kcal) relative to that of Pt (121.6 kcal).[24] This is significant since the heat of sublimation is a measure of metal–metal bond strength in the pure metal.

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Registry No. K_2PtCl_4, 10025-99-7; *cis*-$PtCl_2(NH_3)_2$, 15663-27-1; $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$, 62782-86-9; *trans*-$PtCl_2(TMA)_2$ (form I), 24411-25-4; *trans*-$PtCl_2(TMA)_2$ (form II), 24380-93-6; dichloroplatinum trimethylacetamide blue (form III), 24411-26-5; platinblau, 30685-25-7; *cis*-$Pt(CH_3CN)_2Cl_2$, 21264-32-4.

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(24) "Handbook of Chemistry and Physics", 59th ed., CRC Press, West Palm Beach, FL, 1978–1979, pp D73-4.

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Oxy and Thio Phosphorus Acid Derivatives of Tin. 1. Triorganotin(IV) Dithiophosphate Esters

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Twelve triorganotin dithiophosphate esters $R_3SnS_2P(OR')_2$, where $R = C_6H_5$ when $R' = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, or C_6H_5, where $R = CH_3$ when $R' = CH_3$, C_2H_5, n-C_3H_7, or i-C_3H_7, and where $R = C_6H_{11}$ when $R' = i$-C_3H_7, can be synthesized in high yield by the condensation of the organotin hydroxide with the *O,O'*-diorganodithiophosphoric acid to release water which is distilled azeotropically, or taken up in an alcohol solvent corresponding to the phosphoric acid ester group, or by the reaction of the triorganotin chlorides with an alkali-metal salt of the dithiophosphoric acid. The products are colorless, crystalline solids except for the trimethyltin derivatives which are oils. The synthesis of the diisopropyl ester in the triphenyltin series is accompanied by protodemetalation to yield the bis compound $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$. Infrared spectral bands were assigned to ν(CO) (1170–1095 cm^{-1}), $\nu_{asym}(PS_2)$ (675–635 cm^{-1}), and ν(POR) (1015–965 cm^{-1}), but the $\nu_{sym}(PS_2)$ absorption obscures the $\nu_{sym}(SnC_3)$ modes. NMR $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ coupling constants for the methyltin series are consistent with four-coordinated tin in solution and mass spectral data with monomers. Tin-119m Mössbauer data, on the other hand, specify a five-coordinated structure for the methyltin but a four-coordinated structure for the cyclohexyl- and phenyltins. The triphenyltin ethoxy and isopropoxy derivatives behave identically in a variable-temperature Mössbauer study, where the slope of the temperature dependence of the log of the resonance area is consistent with a monomeric structure packed in the solid into a rather tight lattice. With the use of low-energy, lattice-mode Raman data in the effective vibrating-mass treatment, the molecularity of the vibrating unit is found to be monomeric. The predicted monomeric, monodentate structure for these two esters is extremely rare among dithiophosphate–metal systems.

Organotin compounds are powerful biocides and have found wide application as agricultural fungicides and miticides, surface disinfectants, anthelminthics, and marine antifouling agents.[1,2] A particularly intriguing idea is to combine the triorganotin moieties which show the strongest biocidal activity with organophosphorus moieties which are also known for their potent biocidal effect. The combination of the two kinds of biological activity in a single molecule could produce a still more powerful and lasting effect and prevent the problems associated with the development of tolerance to each kind.

Several model organotin dithiophosphorus systems suggest themselves as subjects for study. We initiate this series of papers with a description of the synthesis of the triorganotin dithiophosphate esters. This class of compounds was first introduced in 1955 and has been the subject of several patents describing applications as bactericides, insecticides, fungicides, etc.,[3-15] but a satisfactory answer to the question of the structure–function relationships in the known systems[16-19] has not yet been given. The systems are also of interest structurally[20] since several modes of attachment of the dithiophosphate ester ligand are in principle possible, including those of a monodentate, bidentate, or bridging ligand in an oligomeric form as in a dimer and that of a bridging ligand in an associated polymer chain. The X-ray crystallographic results for certain key examples will be published as a part of this series.

We report here the synthesis of 12 compounds, nine not reported before, by two preparative methods.[21]

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(1) Zuckerman, J. J. *Adv. Chem. Ser.* **1976**, *No. 157*.

(2) Zuckerman, J. J.; Reisdorf, R. P.; Ellis, H. V., III; Wilkinson, R. R. *ACS Symp. Ser.* **1978**, *No. 82*, 388.

(3) Kubo, H. *Agr. Biol. Chem.* **1965**, *29*, 43.

(4) ESSO Research and Engineering Co. British Patent 737 392, 1955; *Chem. Abstr.* **1955**, *50*, 9010.

(5) McDermott, J. P. U.S. Patent 2 786 812, 1957; *Chem. Abstr.* **1957**, *51*, 10892.

(6) Homberg, O. A.; Hedrenbleikner, I. French Patent 1 365 375, 1964; *Chem. Abstr.* **1964**, *61*, 14711.

(7) Nagae, Y.; Wakamori, K. Japanese Patent 4576, 1966; *Chem. Abstr.* **1966**, *65*, 2298.

(8) Nakanishi, M.; Tsuda, A. Japanese Patent 15 290, 1966; *Chem. Abstr.* **1966**, *65*, 20164.

(9) Bliznyuk, N. K.; Khokhlov, P. S.; Andrianov, Tu. A. USSR Patent 181 103, 1966; *Chem. Abstr.* **1966**, *65*, 8962.

(10) Walsh, E. N.; Kopacki, A. F. U.S. Patent 3 296 193, 1967; *Chem. Abstr.* **1967**, *66*, 55 981; U.S. Patent 3 358 006, 1968; *Chem. Abstr.* **1968**, *68*, 30705.

(11) Walker, D. R.; Ramsden, E. H. U.S. Patent 3 410 797, 1968; *Chem. Abstr.* **1969**, *70*, 21592.

(12) Chas. Pfizer and Co. British Patent 1 163 738, 1969; *Chem. Abstr.* **1970**, *72*, 2550.

(13) Bliznyuk, B. K.; Protusova, L. O.; Kvash, Z. M. USSR Patent 248 673, 1969; *Chem. Abstr.* **1970**, *72*, 100889.

(14) Toda, T.; Ida, K.; Kimoto, K. Japanese Patent 19 512, 1970; *Chem. Abstr.* **1970**, *73*, 77830.

(15) Baker, D. R. South African Patent 72-02699, 1972; *Chem. Abstr.* **1973**, *79*, 78964; U.S. Patent 3 917 827, 1975; *Chem. Abstr.* **1976**, *84*, 85648; U.S. Patent 3 919 418, 1975; *Chem. Abstr.* **1976**, *84*, 85644; U.S. Patent 3 947 481, 1976; *Chem. Abstr.* **1976**, *85*, 46858; U.S. Patent 3 992 425, 1976; *Chem. Abstr.* **1977**, *86*, 90031; U.S. Patent 4 012 412, 1977; *Chem. Abstr.* **1977**, *87*, 6201.

(16) Pudovik, A. N.; Chenkasov, R. A.; Bykova, I. V.; Evstafev, G. I.; Zemkaya, Z. I.; Nazypov, M. N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1972**, *42*, 76.

