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STRUCTURAL RESEARCHES ON NITRATO COMPLEXES OF ORGANOTIN: COORDINATIVE INTERACTIONS Sn—O IN NITRATOTRIPHENYL(PYRIDINE *N*-OXIDE)TIN(IV)

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Summary

A molecular adduct of nitratotriphenyltin with pyridine *N*-oxide, $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{NO}_3)(\text{C}_5\text{H}_5\text{NO})]$, has been synthesized and characterized by infrared spectroscopy and X-ray structural analysis. The compound crystallizes in space group $P2_1/n$, with a 10.59(1), b 17.59(2), c 11.71(1) Å, β 93.0(1)°; Z 4. The structure has been determined from diffractometer data by the heavy-atom technique and refined by least-squares calculation to R 5.0% for 2416 independent reflections. The tin atom has a slightly distorted trigonal bipyramidal coordination, with the unidentate nitrate group and the pyridine *N*-oxide at the apices of the bipyramid and the phenyl rings in equatorial positions. X-ray results are correlated with the spectroscopic data.

Introduction

It is well known that organotin compounds show biological activity towards most types of living species. In particular, the triphenyltin derivatives are highly fungitoxic and have been used in various agricultural contexts to provide resistance against fungal attack [1,2,3].

The synthesis and the chemical investigation of molecular adducts of triphenyltin(IV) derivatives with oxygen-containing donor molecules are in progress in our laboratory [4]. The present paper deals with the synthesis of nitratotriphenyl(pyridine *N*-oxide)tin(IV) and its characterization by infrared spectroscopy and X-ray analysis.

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TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS (\AA^2) u , WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR NON-HYDROGEN ATOMS

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(a)$	$B_{22}(a)$	$B_{33}(a)$	$B_{12}(a)$	$B_{13}(a)$	$B_{23}(a)$
Sn	1869(1)	2068(0)	2388(1)	4.33(2)	5.03(3)	6.35(3)	-0.14(3)	0.52(2)	0.06(3)
O(1)	2538(6)	1725(4)	4165(6)	5.5(3)	9.2(4)	7.3(4)	-0.5(3)	1.8(3)	1.5(3)
O(2)	654(6)	1674(5)	4684(7)	6.1(4)	8.9(5)	10.3(5)	-0.3(3)	1.3(4)	-1.3(4)
O(3)	2163(9)	1259(5)	5773(7)	1.27(6)	9.8(5)	7.3(4)	3.2(5)	1.4(4)	1.9(4)
N(1)	1778(8)	1548(5)	4880(7)	6.4(4)	6.3(5)	7.2(5)	0.9(4)	0.1(4)	0.1(4)
C(1)	1023(8)	3099(5)	2820(8)	4.3(4)	5.2(5)	6.4(5)	0(3)	0(3)	0.3(4)
C(2)	-257(9)	3146(6)	2956(10)	5.5(5)	5.7(6)	9.9(7)	0.3(4)	-0.8(5)	-0.9(6)
C(3)	-832(10)	3835(7)	3162(12)	4.9(5)	7.7(7)	14.1(10)	1.8(5)	-0.2(6)	-1.0(7)
C(4)	-147(11)	4479(6)	3251(11)	9.2(7)	5.3(5)	11.1(8)	1.8(5)	0(6)	-0.9(6)
C(5)	1102(11)	4451(6)	3134(11)	8.1(7)	5.3(5)	12.5(9)	-0.8(5)	1.6(6)	-0.2(6)
C(6)	1691(10)	3771(6)	2942(10)	6.6(6)	6.0(6)	9.8(7)	0.1(5)	1.4(6)	-0.7(5)
C(7)	3840(7)	2069(5)	2124(7)	4.8(4)	4.8(4)	5.5(4)	-0.1(4)	0.8(3)	1.0(4)
C(8)	4673(8)	2535(5)	2765(9)	5.4(5)	5.2(5)	7.5(6)	-0.4(4)	0.5(4)	1.4(4)
C(9)	5953(9)	2511(6)	2361(9)	5.1(5)	8.2(6)	7.5(6)	-1.1(4)	-0.6(4)	2.1(5)
C(10)	6399(9)	2058(7)	1753(10)	4.9(4)	8.8(6)	9.6(7)	1.0(5)	1.2(4)	3.0(6)
C(11)	5586(10)	1600(6)	1109(10)	7.3(6)	7.0(6)	8.2(6)	1.7(5)	1.5(5)	0.6(5)
C(12)	4296(8)	1613(5)	1298(8)	5.3(4)	5.5(5)	7.3(6)	0.2(4)	0.7(4)	0.7(4)
C(13)	767(8)	1081(5)	2084(9)	4.8(4)	5.2(5)	7.7(6)	-0.3(4)	1.4(4)	-0.8(4)
C(14)	-208(10)	1072(6)	1270(11)	6.0(5)	6.3(6)	12.8(9)	-1.6(5)	0.1(6)	-0.6(6)
C(15)	-995(11)	431(8)	1096(14)	6.4(6)	10.2(9)	16.1(12)	-1.3(6)	-1.5(7)	-0.6(8)
C(16)	-736(12)	-180(7)	1774(14)	8.2(7)	6.3(7)	14.8(13)	-2.3(6)	0.8(8)	-1.4(7)
C(17)	193(12)	-193(6)	2568(12)	8.7(7)	5.2(6)	14.9(10)	0.5(5)	3.1(7)	0.5(6)
C(18)	955(10)	433(6)	2751(10)	6.9(6)	4.7(5)	11.3(8)	4.6(4)	2.3(5)	-0.6(5)
N(2)	1603(6)	3052(4)	162(6)	4.5(3)	5.6(4)	6.3(4)	0.1(3)	-0.3(3)	0(3)
C(19)	653(8)	3467(6)	-51(9)	5.0(4)	6.3(5)	7.3(6)	0.7(4)	-0.4(4)	-0.4(4)
C(20)	656(10)	4164(6)	-534(10)	7.3(6)	6.2(6)	10.1(8)	1.8(5)	-0.8(5)	-0.1(5)
C(21)	1790(11)	4457(6)	-756(11)	8.6(7)	5.8(6)	10.6(8)	0.1(5)	-1.2(6)	1.5(6)
C(22)	2862(10)	4029(6)	-519(10)	6.8(6)	7.1(6)	8.7(7)	-1.5(5)	0(5)	1.7(5)
C(23)	2743(8)	3325(6)	-61(8)	4.2(4)	7.2(5)	7.0(5)	-0.2(4)	-0.4(4)	1.4(5)
O(4)	1479(6)	2388(3)	545(6)	6.0(3)	5.1(3)	7.3(4)	-0.6(2)	0.2(3)	0.3(3)

