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STRUCTURAL RESEARCHES ON ORGANOTIN(IV) COMPOUNDS. SYNTHESIS AND STRUCTURE OF NITRATOTRIPHENYL(TRIPHENYLPHOSPHINE OXIDE)TIN(IV)

MARIO NARDELLI, CORRADO PELIZZI * and GIANCARLO PELIZZI
Istituto di Chimica Generale ed Inorganice, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma (Italy)

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Summary

A nitrato-complex of organotin(IV) containing triphenylphosphine oxide, $Sn(C_6H_5)_3(NO_3)$ $[(C_6H_5)_3PO]$, has been synthesized and characterized by infrared spectroscopy and X-ray structural analysis. The compound crystallizes in space group $P\bar{1}$, with $a = 11.817(6)$, $b = 11.086(6)$, $c = 12.471(6)$, $\alpha = 99.6(1)$, $\beta = 90.8(1)$, $\gamma = 97.8(1)$, $Z = 2$. The structure has been solved from X-ray diffractometer data by Patterson and Fourier methods and refined by least-squares calculations to $R = 6.4\%$ for 4301 independent reflections. The structure consists of discrete monomer units in which tin shows trigonal bipyramidal geometry.

Introduction

Our studies of the synthesis and the structure of nitrato-complexes of tin have revealed: (i) the interesting behaviour of the coordinated nitrate group in nitratotriphenylstannyltin(II) [1] and in (2-aminobenzothiazolato)nitratotin(II) [2]; (ii) an unusual stereochemistry for tin in μ-oxalato-bis[(di-n-propylsulphoxide)-nitratodiphenyltin(IV)] [3] and in tris(dimethylsulphoxide)nitratodiphenyltin(IV) nitrate [4]; and (iii) the presence of tin—tin bonds in nitratotriphenylstannyltin(II) [1] and in nitratotris(triphenylstannyl)tin(IV) [5]. Our studies are now being extended to nitrato-complexes of organotin systems involving substituted phosphines and arsines and their corresponding oxides as ligands. We describe below the synthesis and characterization of a five-coordinated organotin(IV) complex containing triphenylphosphine oxide.

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* To whom correspondence should be addressed .

Experimental

Nitratotriphenyl(triphenylphosphine oxide)tin (I) was prepared under dry nitrogen by adding 0.001 moles of triphenylphosphine oxide (TPPO) in dry acetone to a stirred solution of nitratotriphenyltin(IV) (0.001 mol) in this same solvent. The solution was set aside at room temperature under nitrogen for 48 h and subsequently slow evaporation of the solvent gave colourless prismatic crystals of formula $C_{36}H_{30}NO_4PSn$ (molecular weight 690.29) (Found: C, 62.6; H, 4.5; N, 2.1; Sn, 17.3. Calcd.: C, 62.6; H, 4.4; N, 2.0; Sn, 17.2%). The same compound was obtained from nitratotriphenyltin(IV) and triphenylphosphine under the same conditions; in this case the triphenylphosphine oxide must be formed by the strong oxidising action of the covalent nitrate group.

The IR spectra were obtained on a Perkin—Elmer model 457 spectrophotometer using Nujol mulls between NaCl plates.

The cell dimensions, accurately determined from diffractometer measurements, and other pertinent crystal data, are as follows: $a = 11.817(6)$, $b = 11.086(6)$, $c = 12.471(6)$ Å; $\alpha = 99.6(1)$, $\beta = 90.8(1)$, $\gamma = 97.8(1)°$; $V = 1594.8$ Å^3, $Z = 2$, $D_{calc} = 1.47$, $D_{obs} = 1.40$ g cm^{-3}, $F(000) = 684$, μ(Mo-K_α) = 8.9 cm^{-1}; space group $P\bar{1}$ (from structural analysis).