Table I. Triorganotin Dithiophosphate Esters

$R_3SnS_2P(OR'_2)_2$					% C		% H	
R	R′	prepn[a]	yield, %	mp or bp, °C	calcd	found	calcd	found
C_6H_5	CH_3[c]	2, 3	72	83[c]	6.12[b]	6.00[b]		
	C_2H_5[d]	2, 3	89	105[d]	5.80[b]	5.65[b]		
	n-C_3H_7[e]	2, 3	65	63	5.51[b]	5.40[b]		
	i-C_3H_7	2, 3	52	73.5–74.5	51.16	51.01	5.20	5.27
	n-C_4H_9[f]	2	94	68–69[f]	5.26[b]	5.10[b]		
	i-C_4H_9	1	63	52–54	58.80	52.95	5.64	5.68
	C_6H_5	1	77	121–122	57.07	57.10	4.00	4.17
CH_3	CH_3	3	25	[g]	18.71	20.34	4.71	5.08[h]
	C_2H_5	1, 3	64	112–115 (0.2 torr)	24.09	23.89	5.49	5.41
	n-C_3H_7	3	75	oil				
	i-C_3H_7	3	75	105–109 (0.4 torr)	28.67	28.73	6.15	6.28
C_6H_{11}	i-C_3H_7	4		43–44				

[a] Preparations **1**, **2**, and **3** correspond to the syntheses described by eq 1, 2, and 3; **4** was used as received from the Stauffer Chemical Co. Its preparation was described in ref 15 from the potassium salt of the acid (7.6 g, 0.03 mol) and tricyclohexyltin chloride (10.1 g, 0.025 mol). [b] Analysis data for phosphorus. [c] Reference 3 reports a melting point of 86 °C. [d] Reference 3 reports a melting point of 105 °C; reference 16 reports a melting point of 90–91 °C. [e] Reference 3 reports a melting point of 63 °C. [f] Reference 3 reports a melting point of 69.1 °C. [g] This compound distills over a wide temperature range, indicating some thermal decomposition. Purification could not be affected by gas chromatography. The composition is based upon NMR and mass spectral data. [h] Molecular weight: calculated, 321; found (in benzene), 300.

Experimental Section

Reagent grade chemicals and solvents were used as received, except for triphenyltin chloride (M&T) which was recrystallized from chloroform before use. Trimethyltin hydroxide was prepared from the chloride. Infrared spectra were recorded as KBr disks or Nujol mulls on KBr plates and polyethylene film on a Beckman 4250 or an IR-12 spectrometer. Tin-119m Mössbauer spectra were recorded at 77 K on a Ranger Engineering constant-acceleration spectrometer equipped with a proportional counter and with $Ca^{119m}SnO_3$ (New England Nuclear Corp.) used as the γ-ray source and $Ca^{119}SnO_3$ used as the zero isomer shift (IS) reference standard at room temperature. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS system at 70 eV. Raman spectra were recorded on a Spex Ramalog 5 system. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.

Anaerobic reaction conditions are unnecessary owing to the stability of the starting materials and products. Warning should, however, be given concerning the toxicity of several of the organotin starting materials used, especially trimethyltin chloride, and the unpleasant odors of the organotin dithiophosphates.

The compounds studied are listed with the preparatory method used, their yields, their melting points, and their microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table V.

Preparation of the *O,O′*-Dialkylphosphorodithioic Acids, HS(S)P-(OR′)$_2$. Tetraphosphorus decasulfide (444.5 g, 1 mol) was treated with the corresponding anhydrous alcohol (4 mol) added dropwise with magnetic stirring. Hydrogen sulfide was evolved, and the solid dissolved completely with formation of the crude acid. The reaction was exothermic, and external cooling was applied at initial stages. Toward the end of the reaction, gentle warming with a water bath (ca. 60–80 °C) was necessary to speed up the reaction. The crude acid was distilled in vacuo (as fast as possible to avoid decomposition) at the following temperatures: R′ = CH_3,[21,23] bp 62–64 °C (0.5 torr); C_2H_5,[22,23] bp 75–78 °C (0.3 torr); n-C_3H_7,[23,23] bp 112 °C (0.5 torr); i-C_3H_7,[21-24] bp 72–74 °C (0.7 torr); n-C_4H_9,[23,24] bp 120 °C (0.8–1 torr); i-C_4H_9[25] bp 75–84 °C (0.08–0.1 torr); C_6H_5,[26] mp 60–61 °C.

Preparation of the Sodium Salts, NaS(S)P(OR′)$_2$.[27] Sodium *O,O′*-dialkyl dithiophosphates were prepared via sodium ethoxide formed by dissolving the stoichiometric amount of metallic sodium in absolute ethanol (excess) and treating the solution with an equivalent amount of dialkyldithiophosphoric acid. The solutions were used immediately without isolation of the salt.

Preparation of Ammonium Dialkyl Dithiophosphates, $NH_4S_2P(OR')_2$.[28] Phosphorus decasulfide (88.9 g, 0.2 mol) was treated with anhydrous alcohol (0.8 mol) added dropwise. After all the phosphorus decasulfide had dissolved, the mixture was heated gently on a water bath until the reaction was completed. The acid thus obtained was diluted with 300–400 mL of dry benzene and a stream of anhydrous ammonia bubbled through the solution. The ammonium dialkyl dithiophosphate precipitated was filtered, washed with benzene, and dried. The yields were as follows for R′: CH_3, 46%; C_2H_5, 61%; n-C_3H_7, 61%; i-C_3H_7, 70%; n-C_4H_9, 58%.

Preparation of Triphenyltin Dithiophosphate Esters. **(*O,O′*-Dimethyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OCH_3)_2$.** Triphenyltin chloride (7.70 g, 0.02 mol) was treated with $NaS_2P(OCH_3)_2$ (3.6 g, 0.02 mol) in methanol. The mixture was heated on a water bath for 1 h, filtered, and concentrated to give 3.6 g (35.6%) of the product, mp 83 °C (lit.[3] mp 86 °C).

Alternatively, a suspension of triphenyltin hydroxide (1.22 g, 0.0033 mol) in methanol was heated with dimethyldithiophosphoric acid (0.61 g, 0.004 mol) on a water bath until a clear solution was obtained, which on cooling deposited 1.2 g (71.7%) of the crystalline product, mp 83 °C (lit.[3] mp 86 °C).

(*O,O′*-Diethyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_2H_5)_2$. Triphenyltin chloride (7.7 g, 0.02 mol) was similarly treated with sodium diethyl dithiophosphate (4.16 g, 0.02 mol) to give 6.4 g of the product (60% yield), mp 105 °C (lit.[3] mp 105 °C).

Alternatively, a suspension of triphenyltin hydroxide (18.3 g, 0.05 mol) in absolute ethanol was treated with diethyldithiophosphoric acid (9.3 g, 0.05 mol), diluted with absolute ethanol, and allowed to reflux for 2 h on a water bath until a clear solution was obtained. The solution was concentrated and cooled to give 21.5 g (88.5% yield) of product, mp 105 °C (lit.[3] mp 105 °C).

(*O,O′*-Di-*n*-propyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_3H_7\text{-}n)_2$. Triphenyltin chloride (3.88 g, 0.02 mol) was treated in the same way with sodium di-*n*-propyl dithiophosphate (2.36 g, 0.02 mol) to yield 1.3 g of the product (23%), mp 63 °C (lit.[3] mp 63 °C).

Alternatively, a suspension of triphenyltin hydroxide (5.0 g, 0.014 mol) in 1-propanol was heated with di-*n* propyldithiophosphoric acid

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(17) Ishmaeva, E. A.; Cherkasov, R. A.; Ivantaeva, L. P.; Bykova, I. V. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1975**, *45*, 470.

(18) Cherkasov, R. A.; Kashina, N. V.; Lushchits, I. G.; Vinokurov, A. E.; Pudovik, A. N. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1976**, *46*, 761.

(19) Voronkov, M. G.; Mirsov, R. G.; Stankevich, O. S.; Kuznetson, G. V. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1976**, *46*, 1907.

(20) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(21) In the course of submitting this paper, another publication appeared [Singh, B. P.; Srivastava, G.; Mehrotra, R. C. *J. Organomet. Chem.* **1979**, *171*, 35] which includes the preparation of some of these compounds and reaches the same structural conclusions on the basis of electronic, NMR, and infrared data.

(22) Malatesta, L.; Laverone, F. *Gazz. Chim. Ital.* **1951**, *81*, 596.