u Anisotropic thermal parameters are in the form: $\exp[-\frac{1}{4}(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Experimental

A solution of pyridine *N*-oxide (1.0 g) in dry acetone was added at room temperature under nitrogen to a solution of nitratotriphenyltin (4.1 g) in the same solvent. The colourless microcrystalline product, which was obtained by slow evaporation of the solvent, was recrystallized under nitrogen from chloroform/toluene to yield prismatic crystals. The compound is fairly stable in the air. Found: C, 54.4; H, 4.3; N, 5.7; Sn, 23.2. $C_{23}H_{20}N_2O_4Sn$ calcd.: C, 54.5; H, 4.0; N, 5.5; Sn, 23.4%.

Rotation and Weissenberg photographs were used to determinate preliminary unit-cell dimensions and space group, which was found to be $P2_1/n$. Crystallographic data of $[Sn(C_6H_5)_3(NO_3)(C_5H_5NO)]$, Mol.wt. 507.1, are as follows: a 10.59(1); b 17.59(2); c 11.71(1) Å; β 93.0(1)°; V 2179.2 Å³; Z 4, D_{obs} 1.53 g cm⁻³; D_{calc} 1.55 g cm⁻³; $\mu(Mo-K\alpha)$ = 12.43 cm⁻¹; $F(000)$ = 1016. Intensities for 3850 unique reflections with $2.0^\circ < \theta < 25.0^\circ$ were measured by means of an on line single-crystal Siemens AED diffractometer using Mo- $K\alpha$ radiation and the $\omega - 2\theta$ scan technique. The prismatic crystal (mean radius 0.145 mm), which was used for crystal data and intensity measurements, slowly deteriorated under exposure to X-rays, as shown by its yellowing and by the decreasing of the intensity of a standard reflection monitored every 20 reflections. The usual Lorentz-polarization factors were applied, but no absorption correction was made. For the structure analysis only the 2416 reflections having $I \geq 2\sigma(I)$ were used.

