96. *Tin*(IV) *Nitrate: The Relation between Structure and Reactivity of Metal Nitrates.*

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Tin(IV) nitrate has been prepared by reaction of dinitrogen pentoxide with tin(IV) chloride, followed by sublimation in vacuum at 40°. Infrared spectra indicate that all four nitrate groups are bonded in the same bidentate manner. The compound reacts readily with aliphatic hydrocarbons, and vigorously with diethyl ether. It is postulated that the species responsible for this reactivity is the NO_3 radical and that this is most readily released from compounds containing bidentate nitrate groups. In the adduct $Sn(NO_3)_4,2py$ the nitrate groups are unidentate, and the adduct does not react with aliphatic hydrocarbons or ethers. The ultraviolet spectra of solutions of tin(IV) nitrate in several solvents are recorded.

TIN(IV) NITRATE was first obtained by Schmeisser from the reactions of tin(IV) chloride with dinitrogen pentoxide,[1] chlorine nitrate,[2] or bromine nitrate.[3] No supporting analytical data were given, and the only physical property so far referred to is its ease of sublimation (40° under vacuum). Attempts to prepare the compound by solvolysis of tin(IV) chloride in dinitrogen tetroxide gave only the tetroxide adduct of the chloride; [4,5] Böhme and Boll [6] obtained a precipitate of the compound $Sn(NO_3)_4,6Et_3N$ from aqueous solutions containing tin(IV) bromide and silver nitrate, but did not separate tin(IV) nitrate from this adduct. Because of its high volatility, the tin–nitrate bonds are clearly covalent, and the nature of these bonds is also of interest in the light of the high chemical reactivity of tin(IV) nitrate. We have therefore prepared the compound by reaction of tin(IV) chloride with dinitrogen pentoxide, followed by sublimation at 40°. Analysis, and some physical and chemical properties, are reported. These results, taken together with recent information on some other reactive nitrates enable us to suggest a relationship between the type of bonding, and the reactivity, of the coordinated nitrate group.

DISCUSSION AND RESULTS

Tin(IV) nitrate is obtained as large, transparent crystals on cold parts of the sublimation apparatus. The condensation process from the gas phase is unusual, in that the vapour condenses on a few established crystals, which grow to several mm. in diameter and rarely merge; most volatile metal nitrates condense initially as a film of minute crystals. On exposure to moist air, nitrogen dioxide is evolved and a film of hydrated tin(IV) oxide develops which is highly cohesive and rapidly inhibits further reaction. The compound is soluble in a wide range of polar organic solvents (*e.g.*, ethyl acetate, pyridine, methyl cyanide, dimethyl sulphoxide), and is unusual in being appreciably soluble also in chloroform and carbon tetrachloride.

Thermal decomposition.—Thermogravimetric analysis was not possible because of the volatility of tin(IV) nitrate. A sample was heated in nitrogen in a closed tube carrying a side-arm and cold finger. The compound melted at 91°; a sublimate of the nitrate appeared on the cold finger at 94°, and at 98° decomposition commenced with evolution of brown fumes. At 110° the melt resolidified to a glass, which was partially soluble on extraction with chloroform. The soluble and insoluble components were tin(IV) nitrate

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[1] Schmeisser, *Angew. Chem.*, 1955, **67**, 493.
[2] Schmeisser and Brändle, *Angew. Chem.*, 1957, **69**, 781.
[3] Schmeisser and Brändle, *Angew. Chem.*, 1961, **73**, 388.
[4] Partington and Whynes, *J.*, 1949, 3135.
[5] Addison and Simpson, unpublished results.
[6] Böhme and Boll, *Z. anorg. Chem.*, 1957, **292**, 61.

and tin(IV) oxide, respectively, so that no intermediate oxide–nitrate appears to be formed under these conditions.

Structure and Chemical Reactivity.—The number and position of infrared absorption bands (see below) indicate that in the tin(IV) nitrate molecule all the nitrate groups are bonded to the metal as bidentate groups. The compound also reacts readily with aliphatic hydrocarbons. These observations, taken together with the behaviour of titanium,[7] zirconium,[8] beryllium,[9] and copper [10] nitrates, lead us to postulate that the species responsible for oxidation of organic compounds by anhydrous metal nitrates is the NO_3 radical, and that this is most readily derived from nitrate groups bonded in bidentate fashion.

