

Preparation and structural studies on diorganotin(IV) complexes of *N*-nitroso-*N*-phenylhydroxylamines

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Received 20 September 2006; received in revised form 2 April 2007; accepted 10 April 2007

Available online 14 April 2007

Abstract

Diorganotin(IV)-complexes of the *N*-nitroso-*N*-phenylhydroxylamines (hereinafter cupf), Et₂Sn(cupf)₂ (**1**), Bu₂Sn(cupf)₂ (**2**), {[Bu₂Sn(cupf)₂O]₂O} (**3**), *t*-Bu₂Sn(cupf)₂ (**4**) and Oc₂Sn(cupf)₂ (**5**, **6**) were prepared and characterised by FT-IR and Mössbauer spectroscopic measurements. The binding modes of the ligand were identified by FT-IR spectroscopy, and it was found that the ligand is coordinated in chelating or bridging mode to the organotin(IV) center. The ¹¹⁹Sn Mössbauer and FT-IR studies support the formation of *trans*-O_h (**1**–**6**) structures. The X-ray diffraction analysis of **4** revealed that the tin centre is in a skew-trapezoidal geometry defined by four donors derived from the cupferronato ligands and two carbon atoms from the tin-bound *n*-butyl substituents. The ¹¹⁹Sn NMR investigations indicate that in solution **4** retains its hexacoordinated nature.

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Keywords: Diorganotin(IV); FT-IR; Mössbauer; ¹H; ¹³C and ¹¹⁹Sn NMR spectroscopy; Cupferron; X-ray diffraction

1. Introduction

The ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine, NH₄[PhN(O)NO], cupferron (hereinafter cupf) (Scheme 1), is a well known analytical reagent and it was very popular especially during the classical period of analytical chemistry [1]. This ligand is known to form complexes with many metals but few of them have been structurally characterised. The biological activity of cupf has also been investigated: carcinogenic, mutagenic, genotoxic and DNA-damaging effects were noted [2]. The knowledge of the coordination chemistry of cupferron could provide useful information about the interaction modes of NO with metal centres of biologically important species, and it may also contribute to elucidate the mecha-

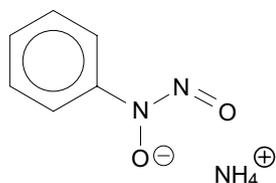
nism of activation of NO-receptor enzyme guanylate cyclase [2].

The organotin(IV) complexes of cupf may be interesting to study, since many organotin compounds are known to display antitumour activity and the ligand itself has some biological activity [3]. Some diaryltin(IV)-cupferronates, Ar₂Sn(cupf) (Ar = Ph, *o*-Tol, *m*-Tol, *p*-Tol), were prepared and characterized by IR spectroscopy [4].

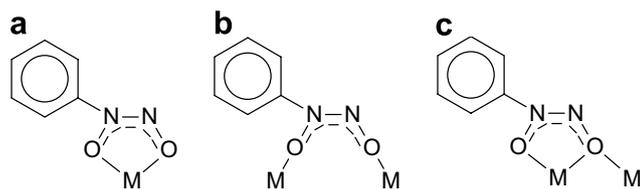
Recently, one of us reported the synthesis and structural characterisation of organotin(IV) cupferronato complexes, such as [Me₃Sn(cupf)]₄ [5], Ph₂Sn(cupf)₂ [6], [Me₂Sn(cupf)₂]₂ [3]. It was found that, depending on the number (2, 3) and the nature (Me, Ph) of the organic substituents at the tin(IV) atom, the cupferronato anion displays various coordination patterns in these molecules, chelating (Scheme 2a), bridging (Scheme 2b), and bridging chelating (Scheme 2c). As a consequence, the central tin(IV) atom assumes a penta-, hexa- or hepta-coordinate state,

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Scheme 1.