(23) Kabachnick, M. I.; Mastrjukova, T. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 121.

(24) Mastin, W.; Norman, G. R.; Weilmuenster, E. A. *J. Am. Chem. Soc.* **1945**, *67*, 1662.

(25) Bencze, P.; Baboczky-Kampos, K. *Acta Chim. Acad. Sci. Hung.* **1962**, *31*, 53; *Chem. Abstr.* **1962**, *52*, 49366.

(26) Fletcher, J. H.; Hamilton, J. C.; Hechenbleikner, I.; Hoegberg, E. I.; Sertl, B. J.; Cassaday, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 2461.

(27) Hoegberg, E. I.; Cassady, J. T. *J. Am. Chem. Soc.* **1951**, *73*, 557.

(28) Sasse, K. *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed.* **1964**, *12* (*Part 2*), 683–8.

Table II. Infrared Spectral Data (cm^{-1}) of the Triorganotin Dithiophosphate Esters, $R_3SnSP(=S)(OR')_2$

R = C_6H_5						
R' = CH_3	R' = C_2H_5	R' = n-C_3H_7	R' = i-C_3H_7	R' = i-C_4H_9	R' = C_6H_5	
	3065 w					
	2995 w					
	2990 w					
	2935 vw					
	2900 vw					
	2370 vw					
					1592 sh	
					1587 m	
			1575 vw	1574 vw	1575 w	
	1485 m				1484 vs	
	1445 vw					
	1433 s			1428 m	1429 s	
	1390 m					
					1364 vw	
					1350 vw	
1328 w	1336 w		1328 vw	1330 vw	1330 w	
1295 w	1310 w	1295 w	1295 w	1295 w	1300 w	
			1254 vw		1261 vw	
					1240 w	
					1199 s	
			1185 sh	1185 vw	1190 m	
			1174 m		1178 vs	
			1155 w	1155 w (br)		
1166 m	1160 m	1145 m (br)	1135 m	1124 w	1157 vs	ν((P)-O-C)[a]
			1095 m			
1154 sh	1102 w					
	1095 w					
1065 m	1075 s	1069 s	1069 m	1070 m		
	1044 s (br)	1048 m (br)	1060 sh	1046 sh	1060 vw	
		1015 sh	1018 vw	1019 w	1022 m	
		1000 sh			1004 m	
1007 vs	1015 vs	990 s	990 vs	991 s	995 m (?)	ν(P-O-(C))[a]
990 s	998 s					
			970 sh		981 w	
	956 vs	967 s (br)	965 vs	959 w	965 w	
	935 s		932 sh		933 vs	
	924 sh	906 vw		908 w	912 vs	
					901 s	
			883 m		894 vs	
				860 m	858 vw	
		832 m	846 vw	850 m		
809 s	805 w	810 w		818 vw	825 w (br)	
794 sh	796 sh					
	790 s					
	770 m				775 vs	
			767 s		764 vs	
		748 s			747 m	
	740 s		741 w		737 s	
722 vs	732 s	722 s	723 s	723 s	729 s	
					720 sh	
	700 s		691 s	692 s	695 s	
					689 m	
633 s (br)	655 vs	655 m	663 s	655 s	675 vs	$\nu_{asym}(PS_2)$
					660 w	
		639 m	648 sh		648 vw	
					610 vw	
				545 w (br)	564 m	
486 m	540 m	514 m (br)	505 s	521 m	525 s	$\nu_{sym}(PS_2)$
	515 w					
			480 w		489 m	
432 m	446 m	435 s	435 s	437 m	437 s	

R = CH_3			
R' = CH_3	R' = C_2H_5	R' = i-C_3H_7	R = C_6H_{11}; R' = i-C_3H_7
2985 m	2990 vs	2975 s	
2940 s	2940 m	2930 m	
2910 m	2910 m	2920 sh	
2920 m	2880 w	2870 w	
	2780 vw		
1460 sh	1480 m		
1452 m	1455 sh	1462 m	
1438 m	1446 m	1447 m	1442 s
	1393 s	1381 s	1370 m
	1370 sh	1370 s	1362 sh
		1348 w	1349 w

Table II (*Continued*)

R = CH_3				
R′ = CH_3	R′ = C_2H_5	R′ = i-C_3H_7	R = C_6H_{11}; R′ = i-C_3H_7	
			1340 vw	
			1325 vw	
	1294 m (br)		1292 w	
	1268 vw		1263 w	
	1190 w			
			1175 sh	
		1175 m	1168 m	
1173 s	1164 s	1138 m	1137 m	ν((P)-O-C)[a]
		1102 s	1103 s	
	1100 s			
			1080 w	
			1060 vw	
1040 sh	1045 vs		1038 w	
1018 vvs (br)	1025 vs	985 vs	987 vs	ν(P-O-(C))[a]
	955 vs (br)	962 vs (br)	965 vs	
		935 sh	905 w	
		883 s	880 m	
			835 w	
			800 vw	
780 vs (br)	788 vs (br)	785 sh		ρ(Sn-C)
		765 vs	768 s	
745 s	730 sh	750 sh	752 w	
700 s			719 vw	
685 sh	675 sh	660 w	665 m	
655 vs	658 vs	645 s	650 s	$\nu_{asym}(PS_2)$
530 s	540 vs	538 s		ν_{asym}(Sn-C)
510 sh	508 s	503 m	541 m	$\nu_{sym}(PS_2)$
495 s				ν_{sym}(Sn-C)
			512 w	
			480 w	
390 w	380 w	380 w		ν(Sn-S)

[a] See ref 32.

(2.9 g, 0.014 mol) until a clear solution was formed. After concentration and cooling, 5.1 g (65.1% yield) of product (mp 63 °C (lit.[3] mp 63 °C)) was obtained.

(*O,O′*-Diisopropyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_3H_7\text{-}i)_2$. A solution of the sodium salt of diisopropyldithiophosphoric acid (0.1 M) in absolute ethanol (20 mL) was added dropwise to a stirred solution of triphenyltin chloride (0.01 M) in freshly distilled diethyl ether (70 mL). After 24 h the white precipitate was separated by filtration through diatomaceous earth and the filtrate concentrated to dryness on a rotary evaporator. The resulting white solid was dissolved in a minimum of warm toluene, the solution was filtered, and the compound was allowed to crystallize at 0 °C, yielding white, prismatic crystals (2.93 g, 52% yield) of the title compound, mp 73.5–74.5 °C.

A second crop of needlelike crystals separated after several days and were identified as bis(*O,O′*-diisopropyl dithiophosphato)diphenyltin, mp 110 °C. Anal. Calcd for $C_{24}H_{38}O_4P_2S_4Sn$: C, 41.20; H, 5.49. Found: C, 41.78; H, 5.37.

(*O,O′*-Di-*n*-butyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_4H_9\text{-}n)_2$. A suspension of triphenyltin hydroxide (4.0 g, 0.011 mol) in *n*-butyl alcohol was allowed to reflux for 3 h with di-*n*-butyldithiophosphoric acid (2.6 g, 0.011 mol). The solution was concentrated and cooled to give 6.1 g (94.3% yield) of the product, mp 68–69 °C (lit.[3] mp 69.05 °C).

(*O,O′*-Diisobutyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_4H_9\text{-}i)_2$. Equimolar quantities (0.02 mol) of triphenyltin hydroxide and diisobutyldithiophosphoric acid were allowed to reflux together in benzene (100 mL), and the water formed azeotropically was distilled into a Dean and Stark trap. Concentration of the resulting solution yielded a colorless oil, from which crystallization was induced by the addition of *n*-hexane at 0 °C. The product was purified by recrystallization from a hexane–benzene (10:1) mixture (8.74 g, 63%), mp 52–54 °C.