A crystal with a mean diameter of 0.16 mm was used for data collection on a Siemens AED diffractometer using Mo-K_α radiation ($\bar{\lambda} = 0.7107$ Å). The intensities of 6953 independent reflections were thus measured within the range 5.0—54.0° in 2θ; of these 4301 were considered "observed" having $I > 2\sigma(I)$. A standard

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ FOR Sn, P; $\times 10^3$ FOR O, N, C) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$		$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$
Sn	185(2)	1945(2)	3089(2)	C(16)	90(2)	—224(3)	152(2)
P	2892(5)	2860(6)	1865(5)	C(17)	57(2)	—201(3)	258(2)
O(1)	168(1)	271(2)	214(1)	C(18)	34(2)	—82(2)	305(2)
O(2)	—244(2)	115(2)	520(2)	C(19)	347(2)	446(2)	199(2)
O(3)	—126(2)	102(2)	391(1)	C(20)	291(2)	533(3)	270(2)
O(4)	147(2)	282(2)	483(2)	C(21)	336(2)	658(3)	285(3)
N	175(2)	170(2)	466(2)	C(22)	435(3)	694(3)	229(3)
C(1)	—85(2)	290(2)	224(2)	C(23)	479(2)	611(3)	152(2)
C(2)	—38(3)	395(3)	182(2)	C(24)	434(2)	487(2)	137(2)
C(3)	—118(3)	454(3)	119(3)	C(25)	382(2)	220(2)	273(2)
C(4)	—229(2)	409(3)	103(2)	C(26)	474(3)	295(3)	335(2)
C(5)	—274(3)	306(3)	144(3)	C(27)	536(2)	238(3)	398(3)
C(6)	198(2)	245(2)	206(2)	C(28)	513(3)	113(3)	401(3)
C(7)	123(2)	272(2)	452(2)	C(29)	420(3)	41(3)	341(3)
C(8)	126(3)	399(3)	494(2)	C(30)	352(2)	95(2)	276(2)
C(9)	204(3)	448(3)	585(3)	C(31)	306(2)	213(2)	49(2)
C(10)	275(2)	375(3)	627(2)	C(32)	394(3)	141(3)	19(2)
C(11)	261(2)	251(3)	582(2)	C(33)	389(3)	86(3)	—94(3)
C(12)	187(2)	199(2)	495(2)	C(34)	311(2)	99(3)	—165(2)
C(13)	46(2)	11(2)	241(2)	C(35)	231(2)	170(3)	—135(2)
C(14)	75(2)	—170(2)	133(2)	C(36)	221(2)	232(2)	—29(2)
C(15)	93(2)	—134(3)	85(2)				

reflection was periodically measured every 20 reflections; its intensity did not vary significantly during data collection indicating that both instrument and crystal stability were good. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction. The atomic coordinates of tin were readily derived from a three-dimensional Patterson map, while the remaining atomic positions for the non-hydrogen atoms were obtained from successive applications of Fourier calculations using an initial set of phases based on the coordinates of tin. Refinement was by block-diagonal least-squares calculations with anisotropic thermal parameters to a conventional R value of 7.2%. The positions of the hydrogen-atoms were calculated and included in the structure factor calculations but not refined. The final R was 6.4%.

The atomic parameters for non-hydrogen atoms are given in Table 1. Lists of final thermal parameters and structure factors can be obtained from the authors. Scattering factors for the non-hydrogen atoms were from Cromer and Mann [6]; those for hydrogen were from Stewart, Davidson and Simpson [7].

All the calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

Results and discussion

Table 2 lists the main bond distances and angles in the compound I. The vibrational bands with relative assignments are listed in Table 3.

A clinographic projection of the structure is shown in Figure 1 together with some relevant bond distances. The tin atom is five-coordinated by three phenyl carbon atoms, an oxygen atom from the NO_3 group, and the oxygen atom from the TPPO molecule. The coordination polyhedron can be described in terms of a slightly distorted trigonal bipyramid with the carbon atoms in equatorial positions. The largest angular distortion from the idealized trigonal bipyramidal

