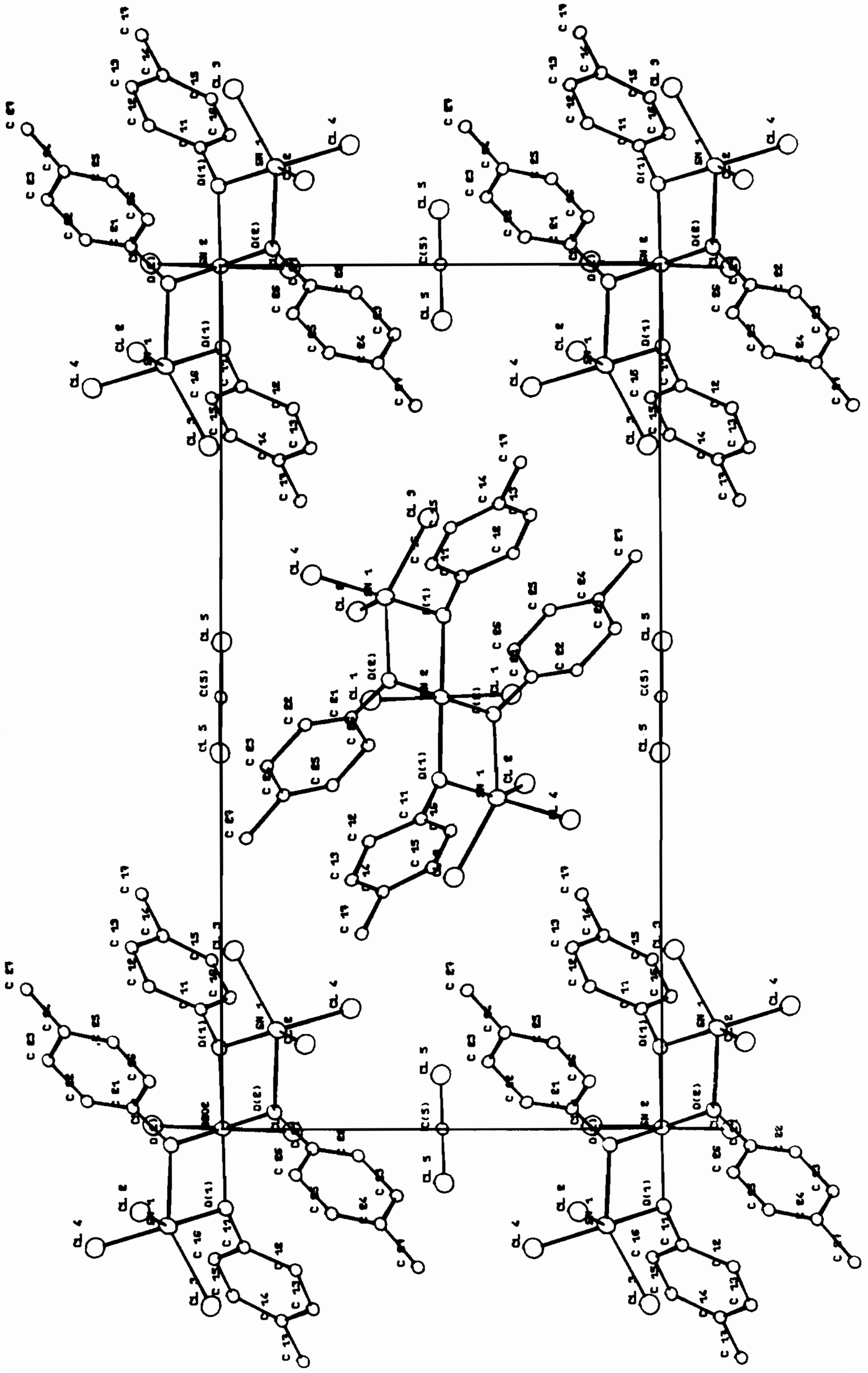
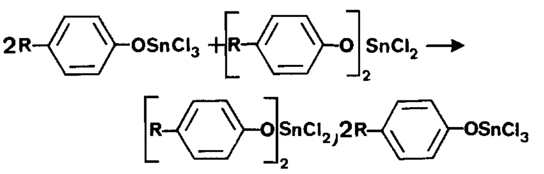


Fig. 3. Projection of the structure packing on the *xy* plane (origin: upper left corner; the dichloromethane molecules lie on two-fold axes too).

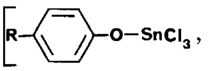
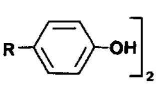
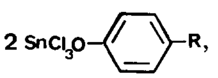
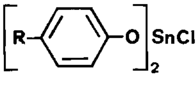
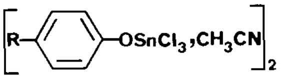
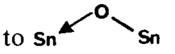
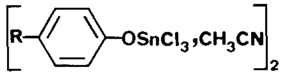


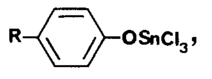
(I) (3)

p-Alkylphenoxytrimethylsilanes are split by tin tetrachloride at the Si–O bond with formation of trimethylchlorosilane (a) and soluble chlorophenoxystannanes (b) and (c).

