and iodine suggested the preparation of the analogous rhodium compound $C_5H_5RhCOI_2$. The reaction between $C_5H_5Rh(CO)_2$ and iodine in diethyl ether solution at room temperature proceeded rapidly with gas evolution to give a nearly quantitative yield of purple-brown crystalline $C_5H_5RhCOI_2$. The expected structure I (M = Rh) is confirmed by the presence of a π-cyclopentadienyl resonance at τ 4.09 in the proton n.m.r. spectrum and a strong metal carbonyl band at 2065 cm.$^{-1}$ in the infrared spectrum.

Acknowledgment.—The author is indebted to Mr. M. B. Bisnette and Mr. A. Fronzaglia for experimental assistance and to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant No. AF-AFOSR-580-64.

CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES,
UNION CARBIDE CORPORATION, PLASTICS DIVISION, BOUND BROOK, NEW JERSEY

Tetraneophyltin[1] and Its Derivatives: The Effects of Steric Hindrance in Organotin Chemistry

BY WALTER T. REICHLE

Received August 5, 1965

Tetraneophyltin has been prepared and its chemical reactions and derivatives subjected to study. The very severe steric crowding inhibits tin–carbon bond cleavage reactions in the tetraneophyltin or chloride displacement reactions in trineophyltin chloride. By various techniques the following compounds were prepared: $[C_6H_5C(CH_3)_2CH_2]_3SnX$: X = F, Cl, Br, I, OH, $S_{1/2}$, N_3, NO_3, ClO_4, O_2CCH_3, O_2CCF_3, O_2CH. The fluoride is a low-melting, hydrocarbon-soluble derivative; the acetate, formate, and perfluoroacetate have normal ester carbonyl absorptions (1650–1700 cm.$^{-1}$). The nitrate and perchlorate are both bidentate ligands attached to five-coordinate tin atoms; all other derivatives have four-coordinate tin atoms. Neither the hydrosulfide nor the oxide (X = SH, $O_{1/2}$) could be prepared. The infrared, nuclear magnetic resonance, and Mössbauer spectra of these compounds have been correlated.

Introduction

Generally speaking, the effect of steric crowding about a reaction center has been explored in depth only in organocarbon chemistry.[2] In organotin chemistry there are relatively few examples of compounds and their reactions which have a sterically hindered tin atom as the focal point of the investigation.

Bähr and Gelius[3,4] prepared tetramesityltin and similar hindered tetraaryltin compounds. These showed considerably depressed reactivities with attacking electrophiles as did tetra-9-fluorenyltin and tetra-1-indenyltin, which were prepared by other investigators.[5] Seyferth[6] prepared tetra(trimethylsilylmethyl)tin and found that its tin–carbon bond cleavage reactions had to be carried out under severe conditions. Recently,[7] a synthetic study of the neopentyltin compounds was reported. It was observed that both the tendency toward tin–carbon bond formation as well as bond cleavage of these compounds was considerably depressed, relative to unhindered alkyl analogs. These authors noted the facile formation of bis(trineopentyltin) oxide and hexaneopentylditin. Bis-9-phenanthryltin has also been prepared and found not to undergo the normal disproportionation to the tetra-9-phenanthryltin and tin metal on heating and to be approximately dimeric in solution.[8] Krause and Weinberg prepared the stable di-*t*-butyl- and di-*t*-amyltin dihydroxides.[9] Here, steric crowding presumably prevented dehydration to the polydialkyltin oxides. Tri-2-tolyltin hydroxide was found to have an unusually high melting point (215°) without decomposition to the oxide and water.[10] Unexpectedly, the di-*t*-butyltin difluoride was found to be a fairly insoluble substance of high melting point (260° dec.),[11] quite comparable in its properties with the trialkyltin fluorides which seem to polymerize by Sn–F–Sn bridging.[12]

The purpose of this paper is to present the physical properties and some chemical reactions of a wide range of derivatives of a single severely hindered tin compound (tetraneophyltin) in order to be able to find what changes, relative to unhindered systems, occur. Inspection of Fisher–Hirschfelder[13] models of tetraneophyltin indicates that the tin atom is virtually enveloped in hydrocarbon. The phenyl groups protrude straight into space from the molecule. The underlying methyl and methylene groups seem to shield the tin atom

---

[1] Neophyl = $C_6H_5C(CH_3)_2CH_2$–

[2] M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956.

[3] G. Bähr and R. Gelius, *Ber.*, **91**, 812 (1958).

