

444. *Dimethyltin Dinitrate.*

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Dimethyltin dinitrate has been prepared by the reaction of tetramethyltin and dinitrogen tetroxide in ethyl acetate solution, and its properties are compared with those of trimethyltin nitrate. The infrared spectrum indicates that the nitrate groups are covalent and unidentate in the solid, and is consistent with a tetrahedral structure. Molar conductivities in water and dimethyl sulphoxide show that the compound is a 1:2 electrolyte in these solvents. The ultraviolet spectra of solutions of the sublimed and unsublimed compound in water, dimethyl sulphoxide, ethyl alcohol, ethyl acetate, and methyl cyanide are discussed. The infrared spectrum of the addition compound $\text{Me}_2\text{Sn}(\text{NO}_3)_2 \cdot 1.5\text{Me}_2\text{SO}$ shows that the sulphoxide acts as a ligand, with consequent weakening of the Sn-NO₃ bonds. Dimethyltin dinitrate is resistant to attack by a solution of dinitrogen pentoxide in chloroform.

RECENT work on trimethyltin compounds, Me_3SnX , has revealed novel features in their structure and properties, and the influence of the group X is not always that which would be expected from its known chemistry. Thus the fluoride, originally thought¹ to be an ionic compound $\text{Me}_3\text{Sn}^+\text{F}^-$, consists of chains of planar Me_3Sn groups linked by bridging fluorine atoms;² acetate³ and perchlorate⁴ groups appear to perform a similar function. In contrast, the nitrate group in trimethyltin nitrate does not act as a bridge between tin atoms, in spite of the fact that in copper nitrate⁵ and basic beryllium nitrate,⁶ for example, it displays ability to bond in this way. The presence of two Sn-C stretching frequencies in the infrared spectrum of Me_3SnNO_3 indicates that the Me_3Sn group is non-planar,⁷ and

¹ Okawara, Webster, and Rochow, *J. Amer. Chem. Soc.*, 1960, **82**, 3287.

² Clark, O'Brien, and Trotter, *Proc. Chem. Soc.*, 1963, 85.

³ Beattie and Gibson, *J.*, 1961, 2585.

⁴ Clark and O'Brien, *Inorg. Chem.*, 1963, **2**, 740.

⁵ Wallwork, *Proc. Chem. Soc.*, 1959, 311.

⁶ Addison and Walker, *Proc. Chem. Soc.*, 1961, 242.

⁷ Okawara, Hathaway, and Webster, *Proc. Chem. Soc.*, 1963, 13.

the nitrate bands can be interpreted on the basis of C_{2v} symmetry.⁴ Bands characteristic of the nitrate ion are absent, although the diammine has the ionic structure $[\text{Me}_3\text{Sn}(\text{NH}_3)_2]^+\text{NO}_3^-$.

We have now prepared dimethyltin dinitrate by the reaction of tetramethyltin with dinitrogen tetroxide. The compound has not previously been reported, although there are early claims to the preparation of diethyltin dinitrate.⁸ Some of its physical and chemical properties have been studied, and are of interest in comparison with those of the dimethyltin dihalides (which are monomeric and tetrahedral⁹) and trimethyltin nitrate.

DISCUSSION AND RESULTS

Dimethyltin dinitrate is a white crystalline solid. It is highly deliquescent, and on exposure to the atmosphere is converted to liquid within one minute, in contrast to trimethyltin nitrate which is not hygroscopic.⁴ On heating, some nitrogen dioxide is evolved, and the compound explodes. The nuclear magnetic resonance spectrum in chloroform solution shows only one peak, at τ 8.48. Under the same conditions, tetramethyltin shows a peak at τ 9.95. This shift to low field suggests that the tin atom in the dinitrate is somewhat electron-deficient compared with its state in tetramethyltin, and is consistent with conclusions drawn from the infrared spectrum.