The infrared spectra were measured in KBr disks using a Perkin-Elmer 457 spectrophotometer. The ultraviolet spectra were registered on a Perkin-Elmer 402 spectrophotometer.

Solution and refinement of the structure

The tin position was deduced from a three-dimensional Patterson map and subsequently three cycles of phase calculations and Fourier synthesis (assuming an overall temperature factor of 4.50 Å²) revealed the positions of all remaining non-hydrogen atoms.

Block-diagonal least-squares refinement, using unit weights and isotropic temperature factors, converged to a conventional R value of 10.3%. The refinement was continued with anisotropic thermal parameters which further reduced R to 5.6%. All hydrogen atoms were located on a difference map and their contributions were allowed for in the calculations assuming isotropic parameters. The final R 's were 5.0% for the observed reflections and 8.0% for the total number of reflections. At the end of the refinement the shifts of the positional parameters were no more than one fourth of the standard deviations.

The function minimized in the least-squares was $\sum w(|F_o| - |F_c|)^2$, in which the weight for each reflection was unity.

The final parameters are tabulated in Tables 1 and 2 together with their estimated standard deviations. The main infrared absorption bands are reported in Table 3. A list of structure factors can be obtained from the authors on request. Atomic scattering factors were taken from Cromer and Mann [5] for non-hydrogen atoms and from Stewart, Davidson and Simpson [6] for hydrogen atoms.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^3$) AND THERMAL PARAMETERS (\AA^2), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR HYDROGEN ATOMS

	$x/a(a)$	$y/b(b)$	$z/c(c)$	B
H(2)	-75(5)	263(3)	283(5)	7(1)
H(3)	-174(5)	382(3)	324(5)	7(2)
H(4)	-53(5)	496(3)	356(5)	8(2)
H(5)	165(5)	492(3)	321(5)	7(1)
H(6)	271(5)	374(3)	291(5)	8(2)
H(8)	430(5)	288(3)	337(5)	8(1)
H(9)	657(5)	287(3)	307(5)	7(1)
H(10)	740(5)	204(3)	162(5)	8(1)
H(11)	586(5)	123(3)	44(5)	8(2)
H(12)	367(5)	127(3)	82(5)	6(1)
H(14)	-37(5)	152(3)	77(5)	6(1)
H(15)	-147(5)	50(3)	37(5)	7(1)
H(16)	-125(5)	-63(3)	163(5)	8(2)
H(17)	45(5)	-63(3)	316(5)	8(2)
H(18)	177(5)	44(3)	344(5)	8(2)
H(19)	-41(5)	324(3)	20(5)	7(2)
H(20)	-21(5)	447(3)	-69(5)	8(2)
H(21)	200(5)	499(3)	-111(5)	8(2)
H(22)	369(5)	432(3)	-73(5)	8(2)
H(23)	354(5)	297(3)	15(5)	6(1)

Results and discussion

Fig. 1 illustrates the molecular structure of the complex, in which the tin atom has a slightly distorted trigonal bipyramidal coordination, with the phenyl rings occupying the equatorial positions and the nitrate group and the pyridine *N*-oxide molecule at the apices of the bipyramid. The geometry is not ideally trigonal bipyramidal as can be seen from the bond angles, which together with bond lengths are shown in Table 4. In particular the angle subtended at tin by the two apical ligands is 171.4° instead of 180° . The tin atom is only 0.06 \AA below the coordination equatorial plane formed by C(1)C(7)C(13), on the same side of the nitrate group (2.27 \AA), while the pyridine *N*-oxide molecule is 2.17 \AA above the plane.