[4] G. Bähr and R. Gelius, *ibid.*, **91**, 818 (1958).

[5] H. Zimmer and H. W. Sparmann, *ibid.*, **87**, 645 (1954).

[6] D. Seyferth, *J. Am. Chem. Soc.*, **79**, 5881 (1957).

[7] H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danzik, *J. Org. Chem.*, **29**, 2632 (1964).

[8] G. Bähr and R. Gelius, *Ber.*, **91**, 829 (1958).

[9] E. Krause and K. Weinberg, *ibid.*, **63**, 381 (1930).

[10] A. Stern and E. I. Becker, *J. Org. Chem.*, **29**, 3220 (1964).

[11] E. Krause and K. Weinberg, *Ber.*, **63**, 383 (1930).

[12] H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963).

[13] These represent covalently bonded atoms which have approximately the van der Waal's radius.

almost completely. Neither the phenyl, methyl, nor methylene groups can rotate freely about their C–C axis; only small oscillations are possible. The *o*-phenyl hydrogens interact strongly with the methyl hydrogens and less so with the methylene hydrogens. No rotation is possible about the Sn–C axis. The trineophyltin–X derivatives are also very hindered molecules. Small substituents (X = OH, F) are surrounded by the adjacent methyl and methylene groups; only a portion of the larger substituents (X = Br, I, NO_3, ClO_4, etc.) project from the molecule in these models. It would seem to be very difficult for the tin atom in this group to assume a coordination number higher than four.

Experimental Section

The melting points were taken with a thermometer calibrated with pure compounds of known melting points. The infrared spectra were recorded on a Perkin-Elmer Model 21 instrument using NaCl or KBr prisms. The nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 instrument.

Tetraneophyltin and trineophyltin chloride were prepared by adding an ether solution of stannic chloride (65 g., 0.249 mole in 300 ml. of ether) to a filtered Grignard solution prepared from neophyl chloride[14] (172 g., 1.03 moles) and magnesium chips (94 g., 3.92 g.-atoms) in dry ether (1.5 l.). The reaction was refluxed for 1 hr. and then left standing overnight. Benzene (1.5 l.) was added to the slurry and excess Grignard decomposed with methanol. The material was filtered and the cake washed twice with benzene. Solvent-free crystals resulting from evaporation were crystallized twice from hexane–benzene (7:3 by volume, −10°). This yielded 61 g. of crystals, m.p. 117.5–118.5°, 44.0% yield of trineophyltin chloride.

Anal. Calcd. for $C_{30}H_{39}SnCl$: C, 65.01; H, 7.06; Cl, 6.43. Found: C, 65.27; H, 6.96; Cl, 6.53.

The solids from the crystal liquors were crystallized twice from benzene–ethanol (1:3, 20°). This resulted in 14.5 g. of crystals, m.p. 90–91.5°, 8.8% yield of tetraneophyltin.

Anal. Calcd. for $C_{40}H_{52}Sn$: C, 73.73; H, 7.99; Sn, 18.28; mol. wt., 651. Found: C, 73.60; H, 8.07; Sn, 17.84, 17.76; mol. wt., 619, 632 (vapor phase osmometer, benzene, 37°).

Trineophyltin hydroxide was prepared by refluxing the corresponding chloride (6.5 g., 11.8 mmoles) in a solution of sodium hydroxide (3.5 g., 88 mmoles) in ethanol–water (250 ml. of 95% ethanol) for 15 hr. The volatiles were removed and the remaining solid washed to neutrality with water. The dry solid was crystallized twice from hot heptane, 4.6 g., 73% yield, m.p. 145–146°.

Anal. Calcd. for $C_{30}H_{40}SnO$: C, 67.28; H, 7.48; Sn, 22.25. Found: C, 68.30; 68.16; H, 7.55, 7.24; Sn, 21.27, 21.46.

Compounds Prepared by Neutralization of Trineophyltin Hydroxide. A small amount of this hydroxide (0.5 g.) was dissolved in the solvent indicated and a little of the concentrated aqueous acid was added to this solution. This was then boiled briefly and crystallized as indicated. These neutralizations proceeded in high yield. In order to obtain analytically pure compounds the crude products were repeatedly crystallized with resultant loss of product. For this reason no yields are stated.

Trineophyltin fluoride[15]; 50% hydrogen fluoride in ethanol, crystallized three times from heptane, m.p. 98–100°.

Anal. Calcd. for $C_{30}H_{39}SnF$: C, 67.07; H, 7.25; F, 3.53. Found: C, 67.10; H, 7.25; F, 3.55.