(*O,O′*-Diphenyl dithiophosphato)triphenyltin, $(C_6H_5)_3SnS_2P(OC_6H_5)_2$. Triphenyltin hydroxide and diphenyldithiophosphoric acid in 0.02 molar quantities were allowed to reflux together in benzene (100 mL), and the water formed azeotropically was distilled into a Dean and Stark separator. After 2 h the requisite amount of water had been collected, and the resulting solution was allowed to cool, filtered, and concentrated to ca. 10 mL on a rotary evaporator. The white precipitate that formed was taken up in a minimum amount of warm toluene and allowed to crystallize at 0 °C, yielding a white crystalline product (9.8 g, 77% yield) identified as (*O,O′*-diphenyl dithiophosphato)triphenyltin, mp 121–122 °C.

Preparation of Trimethyltin Dithiophosphate Esters. **(*O,O′*-Dimethyl dithiophosphato)trimethyltin, $(CH_3)_3SnS_2P(OCH_3)_2$.** Metallic sodium (1.20 g, 0.052 mol) was dissolved in absolute ethanol (30 mL) and dimethyldithiophosphoric acid (8.24 g, 0.052 mol) added. Trimethyltin chloride (9.50 g, 0.048 mol) in absolute ethanol was added with stirring, sodium chloride was filtered out, and the filtrate was concentrated to give the crude product as an oil. This was distilled (bp 75–80 °C (0.01 mm)) to give pure product (6.35 g, 42%).

(*O,O′*-Diethyl dithiophosphato)trimethyltin, $(CH_3)_3SnS_2P(OC_2H_5)_2$. Method A. Trimethyltin hydroxide (3.77 g, 20.9 mmol) and diethyldithiophosphoric acid (3.94 g, 21.2 mmol) were mixed in benzene (65 mL), and the solution was heated at reflux for 3 h. Water produced in the reaction was collected by a Dean and Stark trap. After removal of benzene under vacuum, the product was vacuum distilled to give 4.64 g (13.3 mmol, 64% yield) of the product, bp 112–115 °C (0.2 mm).

Method B. Potassium hydroxide (0.28 g, 5 mmol) was dissolved in ethanol and trimethyltin chloride (0.995 g, 5 mmol) added to give a precipitate. Diethyldithiophosphoric acid (0.93 g, 5 mmol) was added, the mixture refluxed for 1 h and filtered, and the filtrate evaporated to give 1.3 g (80% yield) of the product as an oil.

(*O,O′*-Di-*n*-propyl dithiophosphato)trimethyltin, $(CH_3)_3SnS_2P(OC_3H_7\text{-}n)_2$. Potassium hydroxide (0.28 g, 5 mmol) in ethanol was treated with trimethyltin chloride (0.995 g, 5 mmol). After the addition of di-*n*-propyldithiophosphoric acid (1.02 g, 4.8 mmol), the mixture was refluxed for 1 h and then filtered, and the solvent was evaporated to give an oil (1.37 g, 75% yield).

(*O,O′*-Diisopropyl dithiophosphato)trimethyltin, $(CH_3)_3SnS_2P(OC_3H_7\text{-}i)_2$. To a solution of trimethyltin chloride (3.98 g, 20 mmol) in diethyl ether (30 mL) was added a solution of the sodium salt of diisopropyldithiophosphoric acid (4.86 g, 20.5 mmol) in anhydrous ethanol. Formation of a white precipitate began immediately. The mixture was heated at reflux for 1 h, cooled, and filtered through diatomaceous earth. Solvent was removed under vacuum on the rotary evaporator. The residual oil was purified by vacuum distillation to yield 5.65 g of the product (15 mmol, 75% yield), bp 105–109 °C (0.4 mm).

Results and Discussion

The synthesis of the triorganotin dithiophosphate esters proceeds in high yield from the reaction of a triorganotin hydroxide with the *O,O'*-diorganodithiophosphoric acid (eq 1).

$$R_3SnOH + HSP(=S)(OR')_2 \xrightarrow{\text{benzene}} R_3SnSP(=S)(OR')_2 + H_2O \quad (1)$$

$$R = CH_3;\ R' = C_2H_5$$

$$R = C_6H_5;\ R' = C_4H_9,\ C_6H_5$$

The released water is azeotropically distilled to drive the reaction. Reaction 1 also proceeds in a solvent of the alcohol corresponding to the phosphoric acid ester group (see eq 2).

$$R_3SnOH + HSP(=S)(OR')_2 \xrightarrow{R'OH} R_3SnSP(=S)(OR')_2 + H_2O \quad (2)$$

$$R = C_6H_5;\ R' = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9$$

In addition, triorganotin chlorides react with the alkali metal salts of the dithiophosphoric acid (eq 3). These derivatives

$$R_3SnCl + MSP(=S)(OR')_2 \rightarrow R_3SnSP(=S)(OR')_2 + MCl \quad (3)$$

$$R = C_6H_5;\ R' = CH_3,\ i\text{-}C_3H_7;\ M = Na$$

$$R = CH_3;\ R' = i\text{-}C_3H_7,\ CH_3;\ M = Na$$

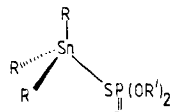
$$R = c\text{-}C_6H_{11};\ R' = i\text{-}C_3H_7;\ M = K$$

have also been synthesized by the protodemetalation of tetraorganotins (see eq 4).[16,18] The organotin dithiophosphate

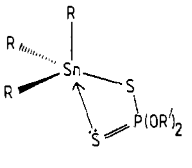
$$R_4Sn + HSP(=S)(OR')_2 \rightarrow R_3SnSP(=S)(OR')_2 + RH \quad (4)$$

esters listed in Table I are colorless, crystalline solids, soluble in polar and nonpolar solvents, except for the trimethyltin derivatives which are liquids or oils in the case of the higher esters. The synthesis of (*O,O'*-diisopropyl dithiophosphato)triphenyltin from the sodium salt of the dithiophosphoric acid was accompanied by the cleavage of the phenyl–tin bond to produce the bis compound.

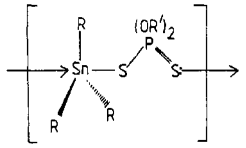
Three different covalent structures (A–C) must be considered for the triorganotin dithiophosphate esters. In addition, an ionic form (D) is also possible. The ionic form (D) and the polymeric form (C) are improbable in view of the good solubility of the species in nonpolar organic solvents. The dithiophosphate group is known to act as a bidentate ligand through sulfur in many transition-metal chelate complexes, but monodentate behavior as in A is apparently extremely rare.[29]



(A)



(B)



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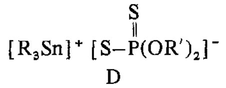

$$[R_3Sn]^+\,[S\text{-}\overset{\overset{\large S}{\|}}{P}(OR')_2]^-$$

D

Infrared Data. Infrared data cannot distinguish between the various structural possibilities since it is impossible to assign with confidence the P—S and P=S stretching frequencies. Thus, for the free acids ($(RO)_2P(=S)SH$) and their esters ($(RO)_2P(=S)SR$), the P—S stretching bands appear in the same region as for the transition-metal complexes $M[S_2P(OR)_2]_n$ which contain bidentate dithiophosphate ligands.[30] The P—S absorptions appear in the ranges 560–530 and 670–630 cm^{-1} [31] and can probably best be described as $\nu_{sym}(PS_2)$ and $\nu_{asym}(PS_2)$, respectively. There seems to be little sensitivity on the part of these frequencies to the groups connected to sulfur.[31,32]

The infrared spectral assignments for our compounds are listed in Table II. It is possible to assign with confidence only the $\nu(CO)$, $\nu_{asym}(PS_2)$, and $\nu(POR)$ bands. The $\nu_{asym}(PS_2)$ absorption is found in the range 675–635 cm^{-1} for our compounds with $\nu(CO)$ at 1170–1095 cm^{-1} and $\nu(POR)$ at 1015–965 cm^{-1}.[33] The $\nu_{sym}(PS)_2$ absorptions apparently obscure the $\nu_{sym}(SnC_3)$ region, thus denying us important information on the configuration of the triorganotin skeleton. The assignment of the $\nu(PS_2)$ modes is done by analogy with those reported for the corresponding organolead,[34] -thallium,[32] and -mercury[35] derivatives.

