Heptacoordinate Dimethyltin(IV)cupferronato Complexes − X-ray and Solid-State NMR Structural Analysis − Hydrogen Bond Supramolecular Self-Assembly

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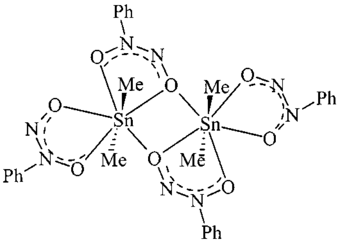
Keywords: Chelates / Hypervalent compounds / N ligands / Self assembly / Tin

Reaction of the dimeric dimethyltin(IV)cupferronato complex $[Me_2Sn(O_2N_2Ph)_2]_2$ (**1**) with 4,4′-bipyridine (bipy), pyridine (py), and 2,6-diamino-4-phenyl-1,3,5-triazine (dpt) afforded three new hepta-coordinated derivatives, $[\mu\text{-}(4,4'\text{-bipy})\{Me_2Sn(O_2N_2Ph)_2\}_2]\cdot MeOH$ (**2**), $Me_2Sn(O_2N_2Ph)_2(py)$ (**3**), and $[Me_2Sn(O_2N_2Ph)_2(MeOH)]\cdot dpt$ (**4**). These were characterised by X-ray structural analysis and solid-state ^{119}Sn, ^{13}C CP MAS NMR-, and multinuclear solution NMR spectroscopy. Single-crystal X-ray diffraction analysis of **2**–**4** showed that in all three compounds tin was hepta-coordinated, and the cupferronato anions were chelated to the Me_2Sn^{IV} centre in a nearly symmetrical arrangement. Compound **4** contained supramolecular self-assembled ribbons, formed by hydrogen bonds between Me_2SnO_5 moieties and pairs of dpt molecules.

Introduction

Recently, we reported the synthesis and structural characterisation of *N*-nitroso-*N*-phenylhydroxylaminato (cupferronato, $PhN_2O_2^-$, hereinafter cupf) tin(IV) complexes, such as $[Me_3Sn(cupf)]_4$ (**5**),[1] $Ph_2Sn(cupf)_2$ (**6**), $[Me_2Sn(cupf)_2]_2$ (**1**), and $Sn(cupf)_4$ (**7**).[2] We found that, depending on the number (0, 2, 3) and the nature (Me, Ph) of the substituents at the Sn^{IV} atom, the cupferronato anion displays various coordination patterns in these molecules: chelating (**6**, **1**, **7**), bridging (**5**), and bridging-chelating (**1**). As a consequence of this, the central Sn^{IV} atom assumes a penta- (**5**), hexa- (**6**), hepta- (**1**), or octacoordinate (**7**) state, respectively, and the resulting complexes display different coordination geometries at the central Sn^{IV} atom.[1,2] Bridging-chelating coordination of the cupferronato ligand to Me_2Sn^{IV} gives the dimeric species **1** (Scheme 1),[2] whereas a bridging coordination affords the tetrameric complex **5** (Scheme 2).[1]

Compound **5** seemed an attractive starting material for building supramolecular structures based upon chains of alternating trigonal planar $SnMe_3$ units with rigid linear spacers, such as 4,4′-bipyridine (4,4′-bipy). The reaction of **5** with 4,4′-bipy, however, afforded a dimethyltin derivative **2**, following tin−carbon bond redistribution (vide infra). This led us to investigate the reactions of the dimethyltin derivative **1** with 4,4′-bpy and with pyridine (py) as a model. Formation of **2** and **3** suggested that a nitrogen-donor base coordinates easily to the tin atom of a $Me_2Sn(cupf)_2$ moiety and we decided to use 2,6-diamino-4-phenyl-1,3,5-triazine (dpt) as a coordinated ligand able to participate in intermolecular hydrogen bond interactions and thus to connect the tin coordination centres into supramolecular architectures. This approach is well documented by several examples of hydrogen bond self-assembled supramolecular structures formed by interactions between amino substituents and heteroatoms.[3] From our previous experience with cobalt and nickel cupferronato adducts of dpt[4] we knew that metalcupferronates could form supramolecular structures based upon this strategy. Although only in its



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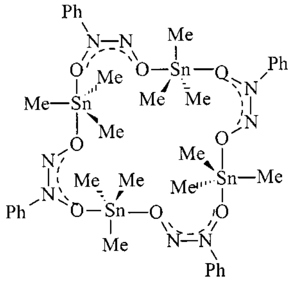
Scheme 1



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Scheme 2

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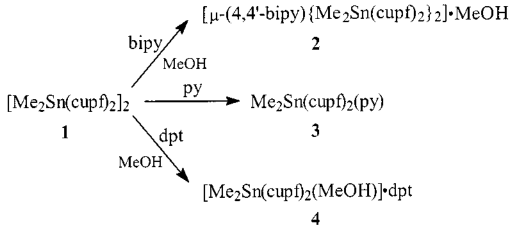
infancy, the combination of coordination dative and hydrogen bonds in the construction of supramolecular architectures opens a wide area of investigation, and has already provided some interesting results.[4] On the other hand, some organotin supramolecular assemblies based on hydrogen bonds are known,[6] opening a potentially broad field for novel materials of this type.

The reactions investigated in this research are illustrated in Scheme 3. The structural analyses of the products thus obtained, [μ-(4,4′-bipy){$Me_2Sn(cupf)_2$}$_2$]·MeOH (**2**), $Me_2Sn(cupf)_2(py)$ (**3**), and [$Me_2Sn(cupf)_2(MeOH)$]·dpt (**4**), are reported here. To this end, X-ray analyses of **2**−**4** were carried out and the resulting structures compared with those of **1** and **5** reported previously.[1,2]



Scheme 3

Solid-state ^{119}Sn NMR spectroscopy is known to give insight into the local symmetry properties of the central tin(IV) atom, and, combined with solution ^{119}Sn NMR spectroscopic data, provides information about the structural changes occurring upon dissolution of the organotin compounds.[7] The availability of X-ray data on a set of structurally related organotin(IV) molecules (**1**−**5**) prompted us to complement the present work with the solid-state and solution NMR spectroscopic data.