Infrared Spectrum.—The bands observed, together with suggested assignments, are as follows: 1554vs,sp and 1540vs,sp (asym. NO_2 stretch); 1411w,sp (asym. CH_3 deform.); 1285vs,sp and 1257vs,sp (sym. NO_2 stretch); 1212w,sh; 1208m,sp (sym. CH_3 deform.); 1006m,sp and 996s,sp (N—O stretch); 812w,sh; 800s,sp (NO_3 out-of-plane rock); 760s,sp (CH_3 rock¹); 720w and 702w (NO_2 bend); 588m,sp (Sn—C asym. stretch); 527w,sp cm^{-1} (Sn—C sym. stretch). Various structures for the compound are possible, depending on whether the nitrate group is bonded to the tin as a unidentate, bidentate, or bridging group. The infrared spectrum can be interpreted satisfactorily on the assumption that the molecule is tetrahedral (like the halides Me_2SnX_2 , where X = Cl, Br, or I)⁹ and that all nitrate groups in the solid are covalent and unidentate. The C_{2v} symmetry of the unidentate nitrate gives rise to two stretching vibrations of type A_1 , and one of type B_1 . For a tetrahedral molecule containing two such groups (assuming free rotation of the Sn—O bonds), all three stretching vibrations should be split, as is observed (see above). The two tin-carbon stretching frequencies required by the tetrahedral model are also observed. For bridging or bidentate nitrate groups,^{5,6} a band of frequency *ca.* 1640 cm^{-1} or higher (corresponding to the N=O stretch) is characteristic. No such band occurs in the spectrum for $\text{Me}_2\text{Sn}(\text{NO}_3)_2$, whereas the observed bands at 1554 and 1540 cm^{-1} are quite consistent with the ν_4 vibration of a unidentate $-\text{ONO}_2$ group. For the compound (bipy)Pd(NO_3)₂, for example, $\nu_4 = 1517 \text{ cm}^{-1}$.¹⁰ It is of interest to compare those bands in the spectra of the mononitrate⁴ and dinitrate which are more directly related to bond order (Table I).

TABLE I.

Infrared absorption bands (cm^{-1}).

	Sn—C stretch	Asym. NO_2 stretch	Sym. NO_2 stretch	N—O stretch
$\text{Me}_2\text{Sn}(\text{NO}_3)_2$	588, 527	1554, 1540	1285, 1257	1006, 996
$\text{Me}_3\text{Sn}(\text{NO}_3)$	557, 520	1488	1268	1031

The symmetrical NO_2 stretching frequency is not sensitive to changes in the degree of covalency, but the increase in the asymmetric stretching frequency which occurs in the dinitrate indicates that the Sn—O bonds in this molecule are slightly more covalent than in the mononitrate. Consistent with this, the N—O stretching frequency in the dinitrate is slightly lower than in the mononitrate. This effect alone might have been expected

⁸ Cahours, *Annalen*, 1860, **114**, 354; Löwig, *ibid.*, 1852, **84**, 308.

⁹ Skinner and Sutton, *Trans. Faraday Soc.*, 1944, **40**, 163.

¹⁰ Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

to result in a weakening of the Sn-C bonds in the dinitrate compared with the mononitrate, whereas the reverse is the case (Table 1). Account must also be taken, however, of the fact that each metal-nitrate bond has partial ionic character, and even though this is slightly less with the dinitrate than with the mononitrate, the overall effect of introducing a second nitrate group is to confer a greater positive charge (or electron deficiency) on the tin atom in the dinitrate, with a consequent increase in the Sn-C frequency.

Solution Properties.—Dimethyltin dinitrate is soluble in water and in many polar organic solvents (ethyl alcohol, ethyl acetate, methyl cyanide, dimethyl sulphoxide), giving clear solutions. It has a slight solubility in chloroform, from which it crystallises readily, but is insoluble in carbon tetrachloride, benzene, and nitrobenzene. No solvent suitable for molecular-weight measurements has yet been found, since solution appears to be accompanied by ionic dissociation.

Conductivity of Solutions.—Molar conductivity values for solutions in water and in dimethylsulphoxide are given in Table 2.