The compound has a structure similar to that of nitratotriphenyl(triphenylphosphine oxide)tin(IV) [4], which is also trigonal bipyramidal with the phenyl rings in the equatorial plane and the oxygenated ligands at the apices. The difference in stoichiometry between the two compounds is confined to replacement of pyridine *N*-oxide by triphenylphosphine oxide. Detailed comparison of the structural parameters in the two compounds shows that the corresponding bond lengths and angles are similar. The only possible difference concerns the Sn—O bond distances in the two coordination polyhedra: while the Sn—O(NO₃) bond is slightly longer in the present compound (2.245 \AA) than in the triphenylphosphine derivative (2.22 \AA), the reverse is true for the Sn—O(org. lig.) bond (Sn—O(pyO) 2.227 ; Sn—O(TPPO) 2.29 \AA). Whether or not these differences are significant is uncertain, and a systematic structural study on $\text{Sn}(\text{C}_6\text{H}_5)_3(\text{NO}_3)\text{X}$

TABLE 3
MAIN VIBRATIONAL BANDS (cm^{-1}) WITH RELATIVE ASSIGNMENTS

3120m	ν(CH)	1000(sh)	ring
3070m		993s	breath
1765vw	ν ₁ + ν ₄	930w	δ(CH) _{out}
1750vw		920w	
1575w	ν(CC), ν(CN)	905w	
1490vs		830s	
1476s		820m	
1465vs		805mw	δ(NO ₂)
1425s	ν(NO ₃) _{as}	775ms	δ(CH) _{out}
1380s	ν(CC), ν(CN)	730vs	
1330w		700s	
1285vs	ν(NO ₃) _s	678s	
1203s	ν(NO) _{pvt}	660m	
1195(sh)		558m	ring
		550(sh)	skeletal
1185(sh)		458m	δ(NO) _{pvt}
		450s	
1170m	δ(CH) _{in}	325m	ν(SnO)
1155(sh)		305(sh)	
1145w			
1090w			
1073m			270ms
1065(sh)			
1020m	ν(NO)		

(X = unidentate oxygenated ligand) compounds is now in progress in our laboratory.

Sn—C and Sn—O bond lengths have been reported previously for five-coordinated monomer organotin compounds [4]. The agreement with the tabulated values is fairly-good for the Sn—C bonds, which in the present compound are 2.096, 2.112 and 2.126 Å, 2.10–2.20 Å being the observed range. As discussed previously, the analysis of the Sn—O bond lengths is complicated by the fact that the ligands with oxygen involved in coordination are different. However, while no structures are known for five-coordinated tin(IV) compounds having the pyridine *N*-oxide as a ligand, the nitrate group is present in two five-coordinated tin derivatives, viz. aquatrimethylnitratotin [7] and nitratotriphenyl(triphenylphosphine oxide)tin [4]. The value of the Sn—O(NO₃) bond in both these compounds, (2.22 Å), is very close to that in the present compound (2.245 Å).

The pyridine ring is planar, as expected, with O(4) out of the plane by only 0.10 Å. The X-ray results do not reveal significant differences in the bond distances compared with those observed by Ülkü, Huddle and Morrow [8] in the uncoordinate pyridine *N*-oxide. (Corresponding values do not differ by more than 0.01 Å.)

Unlike the structure, the N—O stretching frequency is influenced by coordination; the vibration decreases as consequence of a decrease in the double-bond character of the N—O bond. The magnitude of the shift ($\Delta\nu = 37 \text{ cm}^{-1}$) with respect to the free ligand (1240 cm^{-1}) is in agreement with that observed in other tin or organotin complexes [9,10,11,12]. Also the electronic absorption