Results and Discussion

Synthesis of the Complexes

The reaction of **5**, a tetrameric complex, with bipy in methanol, and the reaction of dimer **1** in *n*-heptane with bipy, followed by recrystallisation from MeOH, both yielded the solvated binuclear complex **2** (Scheme 3).

Mössbauer spectroscopic studies[8] have shown that in concentrated methanolic solution, **5** undergoes a redistribution[9] involving Sn−Me bond cleavage (Scheme 4).

$$\underset{\mathbf{5}}{[Me_3Sn(cupf)]_4} \xrightarrow{MeOH} \underset{\mathbf{1}}{[Me_2Sn(cupf)_2]_2} + 2\ Me_4Sn$$

Scheme 4

Slow evaporation of a pyridine solution of **1** afforded mononuclear **3** as colourless crystals after several days. Addition of a methanolic solution of dpt to **1** in methanol readily gave **4** as a crystalline compound.

X-ray Analyses

Molecular Structures

The molecular structures of **2**−**4**, established by single-crystal X-ray diffraction, are shown in Figures 1−3, with the atom numbering schemes. The relevant geometric parameters are collected in Table 1. The data obtained for **2** reveal that the Sn^{IV} centres are heptacoordinate and located

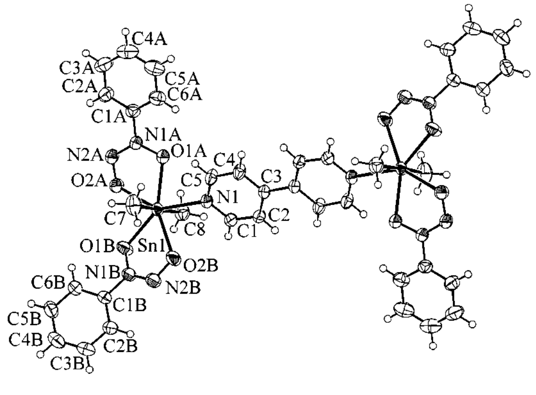


Figure 1. Molecular structure of **2**, the disordered MeOH molecules were omitted

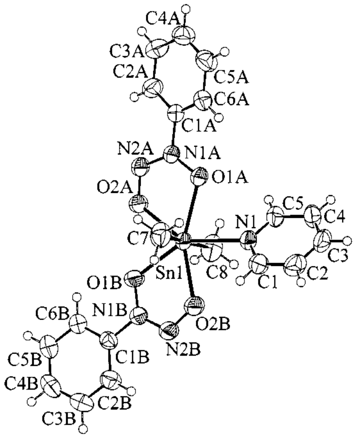


Figure 2. Molecular structure of **3**

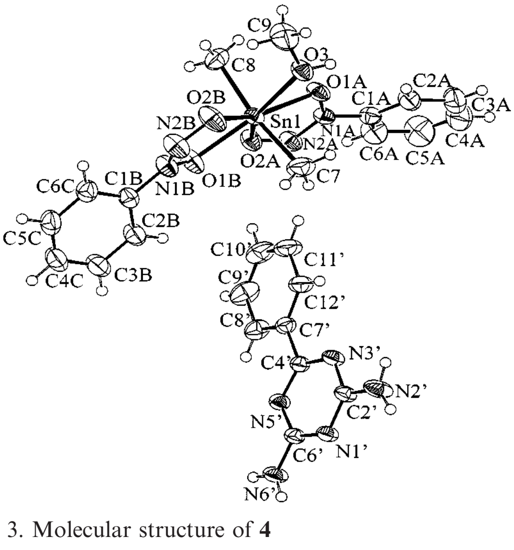


Figure 3. Molecular structure of **4**

Table 1. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **2**−**4**

	2[a]		**3**		**4**	
	L = *A*	*L* = *B*	*L* = *A*	*L* = *B*	*L* = *A*	*L* = *B*
Sn(1)−O(1*L*)	2.2831(12)	2.2769(13)	2.3104(14)	2.2306(14)	2.3435(10)	2.2012(10)
Sn(1)−O(2*L*)	2.2738(12)	2.3313(13)	2.2584(14)	2.3167(15)	2.2792(9)	2.2804(12)
Sn(1)−N(1)	2.4497(13)		2.4677(16)			
Sn(1)−O(3)					2.4119(9)	
Sn(1)−C(7)	2.123(2)			2.114(3)	2.1100(15)	
Sn(1)−C(8)	2.1124(18)			2.109(3)	2.1129(14)	
O(1*L*)−N(1*L*)	1.3134(16)	1.3132(16)	1.3168(18)	1.314(2)	1.3133(13)	1.3243(14)
O(2*L*)−N(2*L*)	1.3004(18)	1.288(2)	1.293(2)	1.287(2)	1.3025(15)	1.2948(17)
N(1*L*)−N(2*L*)	1.2852(18)	1.2896(19)	1.284(2)	1.286(2)	1.2878(14)	1.2864(16)
O(1*L*)−Sn(1)−O(2*L*)	67.51(4)	66.87(4)	67.53(5)	67.71(5)	66.12(3)	69.43(4)
C(7)−Sn(1)−C(8)		177.91(7)		174.30(9)		170.75(6)
O(1*L*)−N(1*L*)−N(2*L*)−O(2*L*)	0.4(2)	−0.4(3)	0.9(3)	0.3(3)	−0.2(2)	0.8(2)
O(1*L*)−N(1*L*)−C(1*L*)−C(6*L*)	−7.5(2)	−16.6(2)	15.7(3)	−1.8(3)	16.7(2)	−145.1(1)
N(2*L*)−N(1*L*)−C(1*L*)−C(2*L*)	−9.0(2)	−18.4(2)	18.5(3)	−1.9(3)	19.3(2)	−143.5(1)

[a] *L* = *A* and *L* = *B* represent the two different cupferronato ligands chelated to tin.