TABLE 2.

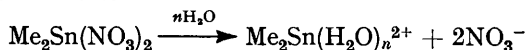
Molar conductivities of solutions of dimethyltin dinitrate at 25°.

In water		In dimethyl sulphoxide	
Molar concn.	Molar conductivity (ohm ⁻¹ cm. ²)	Molar concn.	Molar conductivity (ohm ⁻¹ cm. ²)
0.00025	464	0.001	76.3
0.0005	440	0.0032	67.8
0.001	403	0.0065	59.7
0.014	242	0.012	52.5

The conductivity values in dimethyl sulphoxide agree very closely with those for 1 : 2 electrolytes [*e.g.*, Ba(NO₃)₂] in this solvent.¹¹ No change in conductivity with time was observed at any concentration, and the behaviour is entirely consistent with the immediate ionisation



the solvated Me₂Sn²⁺ ion being a stable species in this medium. The conductivity values in aqueous solution greatly exceed the expected value (*ca.* 240 ohm⁻¹ cm.² at 0.001M) for a 1 : 2 electrolyte. The aqueous solutions were strongly acid, so that the solvated cation produced by the initial ionisation



is presumably unstable, and undergoes further dissociation of the type



to produce highly-conducting hydrogen ions. Equilibria between the various species in aqueous solution are established rapidly, since no variation of conductivity with time was observed, and even after boiling for several minutes, the conductivities of the 0.001M- and 0.014M-solutions were unchanged.

Sublimation.—On heating dimethyltin dinitrate at 85°/10⁻² mm., a crystalline sublimate was obtained. The chemical analysis, infrared spectrum, and X-ray diffraction powder pattern were virtually identical with those of the unsublimed product, but differences between the ultraviolet spectra of solutions prepared from the two products were observed.

Ultraviolet Spectra of Solutions.—The spectrum of an aqueous solution at 25° (Fig. 1, curve A) shows two peaks. The peak at 302 mμ (ε 15.7) corresponds to dissociation of the molecule to give two free nitrate ions in solution. This spectrum is unchanged with time at 25°, but on boiling the solution, the peak at 265 mμ diminished (*e.g.*, curve B) and

¹¹ Addison and Johnson, unpublished results.

eventually disappears leaving curve C as the final spectrum. The spectrum of sublimed dimethyltin dinitrate (curve D) shows only the characteristic 302 $m\mu$ nitrate band, and closely resembles curve C.

The 265 $m\mu$ peak does not arise from impurity, since the spectrum was found to be unchanged throughout the course of extensive recrystallisation and different samples gave the same ϵ value. It is believed to arise from a species in which nitrate groups are covalently bonded to the dimethyltin cation, and which breaks down on boiling the solution. Since the conductivity of the solution is unchanged on boiling, the concentration of this species must be very small, and the high initial ϵ value at 265 $m\mu$ suggests that this is a charge-transfer band. Co-ordination of a nitrate group to a metal atom is

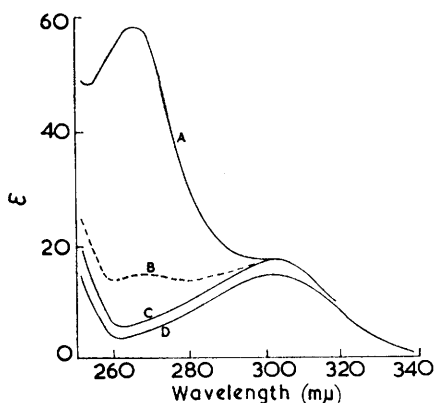


FIG. 1. Ultraviolet spectra of solutions of dimethyltin dinitrate in water. A, fresh solution of unsublimed compound at 25°. B, solution A after heating at 100° for 5 min. C, solution A after heating at 100° for 15 min. D, fresh solution of sublimate at 25°.