Trineophyltin bromide; 48% hydrobromic acid in ethanol, crystallized twice from ethanol; m.p. 109.5–110°.

Anal. Calcd. for $C_{30}H_{39}SnBr$: C, 60.22; H, 6.52; Br, 13.38; Sn, 19.88. Found: C, 59.90; H, 6.08; Br, 13.44; Sn, 19.77.

Trineophyltin iodide; 47% hydriodic acid in ethanol; crystallized twice from ethanol, m.p. 116.5–117.5°.

Anal. Calcd. for $C_{30}H_{39}SnI$: C, 55.82; H, 6.05; I, 19.68. Found: C, 56.39; H, 5.99; I, 19.31.

Trineophyltin acetate; glacial acetic acid (plus a trace of anhydride); crystallized twice from heptane; m.p. 86.5–87.0°; infrared C=O asymmetric stretch at 1660 cm.$^{-1}$, vs (cryst.).

Anal. Calcd. for $C_{32}H_{42}SnO_2$: C, 66.62; H, 7.24; Sn, 20.60. Found: C, 67.10; H, 7.23; Sn, 20.20.

Trineophyltin formate; 90% formic acid in benzene; crystallized twice from heptane; m.p. 81.5–82.5°; infrared C=O asymmetric stretch at 1655 cm.$^{-1}$, vs (cryst.).

Anal. Calcd. for $C_{31}H_{40}SnO_2$: C, 66.00; H, 7.11. Found: C, 65.64; H, 7.28.

Trineophyltin perfluoroacetate; 100% perfluoroacetic acid in heptane; crystallized twice from heptane; m.p. 108.5–109.5°; infrared C=O asymmetric stretch at 1720 cm.$^{-1}$, vs, broad (cryst.).

Anal. Calcd. for $C_{32}H_{39}SnO_2F_3$: C, 60.87; H, 6.18. Found: C, 60.85; H, 5.98.

Trineophyltin azide; about 5% hydrogen azide in methanol: crystallized twice from heptane; m.p. 96.0–96.5°; infrared $-N_3$ asymmetric stretch at 2072 cm.$^{-1}$, s (cryst.).

Anal. Calcd. for $C_{30}H_{39}SnN_3$: C, 64.30; H, 6.96; N, 7.50. Found: C, 64.28; H, 6.95; N, 7.78.

Trineophyltin nitrate; concentrated nitric acid in heptane; crystallized once from heptane: m.p. 122–123°.

Anal. Calcd. for $C_{30}H_{39}SnNO_3$: C, 62.05; H, 6.73; N, 2.31; mol. wt., 580. Found: C, 62.18; H, 6.90; N, 2.65; mol. wt., 591 (vapor phase osmometer, benzene, 37°, 0.9%).

Trineophyltin perchlorate; 70% perchloric acid in ethanol; crystallized twice from heptane; m.p. 162–163°.

Anal. Calcd. for $C_{30}H_{39}SnClO_4$: C, 58.36; H, 6.31; Cl, 5.67; mol. wt., 617. Found: C, 57.33; H, 6.49; Cl, 5.65; mol. wt., 608 (vapor phase osmometer, benzene, 37°, 1.0%).

Preparation of Bis(trineophyltin) Sulfide. (A) **Reaction of Trineophyltin Hydroxide with Carbon Disulfide.**—The hydroxide (0.5 g.) and carbon disulfide (50 ml.) were heated in a sealed glass tube for 18 hr. at 110°. After solvent removal the resulting oil was crystallized three times from ethanol, m.p. 97.5–98.0°.

Anal. Calcd. for $C_{60}H_{78}Sn_2S$: C, 67.40; H, 7.30; S, 3.00. Found: C, 67.3; H, 7.25; S, 2.79, 2.92.

(B) **Reaction of Trineophyltin Hydroxide with Aqueous Sodium Sulfide.**—The hydroxide (0.5 g.) and an equal weight of sodium sulfide nonahydrate were refluxed for 6 hr. in 50 ml. of 90% ethanol–water. The solution was then acidified with acetic acid and diluted with water (100 ml.), and the precipitate was filtered, dried, and crystallized three times from heptane, m.p. 97.5–98.0°.

Anal. Calcd. for $C_{60}H_{78}Sn_2S$: C, 67.40; H, 7.30; S, 3.00. Found: C, 67.3; H, 7.3; S, 3.00.

