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A Contribution to the Chemistry of Tin(IV) Nitrate

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Triphenylphosphine and -arsine react with tin(IV) nitrate in carbon tetrachloride to afford dinitratotin(IV) bis(diphenylphosphonate and arsonate), $(Ph_2EO_2)_2Sn(NO_3)_2$ *(E = P and As), respectively, as white amorphous solids. These compounds are suggested to have polymeric structures involving bridging phosphonate or arsonate groups and unidentate nitrate groups raising the coordination number of tin to six. Polymeric* $\{OSn(NO_3)_2\}$ *is obtained from the reaction of tin(IV) nitrate with nitric oxide in both carbon tetrachloride solution and the gas phase. Again the tin atom is considered to be six coordinated by oxygen atoms from bridging oxide and bidentate or bridging nitrate groups. Solvolysis occurs on dissolution of tin(IV) nitrate in acetic or trifluoroacetic acids and their anhydrides. From acetic acid or anhydride, tin(IV) acetate,* $Sn(O_2CCH_3)_4$*, was isolated as a white crystalline solid but the nitronium salt* $2NO_2^+\{Sn(O_2CCF_3)_6^{2-}\}$ *was recovered from trifluoroacetic anhydride, whilst the acid solvate* $2NO_2^+\{Sn(O_2CCF_3)_6^{2-}\}\cdot CF_3CO_2H$ *was obtained from trifluoroacetic acid.*

Introduction

Although a large number of nitratotin(IV) derivatives have been characterised and their spectroscopic properties and solid-state structures extensively investigated [1], very few studies of the chemical reactions of this type of compound have been reported. Both trimethyltin nitrate and dimethyltin dinitrate form adducts with pyridine [1a], however, the reaction of diphenyltin dinitrate with a much wider range of bases have been reported. The addition of hot DMSO to a solution of $Ph_2Sn(NO_3)_2$ in anhydrous acetone yields the ionic complex $\{Ph_2Sn(NO_3)(DMSO)_3\}^+NO_3^-$ [2], whilst reaction with di-n-propyl sulphoxide produces μ-oxalatobis(di-n-propylsulphoxide)nitratodiphenyltin [3]. Recrystallisation of the initial product from the reaction of triphenylarsine with $Ph_2Sn(NO_3)_2$ yields $Ph_3SnSn(NO_3)$, in which partial reduction to bivalent tin has occurred [4], whilst an identical procedure using the DMSO complex $\{Ph_2Sn(NO_3)(DMSO)_3\}^+NO_3^-$ affords $(Ph_3Sn)_3SnNO_3$ [5]. Repeated recrystallisation of the initial product from the reaction of $Ph_2Sn(NO_3)_2$ with 2-aminobenzthiazole results in the isolation of a product, (2-aminobenzthiolato)tin(II) nitrate, containing solely bivalent tin [6]. The formation of these bivalent tin products is, to say the least, surprising, since they contain the strongly oxidising nitrate ligand bonded directly to an easily oxidisable bivalent tin atom.

The reactivity of metal nitrates appears to be largely associated with the mode of bonding of the nitrate group, bidentate nitrate exhibiting a far greater reactivity than unidentate nitrate. Tin(IV) nitrate has a structure in which all four nitrate groups chelate the tin atom which experiences distorted dodecahedral eight-fold oxygen coordination [1f]. In this Paper we report our studies of the reactions of tin(IV) nitrate with triphenylphosphine and -arsine, nitric oxide, and acetic and trifluoroacetic acids and their anhydrides.