Chlorotrimethylsilane was isolated by distilling the supernatant liquid of the reaction and identified on the basis of its IR and NMR spectra. Since the reaction is carried out at high temperatures (*ca.* 100 ℃), the highly volatile trimethylchlorosilane is eliminated and the two equilibria (1) and (2) are displaced towards the formation of (I) which precipitates slowly, arising by complexation from (a) and (b).

Note about Infrared Spectra

When we compare the compounds ,  (noted a) with   (noted b) and  noted (c), the evidence for the dimeric framework is provided by the presence of strong intensity bands in the 560–580 and 450–490 cm^{-1} regions, which might be assigned to  vibrations in the Sn_2O_2 ring. Similar bands present in the dimeric adduct  favour the above assignment.

A further support is provided by the fact that these bands are quite absent from the 1:2 complex with pyridine  2 pyridine where the Sn_2O_2 ring is missing. These assignments are in fair agreement with earlier results reported in the literature [14–17].

The three mentioned adducts (a), (b) and (c) show strong vibrations in 320–370 cm^{-1} spectral region which arise from tin-chlorine vibrations [15–19].

The IR spectra of the compounds (a) and (b) have most bands in common. However, two striking differences can be noted. The presence of a broad and strong band in the 3200 cm^{-1} region in the compound (a) due to the hydrogen bonded νOH (3500 cm^{-1} in the free phenol); the shift to this lower spectral regions demonstrates the coordination to tin atom through the oxygen atom of the phenol. The OH stretching frequency is obviously not present in compounds (b) or (c).

The other important difference is the presence of a strong and sharp band in the region 385–395 cm^{-1} only for the compound (b). This band may be associated either with new O → Sn vibrations, (involvin two adjacent Sn_2O_2 rings), or to a Sn–Cl stretching. It is difficult however to assign this band unambiguously.

References

1 W. Jasiobedzki, *Roczniki Chem.*, *36*, 455 (1962).
2 Wilhelm, P. Neumann, 'The Organic Chemistry of Tin', Interscience Publishers, 238–246 (1967).
3 V. V. Yastrebov and A. I. Chernyshev, *Kinetika I. Kataliz*, *14*, 933 (1973).
4 V. V. Yastrebov and A. I. Chernyshev, *Journal of General Chemistry of the USSR*, *40*, 604 (1970).
5 V. V. Yastrebov, A. V. Krylov and A. I. Chernyshev, *Journal of General Chemistry of the USSR*, *46*, 148 (1976).
6 V. V. Yastrebov and A. V. Krylov, *Journal of General Chemistry of the USSR*, *46*, 2298 (1976).
7 M. Usanovich and E. Pichugina, *Journal of General Chemistry of the USSR*, *26*, 2371 (1956).
8 J. L. Speier, *J. Am. Chem. Soc.*, *74*, 1003 (1952).
9 P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J. P. Declercq, Multan 77 (1977). A system of Computers Programs for the Automatic Solution of Crystal Structures from X-ray diffraction data. University of York, England and Louvain, Belgium.
10 G. M. Sheldrick (1976). SHELX. A program for the Resolution of Crystal Structures, Cambridge University, England.
11 R. Graziani, G. Bombieri, E. Forsellini, P. Furlan, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.*, *125*, 45 (1977).
12 Y. M. Chow, *Inorg. Chem.*, *10*, 673 (1971).
13 N. G. Bokii and Yu. T. Struchkov, *J. Struct. Chem. (USSR)*, *12*, 253 (1971).
14 Y. Kawasaki, T. Tanaka and R. Okawara, *J. Org. Chem.*, *6*, 95 (1966).
15 R. C. Paul, H. S. Makhni, P. Singh, S. L. Shadha, *Zeit. Anorg. Allg. Chem.*, *377*, 108 (1970).
16 R. C. Paul and S. L. Shadha, *J. Inorg. Nucl. Chem.*, *31*, 2753 (1969).
17 R. C. Paul, H. Singh and S. L. Shadha, *Indian Journal of Chemistry*, 121 (1977).
18 R. C. Paul and P. Scharma, *J. Inorg. Nucl. Chem.*, *38*, 169 (1976).
19 I. R. Beattie, G. P. McQuillan, L. Rule and M. Webster, *J. Chem. Soc.*, 1514 (1963).
20 A. W. Laubengayer and W. C. Smith, *J. Am. Chem. Soc.*, *76*, 5985 (1954).
21 D. C. Bradley, E. V. Caldwell and W. Wardlaw, *J. Chem. Soc.*, 3039 (1957).