(C) **Reaction of Trineophyltin Chloride with Sodium Sulfide.**—The trineophyltin chloride (0.5 g.) was allowed to react with sodium sulfide nonahydrate (1.0 g.) for 24 hr. in refluxing ethanol. The solution was acidified with acetic acid, diluted with water, and filtered, and the dry precipitate was crystallized twice from heptane, m.p. 96.5–97.0°.

Anal. Calcd. for $C_{60}H_{78}Sn_2S$: C, 67.40; H, 7.30; S, 3.00; mol. wt., 1068. Found: C, 67.5; H, 7.28; S, 2.84; mol. wt., 936, 976 (vapor phase osmometer, benzene, 37°, 0.5 and 0.8%).

This sulfide was identical with the above products derived from the hydroxide and carbon disulfide or sodium sulfide by mixture melting point and X-ray powder diffraction patterns.

Reaction of Tetraneophyltin with Hydrogen Bromide.—This compound was refluxed in xylene for 7 hr. while being sparged with anhydrous hydrogen bromide. Crystallization of the solvent-free residue from heptane (twice) yielded a few crystals of trineophyltin bromide, m.p. 102–104°.

Anal. Calcd. for $C_{30}H_{39}SnBr$: Br, 13.40. Found: Br, 13.67.

---

[14] W. T. Smith, Jr., and J. J. Sellers, *Org. Syn.*, **32**, 90 (1952).

[15] This compound could not be prepared from the chloride and cesium fluoride in dimethyl sulfoxide at reflux nor by addition of the chloride in ethanol to a saturated aqueous sodium fluoride solution.

Reaction of Tetraneophyltin with Stannic Bromide.—This compound (5.88 g., 9.11 mmoles) was mixed with anhydrous stannic bromide (4.01 g., 9.11 mmoles) and heated for 13 hr. in an oil bath (200–235°). The volatiles (at 200° and 50 mm. pressure) were removed (1.15 g. loss, 2.0 g. theory for R_3SnBr) and the remainder extracted with hot heptane. The filtered heptane liquors contained a solid which after crystallization (three times from heptane) was still very impure bromide, m.p. 98–110°; 1.3 g., 23%.

Reaction of Tetraneophyltin with Bromine.—A stoichiometric amount of bromine (1:1) was added to a carbon tetrachloride solution of the tin compound. Refluxing (1 hr.), solvent removal, and three recrystallizations from ethanol still yielded an impure bromide, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{30}H_{39}SnBr$: Br, 13.38. Found: Br, 15.12, 15.27. Evidently the phenyl groups had also been brominated.

Preparation of Trineophyltin Deuterium Oxide.—A small amount (0.5 g.) of the hydroxide was heated in 50 ml. of heptane and 10 ml. of deuterium oxide for 36 hr. at 110° in a sealed tube. The deuterium oxide was distilled off and the solid crystallized from heptane, m.p. 143–144°; νO–D 2670 cm.$^{-1}$; vvw (cryst.).

Pyrolysis of Trineophyltin Hydroxide.—A quantity (6.0 g.) of the hydroxide was gradually heated under argon in an alloy bath. At 340–350° pronounced gas evolution set in; a sublimate and a liquid appeared in the air condenser. After 15 min. at 400°, vacuum was applied and the liquid drawn off (1.75 g.).

Anal. Found (liquid): C, 88.79; H, 10.17; mole ratio C:H, 1:7.3. The vapor phase chromatography showed twelve compounds to be present. Both infrared and nuclear magnetic resonance showed the presence of monosubstituted phenyl, methyl, methylene, and vinyl groups. The solid in the air condenser (3.1 g.) was flash distilled to yield an oil (b.p. 160–180° (0.05 mm.)).

Anal. Found (oil): C, 69.30; H, 7.50; Sn, 18.78; mol. wt., 429, 448 (vapor phase osmometer, benzene, 37°).

No tetraneophyltin could be isolated from this oil. The pyrolysis tube residue (0.7 g.) was a gray solid.

Anal. Calcd. for SnO: Sn, 88.2. Found: Sn, 90.6.

Results

It is likely that replacement of the ether with tetrahydrofuran or the use of neophyllithium[3,4,6] would increase the yield of the tetraneophyltin considerably. Attempts to cleave a neophyl radical from the tetraneophyltin using hydrogen bromide (in refluxing xylene), stannic bromide (230°), or bromine (refluxing carbon tetrachloride) were only partially successful; the direct preparation of the trineophyltin chloride seems to be preferable. Hydrolysis of the chloride to the hydroxide required relatively severe conditions. Displacement reactions on the trineophyltin chloride, to form the fluoride, were unsuccessful. Sodium sulfide (in refluxing aqueous ethanol) did yield the bis(trineophyltin) sulfide. Derivatives of the trineophyltin moiety were best prepared by neutralization of the hydroxide with the appropriate acid.