Experimental

All manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried and freed from oxygen by standard methods. Tin(IV) nitrate was prepared by the method of Addison and Simpson [7]. Pure N_2O_5 was collected at –78 °C, and $SnCl_4$ added in portions with continuous shaking. Excess of reagents were removed by evacuation, and the crude product was sublimed under vacuum (10^{-2} Torr) at 50 °C. Triphenylphosphine and -arsine were commercial products (B. D. H.) and were used without further purification. Commercial nitric oxide was purified by passing through KOH pellets and subsequently a P_2O_5 column. Infrared spectra were recorded as nujol and halocarbon mulls with AgCl windows using a Perkin Elmer 457 spectrometer. Electronic spectra were determined using a Unicam SP800 spectrophotometer. Tin-119*m* Mössbauer

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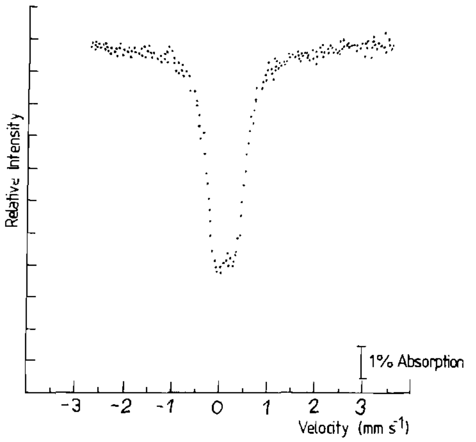


Figure 1. Tin-119*m* Mössbauer spectrum of $(Ph_2PO_2)_2Sn(NO_3)_2$.

data were collected versus a $BaSnO_3$ source at the PCMU (Harwell), and were fitted to Lorentzian line shapes by usual least-squares methods. A typical spectrum is shown in Fig. 1.

Reaction of Tin(IV) Nitrate with Triphenylphosphine

A solution of triphenylphosphine (0.626 g, 2.4 mmol) in CCl_4 was added to a solution of tin(IV) nitrate (0.455 g, 1.2 mmol) also in CCl_4 resulting in the formation of a milky emulsion. After a short time, a pale yellow precipitate was formed together with a feint atmosphere of nitrogen dioxide above the solution. After allowing the precipitate to settle completely, it was filtered off and dried *in vacuo*. Found: C, 43.2; H, 3.0; N, 4.3; Sn, 15.9% $(Ph_2PO_2)_2Sn(NO_3)_2$ requires: C, 42.5; H, 3.0; N, 4.2; Sn, 17.6%.

Reaction of Tin(IV) Nitrate with Triphenylarsine

A turbid solution was formed on the addition of triphenylarsine (1.078 g, 3.5 mmol) in CCl_4 to tin(IV) nitrate (0.647 g, 1.76 mmol) also in CCl_4. A massive white precipitate was then formed suddenly with evolution of nitrogen dioxide and heat. The product was filtered and dried *in vacuo* yielding $(Ph_2AsO_2)_2Sn(NO_3)_2$ as a white amorphous powder. Found: C, 37.7; H, 3.2; N, 3.8; Sn, 15.1%. Required: C, 37.7; H, 2.6; N, 3.7; Sn, 15.5%. The filtrate was yellow in colour, and exhibited bands in the ultraviolet at *ca.* 30,000 (weak), 36,300 (strong) and 37,300 (strong) cm^{-1} characteristic of nitroaromatic compounds (*cf.* nitrobenzene in CCl_4 exhibits bands at 30,000 (weak) and 37,000 (strong) cm^{-1}). When excess triphenylarsine was employed in the reaction, a similar white amorphous solid, which appeared to be $(Ph_3AsO_2SnO(NO_3)_2$ was obtained (found: C, 45.7; H, 3.6; N, 3.3; Sn, 13.1%. Required: C, 47.8; H, 3.3; N, 3.1; Sn, 13.2%), and tetraphenylarsonium nitrate (found: C, 62.1; H, 4.3; N, 3.1%. Required: C, 64.7; H, 4.5; N, 3.4%) was recovered from the filtrate.

Reaction of Tin(IV) Nitrate with Nitric Oxide

Reaction in carbon tetrachloride solution

Pure dry nitric oxide was slowly bubbled through a solution of tin(IV) nitrate in carbon tetrachloride. An immediate reaction was observed, and an intense atmosphere of nitrogen dioxide developed above the surface of the solution. Simultaneously a white precipitate was formed, and the reaction was stopped when the formation of the product was complete. Excess nitric oxide was swept out of the apparatus with nitrogen, and the product filtered and dried *in vacuo*. Found: Sn, 46.8; N, 9.0%. $SnO(NO_3)_2$ requires: Sn, 45.9; N, 9.3%.