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Sn—O(1)	2.29(2)	O(1)—Sn—O(3)	174.1(7)	O(1)—P—C(19)	111(1)
Sn—O(3)	2.22(2)	O(1)—Sn—C(1)	87.1(7)	O(1)—P—C(25)	114(1)
Sn—C(1)	2.10(2)	O(1)—Sn—C(7)	86.1(8)	O(1)—P—C(31)	110(1)
Sn—C(7)	2.14(2)	O(1)—Sn—C(13)	89.4(7)	C(19)—P—C(25)	106(1)
Sn—C(13)	2.13(2)	O(3)—Sn—C(1)	94.7(8)	C(19)—P—C(31)	108(1)
P—O(1)	1.47(2)	O(3)—Sn—C(7)	97.3(8)	C(25)—P—C(31)	107(1)
P—C(19)	1.79(3)	O(3)—Sn—C(13)	84.9(8)	C(20)—C(19)—P	117(2)
P—C(25)	1.83(3)	C(1)—Sn—C(7)	126.0(9)	C(24)—C(19)—P	122(2)
P—C(31)	1.79(3)	C(1)—Sn—C(13)	120.0(9)	C(26)—C(25)—P	121(2)
N—O(2)	1.22(3)	C(7)—Sn—C(13)	113.4(9)	C(30)—C(25)—P	115(2)
N—O(3)	1.30(3)	Sn—C(1)—C(2)	121(2)	C(32)—C(31)—P	123(2)
N—O(4)	1.22(3)	Sn—C(1)—C(6)	119(2)	C(36)—C(31)—P	115(2)
C(1) ··· C(6) av.	1.41(4)	Sn—C(7)—C(8)	118(2)	Sn—O(3)—N	117(1)
C(7) ··· C(12) av.	1.39(4)	Sn—C(7)—C(12)	119(2)	O(2)—N—O(3)	116(2)
C(13) ·· C(18) av.	1.39(4)	Sn—C(13)—C(14)	120(2)	O(2)—N—O(4)	124(2)
C(19) ·· C(24) av.	1.40(4)	Sn—C(13)—C(18)	121(2)	O(3)—N—O(4)	120(2)
C(25) ·· C(30) av.	1.39(4)	Sn—O(1)—P	153(1)		
C(31) ·· C(36) av.	1.39(4)				

TABLE 3

VIBRATIONAL BANDS (cm^{-1}) AND ASSIGNMENTS

3070 w	ν(CH)	1077 m	β(CH)
3050 w	ν(CH)	1070 (sh)	β(CH)
1765 vw	$\nu_1 + \nu_4$	1010 m	ν(NO)
1705 vw		997 m, (sh)	ring
1580 w	ν(CC)	810 m, w	$\partial(NO_2)$
1570 w	ν(CC)	750 m	γ(CH)
1475 s	ν_{as}(NO)	722 s	γ(CH) + ν(PC)
1430 m	ν(CC)	695 (sh)	—
1420 m	ν(CC)	690 s	φ(CC)
1370 m	ν(NO)	540 s	∂(PC)
1330 w	ν(CC)	530 s	∂(PC)
1290 vs	ν_s(NO)	450 s	ν(PC)
1188 w	β(CH)	440 m	ν(PC)
1150 m	ν(PO)	300 w	∂(PO)
1120 m	ν(PC)	275 (sh)	—
1090 m	2∂(PC)	268 m	ν(SnC)

