Synthesis and Structural Characterization of Tin(IV) *N*-nitroso-*N*-phenylhydroxylaminato Complexes: Crystal Structures of $Sn(O_2N_2Ph)_4$, $Ph_2Sn(O_2N_2Ph)_2$ and $[Me_2Sn(O_2N_2Ph)_2]_2$

Andrea Deák,[a,b] Monica Venter,[b] Alajos Kálmán,*[a] László Párkányi,[a] Lajos Radics,[a] and Ionel Haiduc*[b]

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Reaction of cupferron [NH_4L, L = PhN(O)NO$^-$] with tin(IV), diphenyltin(IV) and dimethyltin(IV) halides yields the cupferronato complexes SnL_4 (**1**), Ph_2SnL_2 (**2**) and $[Me_2SnL_2]_2$ (**3**). All were characterized by FT-IR, FT-Raman, NMR (^{1}H, ^{13}C and ^{119}Sn) spectroscopic methods and X-ray structural analysis. An almost ideal, very rare dodecahedral geometry is found in the structure of **1**. The hexacoordinated tin center exhibits a bicapped tetrahedral geometry in complex **2**. The tin centers are heptacoordinated in a pentagonal bipyramidal geometry in the dimeric complex **3**. These complexes incorporate five-membered SnO_2N_2 and four-membered Sn_2O_2 inorganic rings. Vibrational spectral data are consistent with the structures determined. The ^{119}Sn NMR spectra indicate that in solution **1** retains its octacoordinated nature; in compound **2** the tin atom is hexacoordinated, while in **3** the tin atom is pentacoordinated.

Introduction

We became interested in tin and organotin(IV) *N*-nitroso-*N*-phenylhydroxylaminato (cupferronato) complexes since many organotin compounds are known to display antitumor activity.[1] In addition, the biological activity of cupferron [NH_4L, L = PhN(O)NO$^-$] has also been investigated, carcinogenic, genotoxic, mutagenic and DNA-damaging effects being observed.[2] The knowledge of the coordination chemistry of cupferron could provide more information about the interaction modes of nitric oxide with metal centers of biologically important species (e.g. hemes or heme models) and could help to elucidate the mechanism of activation of the NO-receptor enzyme guanylate cyclase.[2] Moreover, a large structural diversity of cupferronato complexes is expectable due to the ability of tin to exhibit various coordination geometries[3] and to the diverse coordination patterns of cupferronato anion.[4] In order to accumulate precise structural data concerning the binding modes of *N*-nitroso derivative with tin we prepared tin and diorganotin(IV) cupferronato complexes: $Sn(O_2N_2Ph)_4$ (**1**), $Ph_2Sn(O_2N_2Ph)_2$ (**2**) and $[Me_2Sn(O_2N_2Ph)_2]_2$ (**3**) which were investigated by FT-IR, FT-Raman, multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR as well as X-ray diffraction analysis.

Results and Discussion

Reaction of cupferron [NH_4L, L = PhN(O)NO$^-$] with SnI_4 in chloroform (Equation 1) results in the formation of **1**.

$$SnI_4 + 4\,NH_4L \xrightarrow{CHCl_3} \underset{\mathbf{1}}{SnL_4} + 4\,NH_4I \quad (1)$$

In similar manner, cupferron reacts with diorganotin dichlorides R_2SnCl_2 (R = Ph and Me) in acetone or dried MeOH (Equation 2) to give **2** and **3**.

$$n\,R_2SnCl_2 + 2\,n\,NH_4L \xrightarrow[\text{or MeOH}]{\text{acetone}} [R_2SnL_2]_n + 2\,n\,NH_4Cl \quad (2)$$

$$\mathbf{2}\text{: } n = 1, R = Ph \qquad \mathbf{3}\text{: } n = 2, R = Me$$

All the complexes **1−3** are stable and are soluble in $CHCl_3$ and *n*-heptane.

Structures in the Solid State

Vibrational Behavior

The FT-IR and Raman spectra were recorded for the complexes **1−3** in the 3500−100 cm^{-1} spectral range. As was expected all these new compounds display ν(N−N), ν(N=O) and δ(ONNO) absorption bands typical for the $PhN_2O_2^-$ ligand.[4] Taking into account the coordination of the anionic cupferronato ligand to the metal centers through the oxygen atoms, the Sn−O stretching vibration

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[a] Institute of Chemistry, Chemical Research Center of the Hungarian Academy of Sciences,
P. O. Box 17, H-1525 Budapest, Hungary
Fax: (internat.) + 36-1/325-7554
E-mail: akalman@cric.chemres.hu

[b] Chemistry Department, Babes-Bolyai University,
RO-3400 Cluj-Napoca, Romania
Fax: (internat.) + 40-64/190-818
E-mail: ihaiduc@chem.ubbcluj.ro

was also characteristic.[4] Selected bands and assignments are listed in Table 1.