in a nearly pentagonal bipyramidal environment, with the equatorial plane defined by the O_4N donor set of the cupferronato and the bipy ligands, and the two methyl groups in the apical positions. The formation of **2** occurs through the cleavage of the dative Sn←O bonds of the dimer **1**, with the bipy ligands acting as spacers that link the two Me_2Sn^{IV} centres. One should note that the four-membered Sn_2O_2 ring, typical for all structurally characterised pentagonal bipyramidal C_2SnO_4N cores of Me_2Sn^{IV} dimers,[10] is absent in **2**. Consequently, each half of **2** contains two SnO_2N_2 units as five-membered chelate rings (*A* and *B*) with O(1*L*)−Sn(1)−O(2*L*) bite angles of 67.51(4)° (*A*) and 66.87(4)° (*B*). The lengths of the two Sn−O bond formed in ligands *A* are nearly equal ($\Delta = 0.009$ Å), while those in ligands *B* are slightly different ($\Delta = 0.054$ Å). It should be mentioned here that the chelating cupferronato anions in the parent **1** are isobidentate when coordinated to the dimethyltin(IV) centre ($\Delta = 0.076$ Å), whereas the triconnective cupferronato ligands exhibit different Sn−O bond lengths ($\Delta = 0.148$ Å). In a manner similar to the tridentate aminodicarboxylato anions in dimethyltin(IV) dimers,[10] the latter finding may be ascribed to the triconnective coordination of the cupferronato O atoms. The Sn−N bond length of 2.4450 (1) Å in **2** is slightly longer than the 2.402(2) Å observed in the polymeric $[Me_2SnCl_2(4,4'\text{-bipy})]_n$ complex.[11] There are two positionally disordered MeOH molecules in the unit cell (space group $P2_1/n$) with their O atoms in special positions (inversion centres).

Dissolution of **1** in anhydrous pyridine affords **3**, the "monomeric" form of **2**. Consequently, each tin(IV) centre retains its nearly pentagonal bipyramidal coordination. To the best of our knowledge this is the first reported case where a Me_2Sn^{IV} complex is built from C_2SnO_4N core, despite the fact that this core is known to be ubiquitous in multinuclear complexes.[7,10] The structural similarity between **3** and **2** is reflected by the practically unaltered O(1*L*)−Sn(1)−O(2*L*) bite angles [67.53(5)° for *A* and 67.71(5)° for *B*] and differential Sn−O distances ($\Delta = 0.052$ Å for *A*, $\Delta = 0.086$ Å for *B*). The Sn−N distance is somewhat longer than those found for dimer **2** and $Me_2SnCl_2\cdot 2py$ (2.39 Å).[12] In a manner similar to **2**, the nitrosohydroxylaminato groups of the cupferronato anions are essentially planar in **3**, while the phenyl ring is nearly coplanar with the plane of the N(O)NO group, although the O(1*L*)−N(1*L*)−C(1*L*)−C(6*L*) and O(1*L*)−N(1*L*)−C(1*L*)−C(2*L*) torsion angles show some variation (Table 1).

The crystal lattice of **4** contains the complex $Me_2Sn(cupf)_2(MeOH)$ (**4a**) and dpt molecules. The coordination geometry of the Sn^{IV} atom in **4** was found to be closely similar to that in **2** and **3**. Coordination of the bulky dpt unit to the Me_2Sn^{IV} centre via the pyridyl nitrogen atoms is sterically hindered by the likewise bulky cupferronato ligands. Therefore, only one MeOH molecule may occupy the vacant seventh position of the coordination sphere. In this arrangement, the O atom of the MeOH molecule occupies the position of the N atom of bipy (**2**) or py (**3**). This results in a pentagonal bipyramidal C_2SnO_5 core, like the one found for the parent **1**. The latter core is known to occur both in mononuclear[13] and dinuclear[2,14] Me_2Sn^{IV} complexes, although **4** represents the first structurally characterised compound containing methanol coordinated to a dimethyltin(IV) centre.

In complex **4**, the cupferronato *A* and *B* ligands display fairly similar coordination, but remarkably different hydrogen bonding. Both *A* and *B* form five-membered inorganic SnO_2N_2 rings that assume different O(1*L*)−Sn(1)−O(2*L*) bite angles [66.12(3)° for *A* and 69.43(4)° for *B*] and unequal differential Sn−O bond lengths: $\Delta = 0.064$ Å in ligand *A* and $\Delta = 0.079$ Å in ligand *B*. Finally, in anion *B*, the plane of the phenyl group is markedly twisted away from the plane of the N(O)NO group with the O(1*B*)−N(1*B*)−C(1*B*)−C(6*B*) torsion angle taking a value of −145.1(1)°.

Crystal Packing and Supramolecular Organisation

The data collected in Table 2 reveal that the crystal lattices of the complexes reported in this work are supramolec-

Table 2. Selected interatomic distances (Å) and angles (°) for the hydrogen bonding and C−H···π interactions in **2**−**4**; Symmetry codes see footnotes

Compd.	D−H···A[a]	H···A (Å)	D···A (Å)	D−H···A (°)
2	C(1)−H(1)···O(2A)[b]	2.56	3.41	151
	C(2)−H(1)···O(1B)[b]	2.58	3.43	153
	C(4A)−H(4A)···π(Ph_B)[c]	2.86	3.44	121
	C(5)−H(5)···π(Ph_B)[d]	3.21	3.72	117
	C(4)−H(4)···π(Ph_B)[d]	3.24	3.72	115
	C(4A)−H(4A)···π(bipy)[e]	3.29	3.34	85
	C(1S)−H(11S)··· π(bipy)[f]	3.05	3.77	133
3	C(5)−H(5)···π(Ph_B)[g]	3.195	3.96	141
	C(7)−H(7A)···π(py)[h]	3.23	3.63	107
	C(7)−H(7B)···π(py)[h]	3.14	3.63	113
4	O(3)−H(3O)···N(3′)[i]	1.96	2.77	160
	N(2′)−H(2′A)···O(1A)[i]	2.11	2.96	171
	N(2′)−H(2′B)···O(2A)[j]	2.32	3.10	161
	N(6′)−H(6′B)···N(1′)[k]	2.18	3.02	171
	N(6′)−H(6′A)···O(2A)[l]	2.46	3.13	134
	C(4A)−H(4A)···π(Ph_{dpt})[m]	2.875	3.78	165
	C(7)−H(7B)···π(Ph_A)[n]	3.00	3.73	133
	C(9′)−H(9′)···π(Ph_B)[o]	3.09	3.78	132