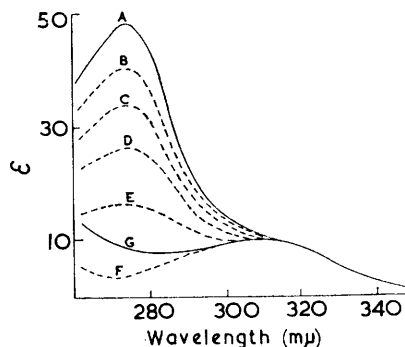


FIG. 2. Ultraviolet spectra of solutions of dimethyltin dinitrate in dimethyl sulphoxide. A, fresh solution of unsublimed compound at 25°. B, C, D, E, and F, solution A held at 25° for $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2 $\frac{1}{2}$, and 22 hr., respectively. G, fresh solution of sublimate at 25°.

already known¹² to give rise, under appropriate conditions, to charge transfer at wavelengths lower than the 302 $m\mu$ characteristic of the free ion. The absence of the 265 $m\mu$ band in solutions of the sublimed product is as yet unexplained. It should be noted, however, that the compound $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_4$ gives a sublimate which has the same chemical analysis, but which gives solutions having quite different properties from those of the unsublimed compound.¹³

The spectra obtained for solutions in dimethyl sulphoxide (Fig. 2) closely resemble those for the aqueous solutions. Initially, two bands are observed at 273 (ϵ 48) and 312 $m\mu$ (ϵ 10.3), and the latter is entirely consistent with ionic dissociation to give two free nitrate ions.¹⁴ However, the spectrum of the dimethyl sulphoxide solution changes with time at 25° (curves B—E, Fig. 2), and the final curve, F, achieved after 22 hours at 25°, shows only the nitrate ion band at 312 $m\mu$. The spectrum of solutions of the sublimate (curve G) is again very similar to that of the final state reached with the unsublimed compound. Dimethyl sulphoxide is a stronger ligand than water, and will more readily displace those nitrate groups which remain co-ordinated to the metal atoms. The 273 $m\mu$ band therefore slowly disappears at 25°, whereas it is necessary to heat the aqueous solution in order that the corresponding replacement can occur.

On the above interpretation, the spectra of solutions in a solvent of much lower

¹² Addison, Hathaway, Logan, and Walker, *J.*, 1960, 4308.

¹³ Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51.

¹⁴ Addison and Sutton, unpublished results.

dielectric constant should present a different pattern, since free nitrate ions should no longer be produced. The spectra of solutions of dimethyltin dinitrate (unsublimed) in ethyl alcohol illustrate this effect (Fig. 3). Only one absorption band now occurs in this region; both ϵ and λ_{max} change with time, but in a way which is more readily interpreted in terms of the weakening of the Sn-NO₃ co-ordinate bond as a result of solvation by ethyl alcohol molecules. The limiting curve, C, is no longer the spectrum of the free nitrate ion. Since ethyl alcohol has a low dielectric constant (*ca.* 25), the free nitrate ion in this solvent would be expected to show an $n_p \rightarrow \pi^*$ transition at longer wavelengths than in water. The observed maximum at 285 m μ indicates that the energy of the ground state of the ion has been lowered as a result of covalent bonding to the metal ion. Similar spectra were obtained for solutions in ethyl acetate and methyl cyanide (Fig. 4), but in these solutions

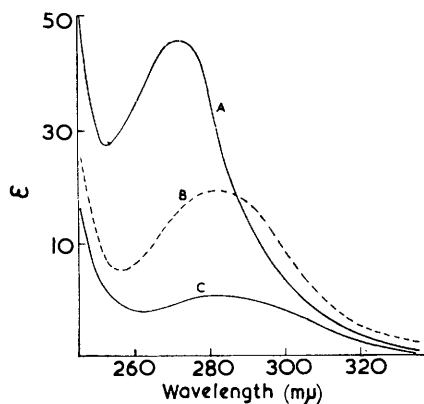


FIG. 3. Ultraviolet spectra of solutions of dimethyltin dinitrate in ethyl alcohol. A, fresh solution of unsublimed compound at 25°. B, solution A after 23 hr. at 25°, or 10 min. at 70°. C, solution A after 4½ hr. at 70°.