Table 1. Selected FT-IR/Raman data and vibrational assignments for complexes **1−3**

1		**2**		**3**		Assign-
IR	Raman	IR	Raman	IR	Raman	ment
1356 s	1361 w	1344 ms	1345 m	1351 ms 1336 ms	1353 mw	ν(N−N)
1205 ms	−	1214 w	−	1216 s	1218 w	ν(N=O)
1168 ms	1167 w	1181 s	−	1180 ms	1199 w	
949 s	940 m	926 s	930 m	923 s	929 mw	δ(ONNO)
401 s	−	400 s	−	401 vs	−	ν(Sn−O)

w: weak, m: medium, ms: medium strong, mw: medium weak, s: strong, vs: very strong.

X-ray Crystallographic Studies

The molecular structures of compounds **1**, **2** and **3** are shown in Figures 1−3, respectively. Selected bond lengths and angles are listed in Table 2 and Table 4.

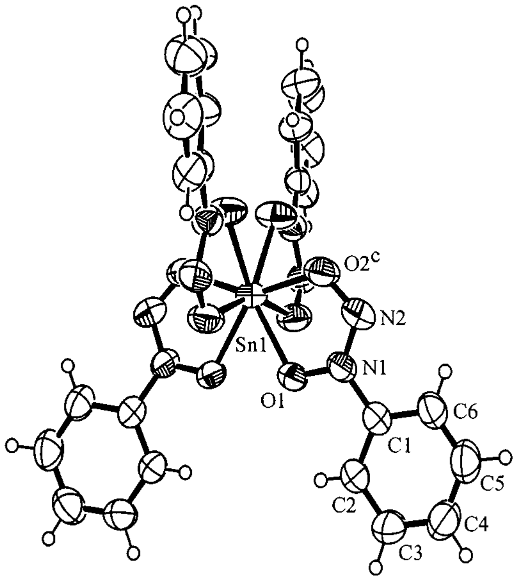

Figure 1. Molecular structure of **1**

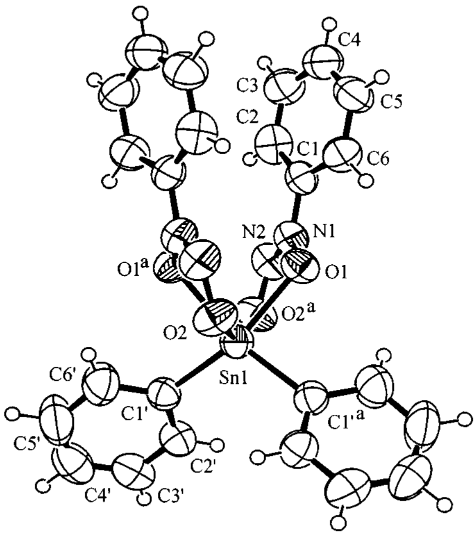

Figure 2. Molecular structure of **2**

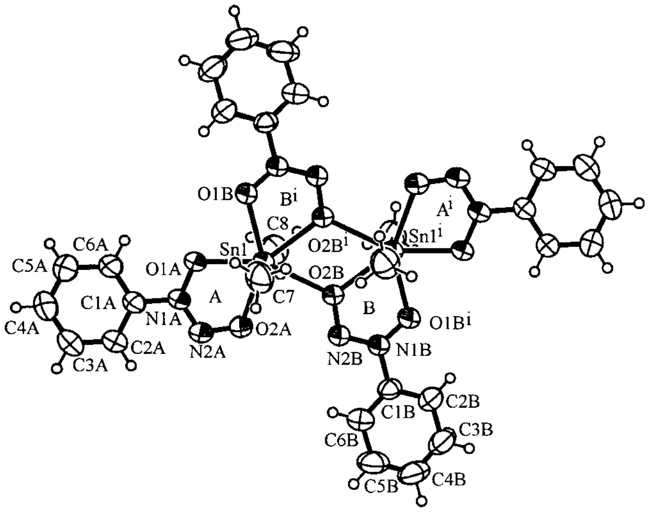

Figure 3. Molecular structure of **3**

The molecular structure of **1** provides a new example of an octacoordinated Sn^{IV} species in an almost perfect dodecahedral geometry of the metal center coordination environment defined by eight oxygen atoms from the four cupferronato ligands. Hitherto, only four Sn^{IV} complexes with octacoordinated tin centers have been characterized by X-ray crystallography: tin tetranitrate,[5] stannic phthalocyanine,[6] tin tetraacetate,[7] and tetrakis(tropolonato)tin.[8] The distortion of the idealized dodecahedron towards the bicapped trigonal prism and/or square antiprism can be described by δ and φ parameters.[9] As shown in Table 3, the four δ (29.5°) and two φ (0°) values are identical in an ideal dodecahedron, while this equality becomes more or less changed for the bicapped trigonal prism and square antiprism. The δ and φ values observed for **1** reveal an almost perfect dodecahedral geometry around the tin atom.