[a] for intermolecular C−H···π contacts the H···ring-centroid distances must be less than 3.4 Å[15a] [b] 3/2 − *x*, 1/2 + *y*, 1/2 − *z*; [c] 1 − *x*, 1 − *y*, − *z*; [d] 1/2 + *x*, 3/2 − *y*, − 1/2 + *z*; [e] 2 − *x*, 1 − *y*, − *z*; [f] *x*, *y*, *z*; [g] 3/2 − *x*, 1/2 + *y*, 3/2 − *z*; [h] 2 − *x*, −*y*, 2 − *z*; [i] −*x* + 1, − *y* + 1, − *z*; [j] *x*, *y* − 1, *z*; [k] − *x* + 1, − *y*, − *z* + 1; [l] − *x* + 1, − *y* + 1, − *z* + 1; [m] − *x*, 1 − *y*, − *z*; [n] 1 − *x*, 1 − *y*, − *z*; [o] −1 + *x*, *y*, *z*.

ular architectures involving more than just van der Waals interactions. Thus, molecules **2** and **3** form crystal lattices stabilised by weak C−H···π intermolecular interactions. An additional interaction via weak C−H···O hydrogen bonding between individual molecules can also be observed in the crystal lattice of **2**.

Compound **4** forms an infinite supramolecular structure (Figure 4) where units of **4a** and dpt molecules are interconnected by regular N−H···O and O−H···N hydrogen bonds, mediated in part by the MeOH molecules. On the one hand, this is achieved in such a way that the MeOH molecules form short (1.96 Å) O−H···N hydrogen bonds with the neighbouring dpt units. In competition with the MeOH molecules, the dpt units, in their turn, interact with the two oxygen atoms of cupferronato anions of the **4a** complex via N−H···O hydrogen bonds (2.11 Å and 2.46 Å). The intermolecular O−H···N and N−H···O hydrogen bonds together assemble the units **4a** and dpt in infinite chains. These chains then become cross-linked to their respective symmetry-related neighbouring chains through N−H···O and N−H···N hydrogen bonds (2.32 Å and 2.18 Å, respectively) to form infinite one-dimensional double-chains (ribbons). In the supramolecular structure thus formed, the Sn···Sn separation between neighbouring **4a** units amounts to ca. 6.8 Å. It may be noted that the N−H···N hydrogen bonds between neighbouring dpt units lead to the formation of eight-membered $(N-C-N-H\cdots)_2$ rings (see Figure 4), while, using the hydrogen atoms of their NH_2 groups, the dpt units also formed N−H···O hydrogen bonds with the cupferronato O atoms of **4a** in the adjacent chain.

Alternatively, the supramolecular arrays can be described as containing pairs of hydrogen-bonded dpt molecules (via N−H···N bonds), interconnected through two separate **4a** molecules, via N−H···O bonds (to the chelate rings) and N···H−O bonds (to the coordinated methanol molecules). Therefore, the supramolecular architecture is a result of the co-operative use of hydrogen bonds and dative coordinate bonds (provided by the methanol ligand).

The neighbouring supramolecular sheets are ordered by C−H···π (Table 2) and π···π interactions. These weak C−H···π and π···π interactions influence the nature of hydrogen-bonding and vice versa.[15]

Structure Determination by NMR Spectroscopy

The structurally relevant NMR spectral parameters for **1**−**5** are collected in Table 3. (For the fully assigned, solution, ^1H, ^{13}C, and ^{119}Sn NMR parameters see the Exp. Sect. and ref.[2]).

Within a given set of related organotin complexes, the chemical shift of the ^{119}Sn nuclei has been shown to reflect the coordination number, the size of the chelate ring, and the nature of the donor atom directly bonded to the central tin(IV) atom: higher coordination numbers, larger ring sizes, and lower electronegativities of the donor atoms shift the ^{119}Sn resonance to lower frequencies.[3,16] Although an exact separation of the various contributions to the nuclear shielding is beyond current theoretical knowledge, the ^{119}Sn chemical shift values in Table 3 do, in general, follow the expected trends. The highest value of the chemical shift of tetrameric (**5**) clearly reflects its pentacoordinated geometry,[1] while the nuclear shielding found for **1**−**4** falls in the range typical of hexa- and heptacoordinated organotin complexes.[3,12] One may tentatively assume that the rela-

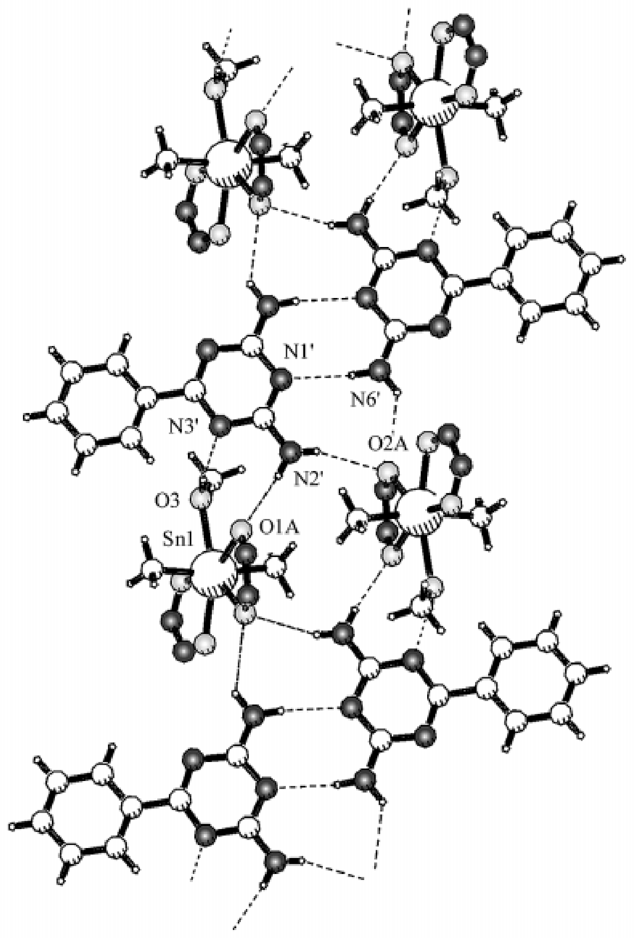


Figure 4. Section of the crystal structure of **4** showing the infinite one-dimensional double-chains (ribbons) formed through O−H···N and N−H···X (X = O, N) hydrogen bonds; the phenyl groups were omitted for clarity.