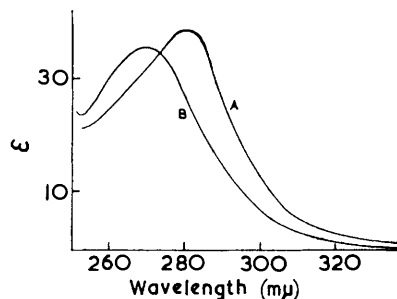


FIG. 4. Ultraviolet spectra of solutions of dimethyltin dinitrate at 25°. A, ethyl acetate solution. B, methyl cyanide solution.

the spectra did not change with time. Only one absorption band occurs, and the spectra are reminiscent of those obtained from solutions of covalent transition-metal nitrates $M(\text{NO}_3)_2$ in these solvents.¹⁴

Addition Compound with Dimethyl Sulphoxide.—Dimethyltin dinitrate crystallises from dimethyl sulphoxide as the solvate $\text{Me}_2\text{Sn}(\text{NO}_3)_2 \cdot 1.5 \text{Me}_2\text{SO}$. Unlike the parent compound, this solvate is not affected by moist air. It is soluble in water and in many polar organic solvents, but is insoluble in non-polar solvents. On heating under a vacuum it melts at 90°, and dimethyl sulphoxide is evolved. In view of the strong ligand properties of dimethyl sulphoxide, the infrared spectrum of the adduct has been examined to determine the extent to which the sulphoxide is acting as a ligand, and the consequences of such bonding on the nature of the tin-nitrate bond. The bands observed, together with suggested assignments, are as follows (* indicates bands associated with the Me_2SO molecule): 2970w* (asym. C-H stretch); 2890w* (sym. C-H stretch); 1496vs,sp and 1463vs,sp (asym. NO₂ stretch); 1424w,sp* and 1410m,sp* (asym. CH₃ deform.); 1328m,sp* (sym. CH₃ deform.); 1302m,sp and 1293vs,sp (sym. NO₂ stretch); 1196w,sp (sym. CH₃ deform.); 1041m,sh*, 1036m,sp*, 1030m,sp*, and 1014s,sp* (CH₃ rock); 993vs, sp(N-O stretch); 954vs,sp* (S=O stretch); 808s,sp and 798s,sh [NO₃ out-of-plane rock and CH₃ (-Sn) rock]; 744w (NO₂ bend); 717w* (asym. C-S stretch); 687w* (sym. C-S stretch); 594m,sp (asym. Sn-C stretch); 435vs,b cm.⁻¹ (Sn-O stretch). The very strong band at 954 cm.⁻¹ is characteristic of dimethyl sulphoxide which is bonded through its oxygen atom

to a metal atom,¹⁵ and the weak bands at 717 and 687 cm^{-1} support this. The broad band at 435 cm^{-1} is absent in the spectrum of $\text{Me}_2\text{Sn}(\text{NO}_3)_2$.

The bond which appears to exist between the tin atom and the oxygen atom of dimethyl sulphoxide in the adduct has its influence on the infrared spectrum of the dimethyltin dinitrate part of the complex. While the spectrum (see above) is still characteristic of covalent nitrate groups, the much smaller difference between the symmetric and asymmetric NO_2 stretching frequencies, compared with dimethyltin dinitrate itself, indicates a weakening of the tin-nitrate bonds on introduction of dimethyl sulphoxide. Only the asymmetric Sn-C stretch is observed at 594 cm^{-1} , the much weaker symmetric stretch being presumably overlapped by the broad and strong Sn-O stretch at 435 cm^{-1} .