The cupferronato anions are bound to the Sn^{IV} center in a bidentate chelating fashion leading to five-membered carbon-free chelate rings SnO_2N_2 with an O(1)−Sn(1)−O(2)^c bite angle of 70.1(1)°. The Sn−O(2) bond length is slightly shorter (by 0.041 Å) than that of Sn−O(1), and somewhat longer than the ideal value of 2.14 Å.[3] The average Sn−O bond length of 2.164 Å is, however, consistent with tin-oxygen distances observed in other octacoordinated tin(IV) species, such as $Sn(NO_3)_4$ (average Sn−O = 2.161 Å)[5] and the recently reported $Sn(tropolonato)_4$ (average Sn−O = 2.168 Å).[8]

The crystal lattice is built up from infinite one-dimensional C−H···O interactions, C(3)−H(3)···O(2) [C−H = 0.94 Å; H···O = 2.45 Å; C···O = 3.37 Å; C−H···O = 165.8°] that extends through (x, 0.5 − y, −0.5 − z). This hydrogen-bonding interaction has no significant impact on the adoption of the almost ideal dodecahedral geometry.

Table 2. Selected interatomic bond lengths (Å), bond angles (°) and torsion angles (°) for **1** and **2**

	1	**2**
Sn(1)−O(1)	2.185(1)	2.206(2)
Sn(1)−O(2)^{i}	2.144(1)	2.158(2)
O(2)^{i}−N(2)	1.303(2)	1.306(4)
O(1)−N(1)	1.309(2)	1.314(3)
N(1)−N(2)	1.278(2)	1.287(4)
C(1)−N(1)	1.428(2)	1.445(5)
Sn(1)−C(1′)	−	2.132(3)
O(1)−Sn(1)−O(2)^{i}	70.1(1)	69.7(1)
Sn(1)−O(1)−N(1)	112.8(1)	108.7(2)
O(1)−N(1)−N(2)	122.0(2)	122.8(3)
N(1)−N(2)−O(2)^{i}	113.2(2)	112.1(3)
N(2)−O(2)^{i}−Sn(1)	119.1(1)	116.3(2)
C(1′)−Sn(1)−O(2)	−	108.2(1)
C(1′)−Sn(1)−C(1′)^{i}	−	107.7(2)
O(1)−N(1)−N(2)−O(2)^{i}	1.8(2)	3.3(5)

Equivalent atoms (i) generated for **1** by *c* = (x, −y + 0.5,−z + 0.5), and for **2** by *a* = (−x, y, −z + 0.5).

Table 3. Ideal and observed δ (°) and φ (°) for octacoordinated complexes

Complex	δ				φ	
dodecahedron[9]	29.5	29.5	29.5	29.5	0	0
bicapped trigonal prism[9]	0	21.7	48.2	48.2	16.1	16.1
square antiprism[9]	0	0	52.5	52.5	10.8	10.8
1	28.4	28.4	25.7	25.7	−1.9	1.1

Table 4. Selected interatomic bond lengths (Å), bond angles (°) and torsion angles (°) for **3**