The trineophyltin hydroxide was found to be stable to loss of water to 340–350° at which temperature a catastrophic decomposition to a wide variety of volatile hydrocarbons and a residue occurred. No tetraneophyltin was produced by rearrangement as could have been expected.[16] All trineophyltin derivatives appeared to be hydrolytically stable. This is much in contrast with the corresponding trimethyltin nitrate and perchlorate.[17] The trineophyltin fluoride is probably the lowest melting organotin fluoride prepared to date and the only generally soluble one.[18]

TABLE I

MÖSSBAUER SPECTRAL DATA OF TIN COMPOUNDS

Absorber	Isomer shift[a] I.S., mm. sec.$^{-1}$	Quadrupole splitting Q.S., mm. sec.$^{-1}$	Q.S./I.S.[b]
SnO_2[c]	0	0	0
(neophyl)$_4$Sn	1.339	0	. . .
$(CH_3)_3SnCl \cdot py$[d]	1.417	3.348	2.36
(neophyl)$_3SnNO_3$	1.397	3.180	2.28
(neophyl)$_3SnClO_4$	1.568	3.830	2.44
(neophyl)$_3$SnF	1.332	2.787	2.09
(neophyl)$_3$SnCl	1.392	2.652	1.90
(neophyl)$_3$SnBr	1.416	2.645	1.87
(neophyl)$_3$SnI	1.407	2.401	1.77
(neophyl)$_3SnN_3$	1.322	2.476	1.86
(neophyl)$_3SnO_2CCH_3$	1.35	2.447	1.81
(neophyl)$_3$SnOH	1.129	1.078	0.95

[a] All shifts relative to SnO_2. [b] See ref. 25 for details. [c] Absorber 78°K., source $Sn^{118}O_2$, 300°K. [d] Crystal structure shows planar $(CH_3)_3Sn$ and a five-coordinated Sn atom; *cf.* R. Hulme, *J. Chem. Soc.*, 1524 (1963).

The trineophyltin hydroxide showed the expected[19–21] O–H stretching frequency at 3620 cm.$^{-1}$ (liquid, 160°). This band shifted to 2670 cm.$^{-1}$ on replacement of the hydrogen with deuterium.[21] This hydroxide also underwent the known reactions with carbon disulfide[19,21,22] and with aqueous sodium sulfide[23] to yield bis(trineophyltin) sulfide. The corresponding hydrosulfide was never in evidence. The trineophyltin nitrate and perchlorate were examined in the infrared in some detail (Tables II and III). The bands due to the neophyl vibrations were located with the aid of the tetraneophyltin and trineophyltin chloride spectra. The remaining bands were evidently due to tin–oxygen or nitrate and perchlorate vibrations.

Discussion

The lack of carbon–tin bond reactivity[3–7] in the tetraneophyltin, the sluggishness of displacement reactions of the trineophyltin chloride, as well as the considerable stability of the trineophyltin hydroxide toward loss of water[10] and rearrangement[16] could have been predicted on the basis of previous work and chemical intuition. Yet, several observations were made which were not predictable and quite unexpected. The trineophyltin fluoride had a surprisingly low melting point (99–100°), a very high solubility in hydrocarbons, and a Mössbauer Q.S./I.S. of 2.09 (Table I).[24] The

---

(16) (a) O. Schmitz-DuMont, *Z. anorg. allgem. Chem.*, **248**, 289 (1941); (b) C. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.*, **51**, 3605 (1929).

(17) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

(18) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960), and previous reviews listed therein.

(19) R. Okawara and K. Yasuda, *J. Organometal. Chem.*, **1**, 356 (1964).

(20) H. Kriegsmann and H. Hoffmann, *Z. anorg. allgem. Chem.*, **321**, 224 (1963).

(21) E. Friebe and H. Kelker, *Z. analyt. Chem.*, **192**, 267 (1963).

(22) W. T. Reichle, *Inorg. Chem.*, **1**, 650 (1962).

(23) W. T. Reichle, *J. Org. Chem.*, **26**, 4634 (1961).