tively lower δ_i^{Sn} values observed for solid **1** and **4** are due to the higher electronegativity of the directly bonded oxygen atom as compared to the N-linkage in **2** and **3**.[16]

The chemical shift anisotropy, $\Delta\sigma$, for **1−4** varies in the range between +383 and +532 ppm, while it becomes negative (−262 ppm) in **5**. An analogous dissimilarity can be seen in the case of the asymmetry parameter, η: it is zero, or nearly zero, in complexes **1−4** while it has a substantial value (0.6) in **5**. Low values of η are known to reflect axial symmetry of the tin(IV) centre,[17] an expectation fully supported by X-ray results showing pentagonal bipyramidal coordination geometry for **1−4**. By contrast, the asymmetry parameter measured for **5** may be rationalised by considering the X-ray structure of this molecule.[1] It has been found that a weak, secondary, nonbonded Sn···O interaction removes the axial symmetry of the Sn^{IV} centre, which then assumes a distorted trigonal bipyramidal (TBP), pseudo hexagonal, geometry.

The magnitude of the solid state one bond tin−carbon scalar coupling, $^1J(^{119}Sn-^{13}C)$, (measured here as the frequency difference between ^{119}Sn satellite signals in the ^{13}C CP MAS spectra) can be used for estimating the Me−Sn−Me angle.[7] The coupling data obtained for **1−4** fall in the range ≈ 1060−1160 Hz (Table 3), and according to the Lockhart−Manders approximation,[7] give a value of 170−179°, in good overall agreement with X-ray observations. It should be noted, however, that the slight changes in the Me−Sn−Me angles show opposite trends according to whether the angles were inferred from X-ray or $^1J(^{119}Sn-^{13}C)$ coupling data (see Table 4). The value of 520 Hz measured for **5** gives 122°, in excellent agreement with the X-ray-derived average value, 120°.

Table 4. Values of Me−Sn−Me angles(°) from X-ray and from ^1J and ^2J[7a]

Compd.	Me−Sn−Me (°) X-ray	^1J(solid)[a]	^1J(solution)[a]	^2J(solution)[b]
1	173.6(1)[2]	171.6	136.3	127.3
2	177.91(7)	173	142.8	135.6
3	174.30(9)	173.8	151	145.8
4	170.75(6)	181.5	175.8	191.7
5	119.91(12)[1] [c]	121.3	110.4	109.5

[a] Me−Sn−Me (°) = $(|^1J| + 778)/10.7$ [b] Me−Sn−Me (°) = $0.0161(|^2J|)^2 - 1.32(|^2J|) + 133.4$ [c] average value

Some additional features of the ^{13}C CP MAS spectra deserve attention. Mirroring the slight changes in the steric environments of the two Sn^{IV}-bonded Me carbon atoms, the ^{13}C spectra of **1−4** display two methyl signals separated by 1.3−2.7 ppm (Table 3). No such effect could be resolved (at 100 MHz) in the spectrum of **5** having three, equatorially oriented, methyl groups attached to the central Sn^{IV} atom. The ^{13}C CP MAS spectrum of **4** also displays a sharp resonance at δ = 49.5 attributable to the methanol Me signal.

Table 3. Selected NMR spectral parameters of complexes **1−5**

Compd.	σ_i [a] Solid-state	σ_{33}	σ_{22}	σ_{11}	$\Delta\sigma$	δ_A	η	δ_i^{Sn} [b]	$^1J(^{119}Sn-^{13}C)$	$\Delta\delta^{Me}$	δ_i^{Sn}(sol.) Solution	$^1J(^{119}Sn-^{13}C)$	$^2J(^{119}Sn-^1H)$
1	184.7	464.0	47.6	−2.7	419.0	279.3	0.2	−184.7	1058±15	1.21	−185.5	680.8	77.1
2	273.2	628.1	74.5	21.2	532.4	354.9	0.2	−273.2	1073±15	2.68	−216.4	750.5	83.6
3	252.6	523.0	58.7	58.7	405.6	270.4	0.0	−252.6	1082±15	2.66	−258.5	837.6	90.5
4	246.6	502.0	70.0	70.0	383.0	255.3	0.0	−246.6	1164±15	1.36	−368.2	1103.3	113.8
5	−1.5	−173.1	81.6	136.8	−261.9	−174.6	0.6	1.5	520±10	0.0	95.9	403.8	54.9

[a] $\sigma_i = 1/3(\sigma_{33} + \sigma_{22} + \sigma_{11})$; $|\sigma_{33} - \sigma_i| > |\sigma_{11} - \sigma_i| > |\sigma_{22} - \sigma_i|$; $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$; $\Delta\sigma = 3/2\delta_A$; $\delta_A = \sigma_{33} - \sigma_I$; $\eta = 3/2(\sigma_{22} - \sigma_{11})(\Delta\sigma)^{-1}$ [b] Chemical shifts are in ppm, coupling constants in Hz;

Dissolution of the complexes results in several changes in the spectral parameters (see Table 3) that suggest differences between the molecular conformations in the solid and solution states. The solution ^{119}Sn chemical shifts, δ^{Sn}(sol.), for **1−3** are fairly close to their isotropic values, δ_i^{Sn}, found in the solid state, suggesting that the coordination geometry of these complexes remains unaffected by dissolution. The marked shift to lower frequency of the ^{119}Sn resonance in **4** may be tentatively rationalised by assuming that due to the presence of DMSO in the solvent (which may replace the coordinated methanol molecule), the coordination pattern of the complex undergoes some modifications. In contrast to the near-constancy of the overall molecular geometry in the two states, as mirrored by the ^{119}Sn chemical shifts, $^1J(^{119}Sn-^{13}C)$ and in part $^2J(^{119}Sn-^1H)$, couplings suggest that the solvent-solute interactions may, in reality, give rise to some changes in the molecular geometry. As attested by the coupling data, these are highest in **1** while practically absent in **4**. For **1** we find that the Me−Sn−Me angle assumes a value of approx. 130° in solution as opposed to 170° (X-ray: 173.6°) in the solid-state (see Table 4). It seems justified to assume that so significant a decrease of the bond angles at the Sn^{IV} centre of the complex should entail further changes in the molecular conformation. However, at this stage of our work we cannot suggest a plausible correlation between the extent of solvent-induced geometrical changes and the structure of the complexes.