	3 *L* = *A*; X = 7	 *L* = *B*; X = 8
Sn(1)−O(1*L*)	2.198(2)	2.247(1)
Sn(1)−O(2*L*)	2.274(2)	2.440(1)
Sn(1)−O(2*L*)^{i}	−	2.395(1)
O(2*L*)−N(2*L*)	1.294(3)	1.303(2)
O(1*L*)^{i}−N(1*L*)	1.321(2)	1.306(2)
N(1*L*)−N(2*L*)	1.280(2)	1.284(2)
C(1*L*)−N(1*L*)	1.433(2)	1.436(2)
Sn(1)−C(X)	2.092(3)	2.103(3)
O(1*L*)−Sn(1)−O(2*L*)^{i}	69.5(1)	65.5(1)
O(1*A*)−Sn(1)−O(1*B*)	77.4(1)	
O(2*B*)−Sn(1)−O(2*A*)	83.9(1)	
O(2*B*)−Sn(1)−O(2*B*)^{i}	63.7(1)	
Sn(1)^{i}−O(1*L*)^{i}−N(1*L*)	113.8(1)	116.7 (1)
O(1*L*)^{i}−N(1*L*)−N(2*L*)	123.7(2)	124.2(2)
N(1*L*)−N(2*L*)−O(2*L*)	114.5(2)	112.2(1)
N(2*L*)−O(2 *L*)−Sn(1)^{i}	116.7(1)	117.4(1)
C(7)−Sn(1)−C(8)	173.6(1)	
O(1 *L*)^{i}−N(1 *L*)−N(2 *L*)−O(2 *L*)	−1.7(4)	1.0(3)

Equivalent atoms (i) generated for *L* = *B* by (−x, −y, −z).

In the class of hexacoordinated tin(IV) compounds the octahedral geometry is predominant.[3] Distorsions in the solid state can be attributed to a compromise between the close packing and the ideal shape of the molecules.[9] In complex **2** the hexacoordinated metal center surrounded by two carbon atoms of two phenyl groups and four oxygen atoms of the chelating cupferronato anions exhibits a slightly distorted bicapped tetrahedral arrangement.[10] In this arrangement the capping ligand atoms O(1) and O(1)^{a} are located in the middle of two faces of the nearly regular tetrahedron C(1′)^{a}···C(1′)···O(2)···O(2)^{a}. The basic tetrahedral geometry around the tin center is retained with angles C(1′)^{a}−Sn(1)−C(1)′ of 107.74(2)°, C(1)′−Sn(1)−O(2) and symmetry equivalent C(1′)^{a}−Sn(1)−O(2)^{a} of 108.2(1)°, and these values are close to the ideal tetrahedral value. The Sn(1)−C(1)′, Sn1−C(1′)^{a} and Sn(1)−O(2), Sn(1)−O(2)^{a} distances belonging to the tetrahedral core are almost equal. Otherwise, the Sn(1)−O(2) distances are close to the ideal value for a normal covalent bond 2.14 Å, while the Sn(1)−O(1) distances are somewhat longer. The O(1)−Sn(1)−O(2)^{a} bite angle of 69.7(1)° is comparable to the bite angle measured in **1** and depends partially on the strain in the five-membered inorganic SnO_2N_2 ring.

The ligand hydrogens in the *para* position interact with the π system of the phenyl rings (1 − x, y, 1.5 − z) bound directly to the tin atom via weak C−H···π interactions [C(4)···π = 3.84 Å, H(4)···π = 3.09 Å, C(4)−H(4)···π = 139.4°].

According to the X-ray data compound **3** is represented by the centrosymmetric dimeric structure $[Me_2Sn(O_2N_2Ph)_2]_2$. Both tin(IV) centers are heptacoordinated. The nearly pentagonal bipyramidal coordination is achieved by one bidentate chelating (*A* and its symmetry equivalent, *A*^{i}) and two triconnective bridging cupferronato ligands (*B* and its symmetry equivalent *B*^{i}) lying in the equatorial plane, and two methyl groups occupying the axial positions. This arrangement with five equatorial oxygen atoms is similar to those reported for the bridged binuclear and polynuclear pentagonal bipyramidal dimethyltin(IV) complexes of aminocarboxylate and aminopolycarboxylate ligands.[11−14] In the majority of these structures,[11−13] while the methyl groups are invariably in the axial position, one oxygen is replaced by a nitrogen atom. There is an additional case where two oxygen atoms are replaced by two nitrogen atoms.[14]

A notable feature in the structure of **3** is the occurrence of a central planar [torsion angle: O2(B)^{i}−Sn(1)^{i}−O(2B)−Sn(1) = 0.(0)°] four-membered Sn_2O_2 ring. In this ring, the two pairs of Sn−O distances [Sn(1)−O(2B)^{i} and Sn(1)−O(2B)] are unequal, and the bridging oxygen atoms [O(2B) and O(2B)^{i}] participate in two additional, planar, five-membered SnO_2N_2 rings resulting in a Sn···Sn separation of 4.108 Å. Distannoxanes generally form dimeric ladder-type structures that also contain a planar four-membered Sn_2O_2 ring,[3][15] a feature which can be found in the bridged binuclear and polynuclear pentagonal bipyramidal dimethyltin(IV) complexes discussed.[11−14] The Sn(1)−O(2B)^{i} bond length in the triconnective bridging ligand seems to be significantly longer by 0.121 Å than the corresponding distance of 2.274(2) Å for the chelating ligand. The O(1B)−Sn(1)−O(2B)^{i} bite angle in ligand *B* deviates by ca 4° from the bite angle of the chelating ligands.