(24) It has been demonstrated elsewhere[25] that for organotin(IV) compounds a quadrupole splitting–isomer shift (Q.S./I.S.) ratio of less than 1.9 implies a tin atom with coordination number of four while a ratio of 2.2 or higher is due to five-coordinated tin. In the interval of 1.9–2.2 the coordination number of the tin atom is uncertain.

(25) R. Herber, H. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965).

TABLE II

INFRARED ABSORPTIONS OF BIDENTATE PERCHLORATE LIGAND

	Cu-(O_2ClO_2)[a]	$(CH_3)_3$-$SnClO_4$[b]	$(CH_3)_3$-$SnClO_4$[c]	(neophyl)$_3$-$SnClO_4$[d]
ν_1	1030	1005	998	1015 s
ν_2	948–920	915	908	922 vw
ν_3	650	633–609		
ν_4	466	470		
ν_6	1130	1125	1112	1105 s
ν_7	624–600			621, 616 m
ν_8	1270–1245	1202	1212–1192	1170–1195 s
ν_9	497	556		504 vw

[a] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961); also A. E. Wickenden and R. E. Krause, *Inorg. Chem.*, **4**, 404 (1965). [b] K. Yasuda and R. Okawara, *J. Organometal. Chem.*, **3**, 76 (1965). [c] Ref. 17. [d] Crystalline state, capillary thickness.

TABLE III

INFRARED ABSORPTIONS OF BIDENTATE NITRATE LIGAND

	$[(CH_3)_3PO]_2$Co-$(NO_3)_2$[a,b]	$Sn(NO_3)_4$[c]	$(CH_3)_3$-$SnNO_3$[d]	(neophyl)$_3$-$SnNO_3$[e]
ν_1	1517 s, 1492 s, 1469 s	1630 vs	1452 s	1528 s
ν_2	1024 m	983 s	1012 s	1040 sh
ν_3	812 w	807 m, 786 m	803 sh	797 sh
ν_4	1282 s, 1304 sh, 1317 sh	1255 s	1300 s	1280 vs
ν_5	. . .	750 w, 702 m	. . .	735
ν_6	. . .	698 w	902 m	. . .

[a] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2,** 1163 (1963). [b] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85,** 2402 (1963). [c] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965). [d] Ref. 17 and K. Yasuda and R. Okawara, *J. Organometal. Chem.*, **3,** 76 (1965). [e] Crystalline state, capillary thickness.

nonspectral evidence would imply a normal four-coordinate tin atom in which the bulky neophyl groups completely suppress the tendency for Sn–F–Sn bridging to occur[12]; the more subtle and accurate Mössbauer spectrum showed that there may be a certain amount of fluoride bridging in this system. This would then call for an unusually long Sn–F bond.

TABLE IV

COUPLING CONSTANTS AND CHEMICAL SHIFTS FOR TRINEOPHYLTIN DERIVATIVES

Compound (neophyl)$_3$SnL, L =	Solvent	Chemical shift, p.p.m.[a,b]			Coupling constant, c.p.s.		
		δCH_3	δCH_2	δ(X)	J_{SnCH_3}	J_{SnCH_2}	J_{SnX}
neophyl	CCl_4	−1.11	−0.984		*c*	48.2	3.9 (SnF)
F	CCl_4	−1.22	−0.948		*c*	52.4	
Cl	CCl_4	−1.19	−1.05		5.8	47.8	
Br	CCl_4	−1.195	−1.065		5.9	48.4	
I	CCl_4	−1.190	−1.335		6.2	44.5	
OH	CCl_4	−1.25	−1.02		3.5	50.8	
$\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$	CCl_4	−1.15	−1.04	−1.82 ($\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$)	5.15	51.7	<5 ($\mathrm{SnO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$)
$\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$	CCl_4	−1.16	−1.08	−7.90 ($\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$)	5.76	51.2	31.4 ($\mathrm{SnO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$)
$\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$	Acetone-d_6	−1.18	−1.16		. . .	. . .	
$\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}$	Acetone-d_6	−1.195	−1.15		. . .	. . .	
Cl	Acetone-d_6	−1.205[d]	−1.205[d]		5.53	48.0	
ClO_4	Acetone-d_6	−1.34	−1.755		3.84	48.6	
NO_3	Acetone-d_6	−1.205	−1.29		6.13	48.4	

[a] $(CH_3)_3SnCl$ in $CDCl_3$, δCH_3 −0.613 (TMS): E. V. van den Berghe and G. P. van der Kelen, *Ber. Bunsengeselsch.*, **68**, 652 (1964). [b] Relative to TMS, 25° (hydroxide 55°). [c] Not found. [d] Unresolved.