Gas phase reaction

The same product was obtained when the two reactants were allowed to mix in the gas phase at 86 °C using nitrogen as the carrier gas in a flow apparatus. An immediate reaction was observed in the zone of mixing with the formation of an intense atmosphere of nitrogen dioxide. The reaction was allowed to proceed for five hours, after which time a thin layer of white solid was trapped by the glass sinter and a dark blue condensate was collected in a –78 °C trap (N_2O_3?). The solid product appeared to be identical to that obtained in CCl_4 solution (found: Sn, 47.0%).

Reaction of Tin(IV) Nitrate with Acetic Acid and Anhydride

A clear solution was initially obtained when tin(IV) nitrate (0.5 g) was dissolved in acetic anhydride (5 ml), but after five minutes white needle crystals began to appear. The reaction mixture was allowed to stand for two hours by which time precipitation of product was complete, and the solution was an intense yellow in colour. The product was filtered off, washed with the minimum of CCl_4, and dried *in vacuo*. Found: C, 25.5; H, 3.1; Sn, 32.8%. $Sn(OOCCH_3)_4$ requires: C, 27.0; H, 3.4; Sn, 33.4%. The same compound slightly solvated by acid was obtained by a similar procedure using acetic acid.

Reaction of Tin(IV) Nitrate with Trifluoroacetic Anhydride

Tin(IV) nitrate (0.5 g) dissolved readily in trifluoroacetic anhydride (0.5 ml) to give a colourless solution which became yellow and then brown on standing. After two hours the solution was an intense brown colour but no solid products were apparent. However, after allowing to stand overnight white needle crystals of the product, $2NO_2^+Sn(O_2CCF_3)_6^{2-}$, and a clear colourless supernatant liquid were obtained. The product was filtered, washed with CCl_4, and dried *in vacuo*. Found: C, 16.2; H, 0.12; N, 3.2; Sn, 13.5%. Required: C, 16.2; H, 0.0; N, 3.15; Sn, 13.35%.

Reaction of Tin(IV) Nitrate with Trifluoroacetic Acid

Tin(IV) nitrate (0.5 g) was dissolved in excess acetic acid and the mixture allowed to stand for three days. A yellow solution was obtained, but no precipitate. Dry CCl_4 was then added and the mixture set aside overnight to permit crystallisation of the product, $2NO_2^+Sn(O_2CCF_3)_6^{2-}\cdot CF_3CO_2H$, which was filtered and dried *in vacuo*. Found: C, 15.45; H, 0.2; N, 2.1; Sn, 12.35%. Required: C, 17.6; H, 0.1; N, 1.5; Sn, 12.4%.

TABLE I. Tin-119*m* Mössbauer Data for $(Ph_2EO_2)_2Sn(NO_3)_2$ (E = P, As) and $\{OSn(NO_3)_2\}$ (mm s^{-1}).

Compound	I. S.	Q. S.	Γ_1[a]	Γ_2[a]	I[b]
$(Ph_2PO_2)_2Sn(NO_3)_2$	0.23	0.79	0.99	0.97	1.11
$(Ph_2AsO_2)_2Sn(NO_3)_2$	0.19	–	2.24	–	–
$\{OSn(NO_3)_2\}$	0.24	0.96	1.18	1.25	1.10
SnO_2[c]	0	0.48			

[a] Full peak width at half height. [b] Relative intensity. [c] Ref. 8.