There are weak intramolecular hydrogen bonds such as C−H···O [C(6A)···O(1A) 2.69 Å, H(6A)···O(1A) 2.35 Å, C(6A)−H(6A)···O(1A) 100.8°] between the phenyl hydrogens and the ONNO group.

In the crystal lattice the symmetry-related dimeric molecules interact along the *a* axis *via* weak C−H···π interactions [C(6B)···π 3.56, H(6B)···π 3.30 Å, C(6B)−H(6B)···π 98.8°].

Structures in Solution

^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded (in $CDCl_3$) to gain some insight into the solution structure of the complexes. For proton-containing groups directly attached to the Sn atom (Me, Ph), proton spectra exhibited ^{119}Sn (and ^{117}Sn) satellite signals due to $^2J(^{119}Sn-^1H)$ or $^3J(^{119}Sn-^1H)$ couplings. In a similar fashion, resonances due to the carbon atoms in groups attached to tin exhibited ^{119}Sn (and ^{117}Sn) satellites arising from one-bond and multiple bond $^nJ(^{119}Sn-^{13}C)$ spin−spin couplings. The relationship[16,17] $|^1J(^{119}Sn-^{13}C)| > |^3J(^{119}Sn-^{13}C)| > |^2J(^{119}Sn-^{13}C)| > |^4J(^{119}Sn-^{13}C)|$ was used to assign the ^{13}C resonances of the phenyl moiety. All the ^{1}H and ^{13}C chemical shifts have the values normally expected and can be found in the Experimental Section.

The chemical shift values of the ^{119}Sn resonance signals of similar tin(IV) complexes are known to reflect the coordination of the Sn atoms in the solution state.[17] Thus in **1**, the observed −747.9 ppm, falls within the range observed in chloroform solutions of other octacoordinated tin(IV) compounds such tetrakis(tropolonato)tin(IV) [$\delta(^{119}Sn)$ = −793.10 ppm][8] and tetrakis(1-pyrrolecarbodithioato)tin(IV) [$\delta(^{119}Sn)$ = −729.2 ppm].[18]

The magnitude of the vicinal Sn−H coupling, $|^3J(^{119}Sn-^1H)| = 77$ Hz exhibited by the resonance due to the *ortho* protons of the Sn−Ph rings in **2** reflects the (equilibrium) rotational angle of the aromatic ring in liquid state.[17] The angle C−Sn−C calculated from the available relationships with the $|^1J(^{119}Sn-^{13}C)|$ coupling[19] indicates an increase in C−Sn−C angle from 107.7° in the solid to 176.4° in solution, which is consistent with octahedral Sn^{IV} units with two phenyl groups in *trans* positions.[19]

Lockhart and Manders noticed that the $|^2J(^{119}Sn-^1H)|$ coupling constant is a function of coordination number of dimethyltin(IV) compounds, ranging between 64 and 79 Hz for pentacoordinated compounds.[20] For **3** the $|^2J(^{119}Sn-^1H)|$ coupling constant of 76.8 Hz indicates pentacoordination in chloroform solution. A single resonance at −159.2 ppm observed in the ^{119}Sn NMR spectra is compatible with the pentacoordinated geometry proposed for the structure in solution. Comparison with ^{119}Sn chemical shifts (−126, −129, −121, and −133 ppm, respectively) of pentacoordinated dimethyltin(IV) alkoxides $Me_2Sn(OR)_2$ (R = Et, ^{n}Pr, ^{i}Bu and ^{n}Bu) serves to confirm this interpretation.[21] These data, combined with the $|^1J(^{119}Sn-^{13}C)|$ coupling constants, tend to confirm that this compound has a pentacoordinated geometry in solution.[19]