NMR Data. Proton NMR data are listed in Table III. The spectra exhibit the resonances arising from the aromatic protons in the range 7.00–8.30 ppm and for the organic ester groups attached to phosphorus through oxygen with the expected integrated areas and spin–spin coupling constants. Thus, in the spectrum of $(C_6H_6)_3SnSP(=S)(OCH_3)_2$, the methoxy group signal appears as a doublet arising from the coupling $|^3J(^{31}P\text{-}O\text{-}C\text{-}^1H)| = 15.5$ Hz, and in the ethoxy derivative, the methylene protons appear as a doublet of quartets arising from the coupling $|^3J(^{31}P\text{-}O\text{-}C\text{-}^1H)| = 10$ Hz and the coupling $|^3J(^1H\text{-}C\text{-}C\text{-}^1H)| = 7.0$ Hz with the terminal methyl protons. The methyltin $|^2J(^{119}Sn\text{-}C\text{-}^1H)| = 57.5$ Hz couplings are in the range expected for four-coordinated triorganotin species in the neat liquid or dilute solutions in which they were measured.[36] The magnitude of this coupling increases from 57.5 to 70.0 Hz for the isopropyl ester in pyridine solution, indicating the formation, in situ, of a five-coordinated complex with the pyridine solvent and establishing the lower J value as corresponding to the four-coordinated situation.

Mass Spectrometric Data. The mass spectra of the three trimethyltin dithiophosphate esters show certain similarities, but the cracking pattern is very different for the *O,O'*-dimethyl dithiophosphate compound. In all three spectra the highest mass fragment observed arises from the loss of one methyl group from tin. In none of the spectra are there any fragments

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(29) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65.

(30) Chittenden, R. A.; Thomas, L. C. *Spectrochim. Acta* **1964**, *20*, 1679.

(31) Adams, D. M.; Cornell, J. B. *J. Chem. Soc. A* **1968**, 1299.

(32) Walther, B. *Z. Anorg. Allg. Chem.* **1972**, *395*, 211.

(33) The $\nu((P)\text{-}O\text{-}C)$ and $\nu(P\text{-}O\text{-}(C))$ modes have been assigned to the 1170–1095- and 1015–965-cm^{-1} ranges, respectively, with reference to the data of: Thomas, L. C.; Chittendon, R. A. *Spectrochim. Acta* **1964**, *20*, 489. However, other authors [i.a.: Corbridge, D. E. C. *Top. Phosphorus Chem.* **1969**, *6*, 235] indicate that these stretching modes occur in the 1060–905- and 875–730-cm^{-1} regions, respectively, while bands occurring in the range 1240–1085 cm^{-1} arise from deformation vibrations involving the carbon atom of the P–O–C linkage.

(34) Haiduc, I.; Martinas, F.; Ruse, D.; Curtui, M. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, *5*, 103.

(35) Haiduc, I.; Veres, E. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, *5*, 115.

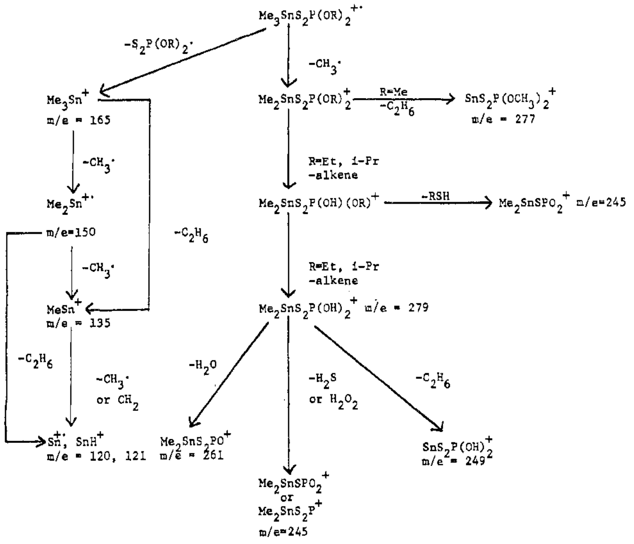
(36) Petrosyan, V. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 115.

Table III. Proton Magnetic Resonance Data for the Triorganotin Dithiophosphate Esters, $R_3SnSP(=S)(OR')_2$

R	R′	$(C_6H_5)_3Sn^a$	$(CH_3)_3Sn^a$	$(C_6H_{11})_3Sn^a$	$H_\alpha{}^{a,b}$	$H_\beta{}^{a,b}$	$H_\gamma{}^{a,b}$
C_6H_5	CH_3	7.1–7.8 m (15)			3.46 d (6) $\|^3J(^{31}P–O–C–^1H)\| = 15.5$		
C_6H_5	CH_2CH_3	7.2–7.8 m (15)			3.91 dq (4) $\|^3J(^{31}P–O–C–^1H)\| = 10.0$ $\|^3J(^1H–C–C–^1H)\| = 7.0$	1.09 t (6) $\|^3J(^1H–C–C–^1H)\| = 7.0$	
C_6H_5	$CH_2CH_2CH_3$	7.2–7.8 m (15)			3.79 t (4) $\|^3J(^{31}P–O–C–^1H)\| = 9.5$ $\|^3J(^1H–C–C–^1H)\| = 6.0$	0.7–1.7 m (10)^{c,d} $\|^3J(^1H–C–C–^1H)\| = 6.0$	
C_6H_5	$CH(CH_3)_2$	7.12–7.87 m (15)			4.71 m (2) $\|^3J(^{31}P–O–C–^1H)\| = 12.0$ $\|^3J(^1H–C–C–^1H)\| = 6.0$	1.15 d (12) $\|^3J(^1H–C–C–^1H)\| = 6.0$	
C_6H_5	$CH_2CH(CH_3)_2$	7.23–7.93 m (15)			3.64 m (4) $\|^3J(^{31}P–O–C–^1H)\| = 9.0$ $\|^3J(^1H–C–C–^1H)\| = 6.5$	1.4–2.0 m (2)^d $\|^3J(^1H–C–C–^1H)\| = 6.5^f$	0.79 d (12)
C_6H_5	C_6H_5	7.0–8.2 m (25)					
CH_3	CH_3		0.66 s (9) $\|^2J(^{119}Sn–C–^1H)\| = 57.0$		3.65 d (6) $\|^3J(^{31}P–O–C–^1H)\| = 15.0$		
CH_3	CH_2CH_3		0.68 s (9) $\|^2J(^{119}Sn–C–^1H)\| = 57.5$		4.16 m (4) $\|^3J(^{31}P–O–C–^1H)\| = 10.0$ $\|^3J(^1H–C–C–^1H)\| = 7.5$	1.36 t (6) $\|^3J(^1H–C–C–^1H)\| = 7.5$	
CH_3	$CH(CH_3)_2$		0.68 s (9) $\|^2J(^{119}Sn–C–^1H)\| = 57.5$		4.83 m (2) $\|^3J(^{31}P–O–C–^1H)\| = 13.0$ $\|^3J(^1H–C–C–^1H)\| = 6.5$	1.36 d (12) $\|^3J(^1H–C–C–^1H)\| = 6.5$	
$CH_3{}^e$	$CH(CH_3)_2$		1.00 s (9) $\|^2J(^{119}Sn–C–^1H)\| = 70.0$		5.02 m (2) $\|^3J(^{31}P–O–C–^1H)\| = 13.0$ $\|^3J(^1H–C–C–^1H)\| = 6.5$	1.38 d (12) $\|^3J(^1H–C–C–^1H)\| = 6.5$	
C_6H_{11}	$CH(CH_3)_2$			1.00–2.50 m (33)^d	4.93 m (2) $\|^3J(^{31}P–O–C–^1H)\| = 12.0$ $\|^3J(^1H–C–C–^1H)\| = 6.0$	1.28 d (12) $\|^3J(^1H–C–C–^1H)\| = 6.0$	

[a] Shifts are in ppm; coupling constants are in Hz; the number of protons in resonance is given in parentheses. Key: s = singlet; d = doublet; t = triplet; m = multiplet; dq = doublet of quartets. All spectra are recorded as $CDCl_3$ solutions, unless otherwise indicated. [b] H_α, H_β, and H_γ refer to $R_3SnS_2P[O(CH_\alpha)_x(CH_\beta)_y(CH_\gamma)_z]_2$. [c] Both H_α and H_β. [d] Satellites unresolvable. [e] Spectrum recorded as a dilute solution in pyridine. [f] For both H_β and H_γ.