Two possible mechanisms have recently been postulated for the reaction of copper(II) nitrate with diethyl ether.[10] The first involves NO_2 radicals produced by the initial dissociation

$$(NO_3)CuO{\cdot}NO_2 \longrightarrow (NO_3)CuO{\cdot} + NO_2{\cdot}$$

The products of reaction are consistent with this mechanism, but the reaction is much more vigorous than any which is known to occur between nitrogen dioxide and ethers at room temperature. The alternative mechanism [10] involves direct release of NO_3 radicals

$$Cu(NO_3)_2 \longrightarrow CuNO_3 + NO_3$$

Powell, Buchholz, and Graham [11] have observed that many gas-phase reactions of nitrogen dioxide can, in fact, be attributed to the small quantity of NO_3 radicals present in kinetic equilibrium in the dioxide. They have confirmed that " NO_3 is a highly reactive species, most if not all of the reactivity of NO_2 with methane or carbon monoxide being attributable to NO_3." This mechanism accounts satisfactorily for both the vigour of the reaction and the reaction products, and more recent evidence on the behaviour of other metal nitrates indicates that this mechanism is the most attractive working hypothesis. The following aspects are relevant:

(*a*) In order to release a NO_3 radical, the metal should have available a lower oxidation state. Reduction to the Cu(I) state would explain why Cu(II) nitrate reacts vigorously with organic compounds, whereas the nitrates of Co(II), Ni(II), and Zn(II) do not. Reduction of Ti(IV) to Ti(III) is not a difficult process, and titanium tetranitrate is so reactive that it will oxidise and nitrate simple aliphatic hydrocarbons.[7] Reduction of Zr(IV) to Zr(III) is more difficult, and zirconium tetranitrate is much less reactive than the titanium compound.[8] From a study of its rate of reaction with Nujol mulling agent, we now find that tin(IV) nitrate reacts with aliphatic hydrocarbons more rapidly than does Ti(IV) nitrate; this is entirely consistent with the ready reduction of Sn(IV) to Sn(II), and the production of two NO_3 radicals in the dissociation

$$Sn(NO_3)_4 \longrightarrow Sn(NO_3)_2 + 2NO_3$$

(*b*) The compounds which can release NO_3 radicals also appear to be those in which the nitrate group is bonded in bidentate fashion. Thus, all nitrate groups are bidentate in tin(IV) nitrate, and in titanium tetranitrate.[12] Copper(II) nitrate is highly reactive in the gas phase, under which conditions both nitrate groups are bidentate,[13] and also in solution in non-aqueous solvents which do not co-ordinate to the copper. In solvents which also act as ligands and thus destroy the bidentate character of the nitrate group (*e.g.*, methyl cyanide), copper(II) nitrate becomes inactive.[10]

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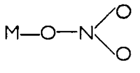
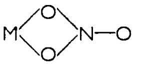
[7] Field and Hardy, *J.*, 1963, 5278.
[8] Field and Hardy, *Proc. Chem. Soc.*, 1962, 76.
[9] Addison and Walker, *J.*, 1963, 1220.
[10] Addison, " Advances in Chemistry," Series No. 36, Amer. Chem. Soc., 1962, p. 131.
[11] Powell, Buchholz, and Graham, *Amer. Chem. Soc. 142nd Meeting Abstracts*, 1962, **142**, 39N.
[12] Addison, Garner, Simpson, Sutton, and Wallwork, *Proc. Chem. Soc.*, 1964, 367.
[13] Bauer and LaVilla, *J. Amer. Chem. Soc.*, 1963, **85**, 3597.

(*c*) It follows from (*a*) and (*b*) above that the NO_3 radical would be most readily released when this group is bonded in bidentate manner to the metal. If NO_3 release involved unidentate bonding as the intermediate step, this conclusion would appear to be untenable, but the only evidence at present available suggests that unidentate bonding is not, in fact, involved. Again, there are no theoretical reasons why bidentate nitrate bonding must necessarily involve two sigma M–O bonds, though the structure is normally written in this way. Bidentate bonding may equally well result from overlap between orbitals of the metal and two oxygen atoms in some form of three-centre bond, in which case all the above observations are mutually consistent.

Infrared Spectrum.—In discussing assignments, it is first necessary to define the terminology to be applied to the vibrational modes for bidentate as opposed to unidentate nitrate groups.


(I)


(II)

Assignments for the unidentate nitrate (I), which belongs to the point group C_{2v}, have been discussed elsewhere.[14] These (see Table) follow the convention that within a point group, vibrational modes are numbered from the highest symmetry species, and, within any given symmetry species, from the highest frequency. Thus, for the unidentate nitrate, the NO_2 symmetric stretch is labelled ν_1, since it is the highest A_1 vibration. The five other absorption bands are then assigned in order. The bidentate group (II) also belongs to point group C_{2v}, so that there are again six vibrational modes. However, as the bond order of the two M–O bonds approaches unity, the terminal N–O bond (structure II) approaches a double bond. The N=O stretching frequency lies in the range 1600—1700 cm.$^{-1}$ (absorption at 1696 cm.$^{-1}$ is assigned [15] to the N=O stretch in the vapour of nitrous acid) so that for the bidentate nitrate group the terminal N–O stretch has the highest frequency, and must be labelled ν_1. The other stretching vibration (the NO_2 symmetric stretch) then becomes ν_2 for the bidentate nitrate. The nomenclature to be used in this and following Papers is set out in the Table, and approximate frequencies (cm.$^{-1}$) are given in parenthesis.