Results and Discussion

Both triphenylphosphine and -arsine react with tin(IV) nitrate in carbon tetrachloride with the evolution of nitrogen dioxide to give dinitratotin(IV) bis(diphenylphosphonate) (Ia) and bis(diphenylarsonate) (Ib), respectively:

$$Sn(NO_3)_4 + 2Ph_3M \longrightarrow (Ph_2MO_2)_2Sn(NO_3)_2$$

Ia M = P
Ib M = As

The products are white (M = P) and pale yellow (M = As) amorphous solids which are generally insoluble and infusible, suggestive of a polymeric nature. Some corroboration of this hypothesis is available from the tin-119*m* Mössbauer data for the two compounds. Both exhibit resonances with isomer shifts of *ca.* 0.2 mm s^{-1}, very close to that of SnO_2 and $BaSnO_3$ (Table I). That of the phosphorus compound exhibits a small resolved quadrupole splitting, but the spectrum of the arsenic analogue appears only as a very broad (Γ = 2.24 mm s^{-1}) single line characteristic of an unresolved quadrupole splitting. Tin(IV) oxide also exhibits a small splitting as a consequence of the tetragonally distorted octahedral coordination of the surrounding oxygen atoms [8]. It would appear, therefore, that the coordination about the tin atoms in Ia and Ib is similar to that in tin(IV) oxide.

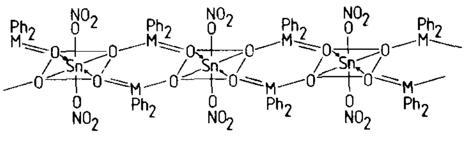
Infrared data for the two compounds are listed in Table II. Coordinated nitrate groups are present in both products, with bands at 1550–1535 ($\nu_{as}(NO_2)$), 1280 ($\nu_s(NO_2)$), 970 ($\nu_s(NO)$) and 790 ($\delta_s(NO_2)$) cm^{-1} typical of unidentate nitrate groups. The analogous bands in $Cs_2Sn(NO_3)_6$ [1a] occur at 1550, 1285, 975 sh, 955, and 795 sh, 790 cm^{-1}. The bands at 1125, 1065 and 483 cm^{-1} in the spectrum of $(Ph_2P)_2)_2Sn(NO_3)_2$ are tentatively assigned to the

TABLE II. Infrared Data for $(Ph_2EO_2)_2Sn(NO_3)_2$ (E = P, As) (cm^{-1}).

$(Ph_2PO_2)_2Sn(NO_3)_2$	$(Ph_2AsO_2)_2Sn(NO_3)_2$	Assignment	
1550 s	1535 s	$\nu_{as}(NO_2)$	(unidentate)
	1530 m		
1485 w	1485 w		
1440 s	1435 s		
1390 w sh			
1335 vw	1340 vw		
1280 s	1280 vs	$\nu_s(NO_2)$	(unidentate)
	1165 m		
1125 vs		$\nu_{as}(PO_2)$	
	1085 s	$\nu_{as}(AsO_2)$	
1065 s		$\nu_s(PO_2)$	
1028 m	1020 w		
1000 m	999 w		
960 vs	970 m	$\nu_s(NO)$	
850 vw	850 w		
790 m	790 s	$\delta_s(NO_2)$	
753 s	740 vs		
	685 vs	$\nu_s(AsO_2)$?	
620 w			
555 sh	560 s br		
545 vs			
483 w		PO_2 scissor	
	470 vs		

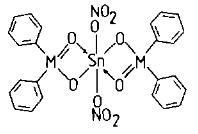
antisymmetric and symmetric PO_2 stretching and PO_2 scissoring vibrations, respectively. The corresponding vibrations in the organotin phosphonates, $R_3SnOP(O)R'_2$ and $R_2SnOP(O)R'R''_2$, occur in the ranges 1119–1141 ($\nu_{as}(PO_2)$), 1042–1071 ($\nu_s(PO_2)$), and 452–490 (PO_2 scissor) [9]. Assignment of the corresponding modes in the arsenic compounds is less satisfactory. The strong band at 1085 cm^{-1} may be assigned as the antisymmetric AsO_2 stretching mode with reasonable confidence. The symmetric mode is also expected to be strong, and therefore cannot be the weak band at 1020 cm^{-1} which is a phenyl ring mode. The most likely candidate for this mode is the very strong band at 685 cm^{-1}, a region where the phosphonate spectrum is blank. Some corroboration is afforded from the spectrum of $Ph_3SnOAs(O)Ph_2$ which exhibits similar bands at 1090 m and 690 s cm^{-1} [10].