Conclusion

A noteworthy trend has been observed in the bonding pattern of the O-donor cupferronato anion in the $[R_nSnL_{4-n}]_m$ series of tin(IV) cupferronate complexes. The nature of the organic moieties attached to tin produces significant changes in coordinational behavior of the ligand: bridging coordination,[4][22] bridging-chelating and chelating coordination patterns are observed. The bonding mode of the ligand to tin is reflected in the length of the Sn−O bonds and in the O(1)−Sn(1)−O(2) bite angles (Table 2 and 4). The Sn(1)−O(1) bond lengths in complexes **1−2** are significantly longer than Sn(1)−O(2), while the opposite was observed for **3** and for the tetrameric trimethyltin(IV) cupferronate $[Me_3SnL]_4$, which contains an unprecedented inorganic metallamacrocycle $Sn_4O_8N_8$.[22] For the chelating ligands the O(1)−Sn(1)−O(2) bite angles lie in the narrow range 69−70° while for the triconnective bridging and bridging ligands[22] this angle tends to close up by approximately 4−5°. In spite of the varied coordination behavior of the nitrosohydroxylaminato [N(O)NO] group in the cupferronato tin complexes, a comparison of the corresponding structural data does not reveal major differences. The N(O)NO moiety is essentially planar. The N(1)−N(2) bond length is shorter than an N−N single bond (1.45 Å) and is closer to an N=N double bond (1.21 Å).[23] The N(1)−O(1) and N(2)−O(2) bond length is between single (1.40 Å) and double bonds (1.21 Å).[23] These data reveal the same electron delocalization along the nitrosohydroxylaminato group in all tin compounds investigated here.

Experimental Section

General Methods: The preparation and purification of the complexes were carried out in the open air, or in dry atmosphere, with anhydrous organic solvents. Organic solvents for reactions and recrystallization were distilled from appropriate drying agents prior to use. The SnI_4 reagent was prepared by a published method.[24] All other starting materials were obtained from commercial sources as pure compounds.

Microanalyses (C, H and N) of the complexes were performed by the Microanalytical Service of the Department of Chemistry, University of Santiago de Compostela (Spain). FT-IR spectra were recorded with a Perkin−Elmer 2000 spectrometer. FT-Raman spectra were recorded with a Bruker FT Raman spectrometer (IFS model 66). Solution NMR data were recorded on a Varian Unity Inova 400 spectrometer in $CDCl_3$, using TMS as internal standard for ^{1}H and ^{13}C, and $SnMe_4$ for ^{119}Sn as external reference.

Preparation of Tetrakis(*N*-nitroso-*N*-phenyl-hydroxylaminato)tin(IV), Sn[PhN(O)NO]$_4$, (1): The ammonium salt $NH_4[PhN(O)NO]$ (0.50 g, 3.25 mmol) was added to a solution of SnI_4 (0.51 g, 0.81 mmol) in 15 mL chloroform. The NH_4I promptly precipitated and the mother liquor became colorless. After stirring for 20 minutes at room temperature, the precipitate was filtered off and the liquid was evaporated. Recrystallization from *n*-heptane gave the product as colorless crystals. Yield 0.22 g, 40%, melting point 168−172°C (decomp.). − FT-IR (KBr): $\tilde{\nu}$ = 1486 cm^{-1}(Ph) (m), 1465 (Ph) (m), 1356 (N−N) (s), 1300 (vs), 1205 (N=O) (ms), 1168 (N=O) (ms), 949 (ONNO) (s), 758 (Ph) (s), 696 (Ph) (s), 684

(OSnO) (m, sh), 410 (s), 401 (Sn−O) (s), 237 (C−H) (vs). − FT-Raman: $\tilde{\nu}$ = 1590 cm^{-1}(C−H) (m), 1487 (C−H) (w), 1361 (N−N) (w), 1314 (vs), 1167 (N=O) (w), 1004 (Ph) (m), 940 (ONNO) (m), 112 (m). − ^{1}H NMR (CDCl$_3$, 399.92 MHz, 30°C): δ = 7.97 (m, 2 H, Ph-H2, -H6), 7.43 (m, 3 H, Ph-H3, -H4, -H5). − ^{13}C NMR (CDCl$_3$, 100.6 MHz, 30°C): δ = 140.0 (s, Ph-C1), 130.3 (s, Ph-C4) ppm; 129.1 (s, Ph-C3, -C5), 119.6 (s, Ph-C2, -C6). − ^{119}Sn NMR (CDCl$_3$, 149.106 MHz, 30°C): δ = −747.9 (s). − $C_{24}H_{20}N_8O_8Sn$ (667.17): calcd. C 43.2, H 3.0, N 16.8; found C 43.1, H 3.3, N 16.8.