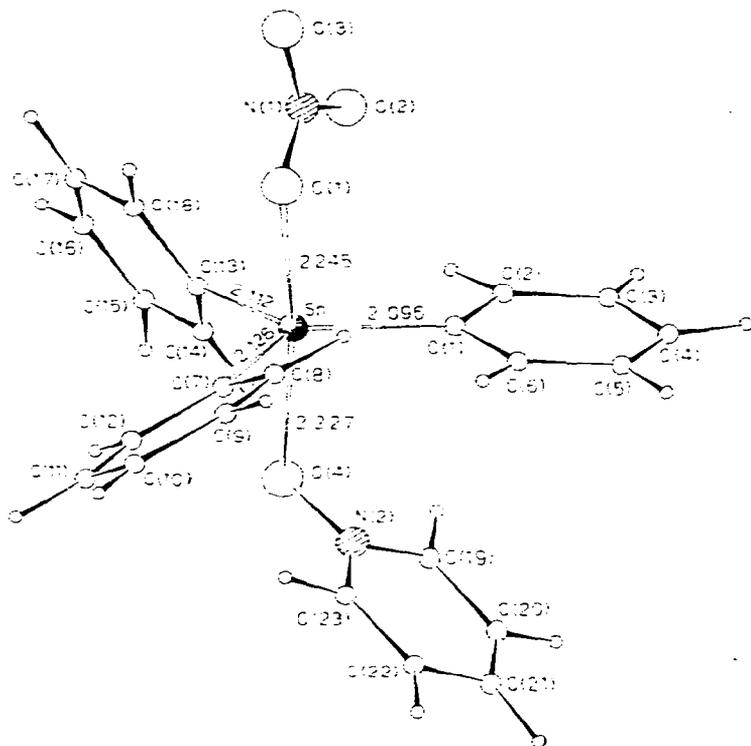


Fig. 1. Clinographic projection of the structure with bond distances (Å) at tin.

maximum of pyridine *N*-oxide (282 nm for the free ligand in ether solution) is influenced by the oxygen coordination (267 nm for the complex in the same solvent).

A summary is given in Table 5 of relevant structural parameters from X-ray studies of some pyridine *N*-oxide complexes. Owing to the large amount of structural information available only most accurately determined structures ($R < 9.2\%$) are listed. Unlike other metal complexes, the pyridine *N*-oxide tin complexes have received very little attention from X-ray structural point of view. The only report we know of refers to dichlorodimethylbis(pyridine *N*-oxide)tin [17], a monomeric octahedral *trans*-complex in which tin is located on a crystallographic centre of symmetry and where the Sn—O bond of 2.25 Å compares fairly well with that found in the present compound (2.227 Å). As can be seen from the data in Table 5, the scatter about the average values for the N—O and N—C lengths as well as for the O—N—C angles is very small, while the M—O bonds reflect the effects of the different nature of the metal. Consideration of the M—O—N angles does not provide any evidence for a recent suggestion [17] that angles nearer to tetrahedral might be expected in the absence of appreciable double-bond character in the N—O bond. The dihedral angle between the Sn—O—N and the pyridine ring plane is 78.9°. This rather large value, which is probably due to steric factors, is typical of pyridine *N*-oxide metal complexes.

The nitrate group acts as unidentate ligand through O(1) (Sn—O(1) 2.225(8)

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°) (STANDARD DEVIATIONS OCCURRING IN THE LAST SIGNIFICANT FIGURE ARE GIVEN IN PARENTHESES)

Sn—O(1)	2.245(8)	C(4)—C(5)	1.34(2)	C(15)—C(16)	1.36(2)
Sn—O(4)	2.227(8)	C(5)—C(6)	1.37(2)	C(16)—C(17)	1.32(2)
Sn—C(1)	2.096(9)	C(6)—C(1)	1.38(1)	C(17)—C(18)	1.38(2)
Sn—C(7)	2.126(9)	C(7)—C(8)	1.39(1)	C(18)—C(13)	1.39(1)
Sn—C(13)	2.112(9)	C(8)—C(9)	1.39(1)	O(4)—N(2)	1.34(1)
O(1)—N(1)	1.23(1)	C(9)—C(10)	1.34(2)	N(2)—C(19)	1.34(1)
O(2)—N(1)	1.22(1)	C(10)—C(11)	1.37(2)	C(19)—C(20)	1.36(2)
O(3)—N(1)	1.21(1)	C(11)—C(12)	1.40(1)	C(20)—C(21)	1.34(2)
C(1)—C(2)	1.38(1)	C(12)—C(7)	1.36(1)	C(21)—C(22)	1.38(2)
C(2)—C(3)	1.38(2)	C(13)—C(14)	1.37(2)	C(22)—C(23)	1.36(2)
C(3)—C(4)	1.35(2)	C(14)—C(15)	1.41(2)	C(23)—N(2)	1.34(1)
O(1)—Sn—O(4)	171.4(2)	Sn—C(1)—C(2)	121.1(7)		
O(1)—Sn—C(1)	97.3(3)	Sn—C(1)—C(6)	122.8(7)		
O(1)—Sn—C(7)	82.6(3)	C(6)—C(1)—C(2)	116(1)		
O(1)—Sn—C(13)	94.6(3)	C(1)—C(2)—C(3)	121(1)		
C(1)—Sn—O(4)	89.4(3)	C(2)—C(3)—C(4)	121(1)		
C(7)—Sn—O(4)	89.6(3)	C(3)—C(4)—C(5)	120(1)		
C(13)—Sn—O(4)	86.5(3)	C(4)—C(5)—C(6)	121(1)		
C(1)—Sn—C(7)	118.0(3)	C(5)—C(6)—C(1)	122(1)		
C(1)—Sn—C(13)	120.8(3)	Sn—C(7)—C(8)	121.4(6)		
C(7)—Sn—C(13)	120.9(3)	Sn—C(7)—C(12)	119.3(6)		
Sn—O(1)—N(1)	120.8(5)	C(12)—C(7)—C(8)	119(1)		
O(1)—N(1)—O(2)	119.5(8)	C(7)—C(8)—C(9)	119(1)		
O(1)—N(1)—O(3)	119.3(8)	C(8)—C(9)—C(10)	121(1)		
O(2)—N(1)—O(3)	121.2(8)	C(9)—C(10)—C(11)	120(1)		
Sn—O(4)—N(2)	120.4(5)	C(10)—C(11)—C(12)	120(1)		
O(4)—N(2)—C(19)	118.4(7)	C(11)—C(12)—C(7)	121(1)		
O(4)—N(2)—C(23)	120.4(7)	Sn—C(13)—C(14)	121.2(7)		
C(23)—N(2)—C(19)	121.0(8)	Sn—C(13)—C(18)	121.2(7)		
N(2)—C(19)—C(20)	119.0(8)	C(18)—C(13)—C(14)	118(1)		
C(19)—C(20)—C(21)	121(1)	C(13)—C(14)—C(15)	122(1)		
C(20)—C(21)—C(22)	119(1)	C(14)—C(15)—C(16)	117(1)		
C(21)—C(22)—C(23)	119(1)	C(15)—C(16)—C(17)	123(1)		
C(22)—C(23)—N(2)	121(1)	C(16)—C(17)—C(18)	120(1)		
		C(17)—C(18)—C(13)	120(1)		