Stability of Dimethyltin Dinitrate towards Dinitrogen Pentoxide.—In reactions of transition-metal compounds, dinitrogen pentoxide is sometimes found to be a more effective reagent for introducing nitrate groups than is dinitrogen tetroxide.^{16,17} It was therefore thought possible that the pentoxide might react with dimethyltin dinitrate to give the unknown methyltin trinitrate, or tin tetranitrate. Solutions of the two compounds in chloroform were thus mixed at room temperature, and allowed to stand for 24 hours. When the solvent and pentoxide were then removed under a vacuum, the crystalline residue consisted of pure dimethyltin dinitrate, and there was no evidence that further replacement of methyl groups had occurred under these conditions.

EXPERIMENTAL

Dimethyltin Dinitrate.—Tetramethyltin was prepared by the reaction of methylmagnesium iodide with tin tetrachloride in di-n-butyl ether.¹⁸ The product distilled at 76–77°/760 mm. The reaction of tetramethyltin with pure liquid dinitrogen tetroxide was violent, even at –78°, and mixing was usually accompanied by explosion and fire. However, when these reagents were each diluted with an equal volume of dry ethyl acetate, reaction was smooth at –78°. The tetroxide solution was added in small quantities to the tetramethyltin solution at –78°; after each addition, the mixture was well stirred and allowed to warm to room temperature, during which time vigorous gas evolution occurred and the original green colour faded. This process was continued until the solution retained its green colour at room temperature, and a slight excess of dinitrogen tetroxide was then added. Removal of solvent under a vacuum gave a residue of colourless *crystals*. These were washed with excess of liquid dinitrogen tetroxide, in which dimethyltin dinitrate is slightly soluble. Tin was determined by heating the compound with concentrated sulphuric acid, evaporating the acid, and igniting to tin(IV) oxide [Found: Sn, 43.7; C, 8.8; H, 2.2; N, 10.5. $\text{Me}_2\text{Sn}(\text{NO}_3)_2$ requires Sn, 43.5; C, 8.8; H, 2.2; N, 10.3%].

Addition Compound with Dimethyl Sulphoxide.—Dimethyl sulphoxide was refluxed over powdered molecular sieve for 12 hr., distilled in vacuum, and stored in a stoppered vessel in a dry-box. The absence of water was confirmed from the infrared spectrum. Dimethyltin dinitrate was dissolved in the minimum amount of dimethylsulphoxide at room temperature; small transparent *crystals* were obtained on evaporation of the solution under a vacuum [Found: Sn, 29.7; C, 15.4; H, 3.7; N, 7.2. $\text{Me}_2\text{Sn}(\text{NO}_3)_2 \cdot 1.5\text{Me}_2\text{SO}$ requires Sn, 30.4; C, 15.4; H, 3.8; N, 7.2%].

Infrared spectra were obtained on a Unicam S.P. 100 spectrophotometer, with sodium chloride and potassium bromide optics. Mulls were prepared in Nujol or Halocarbon Oil, Series 11–14. Cell windows in both sample and reference cells were protected by sheets of Polythene. Nujol was not attacked by dimethyltin dinitrate.

Nuclear magnetic resonance spectra were recorded on an A.E.I. instrument R.S. II, at 60 Mc./sec. Tetramethylsilane was used as internal reference for the spectrum of dimethyltin dinitrate in chloroform. The spectrum of tetramethyltin in chloroform was obtained with cyclohexane as internal reference. Electrical conductivities were measured with a conductivity

¹⁵ Cotton, Francis, and Horricks, *J. Phys. Chem.*, 1960, **64**, 1534.

¹⁶ Field and Hardy, *Proc. Chem. Soc.*, 1963, 11.

¹⁷ Bagnall and Jones, *Proc. Chem. Soc.*, 1962, 376.

¹⁸ Edgell and Ward, *J. Amer. Chem. Soc.*, 1954, **76**, 1169.

cell of the type described by Groeneveld and Zuur.¹⁹ Ultraviolet spectra were recorded on a Unicam S.P. 500 spectrophotometer, by using optically matched fused silica cells fitted with ground stoppers. All solvents were scrupulously dried by standard methods.

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¹⁹ Groeneveld and Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.