Preparation of Diphenylbis(*N*-nitroso-*N*-phenyl-hydroxylaminato)-tin(IV), $Ph_2Sn[PhN(O)NO]_2$ (2): The salt $NH_4[PhN(O)NO]$ (0.20 g, 1.29 mmol) was added to a solution of Ph_2SnCl_2 (0.22 g, 0.64 mmol) in 15 mL acetone. The NH_4Cl promptly precipitated. After stirring for one hour at room temperature, the precipitate was filtered off and the mother liquor was concentrated to low volume, and 5−10 mL *n*-heptane was added. This solution was placed in the refrigerator overnight to yield **2** as a pale yellow solid. Recrystallization from *n*-heptane gave the product as colorless crystals. Yield 0.21 g, 60%, melting point 87−88°C. − FT-IR (KBr): $\tilde{\nu}$ = 1483 cm^{-1} (Ph) (m), 1463 (Ph) (m), 1429 (m), 1344 (N−N) (ms), 1294 (vs), 1214 (N=O) (w), 1181 (N=O) (s), 1156 (s), 926 (ONNO) (s), 762 (Ph) (s), 733 (s), 696 (Ph) (s), 686 (OSnO) (m, sh), 400 (Sn−O) (s), 267 (vs), 122(w). − FT-Raman: $\tilde{\nu}$ = 1591 cm^{-1} (C−H) (s), 1486 (C−H) (w), 1465 (C−H) (vw), 1345 (N−N) (m), 1307 (vs), 1158 (C−H) (mw), 1070 (C−H) (vw), 1025 (C−H) (w), 1005 (Ph) (s), 998 (s), 930 (ONNO) (m), 168 (m), 110 (ms). − ^{1}H NMR (CDCl$_3$, 399.92 MHz, 30°C): δ = 7.97 (m, 2 H, Ph-H2, -H6), 7.72 [m, ^{3}J (^{119}Sn−^{1}H) = 77 Hz, 2 H, Ph$_A$-H2, -H6], 7.46−7.36 (m, 6 H). − ^{13}C NMR (CDCl$_3$, 100.6 MHz, 30°C): δ = 145.6 [m, ^{1}J(^{119}Sn, ^{13}C) = 908.3 Hz, Ph$_A$-C1], 140.0 (s, 1, Ph-C1), 135.6 [m, ^{2}J (^{119}Sn−^{13}C) = 58.8 Hz, Ph$_A$-C2, -C6], 130.6 (s, Ph-C4), 129.5 [m, Ph$_A$-C4, ^{4}J(^{119}Sn−^{13}C) = 17.2 Hz], 129.2 (s, Ph-C3, -C5), 128.6 [m, ^{3}J(^{119}Sn−^{13}C) = 85.0 Hz, Ph$_A$-C3, -C5], 119.7 (s, Ph-C2, C6). − ^{119}Sn NMR (CDCl$_3$, 149.106 MHz, 30°C): δ = −327.2 (b, s). − $C_{24}H_{20}N_4O_4Sn$ (547.13): calcd. C 52.7, H 3.7, N 10.2; found C 52.5, H 3.4, N 10.2.