Å), with a second oxygen atom, O(2), at 3.119 Å from metal. As pointed out by Addison and coworkers [21], the difference between the two Sn—O distances (0.874 Å) is such that only the bonding between tin and O(1) is significant. The structural parameters of the NO₃ group agree with those recently quoted for unidentate nitrate groups in metal complexes [4]. In particular, the length of N—O bonds involving the coordinated oxygen atom, N(1)—O(1) 1.23(1) Å, is slightly longer than those of bonds involving the uncoordinated oxygen atoms (N(1)—O(2) 1.22(1); N(1)—O(3) 1.21(1) Å), although the difference is slight. Moreover the O—N—O angle involving the uncoordinated oxygen is larger (121.2°) than 120° and larger than the other two bond angles (119.5, 119.3°), as usually observed in unidentate nitrates. In keeping with this behaviour, the Sn—O—N angle (120.4°) is larger than 110°.

In the phenyl rings the planarity is fairly good and there are no significant departures from the expected structural parameters. The displacements of the tin atom from their least-squares planes are all less than or equal to 0.14 Å. These

TABLE 5

COMPARISON OF SOME STRUCTURAL PARAMETERS (BOND LENGTHS IN Å, ANGLES IN °) FOR PYRIDINE N-OXIDE COMPLEXES TOGETHER WITH THE COORDINATION NUMBER OF THE METAL