Scheme I



of higher mass than the monomeric species should give, nor are there any arising from polytin species, thus ruling out any gas-phase association of these molecules. All three compounds also give prominent species at *m/e* 165 [$(CH_3)_3Sn^+$]; in fact, this is the base peak (relative abundance 100%) for the methyl and ethyl esters.

The major pathway for decomposition of the isopropyl ester appears to be by sequential loss of the alkene from the dithiophosphate group after initial loss of $CH_3\cdot$ from tin. This pathway is also important for the ethyl ester but is not important for the methyl since the latter has no available β-hydrogen for abstraction. Thus, for the isopropyl ester, prominent fragments arise from *m/e* 321 [$(CH_3)_2SnS_2P(OH)(OC_3H_7)^+$] and *m/e* 279 [$(CH_3)_2SnS_2P(OH)_2^+$, base peak] owing to loss of $CH_3CH{=}CH_2$ twice; and for the ethyl ester, fragments at *m/e* 307 and 279 arise from sequential loss of $CH_2{=}CH_2$.

On the other hand, the dimethyl dithiophosphate cannot eliminate the alkene and, therefore, appears to fragment by loss of methyl radicals from tin to give *m/e* 277 [$SnS_2P(OCH_3)_2^+$] and by loss of the entire dithiophosphate group to give *m/e* 165 [$(CH_3)_3Sn^+$, base peak].

Most of the high-abundance fragments are even-electron ions. Odd-electron ions fragment to give high-abundance even-electron ions by loss of radicals such as $CH_3\cdot$ or $(RO)_2PS_2\cdot$. Even-electron species, where possible, lose neutral alkenes to give other even-electron fragments (see Scheme I and Table IV).

Mössbauer Data. The tin-119m Mössbauer data found in Table V are consistent with those of triorganotin(IV) compounds in a four-coordinated form (ρ values <1.8)[37] for the triphenyl- and tricyclohexyltin derivatives. The trimethyltin compounds studied display larger quadrupole splitting (QS) and ρ values, which indicates that the tin atom is in a higher than four-coordinated state. This suggests, along with the NMR $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ coupling constant data, a monomeric, weakly bidentate chelate arrangement for the solid trimethyltins at 77 K as in structure B as one possible configuration, with the triphenyl-, tricyclohexyl-, and methyltin derivatives (the last in the liquid or dilute solution state) adopting the A structure.

Two compounds have been subjected to variable-temperature Mössbauer study, and the results are depicted in Figure 1. The Mössbauer recoil-free fraction (*f*) is a function of the mean-square displacement $\langle x^2 \rangle$ of the tin atom from its equilibrium position as shown in eq 5, where λ is the wavelength of the Mössbauer γ ray divided by 2π. The parameter *f* thus reflects the binding strength of the lattice. For thin absorbers, the recoil-free fraction is linearly related in a Debye

$$f = \exp[-\langle x^2 \rangle / \lambda^2] \qquad (5)$$

Table IV. Mass Spectral Data for $(CH_3)_3SnS_2P(OR)_2$

mass no.[a]	rel abund	assignt
		R = *i*-C_3H_7
363	29.7	$(CH_3)_2SnS_2P(OC_3H_7)_2^+$
321	21.9	$(CH_3)_2SnS_2P(OH)(OC_3H_7)^+$
279	100.0	$(CH_3)_2SnS_2P(OH)_2^+$
261	14.2	$(CH_3)_2SnS_2PO^+$
249	10.7	$SnS_2P(OH)_2^+$
245	19.6	$(CH_3)_2SnSPO_2^+$ (or $(CH_3)_2SnS_2P^+$)
214	12.2	$HS_2P(OC_3H_7)_2^+$?
183	43.0	$(CH_3)_2SnSH^+$
165	47.5	$(CH_3)_3Sn^+$
153	19.8	$SnSH^+$
150	15.0	$(CH_3)_2Sn^+$
135	24.2	$(CH_3)Sn^+$
		R = C_2H_5
335	97.2	$(CH_3)_2SnS_2P(OC_2H_5)_2^+$
307	19.7	$(CH_3)_2SnS_2P(OH)(OC_2H_5)^+$
279	63.0	$(CH_3)_2SnS_2P(OH)_2^+$
261	27.2	$(CH_3)_2SnS_2PO^+$
249	13.1	$SnS_2P(OH)_2^+$
245	29.3	$(CH_3)_2SnSPO_2^+$ (or $(CH_3)_2SnS_2P^+$)
229	14.5	$(CH_3)_2SnSPO^+$
214	21.7	?
211	28.6	?
185	95.1	SnS_2H^+ or $SnPSH_2^+$
165	100.0	$(CH_3)_3Sn^+$
148–157		overlapping clusters
135	61.7	$(CH_3)Sn^+$
121	33.8	SnH^+
120	23.7	Sn^+
		R = CH_3
307	47.5	$(CH_3)_2SnS_2P(OCH_3)_2^+$
277	39.0	$SnS_2P(OCH_3)_2^+$
209–212	12.0–20.0	overlapping clusters
200	32.7	? (no Sn)
197	45.8	$(CH_3)Sn(OCH_3)_2^+$ or $(CH_3)SnP(OCH_2)^+$
185	99.0	SnS_2H^+ or $SnPSH_2^+$
172	40.0	?
165	100.0	$(CH_3)_3Sn^+$
146–155	13.0–40.6	overlapping clusters
135	58.6	$(CH_3)Sn^+$
125	47.3	?
121	22.1	SnH^+
120	28.9	Sn^+

[a] Represents most intense peak for clusters containing tin (based on ^{120}Sn, ^{32}S, ^{16}O, ^{12}C, ^1H, and ^{31}P).

Table V. ^{119m}Sn Mössbauer Data at 77 K

	IS, mm/s[a]	QS, mm/s[b]	Γ_1, mm/s[c]	Γ_2, mm/s[d]	ρ[e]
$(C_6H_5)_3SnS_2P(OCH_3)_2$	1.27	2.07	1.12	1.22	1.63
$(C_6H_5)_3SnS2P(OC_2H_5)_2$	1.26	2.08	1.10	1.24	1.65
$(C_6H_5)_3SnS_2P(OC_3H_7\text{-}i)_2$	1.28	2.03	1.09	1.23	1.59
$(C_6H_5)_3SnS_2P(OC_3H_7\text{-}n)_2$	1.26	2.03	1.08	1.22	1.61
$(C_6H_5)_3SnS_2P(OC_4H_9\text{-}i)_2$	1.28	1.94	1.08	1.50	1.52
$(C_6H_5)_3SnS_2P(OC_6H_5)_2$	1.31	2.32	1.08	1.30	1.77
$(CH_3)_3SnS_2P(OC_2H_5)_2$	1.38	3.09	1.38	1.55	2.24
$(CH_3)_3SnS_2P(OC_3H_7\text{-}i)$	1.35	2.92	1.21	1.28	2.16
$(c\text{-}C_6H_{11})_3SnS_2P(OC_3H_7\text{-}i)_2$	1.52	2.56	1.08	1.32	1.68

[a] ±0.02 mm/s. [b] ±0.03 mm/s. [c] High-velocity resonance, ±0.04 mm/s. [d] Low-velocity resonance, ±0.05 mm/s. [e] QS/IS.