Vibrational modes for unidentate and bidentate nitrate groups.

Assignment	Species	Vibrational mode Unidentate NO_3	Bidentate NO_3
NO_2 symmetric stretch	A_1	ν_1 (1290)	ν_2 (985)
N–O stretch	A_1	ν_2 (1000)	ν_1 (1630)
NO_2 symmetric bend	A_1	ν_3 (740)	ν_3 (785)
NO_2 asymmetric stretch	B_1	ν_4 (1480—1550)	ν_4 (1250)
NO_2 asymmetric bend	B_1	ν_5 (715)	ν_5 (750)
Out-of-plane rocking	B_2	ν_6 (800)	ν_6 (700)

The observed bands (cm.$^{-1}$) for tin(IV) nitrate are as follows (bidentate assignments in parentheses): 1630vs (ν_1), 1255s (ν_4), 983s (ν_2), 807m and 786m (ν_3), 750w, 732w, and 698w (ν_5 and ν_6). The spectrum is remarkably similar to the corrected spectrum for titanium(IV) nitrate.[7] The simplicity of this spectrum and the absence of band splitting, indicates that all nitrate groups are bonded in the same way, and the band at 1630 cm.$^{-1}$ gives strong support for bidentate bonding. In the compound dimethyl tin(IV) dinitrate there is strong evidence that the nitrate groups are unidentate,[16] and the absorption band of highest frequency occurs at 1554 cm.$^{-1}$. The situation is therefore similar to that observed with

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[14] Addison and Gatehouse, *J.*, 1960, 613.

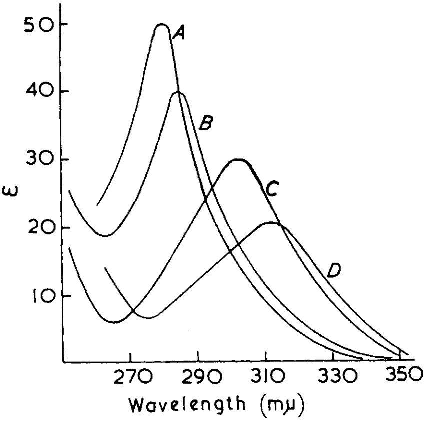
[15] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599.

[16] Addison, Simpson, and Walker, *J.*, 1964, 2360.

the beryllium nitrates. The bridging nitrate groups in basic beryllium nitrate absorb at 1630 cm.$^{-1}$, whereas ν_4 for the simple (unidentate) beryllium nitrate [9] occurs at 1550 cm.$^{-1}$. We therefore regard the metal atom in tin(IV) nitrate as having a co-ordination number of eight, and an examination of the compound by *X*-ray crystallography is in progress.

Reaction with Nujol.—The reaction of tin(IV) nitrate with Nujol mulling agent follows closely the pattern described by Field and Hardy [7] for the reaction of titanium(IV) nitrate with n-dodecane, except for the rate of reaction. The infrared spectrum quoted above was obtained immediately on preparation of the mull, and was confirmed by the spectrum taken with Fluorube as mulling agent. As reaction with Nujol proceeded, the nitrate bands at 1630, 1255, and 807 cm.$^{-1}$ gradually disappeared, and bands at 1565 and 1295 cm.$^{-1}$ (ν_4 and ν_1 for the unidentate nitrate) appeared. The band at 983 cm.$^{-1}$ sharpened, and moved to 992 cm.$^{-1}$. This is consistent with the postulate that only bidentate nitrate groups are reactive; some of the reaction products will no doubt bond to the tin ion, but those nitrate groups which remain are both unidentate and inactive. In addition to new nitrate bands, other bands appear in the spectrum which are characteristic of reaction products, *e.g.* at 3450 cm.$^{-1}$ (C–OH of a carboxylic acid), 1730 cm.$^{-1}$ (C=O of an acid), 1676 cm.$^{-1}$ (ν_4 for an alkyl nitrate), and 1557 cm.$^{-1}$ (nitroalkane). Field and Hardy [7] observed that in the titanium(IV) nitrate reaction, alkyl nitrate bands appeared after 30 min., followed by carboxylic acid and nitroalkane bands after 16 hr. The greater reactivity of tin(IV) nitrate is indicated by clear evidence for the presence of a carboxylic acid after 30 min.