Complex	Coordination number	M—O	N—O	N—C	M—O—N	O—N—C			
[Cu(C ₅ H ₅ NO)Cl ₂] ₂ [13]	4	^a 1.98(1)	2.04(1)	1.35(2)	1.34(2)	124(2)	128(2)	118(3)	118(3)
[Cu(C ₅ H ₅ NO) ₄](BF ₄) ₂ [14]	4	1.93(1)		1.31(1)	1.38(1)	1.35(1)	116.7(6)	120.5(7)	119.5(7)
		1.91(1)		1.36(1)	1.31(1)	1.31(1)	118.6(7)	116.8(10)	117.3(6)
[Cu(C ₅ H ₅ NO) ₂ (NO ₃) ₂] ₂ [15]	5	^a 1.968(5)	2.439(6)	1.362(7)	1.34(1)	1.35(1)	118.6(5)	119.1(5)	116.8(5)
		1.951(5)		1.361(7)	1.37(1)	1.33(1)	119.4(5)	116.9(5)	120.1(6)
[Cu(C ₅ H ₅ NO) ₂ Br ₂] ₂ [16]	5	^a 1.975(4)	2.162(4)	1.365(6)	1.353(8)	1.348(8)	123.6(3)	121.2(4)	118.5(5)
		1.944(4)		1.345(7)	1.351(8)	1.337(8)	119.7(3)	119.2(5)	119.2(6)
		^a 1.976(4)	2.240(4)	1.366(6)	1.327(7)	1.355(9)	121.3(3)	117.6(4)	119.2(5)
		1.949(5)		1.347(6)	1.345(8)	1.334(9)	119.5(4)	118.8(5)	120.9(5)
[Sn(CH ₃) ₂ (C ₅ H ₅ NO) ₂ Cl ₂] [17]	6	2.25(2)		1.37(2)	1.37(2)	1.33(2)	117(1)	118(1)	120(1)
[Hg(C ₅ H ₅ NO) ₆](ClO ₄) ₂ [18]	6	2.35(2)		1.32(2)	1.35(4)	1.36(3)	114(1)	115(2)	122(2)
[Ni(C ₅ H ₅ NO) ₆](BF ₄) ₂ [19]	6	2.060(1)		1.332(1)	1.333(2)	1.349(1)	119.0(1)	120.2(1)	118.3(1)
[Co(C ₅ H ₅ NO) ₆](ClO ₄) ₂ [20]	6	2.088(2)		1.334(4)	1.331(5)	1.343(5)	119.5(2)	120.5(3)	118.7(3)
[Sn(C ₆ H ₅) ₃ (NO) ₃](C ₅ H ₅ NO) [1]	5	2.227(8)		1.34(1)	1.34(1)	1.34(1)	120.4(5)	118.4(7)	120.4(7)

^a These values refer to structures in which the oxygen atom bridges two metal atoms.

TABLE 6
SIGNIFICANT VAN DER WAALS INTERACTIONS (A)

O(1) ... C(19 ⁱ)	3.29(1)	O(3) ... C(10 ⁱⁱ)	3.30(2)
C(8) ... C(19 ⁱ)	3.20(1)	O(2) ... C(23 ⁱⁱ)	3.11(1)
C(9) ... N(2 ⁱ)	3.24(1)	O(3) ... C(21 ⁱⁱⁱ)	3.36(2)
O(3) ... C(9 ⁱⁱ)	3.31(1)		

$$i = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$$

$$ii = x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$$

$$iii = \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$$

rings are differently oriented with respect to the equatorial plane, being twisted out of this plane by 5.3° (C(1) ... C(6)), 33.1° (C(7) ... C(12)), and 61.2° (C(13) ... C(18)). The reciprocal orientation of the rings is defined by the dihedral angles which they form ($\phi_1 \wedge \phi_2$ 38.3° ; $\phi_1 \wedge \phi_3$ 57.3° ; $\phi_2 \wedge \phi_3$ 82.9°).

Comparing the spectroscopic data of the present compound with those of the corresponding triphenylphosphine oxide complex [4] it is noteworthy that: (a) $\Delta\nu(\text{P—O})$ is larger than $\Delta\nu(\text{N—O})$, in agreement with the observations of Das and Kitching [10] on some organotin and -lead complexes with phosphine, arsine and amine oxides; (b) like the Sn—C bond distances, the $\nu(\text{Sn—C})$ frequencies are also insensitive to the nature of the oxygenated ligand (268 cm^{-1} for the TPPO complex; 270 cm^{-1} for pyO complex); (c) the $\nu(\text{Sn—O})$ value is higher than that observed in the TPPO complex, for which the only band confidently assignable to Sn—O stretching is that at 295 cm^{-1} [22]; (d) in contrast to the IR spectrum of the TPPO complex, the spectroscopic characteristics of the nitrate group in the present compound are consistent with an unidentate situation, as indicated by the splittings of the ν_3 ($\Delta\nu = 140\text{ cm}^{-1}$) and $\nu_1 + \nu_3$ ($\Delta\nu = 15\text{ cm}^{-1}$) combination bands [21,23].

As can be seen from the data quoted in Table 6, none of the intermolecular contacts is shorter than the corresponding Van der Waal's distance, so that the whole structure consists of discrete monomer units.

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