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(37) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.

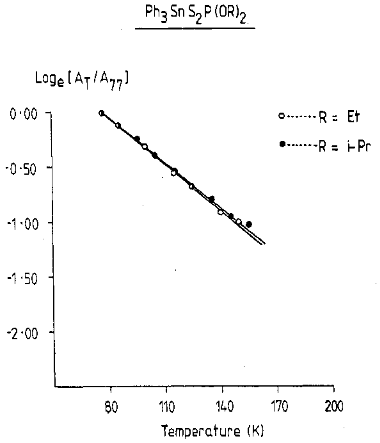

Figure 1. Plot of ln A (normalized to the area under the resonance curve at 77 K) vs. temperature in K. The slopes are -1.43×10^{-2} K^{-1} for the ethyl and -1.40×10^{-2} K^{-1} for the isopropyl ester.

model to the area under the resonance (A_T), and its temperature dependence is given by eq 6 for $T \geq \theta_D/2$, where E_R is

$$A_T \propto f = \exp[-6E_RT/k\theta_D^2] \qquad (6)$$

the Mössbauer recoil energy and θ_D is the Debye temperature of the solid. In the high-temperature limit, plots of ln A_T vs. T should be linear, and the results for the two compounds studied bear this out. For $(C_6H_5)_3SnSP({=}S)(OC_2H_5)_2$ between 77 and 150 K the slope of -1.43×10^{-2} K^{-1} is based upon seven points with intercept at 1.113 and a correlation coefficient of 0.999. For $(C_6H_5)_3SnSP({=}S)(OC_3H_7\text{-}i)_2$ between 77 and 155 K the slope of -1.40×10^{-2} K^{-1} is based upon nine points with intercept at 1.075 and a correlation coefficient of 0.998. These slopes are identical within experimental error and with the isomer shift (IS) and QS data specify that we are dealing here with very similar lattice dynamics in the two cases.

The more tightly bound the tin atoms are in a lattice, the slower appears the decrease in f, and hence A_T, as the temperature is raised. The slope of the plot of ln A vs. T is thus characteristic of the lattice packing of molecules. Noninteracting, monomeric molecules exhibit slopes of ca. -1.8×10^{-2} K^{-1} no matter what the coordination number at tin. A lattice held in part by weak intermolecular interactions such as hydrogen bonding reduces this value to ca. -1.7×10^{-2} K^{-1}. A more complex system of hydrogen bonds can further reduce the slope to ca. -1.3×10^{-2} K^{-1}. Lattices which are strongly hydrogen bonded or lattices in which the tin atom participates in one-, two-, or three-dimensional association exhibit slopes of ca. -1.0×10^{-2} K^{-1}.[38,39] Against this background, the slope of ca. -1.40×10^{-2} K^{-1} found for both the ethoxy and isopropoxy derivatives indicates a monomeric structure packed in a rather tight lattice. Comparison should be drawn with the corresponding slope data for tetraphenyltin (-1.659×10^{-2} K^{-1} [40,41]) for which a spectrum at ambient temperatures can be resolved.[42]

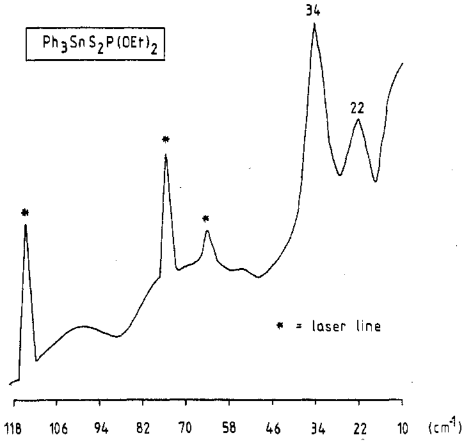

Figure 2. Low-energy, lattice-mode Raman spectrum of (*O,O′*-diethyl dithiophosphato)triphenyltin: λ_0 = 5145 Å at 100 mW.

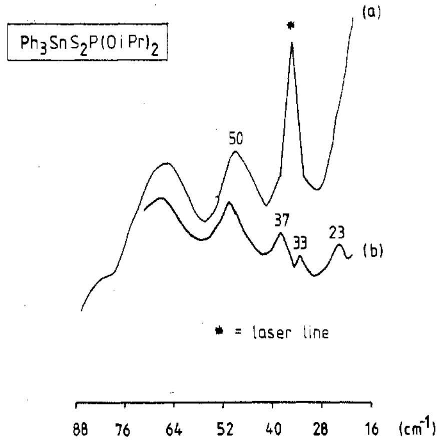

Figure 3. Low-energy, lattice-mode Raman spectrum of (*O,O′*-diisopropyl dithiophosphato)triphenyltin: (a) λ_0 = 4880 Å at 100 mW; (b) λ_0 = 5145 Å at 200 mW.

Table VI. Effective Vibrating-Mass Model: Low-Energy Lattice-Mode Raman Frequencies and $M_{\rm eff}$ Values

	ω	$M_{\rm eff}$	mol wt multiple
$(C_6H_5)_3SnSP({=}S)(OC_2H_5)_2$	22	1487	2.78
	34	623	1.16
$(C_6H_5)_3SnSP({=}S)(OC_3H_7\text{-}i)_2$	23	1390	2.47
	33	675	1.20
	37	537	0.954
	50	294	0.522

The effective vibrating-mass model developed by Herber can be used to obtain the mass of the vibrating unit in the solid from the variation of the recoil-free fraction with temperature and the low-energy (<200 cm^{-1}) lattice mode absorptions in the Raman spectrum.[43] The molecularity of the vibrating unit is calculated from eq 7, where d ln A/dT is the slope of the

$$M_{\rm eff} = -[3E_\gamma^2k/(hc)^2\omega_L^2][dT/d\ln A] \qquad (7)$$

plot of the normalized area under the Mössbauer resonance vs. temperature ($\sim -1.40 \times 10^{-2}$ K^{-1} for the compounds considered in Figure 1) and E_γ is the energy of the Mössbauer γ ray. The low-energy Raman spectra which should contain the lattice mode frequency ω are shown in Figures 2 and 3 for the ethyl and isopropyl esters, while Table VI lists the correlation between the ω frequencies and the $M_{\rm eff}$ values. We are aware of no data in the literature which could serve as a guide for the assignment of the Raman-active bands below 50 cm^{-1}. The molecular weights of the ethyl and isopropyl monomers are 535 and 563, respectively. Thus no band in either spectrum above those found at 34 and 37 cm^{-1}, respectively,

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(38) Harrison, P. G. *Adv. Chem. Ser.* **1976**, *No. 157*, 258.

(39) Harrison, P. G.; Phillips, R. C.; Thornton, E. W. *J. Chem. Soc., Chem. Commun.* **1977**, 603.

(40) Herber, R. H.; Leahy, M. F. *J. Chem. Phys.* **1977**, *67*, 2718.

(41) Reported as -1.60×10^{-2} K^{-1} by: Hazony, Y.; Herber, R. H. "Mössbauer Effect Methodology", Gruverman, I., Seidel, C. W., Eds.; Plenum Press: New York, 1978; Vol. 8, p 107.

(42) Bancroft, G. M.; Butler, K. D.; Shaw, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 1483.