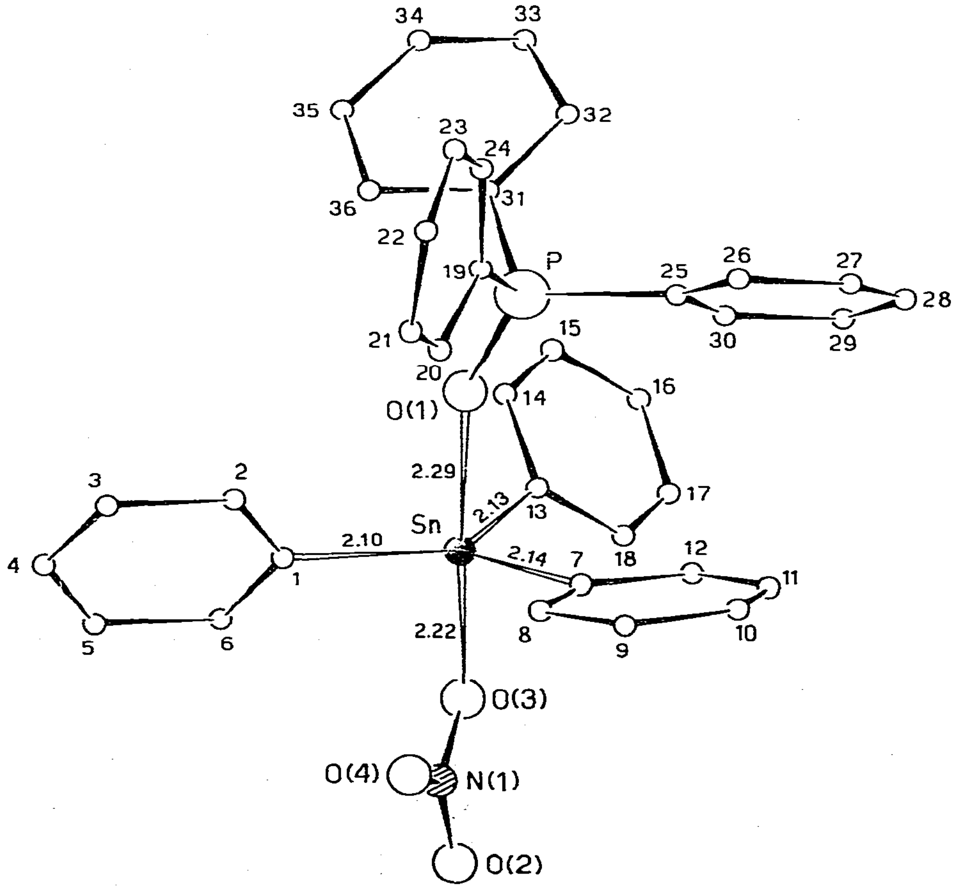


Fig. 1. Clinographic projection of the structure of I. with bond distances in the coordination polyhedron.

geometry, which is characterized by six 90°, three 120° and one 180° angles, is observed for the O(3)—Sn—C(7) angle which is 97.3°.

The crystal is made up of discrete monomer molecules which is unusual for five-coordinated tin. Detailed structural data have been reported only for the eight five-coordinated monomer organotin compounds which are listed in Table 4 together with their bond distances in the coordination polyhedron. All the compounds show distorted trigonal bipyramidal coordinations with the more electronegative ligands bonded preferentially in the axial positions. Moreover, for each type of Sn—X bond, the axial are always longer than the equatorial bonds.

The Sn—C bond distances in complex I fall in the range 2.10—2.20 Å observed for the listed compounds. However, such bond lengths seem, with few exceptions, to be only slightly influenced by the metal coordination number. The tin atom lies 0.09 Å out of the plane formed by the three coordinated carbon atoms. Analysis of the Sn—O bond distances in Table 4 is complicated by the variations in the ligands containing oxygen involved in coordination. A direct comparison can be made only with aquatrimethylnitratotin [8], which also has a nitrate group in the coordination sphere of the metal and which shows an Sn—O distance (viz. 2.22 Å) the same as that in complex I.

Crystal structures have been determined only for a limited number of triphenylphosphine oxide complexes, whose relevant structural parameters are quoted in Table 5, together with those of the orthorhombic [9] and monoclinic [10] polymorphs of the uncoordinated molecule. From the IR data it appears that the ν(P—O) vibration, which appears at 1195 cm^{-1} for the uncomplexed orthorhombic TPPO molecule, shifts to lower frequencies when the molecule is involved in coordination to metals. The rather large range (1048—1194 cm^{-1}) of values is associated with the variation of the central metal [11,12]; on the other hand the value of 1150 cm^{-1} observed in compound I agrees fairly well with those found for substituted phosphine oxide-complexes of tin halides (1125—1167 cm^{-1}) [13].

In contrast with the infrared data, the X-ray results do not show significant differences in the structural parameters compared with those for uncoordinated TPPO. As for bond distances and angles for TPPO complexes it can be noted that the range of values is slightly larger for bond distances (P—O = 1.43—1.53 Å; P—C = 1.75—1.83 Å) than for bond angles (O—P—C = 110—114°, C—P—C = 105—109°; P—C—C = 118—122°).

Both linear and bent coordination by TPPO have been observed, as can be seen from the values of the M—O—P angles quoted in Table 5, which range from 131 to 180°. In view of the rather limited number of entries in this table, a discussion on the metal—oxygen distance would not be appropriate.

Since this is the first Sn—TPPO adduct, no comparison is possible with strictly analogous adducts. However, two compounds have been found to have Sn ··· P interactions via O: $SnCl_4 \cdot 2POCl_3$ [14] and $[(SnCl_3POCl_3)^+(PO_2Cl_2)^-]_2$ [15]. The Sn—O bond distances in these compounds are not far from that found in our compound (2.25, 2.30 Å for the first compound; 2.15 Å for the second).