The δ = 1.5 measured for δ_i^{Sn} in **5** is in accordance[18] with the *trans*-TBP pentacoordinated structure of this complex (see above).[1] The ^{119}Sn resonance was shifted to higher frequency (δ = 95.9) in solution, which is best understood by assuming that the tetrameric complex dissociates into monomeric species featuring *cis*-TBP coordination geometry. This expectation seems to be supported by the reduction of the Me−Sn−Me angle from its original value of 120°, typical of planar Me$_3$Sn groups, to the value of 110° (see Table 4) characteristic for the pyramidal Me$_3$Sn arrangement as in the proposed monomer.[19]

Conclusion

Coordination of N- and O-donor molecules to the Me$_2$Sn^{IV} centre of dimeric **1** results in the cleavage of the stanoxanic dative Sn←O bonds, and subsequent formation of novel heptacoordinated dimethyltin(IV)cupferronato complexes (**2−4**). In these, the cupferronato ligands assume their typical chelating coordination pattern and are nearly symmetrically bound to the Me$_2$Sn^{IV} centre. An X-ray diffraction study of **4** revealed that the pentagonal bipyramidal C$_2$SnO$_5$ moiety might interact with dpt molecules through hydrogen-bonding interactions. Multinuclear solid- and solution NMR spectroscopic data of the novel complexes provide useful complementary information about structural changes accompanying the dissolution of the crystalline complexes.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial suppliers. The preparation and purification of the complexes were carried out in the open air or in a dry atmosphere, as indicated. The syntheses of **1**[2] and **5**[1] were reported previously. All other starting materials were obtained from commercial sources as pure compounds and used as received. − FT-IR spectra were recorded with a Jasco FT/IR 615 spectrometer. − NMR spectroscopy: A Varian Associates model Unity-Inova 400 NMR spectrometer was used to run the NMR spectra using TMS as the internal reference for ^{1}H, ^{13}C, and external SnMe$_4$ for ^{119}Sn spectra. Solution spectra were recorded at 30 °C using solutions of ca. 5% in CDCl$_3$. For solubility reasons, spectra for **4** were taken in a [D$_6$]DMSO/CDCl$_3$ (1:1) solvent mixture. Assignment of the resonances to individual sites in the molecules was inferred from ^nJ(H−H) and ^nJ(C−C) coupling patterns and, when needed, verified through standard, gradient-enhanced, homo-, and heteronuclear 2D (gDQFCOSY,[20] gHSQC[20]) experiments. − Solid-state ^{119}Sn and ^{13}C CP MAS spectra were recorded at room temperature using 7 mm rotors. Typically, two ^{119}Sn CP-MAS spectra were recorded at significantly different spinning rates, ca. 2000 and 4500 rps, respectively. The $\pi/2$ pulse width for ^{119}Sn had a value of 4.1 µs (61 kHz). A recycle delay of 20 s and a CP time of 1 ms were used, and from 30000 to 36000 transients were co-added to obtain the fits. Solid-state ^{119}Sn line-widths varied between 250 to 500 Hz. Solid-state spectral parameters (see Table 3) were inferred by iterative fitting of simulated spectra to the side band manifold of the experimental spectra. The r.m.s. errors of the fitting procedures varied between 0.12 and 0.18 suggesting a 10 to 15 ppm probable error in the values of δ_i and $\Delta\sigma$. However, due to limited pulse power for the uniform excitation of the wide (5000−8000 ppm) ^{119}Sn spectral range, the real errors of these parameters may be larger. ^{13}C CP MAS spectra were taken at spinning rates 3000−4000 rps using a pw90 = 4.1µs (61 KHz) carbon pulse, 5 s recycle delay, 1 ms CP time, and from 4000 to 8000 transients. In alternative runs the TOSS sequence[21] was used to remove the spinning side bands. Solids-state ^{13}C line-widths varied between 100 and 150 Hz.

(µ$_2$–4,4′-Bipyridyl)-bis[di-*N*-nitroso-*N*-phenyl-(hydroxylaminato)-dimethyltin(IV)] Methanol Solvate (2). − Method A: To a solution containing **1** (0.41 g, 0.47 mmol) in 5 mL of *n*-heptane was added a solution of bipy (0.10 g, 0.64 mmol, 35% excess) in 2 mL of *n*-heptane while stirring. Precipitation of the complex occurred immediately. After stirring for one hour at room temperature the precipitate was filtered off and washed with cold MeOH and dried in air. Yield 0.385 g, 81%. The product was recrystallized from MeOH under ambient conditions as large colourless block crystals.