Phosphonate and arsonate groups generally function as bridging ligands via phosphoryl and arsonyl oxygen atoms. In the present case, such behaviour would result in a structure such as II in which the tin atom is octahedrally coordinated by oxygen atoms from the two unidentate nitrate groups, and the bridging phosphonate or arsonate groups. Intramolecular coordination as in III cannot be excluded from the infrared data, although the observation of a strong resonance at ambient temperature in the Mössbauer spectra strongly favour the polymeric structure II.



M=P or As

II



III

Nitric oxide reacts with tin(IV) nitrate both in the gas phase and in carbon tetrachloride solution with the evolution of nitrogen dioxide to afford a white amorphous solid of composition $\{OSn(NO_3)_2\}$ (IV):

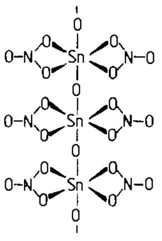
$$Sn(NO_3)_4 + NO \longrightarrow \{OSn(NO_3)_2\} + 3NO_2$$

IV

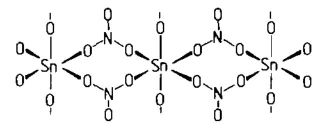
The product is insoluble in all common solvents, again suggesting a polymeric nature, and the ultraviolet spectrum of a sodium hydroxide hydrolysate indicated the presence of nitrate ions only (max. at 31,160 cm^{-1}), and no nitrite ions. The infrared spectrum of IV (Table III) was relatively simple, and exhibited no bands characteristic of NO^+ or NO_2^+ cations, or of molecular N_2O_4, but contained bands at 1600 sh and 1570 ($\nu(NO)$), 1290 ($\nu_s(NO_2)$), 990 ($\nu_{as}(NO_2)$) and 790 ($\delta(NO_2)$) cm^{-1} due to the presence of covalent nitrate groups. A distinction between uni- or bidentate nitrate cannot be made due to the unavailability of Raman data. However, the appearance of a higher energy N–O stretching band (1570, 1600 cm^{-1}) is suggestive of the presence of bidentate or bridging nitrate groups. The broad band at 530 cm^{-1} is assigned to the envelope of Sn–O stretching vibrations. The tin-119*m* Mössbauer spectrum (Table I) was very similar to those of Ia and Ib, and also persisted at ambient temperature indicative of a polymeric structure with six-coordinated tin. The spectroscopic data is therefore consistent with structures such as V and VI containing bidentate and bridging nitrate groups, respectively.

TABLE III. Infrared Data for $\{OSn(NO_3)_2\}$ (cm^{-1}).

Frequency	Assignment	
1600 ms sh 1570 s	$\nu(NO)$	
1290 vs	$\nu_{as}(NO_2)$	(bidentate)
990 vs	$\nu_s(NO_2)$	(bidentate)
833 vw		
790 m	$\delta(NO_2)$	
740 mw		
725 mw		
530 m br	$\nu(Sn–O)$	



V



VI

The product thus is analogous to the compound $OTi(NO_3)_2$ obtained by Gutmann and Tannenburger [11] from the reaction of TiI_4 and N_2O_4, and by Garner [12] from the reaction of $Ti(NO_3)_4$ and N_2O_4.

Tin(IV) nitrate is solvolysed by acetic anhydride or acid to yield tin(IV) acetate VII:

$$Sn(NO_3)_4 + \begin{array}{c}(CH_3CO)_2O\\ \text{or}\\ CH_3CO_2H\end{array} \longrightarrow Sn(O_2CCH_3)_4$$

VII

TABLE IV. Infrared Data of Tin(IV) and Tin(II) Acetate (cm^{-1}).