Preparation of Dimethylbis(*N*-nitroso-*N*-phenyl-hydroxylaminato)-tin(IV), $[Me_2Sn(PhN(O)NO)_2]_2$ (3): The salt $NH_4[PhN(O)NO]$ (0.40 g, 2.58 mmol) dissolved in 15 mL MeOH was added to a solution of Me_2SnCl_2 (0.28 g, 1.27 mmol) in 15 mL MeOH. The NH_4Cl promptly precipitated. After stirring for one hour at room temperature, the solution was concentrated to low volume and cooled in a refrigerator for 24 hours. The microcrystalline product deposited was filtered, dried in an anhydrous atmosphere and recrystallized from *n*-heptane as colorless crystals. Yield 0.31 g, 57%, melting point 112−114°C. − FT-IR (KBr): $\tilde{\nu}$ = 1488 cm^{-1} (Ph) (m), 1465 (Ph) (ms), 1351 (N−N) (ms), 1336 (N−N) (ms), 1294 (vs), 1216 (N=O) (s), 1180 (N=O) (ms), 1156 (s), 923 (ONNO) (s), 756 (Ph) (s), 693 (Ph) (s), 683 (OSnO) (ms sh), 545 (Sn−C) (m), 401(Sn−O) (vs), 217 (C−H) (s), 189 (C−H) (s). − FT-Raman: $\tilde{\nu}$ = 1592 cm^{-1} (C−H) (s), 1489 (C−H) (w), 1353 (N−N) (mw), 1298 (vs), 1218 (N=O) (w), 1199 (N=O) (w), 1005 (Ph) (m), 929 (ONNO) (mw), 546 (Sn−C) (w), 517 (SnC$_2$) (m), 112 (m). − ^{1}H NMR (CDCl$_3$, 399.92 MHz, 30°C): δ = 7.93 (m, 2 H, Ph-H2, -H6), 7.45 (m, 3 H, Ph-H3, -H4, -H5), 0.77 [s, ^{2}J(^{119}Sn−^{1}H) = 76.8 Hz, ^{2}J(^{117}Sn−^{1}H) = 73.4 Hz, ^{1}J(^{13}C−^{1}H) = 132.6 Hz, 3 H, Sn−CH$_3$]. − ^{13}C NMR (CDCl$_3$, 100.6 MHz, 30°C): δ = 140.0 (s, Ph-C1), 130.3 (s, Ph-C4), 129.1 (s, Ph-C3, -C5), 119.6 (s, Ph-C2, -C6), 7.8 [m, ^{1}J(^{119}Sn, ^{13}C) = 647.7 Hz, Sn−CH$_3$]. − ^{119}Sn NMR (CDCl$_3$, 149.106 MHz, 30°C): δ = −159.2 (b, s). − $C_{28}H_{32}N_8O_8Sn_2$ (846.04): calcd. C 39.8, H 3.8, N 13.2; found C 39.8, H 4.0, N 13.2.

X-ray Structure Determination for 1−3

Crystal data and refinement parameters are summarized in Table 5. Intensity data were collected on an Enraf−Nonius CAD-4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using the ω-2θ scan technique. Three standard reflections were monitored every hour; these remained constant within

Table 5. Summary of X-ray diffraction data for **1−3**

	1	**2**	**3**
Empirical formula	$C_{24}H_{20}N_8O_8Sn$	$C_{24}H_{20}N_4O_4Sn$	$C_{28}H_{32}N_8O_8Sn_2$
Formula mass	667.17	547.13	846.04
Crystal size [mm]	0.3 × 0.25 × 0.2	0.40 × 0.15 × 0.15	0.60 × 0.40 × 0.20
Color	colorless	colorless	colorless
Crystal system	tetragonal	orthorhombic	triclinic
Space group	$P4_2/n$	*Pbcn*	$P\bar{1}$
θ range for data collection (°)	2.27 ≤ θ ≤ 31.97	2.32 ≤ θ ≤ 25.97	2.42 ≤ θ ≤ 34.99
a [Å]	12.702(2)	13.258(1)	9.417(2)
b [Å]	12.702(2)	11.683(1)	9.458(1)
c [Å]	8.500(2)	14.973(1)	10.738(1)
α [°]	90.00	90.00	76.17(1)
β [°]	90.00	90.00	64.27(1)
γ [°]	90.00	90.00	78.24(1)
V [Å^3]	1371.4(4)	2319.2(3)	831.1(2)
Z	2	4	1
d_{calc} [Mg/m^3]	1.616	1.567	1.681
μ [mm^{-1}]	0.994	1.140	1.453
F(000)	668	1096	420
Index ranges (°)	$-18 \le h \le 18$	$0 \le h \le 16$	$-15 \le h \le 15$
	$0 \le k \le 18$	$0 \le k \le 14$	$-15 \le k \le 15$
	$0 \le l \le 12$	$0 \le l \le 18$	$-17 \le l \le 17$
No. of reflections collected	5254	4549	15581
No. of indep. reflns./R_{int}	2376/0.021	2231/0.020	7253/0.012
No. of obsd. reflections, $I > 2\sigma(I)$	1312	1133	4828
No. of parameters	99	160	210
GOOF	0.879	0.779	0.977
*R*1 (obsd. data)	0.0283	0.0280	0.0305
*wR*2 (all data)	0.0734	0.0622	0.0831
Largest diff. peak/hole (eÅ^{-3})	0.348/−0.369	0.488/−0.332	1.337/−0.452

experimental error. The structure was solved by direct methods (SHELXS-97)[25a] and refined by full-matrix least-squares (SHELXL-97).[25b] All non-hydrogen atoms were refined anisotropically. Hydrogen atomic positions were generated from assumed geometries. The riding model was applied for the hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-125074 (**1**), CCDC-125075 (**2**) and CCDC-125076 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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