Ultraviolet spectra of solutions of tin(IV) nitrate in A, ethyl acetate; B, methyl cyanide; C, water; D, dimethyl sulphoxide.



Adduct with Pyridine.—This compound has been studied primarily to determine the effect which addition of a ligand such as pyridine to the tin(IV) nitrate molecule has on the metal–nitrate bonds. Tin(IV) nitrate crystallises from pyridine in the form of small, transparent crystals of the bispyridine adduct $Sn(NO_3)_4,2py$. A similar adduct has been reported for silicon tetranitrate.[17] The compound is only slightly hygroscopic. It is soluble in water and many organic solvents to give clear, stable solutions. On heating under vacuum at 75°, a sublimate of tin(IV) nitrate was obtained.

Absorption bands arising from the nitrate groups occurred at the following frequencies: 1552s (ν_4), 1304s (ν_1), 1008m (ν_2), and 827m cm.$^{-1}$ (ν_6). This spectrum is characteristic of unidentate nitrate groups, and the vibrational modes given are assigned on this basis. The ν_4 ν_1 separation (248 cm.$^{-1}$) indicates strong covalency. On the introduction of pyridine into the molecule, therefore, the four bidentate nitrate groups are converted into unidentate groups, and the adduct becomes a 6-co-ordinate complex of tin. Consistent

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[17] Beattie and Leigh, *J.*, 1961, 4249.

with this, the bispyridine adduct does not react with diethyl ether, whereas the parent tetranitrate reacts violently, and no change in the infrared spectrum occurred when the adduct was kept in contact with Nujol mulling agent.

Ultraviolet Absorption Spectra.—The spectra for solutions of tin(IV) nitrate in four solvents are shown in the Figure. No nitrite was formed on solution in water; $\varepsilon_{\text{max.}}$ is 30·1 at 302 mμ corresponding to four nitrate ions per molecule. In dimethyl sulphoxide, $\varepsilon_{\text{max.}}$ is 20·5 at 312 mμ, which again indicates full ionic dissociation.[18] The spectra of solutions in ethyl acetate and methyl cyanide have $\varepsilon_{\text{max.}}$ 50·2 at 281 and $\varepsilon_{\text{max.}}$ 40·1 at 285 mμ, respectively, and are typical of solutions of covalent metal nitrates in these solvents. No time-dependent absorption bands, such as were observed [16] for solutions of dimethyltin dinitrate in water and dimethyl sulphoxide, are present in the spectra of these solutions.

EXPERIMENTAL

Tin(IV) *Nitrate.*—Dinitrogen pentoxide (2—3 g.), prepared from fuming nitric acid and phosphorus pentoxide, was condensed in a flask at −78°, using oxygen–ozone as carrier gas. It was essential to free the pentoxide from any dinitrogen tetroxide, since tin(IV) chloride reacted preferentially with the latter to form the adduct $SnCl_4,N_2O_4$.[5] Tin(IV) chloride (1 g.) was added to the pentoxide at −78°, and the mixture allowed to warm to room temperature with continuous stirring. A smooth reaction took place with fairly vigorous evolution of gas. The mixture was then pumped under vacuum to remove excess of reactants. When the residue was heated under vacuum, a sublimate of ~1·5 g. of tin(IV) nitrate was obtained at 40°.

Nitrogen was determined by the reductive Kjeldahl technique, using Devarda's alloy, and tin by ignition to tin(IV) oxide; to avoid sublimation, the weighed sample was first moistened with concentrated sulphuric acid, after which it could be readily ignited [Found: Sn, 32·2; N, 15·3. $Sn(NO_3)_4$ requires Sn, 32·4; N, 15·3%].

Adduct with Pyridine.—A solution of tin(IV) nitrate in chloroform was added to a solution containing an excess of dry pyridine in chloroform. The solution immediately became bright red, and after 2—3 min. at room temperature, small transparent crystals separated. These were filtered off in a closed system and washed with anhydrous ether. Nitrate was determined as nitron nitrate [Found: Sn, 22·2; NO_3^-, 46·8; C, 23·4. $Sn(NO_3)_4,2C_5H_5N$ requires Sn, 22·6; NO_3^-, 47·3; C, 22·9%].

Spectra.—Infrared spectra were obtained using a Unicam S.P. 200 spectrophotometer. Mulls were prepared in Nujol and Fluorube. Cell windows were of calcium fluoride or sodium chloride; the latter were protected by sheets of polythene in both sample and reference cells. Ultraviolet spectra were recorded on a Unicam S.P. 500 spectrophotometer, matched fused silica cells fitted with ground stoppers being used. Ethyl acetate and methyl cyanide were thoroughly dried, since the slightest trace of water gave rise to a gelatinous suspension.

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[18] Addison and Sutton, unpublished results.