$Sn(O_2CCH_3)_4$	$Sn(O_2CCH_3)_2$ [a]	Assignment
	2924	ν_1 C–H str.
1335 w	1335	ν_2 CH_3 deform.
1475 s	1395	ν_3 COO symm. str.
973 s	930	ν_4 C–C str.
635 vs	661	ν_5 COO symm. str.
3000 vw	3003–2976	ν_7 C–H str.
1570 s	1530	ν_8 COO antisym. str.
1415 s	1429	ν_9 CH_3 antisym. deform.
1025 ms	1015	ν_{10} CH_3 rock
	481	ν_{11} COO rock
3000 vw	3003–2976	ν_{12} C–H str.
1475 s br	1441	ν_{13} CH_3 deform.
1055 s	1046	ν_{14} CH_3 rock
	611	ν_{15} COO out of plane deform.

[a] Ref. 13.

TABLE V. Infrared Data for $2NO_2^+\{Sn(O_2CCF_3)_6^{2-}\}$ and $2NO_2^+\{Sn(O_2CFF_3)_6^{2-}\}\cdot CF_3CO_2H$ (cm^{-1}).

$2NO_2^+\{Sn(O_2CCF_3)_6^-\}$	$2NO_2^+\{Sn(O_2CCF_3)_6^-\}\cdot CF_3CO_2H$	Assignment
	3200 w br	ν(O–H)
2393 s	2395 s	$\nu_{as}(NO_2^+)$
	2380 s	
	1780 s	$\nu_{as}(CO_2)$ $\{CF_3CO_2H\}$
1740 s	1740s	$\nu_{as}(CO_2)\{CF_3CO_2-Sn\}$
1650 s	1650 s	
1565 m	1565 m	
1480 m	1480 m	$\nu_s(CO_2)\{CF_3CO_2-Sn\}$
1400 vs	1410 vs	$\nu_s(CO_2)$ $\{CF_3CO_2H\}$
	1300 m	
1230 sh	1236 sh	
1170 s	1180 s	
855 w	850 w	
785 m	785 m	
730 m	730 m	
690 w	690 w	
630 w	630 w	
530 w	530 w	

as a white crystalline solid. The infrared spectrum of the product is listed in Table IV together with that of tin(II) acetate [13] and suggested assignments. The separation of the antisymmetric and symmetric ν(COO) frequencies, which is characteristic of the mode of coordination of the carboxylate group, is 95 cm^{-1}. This value compares favourably with the separation in zinc(II) acetate [ν_{as}(COO) 1570 cm^{-1}, ν_s(COO) 1452 cm^{-1}, Δ = 188 cm^{-1}] in which the acetate groups are bidentate [14].

In contrast, tin(IV) nitrate is solvolysed by trifluoroacetic anhydride to yield the nitronium salt VIII as white needle crystals:

$$Sn(NO_3)_4 + (CF_3CO)_2O \longrightarrow \underset{\text{VIII}}{2NO_2^+\{Sn(O_2CCF_3)_6^{2-}\}}$$

The material was insoluble in chlorinated solvents, but was soluble in acetonitrile and ethyl acetate, and dissolved with reaction in benzene, acetone, ethanol and water. A similar reaction occurred with trifluoroacetic acid, from which the solvate $2NO_2^+\{Sn(O_2CCF_3)_6^{2-}\}\cdot CF_3CO_2H$, IX, was isolated. The infrared spectra of both VIII and IX are listed in Table V, and are not unexpectedly similar. Both exhibit strong sharp bands at *ca.* 2390 cm^{-1} assigned to the antisymmetric stretching mode of the NO_2^+ ion, as well as a number of strong bands at *ca.* 1700 cm^{-1} characteristic of unidentate carboxylate groups. In addition, the spectrum of the solvate contains bands at 3200 (ν(OH)) and 1780 cm^{-1} (ν_{as}(COO)) of the solvating CF_3CO_2H. The presence of the nitronium ion was confirmed by the ^{14}N nmr spectrum, which exhibited a resonance at +120 ppm relative to the nitrate anion (*cf.* $NO_2^+Ga(NO_3)_4^-$, $\delta = +126$ ppm).

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