Method B: To a solution containing **5** (0.3 g, 0.25 mmol) in 3 mL of MeOH was added a solution of bipy (0.156 g, 1 mmol, 300% excess) in 2 mL of MeOH while stirring. The mixture was stirred for 4 hours. After 2−3 days the compound was separated as large colourless block crystals. The crystals were filtered off, washed with cold MeOH and dried in air. Yield 0.14 g, 53%, melting point 125−126 °C. − FT-IR (KBr): $\tilde{\nu}$ = 3483 cm^{-1} (O−H) (m b), 3104−2823 (m b), 1606 (O−H) (m), 1482 (Ph) (m), 1461 (Ph) (ms), 1415(m), 1337 (N−N) (ms), 1285 (vs), 1215 (N=O) (s), 1166 (N=O) (ms), 1060 (ms), 921 (ONNO) (s), 812 (m), 761 (Ph) (s), 691 (Ph) (s), 627 (ms), 576 (SnC$_2$) (m), 523 (Sn−C) (m), 395 (Sn−O) (vs). − ^{1}H NMR (CDCl$_3$, 399.10 MHz, 30 °C): δ = 0.79 [m, 6 H, CH$_3$, $^1J(^{13}C-^1H)$ = 132.3 Hz, $^2J(^{119}Sn-^1H)$ = 83.6 Hz, $^2J(^{117}Sn-^1H)$ = 80.0 Hz, $^2J(^{115}Sn-^1H)$ = 73.6 Hz], 7.46 (m, 3 H, Ph−H3, −H4, −H5), 7.59 (m, 2 H, Py−H3, −H5), 7.96 (m, 2 H,

Table 5. Summary of X-ray diffraction data for **2−4**

	2	**3**	**4**
Empirical formula	$C_{38}H_{40}N_{10}O_8Sn_2$ CH_4O	$C_{19}H_{21}N_5O_4Sn$	$C_{15}H_{20}N_4O_5Sn$ $C_9H_9N_5$
Formula mass	1034.22	502.10	642.25
Crystal size [mm]	0.25 × 0.25 × 0.50	0.25 × 0.30 × 0.55	0. 35 × 0.45 × 0.60
Colour	colourless	colourless	colourless
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
θ range for data collection (°)	$2.39 \le \theta \le 34.97$	$2.46 \le \theta \le 34.96$	$2.36 \le \theta \le 34.96$
a [Å]	11.047(2)	9.746(1)	10.259(1)
b [Å]	11.395(2)	14.596(2)	11.500(1)
c [Å]	17.025(3)	14.759(2)	12.591(1)
α [°]	90	90	100.31(1)
β [°]	90.70(3)	92.51(1)	100.77(1)
γ [°]	90	90	97.33(1)
V [Å^3]	2143.0(7)	2097.5(5)	1415.7(2)
Z	2	4	2
d_{calc} [Mg/m^3]	1.603	1.590	1.507
μ [mm^{-1}]	1.230	1.253	0.953
F(000)	1040	1008	652
Index ranges (°)	$-17 \le h \le 17$	$-15 \le h \le 15$	$-16 \le h \le 16$
	$0 \le k \le 18$	$0 \le k \le 23$	$-18 \le k \le 18$
	$0 \le l \le 27$	$-23 \le l \le 0$	$-20 \le l \le 20$
No. of reflections collected	9883	9700	26352
No. of indep. reflns./R_{int}	9362/0.0067	9162/0.0092	12379/0.014
No. of obsd. reflns. $I > 2\sigma(I)$	6620	5334	10241
No. of parameters	281	264	356
GOOF	1.001	0.926	1.012
*R*1 (obsd. data)	0.0266	0.0335	0.0268
*wR*2 (all data)	0.0703	0.0786	0.0699
Largest diff. peak/ hole (e Å^{-3})	−0.392/0.670	−1.439/0.742	−0.727/1.112

Ph−H2, −H6), 8.86 (m, 2 H, Py−H2,−H6) ppm. − ^{13}C NMR ($CDCl_3$, 100.56 MHz, 30 °C): δ = 8.9 [m, CH_3, $^1J(^{119}Sn-^{13}C)$ = 750.5 Hz, $^1J(^{117}Sn-^{13}C)$ = 717.5 Hz], 119.6 (s, Ph−C2, −C6), 129.0 (s, Ph−C3, −C5), 121.5 (s, Py−C3, −C5), 140.1 (s, Ph−C1), 130.1 (s, Ph−C4), 145.7 (s, Py−C4), 150.4 (s, Py−C2, −C6). − ^{119}Sn NMR ($CDCl_3$, 149.09 MHz, 30 °C): δ = − 216.4 [br. m, Δ = 42 Hz, $^1J(^{119}Sn-^{13}C)$ = 750 Hz]. − $C_{39}H_{44}N_{10}O_9Sn_2$ (1034.26): calcd. C 45.3, H 4.3, N 13.5; found C 45.3, H 4.5, N 13.5.

Bis(*N*-nitroso-*N*-phenyl-hydroxylaminato)dimethylpyridyltin(IV) (3): Compound **1** (0.30 g. 0.347 mmol) was dissolved in 15 mL of warm pyridine and the yellow solution was stirred for several hours at room temperature. After several weeks the compound separated as large colourless block crystals. Yield 0.32 g, 91%, melting point 84−85 °C. − FT-IR (KBr): ṽ = 1487 cm^{-1} (Ph) (m), 1468 (Ph) (ms), 1342 (N−N) (ms), 1294 (vs), 1228 (N=O) (s), 1193 (N=O) (ms), 1165 (N=O) (ms), 1155 (s), 918 (ONNO) (s), 747 (Ph) (s), 700 (Ph) (s), 623 (ms), 572 (SnC_2) (m), 527 (Sn−C) (m), 395 (Sn−O). − ^{1}H NMR ($CDCl_3$, 399.10 MHz, 30 °C): δ = 0.80 [m, 6 H, CH_3, $^1J(^{13}C-^1H)$ = 132.0 Hz, $^2J(^{119}Sn-^1H)$ = 90.5 Hz, $^2J(^{117}Sn-^1H)$ = 86.5 Hz, $^2J(^{115}Sn-^1H)$ = 79.5 Hz], 7.36 (m, 2 H, Py−H3, −H5), 7.44 (m, 6 H, Ph−H3, −H5), 7.74 (m, 1 H, Py−H4), 7.98 (m, 4 H, Ph−H2, −H6), 8.81 (m, 2 H, Py−H2, −H6). − ^{13}C NMR ($CDCl_3$, 100.56 MHz, 30 °C): δ = 119.4 (s, Ph−C2,−C6), 10.0 [m, CH_3, $^1J(^{119}Sn-^{13}C)$ = 837.6 Hz, $^1J(^{117}Sn-^{13}C)$ = 802.8 Hz, $^1J(^{115}Sn-^{13}C)$ = 774.6 Hz], 123.9 (s, Py−C2, −C5), 128.9 (s, Ph−C3, −C5), 129.8 (s, Ph−C4), 136 (s, Py−C4), 140.2 (s, Ph−C1), 149.1 (s, Py−C2, −C5). − ^{119}Sn NMR ($CDCl_3$, 149.09 MHz, 30 °C): δ = − 258.5 [br. m, Δ = 75 Hz, $^1J(^{119}Sn-^{13}C)$ ≈ 835 Hz]. − $C_{19}H_{21}N_5O_4Sn$ (502.12): calcd. C 45.4, H 4.2, N 13.9; found C 45.5, H 4.4, N 13.9.