Both the trimethyltin and triphenyltin azides have five-coordinated tin atoms,[25,26] and, because the covalent azide group is fairly long (2.37 Å.[27]), it would have seemed reasonable that the trineophyltin azide should have five-coordinated tin. On the contrary, the Mössbauer spectrum showed this compound to have a normal four-coordinated tin atom. Two trineophyltin derivatives with apparently authentic five-coordinated tin were prepared: the nitrate and perchlorate (Mössbauer Q.S./I.S. = 2.28 and 2.44, respectively, Table I). The infrared spectrum (Table II) clearly indicates that the perchlorate group was present as a bidentate ligand (C_{2v} symmetry) as required by the Mössbauer spectrum. The infrared spectrum of the trineophyltin nitrate (Table III) cannot be interpreted as being due to a mono- or bidentate nitrate ligand based on nitrate point group symmetry alone (both are C_{2v}). It has been found that the discrimination between mono- and bidentate nitrato groups by infrared spectroscopy is a very uncertain matter.[28] Compounds which have known bidentate nitrato groups (crystallographic or other reasonable evidence) all have strong absorptions at 1480–1650 cm.$^{-1}$ (symmetric NO_2 stretching) and 1250–1320 cm.$^{-1}$ (asymmetric NO_2 stretching). Both of these absorptions overlap similar bands of the monodentate nitrato group. The Mössbauer spectrum of the trineophyltin nitrate is clearly that of a five-coordinate tin bearing compound. Nuclear magnetic resonance methylene proton chemical shifts of the trineophyltin perchlorate offered a contrast to that of the other compounds which had been examined (Table IV). The δCH_2 was larger than those

---

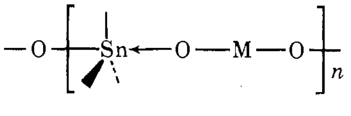
(26) J. G. A. Luijten, M. J. Janssen, and G. J. M. van der Kerk, *Rec. trav. chim.*, **81**, 202 (1962).

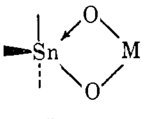
(27) E. H. Egster, *J. Chem. Phys.*, **8**, 135 (1940); value for hydrazoic acid.

(28) R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, 5008 (1964).

of the other trineophyltin compounds examined (probably not a solvent effect, compare the same compounds in carbon tetrachloride and acetone-d_6) and very likely due to a change in coordination number of the tin atom. The evidence in the case of the nitrate is too marginal to reach a conclusion. The large shift of the perchlorate is clear evidence of a substantial change of the methylene proton magnetic environment. This deshielding of the methylene protons may be attributed to the increased ionic character of the tin–oxygen bond.

The trineophyltin perchlorate and nitrate could have either the polymeric structure (I) or the monomeric structure (II). It is difficult to decide between these two. The dilute solution molecular weights (see Experimental Section) indicate clearly a monomeric structure for both.[29]


Polymer


Monomer

Trineophyltin acetate was found to have a four-coordinated tin atom (Q.S./I.S. = 1.81, infrared C═O 1660 cm.$^{-1}$, normal δCH_2). Similar "ester" carbonyl absorptions for the corresponding formate (1655 cm.$^{-1}$) and the perfluoroacetate (1720 cm.$^{-1}$), as well as normal nuclear magnetic resonance δCH_2 absorptions, indicate that here the tin atoms also have the coordination number four. The bulky neophyl groups seem to have forced the "carboxylate"–tin infrared absorptions[30–32] into the normal "ester" conformation.[35]

The above data would seem to indicate that at least two major factors operate when a change of the coordination number of tin in trialkyltin compounds is to be brought about: not only must the ligand have the proper geometry (be large enough to circumvent steric resistance) but it must also be an adequate electron donor to the tin atom. Thus, the perchlorate and nitrate groups are satisfactory bidentate ligands, fluoride would probably be a good one if it were not for its small size, while azide and carboxyl groups (both of proper size) do not coordinate to tin in this case. A qualitative order is: $ClO_4 > NO_3 > F \gg N_3 \simeq RCO_2$.

Acknowledgments.—Dr. W. F. Beach, Mrs. Barbara Petro, and Mrs. Janice Clinard carried out the nuclear magnetic resonance spectroscopy. Professor R. Herber and Mr. H. Stökler of Rutgers University, New Brunswick, N. J., kindly provided the Mössbauer spectra. Dr. G. Omietanski, of the Linde Division, Union Carbide Corp., furnished a generous quantity of the neophyl chloride. The analytical work and molecular weight determinations were carried out at the European Research Associates, Brussels, Belgium.