The nitrate group acts as a unidentate ligand through O(3) (Sn—O = 2.22) with a second oxygen atom, O(4), at 3.07 Å from tin. This mode of coordination is typical for the NO_3 ion and falls in the group of the unidentates with local C_s symmetry identified by Addison and coworkers [16], who emphasized

(continued on p. 271)

TABLE 4

BOND DISTANCES (Å) IN THE COORDINATION POLYHEDRON OF FIVE-COORDINATED MONOMER ORGANOTIN(IV) COMPOUNDS [a]

	Distance								
	I	II	III	IV	V	VI	VII	VIII	IX
Sn—C	2,11(5) e [b] 2,12(4) e	2.17(5) e 2.20(5) e	⟨2.12⟩ e	2,10(2) e 2,12(1) e 2,12(1) e	2,131(7) e 2,142(9) e 2,176(9) a [b]	2,149(7) e 2,181(6) e 2,180(6) a	2,10(2) e 2,11(2) e	2,143(9) e 2,125(10) e 2,130(9) e	2,10(2) e 2,13(2) e 2,14(2) e
Sn—O				2,22(3) a 2,47(2) a	2,091(5) e 2,308(4) a	2,094(7) e 2,276(7) a	2,68(1) a	2,332(6) a	2,22(2) a 2,29(2) a
Sn—Cl	2.32(1) e 2.53(2) a 2.55(2) a	2,46(1) a	2,572(4) a 2,696(3) a				2,403(6) a 2,347(6) e	2,565(2) a	
Sn—S		2,48(1) e 2,79(1) a							

[a] I = 2,2′,2″-terpyridyl(dimethyl)monochlorotin(IV) dimethyl(trichloro)stannate(IV) [30]. II = dimethyltinchloride *N*,*N*-dimethylthiocarbamate [31]. III = tri-(cyclopentadienylmolybdenum)tetrasulfidetrimethyldichlorotin [32]. IV = aquatrimethylnitratotin [8]. V = *N*-benzoyl-*N*-phenyl-*O*-(triphenylstannyl)hydroxylamine [33]. VI = (1,3-diphenylpropane-1,3-dionato)triphenyltin [34]. VII = dichlorodimethyltin-salicylaldehyde (1/1 adduct) [35]. VIII = chlorotrimethyl(triphenylphosphoranylideneacetone)tin [36]. IX = nitratotriphenyl(triphenylphosphine oxide)tin (present work). [b] e = equatorial; a = axial.

TABLE 5

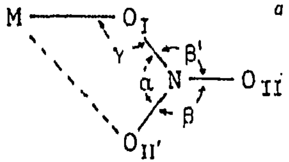
BOND DISTANCES, BOND ANGLES AND VIBRATIONAL FREQUENCIES IN TPPO AND ITS METAL-COMPLEXES [a]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
Bond distances (Å)													
M—O			1.89(2)	1.958(4)	2.12(2)	2.31(2) 2.29(2) 2.43(2)	2.216(7) 2.222(7)	2.33(2) 2.37(2)	2.37(3)	2.34(2)	2.34(1)	2.242(7)	2.29(2)
P—O	1.46(1)	1.49(1)	1.51(2)	1.492(4)	1.50(2)	1.50(2) 1.52(2) 1.50(2)	1.531(8) 1.526(8)	1.43(2) 1.47(2)	1.49(4)	1.49(3)	1.47(2)	1.524(7)	1.47(2)
P—C(mean)	1.76(1)	1.82(1)	1.83(4)	1.80(1)	1.80	1.79(3)	1.82(1)	1.80(3)	1.75(5)	1.82(5)	1.81(2)	1.80(1)	1.80(3)
Bond angles (°)													
M—O—P			180(—)	150.9(3)		131(1) 160(1) 152(1)	169.2(5) 173.2(4)	170.2(1)	143(1)	162(2)	159(1)	165.1(5)	153(1)
O—P—C(mean)	111.3(5)	112.4(9)		111.2(5)		110(1)	109.7(5)	110.1(7)	111(3)	114(2)	111(1)	110.0(5)	112(1)
C—P—C(mean)	107.1(7)	106.2(6)		107.7(3)			109.2(5)	108.7(8)	108(3)	105(2)	108(1)	108.9(6)	107(1)
P—C—C(mean)	121(1)	119(1)		120.2(6)		118(2)	120(1)	119(2)	122(4)	119(3)		120(1)	119(1)
Vibrational frequencies (cm^{-1})													
ν(P—O)	1195		1194 1125				1048		1138 1120	1130 1117	1132 1120	1068	1150