(43) Herber, R. H.; Leahy, M. F. *Adv. Chem. Ser.* **1976**, *No. 157*, 155.

can correspond to the unique intermolecular, intra unit cell vibration sought in this treatment. These two bands correspond to the monomer. None of the other Raman frequencies observed correspond to a reasonable integer unit above the monomer, thus ruling out structure C. This finding corroborates the Mössbauer IS and QS data which specify four-coordination at tin, ruling out structure B, and the magnitude of the slope of the plot of area vs. temperature also rules out a polymeric lattice as in structure C. Thus we are forced to conclude that the triphenyltin dithiophosphate esters adopt a rare, monomeric, monodentate structure such as A.[44]

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Registry No. $(C_6H_5)_3SnS_2P(OCH_3)_2$, 2117-77-3; $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, 2117-78-4; $(C_6H_5)_3SnS_2P(OC_3H_7\text{-}n)_2$, 2117-79-5; $(C_6H_5)_3SnS_2P(OC_3H_7\text{-}i)_2$, 7044-43-1; $(C_6H_5)_3SnS_2P(OC_4H_9\text{-}n)_2$, 2117-80-8; $(C_6H_5)_3SnS_2P(OC_4H_9\text{-}i)_2$, 73002-65-0; $(C_6H_5)_3SnS_2P(OC_6H_5)_2$, 73002-66-1; $(CH_3)_3SnS_2P(OCH_3)_2$, 73002-67-2; $(CH_3)_3SnS_2P(OC_2H_5)_2$, 70558-34-8; $(CH_3)_3SnS_2P(OC_3H_7\text{-}n)_2$, 70558-36-0; $(CH_3)_3SnS_2P(OC_3H_7\text{-}i)_2$, 70573-32-9; $(c\text{-}C_6H_{11})_3SnS_2P(OC_3H_7\text{-}i)_2$, 49538-98-9; $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$, 73002-68-3; $HS(S)P(OC_3H_7\text{-}n)_2$, 2253-43-2; $HS(S)P(OC_4H_9\text{-}i)_2$, 107-55-1; $HS(S)P(OC_2H_5)_2$, 298-06-6; $HS(S)P(OC_4H_9\text{-}n)_2$, 2253-44-3; $HS(S)P(OCH_3)_2$, 756-80-9; $HS(S)P(OC_3H_7\text{-}i)_2$, 107-56-2; $HS(S)P(OC_6H_5)_2$, 2253-60-3; $NH_4S_2P(OC_3H_7\text{-}n)_2$, 1068-31-1; $NH_4S_2P(OC_2H_5)_2$, 1068-22-0; $NH_4S_2P(OCH_3)_2$, 1066-97-3; $NH_4S_2P(OC_3H_7\text{-}i)_2$, 54686-74-7; $NH_4S_2P(OC_4H_9\text{-}n)_2$, 1071-18-7; $NaS_2P(OCH_3)_2$, 26377-29-7; $NaS_2P(OC_2H_5)_2$, 3338-24-7; $NaS_2P(OC_3H_7\text{-}n)_2$, 42401-77-4; $NaS_2P(OC_3H_7\text{-}i)_2$, 27205-99-8; $(C_6H_5)_3SnCl$, 639-58-7; $(C_6H_5)_3SnOH$, 76-87-9; $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_3SnOH$, 56-24-6; tetraphosphorus decasulfide, 12066-62-5; $n\text{-}C_3H_7OH$, 71-23-8; $i\text{-}C_4H_9OH$, 78-92-2; C_2H_5OH, 64-17-5; $n\text{-}C_4H_9OH$, 71-36-3; CH_3OH, 67-56-1; $i\text{-}C_3H_7OH$, 67-63-0; C_6H_5OH, 108-95-2.

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[44] The crystal structure of (*O,O'*-diethyl dithiophosphato)triphenyltin(IV), $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, supports this contention [Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1979**, *18*, 3507].

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Preparation and Properties of a Copper Niobium Oxyfluoride

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A fluorinated phase of copper niobium oxide with the formula $CuNb_2O_{5.3}F_{0.7}$ has been synthesized. The oxyfluoride powder pattern can be indexed on the basis of orthorhombic symmetry with $a = 9.665$ (5), $b = 10.395$ (3), and $c = 7.847$ (3) Å. Magnetic susceptibility data indicate a Curie–Weiss behavior consistent with the quantity of Cu^{2+} (d^9) present. The measured room-temperature resistivity is 0.5 Ω cm, and the electronic activation energy of 0.06 eV indicates some electron delocalization.

Introduction

The chemistry of transition metal oxyfluorides has aroused interest in recent years. In view of the fact that oxygen and fluorine have similar ionic radii[1] the possibility of fluoride incorporation into these systems exists without creation of large structural changes. Such substitutions have been shown to occur in the formation of spinel,[2] magnetoplumbite, garnet,[3] perovskite,[4] and rutile[5] oxyfluorides.

Another group of compounds with rutile related structures are formed when niobium pentoxide reacts with divalent and trivalent ions. In nature the mineral columbite, iron(II) or manganese(II) niobate, occurs with a unique structure. The objective of this work was to prepare and characterize a copper niobium oxyfluoride crystallizing with the columbite structure. The preparation was achieved by a new fluorination technique.

Experimental Section

Material Preparation. The starting material, $CuNb_2O_6$, was prepared by solid-state reaction between CuO, which was synthesized by successive oxidation of metallic copper (Johnson Matthey) under oxygen atmosphere, and Nb_2O_5 (Kawecki Berylco Industries, Inc.). The proper molar ratio of the two oxides was mixed in a high-speed mill and pressed into small pellets. The pellets were then placed on a platinum disk and heated at 1000 °C in a tube furnace for 24 h under a continuous flow of oxygen. The material was obtained as a dark green powder.

Fluorination. The fluorination apparatus[6] consisted of two nickel tubes placed in two separate tube furnaces. HF was generated by means of the thermal decomposition of potassium bifluoride (Research Organic/Inorganic Chemical Corp.), a sufficient quantity of which was placed in a nickel boat and positioned in one of the nickel tubes. The sample was then placed on platinum in a second nickel boat and positioned in the second nickel tube. The two tubes were connected together and also to the carrier gas tanks in such a fashion that as the HF was generated, it was carried by a gas stream which first passed through a flowmeter and a phosphorus pentoxide drying tube and then over the sample and finally exited into a trap containing a 5% solution of sodium hydroxide.

The fluorination reactions were carried out on pressed pellets of copper niobate by using 15% H_2/Ar as the carrier gas which also served as reducing agent. The apparatus described above allowed working temperatures of up to 800 °C. The fluorinations were usually allowed to take place for 4 h. At 800 °C dark brown, well-sintered disks were produced which were then subjected to chemical and physical as well as X-ray measurements.

X-ray Analysis. The X-ray diffraction data were collected on a powder sample by using a Guinier camera with copper Kα radiation ($\lambda = 1.5405$ Å) and silicon ($a = 5.43062$ Å) as an internal standard.

Chemical Analysis. The fluoride content of the sample was leached out by means of sodium hydroxide fusion in a platinum boat. The process was carried out in a closed system to ensure that no fluoride escaped. The fluoride ion concentration was then determined by using a fluorine-sensitive electrode (Orion 94-09) and a Leeds and Northrup 7415 pH meter.

Density Measurements. Density measurements were made by using a hydrostatic technique on Archimedes principle.[7] The liquid medium was perfluoro-1-methyldecaline (Pierce Chemical Co.), and the balance

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(1) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(2) Schieber, M. *J. Appl. Phys.* **1964**, *35*, 1072.
(3) Robbins, M.; et al. *J. Phys. Chem. Solids* **1963**, 24 (6), 759.
(4) Rudorff, W.; Krug, D. *Z. Anorg. Allg. Chem.* **1964**, *329*, 211.
(5) Chamberland, B. L.; et al. *J. Solid State Chem.* **1970**, *2*, 49.
(6) Subbarao, S. N.; et al. *Inorg. Chem.* **1979**, *18*, 488.
(7) Adams, R. L. Ph.D. Thesis, Brown University, 1973.

0020-1669/80/1319-1670$01.00/0