(29) The Mössbauer and infrared spectra were obtained on the crystalline solids, the nuclear magnetic resonance spectra on solutions. In case of the trialkyltin esters[30–32] and imidazoles[33] polymers were found to exist in the crystalline state and also in solution. Increasing dilution tended to increase monomer content,[30] due probably to a shift in the coordination number of tin from five to four in case of the esters (absorption shift from 1590 and 1360 cm.$^{-1}$ RCO_2^- bidentate to 1667 cm.$^{-1}$ RC(═O)O monodentate). Infrared data indicate that trimethyltin nitrate may have the polymer configuration (I) in the crystalline state.[34]

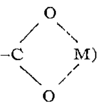
(30) R. Okawara and M. Ohara, *Bull. Chem. Soc. Japan*, **36**, 623 (1963).

(31) R. Okawara and M. Ohara, *J. Organometal. Chem.*, **1**, 360 (1964).

(32) M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. trav. chim.*, **82**, 90 (1963).

(33) M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *J. Organometal. Chem.*, **1**, 286 (1964).

(34) K. Yasuda and R. Okawara, *ibid.*, **3**, 76 (1965).

(35) The normal "ester" –C(═O)O– bonding is found in $(C_6H_5)_3MO_2CC_6H_5$ (M = Si, Ge) and $(C_6H_5)_2MO_2CC_6H_5$ (M = P, As), while the "carboxylate" bonding  $\left(-C\overset{O}{\underset{O}{\diamond}}M\right)$ is found in $(C_6H_5)_3MO_2CC_6H_5$ (M = Sn, Pb), $(C_6H_5)_2MO_2CC_6H_5$ (M = Sb, Bi), and $C_6H_5HgO_2CC_6H_5$ (all as crystalline solids). Evidently there is a sharp break in the bond character in compounds of this nature between the third and fourth row of the atomic table. W. T. Reichle, unpublished results; also see ref. 31.

CONTRIBUTION FROM THE INORGANIC MATERIALS DIVISION, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND

The Electron Paramagnetic Resonance Spectrum of Tetrakis-*t*-butoxyvanadium(IV)

BY GERALD F. KOKOSZKA,[1a] HARRY C. ALLEN, JR.,[1a] AND GILBERT GORDON[1b]

Received June 28, 1965

The electron paramagnetic resonance spectrum of tetrakis-*t*-butoxyvanadium(IV) $[V(OR)_4]$ has been measured in the temperature range of 30 to −196°. The measurements were made on pure $V(OR)_4$, 1–2% $V(OR)_4$ in $Ti(OR)_4$, and 1–2% $V(OR)_4$ in CS_2. The spectrum was essentially the same in all samples. At 30° $\langle g \rangle = 1.964$ and $\langle a \rangle = 0.0064$ cm.$^{-1}$, while at −196° in the solid, the magnetic parameters are $g_{\parallel} = 1.940$, $g_{\perp} = 1.984$, $A_{\parallel} = 0.0125$ cm.$^{-1}$, and $A_{\perp} = 0.0036$ cm.$^{-1}$. These parameters are interpreted in terms of the molecular orbital theory, and the model due to Murao is used to account for the low value of the effective spin–orbit coupling constant, 156 cm.$^{-1}$.

Numerous reports of the e.p.r. spectra and the nature of the bonding in vanadyl complexes[2–7] have been published recently. Usually, the vanadyl ion is found in a distorted octahedral environment with either five or

---

[1] (a) Inorganic Materials Division, National Bureau of Standards, Washington, D. C.; (b) Department of Chemistry, University of Maryland, College Park, Md.

(2) (a) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962); (b) D. Kivelson and S-K. Lee, *J. Chem. Phys.*, **41**, 1896 (1946).

(3) H. R. Gersmann and J. D. Swallen, *ibid.*, **36**, 3221 (1962).

(4) D. E. O'Reilley, *ibid.*, **29**, 1188 (1958); **30**, 591 (1959).

(5) I. Bernal and P. Reiger, *Inorg. Chem.*, **2**, 256 (1963).

(6) E. M. Roberts and W. S. Koski, *J. Chem. Phys.*, **34**, 591 (1961).

(7) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *ibid.*, **42**, 1019 (1965).