[a] I = TPPO (orthorhombic form) [9]. II = TPPO (monoclinic form) [10]. III = $Cu_4OCl_6(TPPO)_4$ [37]. IV = $CuCl_2(TPPO)_2$ [38]. V = $[MnI(TPPO)_4][MnI_2(CO)_4]$ [39]. VI = $Hg_2(TPPO)_6(ClO_4)_2$ [40]. VII = $Ce(NO_3)_4(TPPO)_2$ [41]. VIII = $Th(NO_3)_4(TPPO)_2$ [42]. IX = $[UO_2(CH_3COO)_2TPPO]_2$ [43]. X = $UO_2[(C_2H_5)_2NCS_2]_2TPPO$ [44]. XI = $UO_2(CH_3CS_2)_2TPPO$ [45]. XII = $UCl_4(TPPO)_2$ [46]. XIII = $Sn(C_6H_5)_3(NO_3)TPPO$ (present work).

TABLE 6

DIMENSIONS OF UNIDENTATE NITRATO GROUPS (Å AND DEGREES) IN METAL COMPLEXES, TOGETHER WITH THE COORDINATION NUMBER OF THE METAL AND THE CONVENTIONAL R VALUES



[a]

Complex [b]	Metal	Coordination number	$\mathrm{M{-}O_{I}}$	$\mathrm{M{-}O_{II'}}$	$\mathrm{N{-}O_{I}}$	$\mathrm{N{-}O_{II'}}$	$\mathrm{N{-}O_{II}}$	α	β	β'	γ	R(%)
I	Ni(II)	6	2.08(1)	3.22 [c]	1.28(2)	1.23(2)	1.22(2)	118.7(7)	121.0(7)	120.2(7)	127.4 [c]	8.8
II	Ni(II)	6	2.101(2)	3.24	1.267(3)	1.232(4)	1.258(3)	121.6(3)	121.0(3)	117.4(3)	127.0(2)	4.4
III	Cu(II)	5	1.966(5)	2.802(7)	1.316(9)	1.227(10)	1.222(9)	119.5(5)	123.1(5)	117.3(5)	112.8(5)	7.5
			1.967(5)	2.750(7)	1.304(8)	1.221(8)	1.234(9)	117.9(5)	125.6(5)	116.4(5)	113.2(5)	
IV	Cu(II)	5	2.355(8)	3.126 [c]	1.26(1)	1.22(1)	1.21(1)	119.6(9)	121.9(10)	118.5(9)	115.8 [c]	11.0
V	Cu(II)	5	1.969(3)	2.889 [c]	1.278(4)	1.215(6)	1.218(4)	119.1(3)	121.2(3)	119.7(3)	118.2(2)	3.0
VI	Cu(I)	4	2.206(6)	3.249(2)	1.166(8)	1.247(8)	1.209(8)				[d]	8.1
VII	Au(III)	4	2.02(2)	2.85(2)	1.34(2)	1.24(3)	1.14(3)	118(2)	129(2)	114(2)	114(2)	6.1
			1.99(1)	2.87(2)	1.39(3)	1.22(3)	1.20(2)	118(2)	131(2)	112(2)	114(1)	
VIII	Mn(III)	7	1.896(8)	3.05(1)	1.24(1)	1.23(2)	1.12(1)	112(1)	116(1)	130(1)	131.3(8)	5.9
IX	V(V)	7	1.92(2)	3.12(3)	1.45(3)	1.19(3)	1.24(3)	122(2)	107(2)	130(3)	118.5 [c]	9.5
X	Sn(IV)	7	2.22(3)	3.23 [c]	1.33(2)	1.18(2)	1.26(2)	104(2)	118(2)	134(2)	127(2)	3.9
XI	Sn(IV)	5	2.22(2)	3.07(2)	1.30(3)	1.22(3)	1.22(3)	120(1)	124(2)	116(2)	117(1)	6.4