Bis(*N*-nitroso-*N*-phenyl-hydroxylaminato)methanolato-dimethyltin-(IV) 2,6-Diamino-4-phenyl-1,3,5-triazine Adduct (4): To 8 mL of methanolic solution of **1** (0.52 g, 0.60 mmol) was added dpt (0.225 g, 1.20 mmol) dissolved in 15−20 mL of warm MeOH, and the clear solution was stirred for several hours at room temperature. Precipitation of the compound occurred after 3 hours. Recrystallisation from MeOH gave the product as large colourless block crystals. Yield 0.52 g, 66.6%, m.p. 171−175 °C. − FT-IR (KBr): ṽ = 3447 cm^{-1} (O−H) (ms), 3326 (NH_2) (ms), 3224 (sh), 3154 (NH_2) (ms, br), 3062 (sh) 1661 (NH_2) (m), 1628 (O−H) (s), 1591 (ms), 1540 (C_3N_3) (vs, brd), 1524 (vs, sh), 1488 (Ph) (m), 1459 (Ph) (ms), 1436 (w), 1401 (m), 1340 (N−N) (ms), 1334 (N−N) (ms, sh), 1290 (vs), 1211 (N=O) (s), 1184 (N=O) (ms), 1166 (m), 1159 (m), 1062 (m), 1010 (m), 925 (ONNO) (s), 915(sh), 827 (m), 783(m), 755 (Ph) (s), 703 (C_3N_3), 692 (Ph) (s), 580 (SnC_2) (m), 543 (Sn−C) (b), 395 (Sn−O) (vs). − ^{1}H NMR ([D$_6$]DMSO /$CDCl_3$ (1:1), 399.10 MHz, 30 °C): δ = 0.58 [m, 6 H, CH_3, $^1J(^{13}C-^1H)$ = 132.0 Hz, $^2J(^{119}Sn-^1H)$ = 113.8 Hz, $^2J(^{117}Sn-^1H)$ = 109.2 Hz, $^2J(^{115}Sn-^1H)$ = 100.5 Hz], 6.52 (s, 4 H, dpt−NH_2), 7.41 (m, 1 H, dpt−Ph−H4), 7.45 (m, 2 H, dpt−Ph−H3, −H5), 7.48 (m, 2 H, Ph−H4), 7.53 (m, 4 H, Ph−H3, −H5), 7.96 (m, 4 H, Ph−H2, −H6), 8.29 (m, 2 H, dpt−Ph−H2, −H6). − ^{13}C NMR ([D$_6$]DMSO/$CDCl_3$ (1:1), 100.56 MHz, 30 °C): δ = 13.8 [m, CH_3, $^1J(^{119}Sn-^{13}C)$ = 1103.3 Hz, $^1J(^{117}Sn-^{13}C)$ 1055.0 Hz], 119.4 (s, Ph−C2, −C6), 127.9 (s, dpt−Ph−C2, −C6), 128.0 (s, dpt−Ph−C3, −C5), 129.3 (s, Ph−C3, −C5), 129.6 (s, Ph−C4), 131.0 (s, dpt−Ph−C4), 137.3 (s, dpt−Ph−C1), 140.7 (s, Ph−C1), 167.7 (s, dpt−C2, −C6), 170.7 (s, dpt−C4). − ^{119}Sn NMR ([D$_6$] DMSO/CDCl$_3$ (1:1), 149.09 MHz, 30 °C): δ = −368.2 [br. m, Δ = 17.5 Hz, $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 1103 Hz]. − $C_{24}H_{29}N_9O_5Sn$ (642.26): calcd. C 44.9, H 4.5, N 19.6; found C 44.8, H 4.7, N 19.6.

Solution NMR Spectroscopic Data for Tetrakis[trimethyl(*N*-nitroso-*N*-phenyl-hydroxylaminato)]tin(IV) (5): − ^{1}H NMR (CDCl$_3$, 399.10 MHz, 30 °C): δ = 0.48 [m, 9 H, CH$_3$, $^1J(^{13}\mathrm{C}-^{1}\mathrm{H})$ = 129.6 Hz, $^2J(^{119}\mathrm{Sn}-^{1}\mathrm{H})$ = 54.9 Hz, $^2J(^{117}\mathrm{Sn}-^{1}\mathrm{H})$ = 52.5 Hz, $^2J(^{115}\mathrm{Sn}-^{1}\mathrm{H})$ = 48.2 Hz], 7.46 (m, 3 H, Ph−H3, −H4, −H5), 7.93 (m, 2 H, Ph−H2, −H6). − ^{13}C NMR (CDCl$_3$, 100.56 MHz, 30 °C): δ = 129.1 (s, Ph−C3, −C5), 129.9 (s, Ph−C4), 140.3 (s, Ph−C1), 2.2 [m, CH$_3$, $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 403.8 Hz, $^1J(^{117}\mathrm{Sn}-^{13}\mathrm{C})$ = 386.6 Hz], 119.1 (s, Ph−C2, −C6). − ^{119}Sn NMR (CDCl$_3$, 149.09 MHz, 30 °C): δ = 95.9 [m, Δ = 5 Hz, $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 404 Hz].

X-ray Crystallographic Study: Crystal data and refinement parameters are summarised 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 experimental error. The structures were solved by direct methods (SHELXS-97)[22a] and refined by full-matrix least-squares (SHELXL-97).[22b] All non-hydrogen atoms were refined anisotropically in F^2 mode. 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-162624 (**2**), CCDC-162625 (**3**) and CCDC-162626 (**4**). 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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Received May 2, 2001
[I01150]