[a] The labelling of the distances and the angles is following Addison and coworkers [16]. [b] I = tribenzo[*b,f,j*][1.5.9]triazacycloduodecanenickel nitrate [47]. II = bisaquonitratobispyridenenickel [48]. III = bis(pyridine *N*-oxide)copper nitrate [49]. IV = bis(1,4-diazacycloheptane)copper nitrate hemidrate [50]. V = triaquanitratocaffeinecopper nitrate [51]. VI = nitratotris(diphenylmethylphosphine)copper [25]. VII = potassium tetranitratoaurate [52]. VIII = trinitrato-2,2'-bipyridylmanganese [53]. IX = vanadium oxide trinitrate-acetonitrile complex [26]. X = aquatrimethylnitratotin [8]. XI = nitratotriphenyl(triphenylphosphine oxide)tin (present work). [c] These values were calculated by us on the basis of the coordinates given by the authors. [d] The angles were not reported. Since no coordinates are given, it is impossible to carry out calculations.

the ability of this ion to display a wide range of modes of coordination. The difference (0.85 Å) between the two Sn—O distances lies at the lower limit of the range, 0.8—1.1 Å, taken by Addison and coworkers as excluding bidentate behaviour for the NO_3 group.

The relevant structural parameters of unidentate nitrato groups found from accurate structural analyses are listed in Table 6. Compounds for which sufficient structural information has not been published [17-19] are omitted from the table, as are those characterized by weak M—O interactions [20-24].

Inspection of the data shows that the differences in bond distances and angles are due to bonding effects, since the $N—O_I$ bonds (ranging from 1.24 to 1.39 Å) which involve coordinated oxygen atoms are longer than the others, and consequently the O—N—O angle (β) opposite this bond is larger than the other two and usually greater than 120° (116—131°). Only two structures show unusual values for the NO_3 groups: nitratotris(diphenylmethylphosphine)copper(I) [25] in which steric and electronic factors seem to be responsible for the unexpectedly short $N—O_I$ bond (1.166) and the vanadium oxide trinitrate-acetonitrile adduct [26] in which the $N—O_I$ length of 1.45 Å and the β angle of 107° are significantly different from the usually observed values.

The α and β' angles are both less than 120° for nearly all the compounds listed in Table 6, in agreement with the observations of Addison et al. [16], but there is no clear tendency for α to be $> \beta'$. While this is observed for eight of the nine nitrato groups reported by Addison et al., seven of the twelve nitrato groups quoted in Table 6 show $\alpha > \beta'$, five $\beta' > \alpha$. Moreover, for most of the compounds, the $N—O_{II'}$ (1.18—1.25 Å; mean 1.22 Å) and $N—O_{II}$ (1.12—1.26 Å; mean 1.21 Å) bonds are not significantly different indicating that there is no significant bonding between metal and $O_{II'}$. As usual, the M—O—N (γ) angle is greater than 110° as a consequence of steric hindrance in unidentate coordination [27].

The infrared absorption does not give clear evidence for the unidentate behaviour of the nitrate group. In fact the 1290 and 1475 cm^{-1} bands, which are due to the splitting of the ν_3 band (at ca. 1390 cm^{-1} for an ionic nitrate [16]), and the splitting (60 cm^{-1}) of the $\nu_1 + \nu_4$ combination band at 1765 and 1705 cm^{-1} are more indicative of bidentate than unidentate behaviour [28,29]. In addition, a small shift to lower frequencies (1010 and 810 cm^{-1}) is observed for ν_1 and ν_2, which appear at 1025 and 817 cm^{-1}, respectively, for an ionic nitrate [16]. We were unable to find any bands which could definitely be assigned to ν_4, as the phenyl vibrations interfere with the assignment of the nitrate bands.

Bond distances and angles in the phenyl rings vary within the normal limits for structures of this kind; the departures from the theoretical values for bond distances (max. 0.08 Å) and angles (max. 5°) are not significant.

The three phenyl rings bonded to metal are differently oriented with respect to the coordination equatorial plane formed by C(1)C(7)C(13). One of these rings, C(7) ··· C(12), lies almost in that plane (the dihedral angle being 8.5°), while the other two are tilted in the opposite direction by nearly the same angle [C(1)C(7)C(13)—C(1)···C(6) = 61.1°; C(1)C(7)C(13)—C(13)···C(18) = —50.6°].

The closest non-hydrogen contacts occur between carbon and oxygen atoms not involved in metal coordination: O(2) ··· C(18) ($\bar{x}, \bar{y}, 1-z$) = 3.33; O(2) ··· C(29) ($\bar{x}, \bar{y}, 1-z$) = 3.23; O(2) ··· C(28) ($x-1, y, z$) = 3.21; O(4) ··· C(9) ($\bar{x}, 1-y, 1-z$) = 3.40 Å.

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