Scheme 2.

respectively, and the resulting complexes display different coordination geometries at the central tin(IV) atom [5–7]. Bridging chelating coordination of the cupferronato ligand to $\text{Me}_2\text{Sn(IV)}^{2+}$ cation gives the dimeric species (Scheme 2c) [6], whereas a bridging coordination to $\text{Me}_3\text{Sn(IV)}^+$ affords the tetrameric complex (Scheme 2b) [5].

In order to demonstrate the influence of longer (Et, Bu, Oc) alkyl chains and larger (*t*-Bu) organic substituents on the structure of diorganotin(IV)-cupferronates we prepared the $\text{Et}_2\text{Sn(cupf)}_2$ (**1**), $\text{Bu}_2\text{Sn(cupf)}_2$ (**2**), $\{[\text{Bu}_2\text{Sn(cupf)}]_2\text{O}\}_2$ (**3**), *t*- $\text{Bu}_2\text{Sn(cupf)}_2$ (**4**) and $\text{Oc}_2\text{Sn(cupf)}_2$ (**5**, **6**) complexes. They were characterised by analytical and spectroscopic (FT-IR, Mössbauer) methods. To accumulate precise structural data concerning the binding mode of the cupferronato anion, the X-ray diffraction analysis of **4** was also performed.

2. Experimental

2.1. Materials

Et_2SnCl_2 was purchased from Alfa Aesar, Bu_2SnCl_2 , Bu_2SnO and cupferron were purchased from Fluka. All other compounds were Sigma–Aldrich products. All the starting reagents were of A.R. grade and were used without further purification.

2.2. Syntheses

The complexes **1**, **2**, **4** and **5** were prepared as already described in [8]. The appropriate amount of cupf (2 mmol) and diorganotin(IV)dichloride compounds (1 mmol) were dissolved in dry methanol. After stirring and refluxing, or only stirring, the resulting solution was kept in refrigerator. The precipitated NH_4Cl was filtered off, and the solution was taken for crystallisation. Compounds **3** and **6** were prepared by refluxing appropriate quantity of cupf (2 mmol) and Bu_2SnO or Oc_2SnO in methanol for 3 h. Reaction of ligand and diorganotin(IV) oxides yielded NH_3 which was removed by reflux. Compounds **3** and **6** were crystallised out after slow evaporation of the solvent at room temperature, then washed with methanol. All products were recrystallised from hexane or methanol.

2.3. Analytical and spectroscopic (FT-IR, Mössbauer and multinuclear NMR) measurements

Microanalyses were performed at the Department of Organic Chemistry, University of Szeged. The Sn contents were measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) [8] and found to correspond to the theoretically calculated values. The analytical data on the compounds are presented in Table 1, together with other characteristic physical constants.

FT-IR spectra of the ligand and of the complexes were recorded in Vibrational Laboratory of Szeged University on a BIORAD FTS-65A FT-IR spectrometer in KBr pellets in the range 4000–400 cm^{-1} .

Mössbauer spectroscopic measurements were performed as described previously [8]. In order to determine the steric arrangement of the coordination sphere, the experimental quadrupole splitting values ($|\Delta_{\text{exp}}|$) were compared with those calculated Δ_{calc} for different tetra-, penta- and hexa-coordinated symmetries of the tin(IV) centres on the basis of point charge model formalism (partial quadrupole splitting, pqs) [9]. On the basis of these calculations, the most probable stereochemistry of a given complex can be suggested. The pqs values of the different functional groups in question were taken in part from the relevant literature [10,11].

Solution NMR data were recorded on Bruker Avance 500 spectrometer in CDCl_3 , using TMS as internal

Table 1
Physical and analytic data (calculated % values in parentheses) of diorganotin(IV) cupferronato **1–6** complexes

Complex/starting diorganotin(IV) compounds	Analysis (%)				Colour	Yield (%)	M.p. (°C)
	C	H	N	Sn			
$\text{Et}_2\text{Sn(cupf)}_2$ (1)/ Et_2SnCl_2	42.60 (42.94)	4.44 (4.48)	12.42 (12.56)	26.34 (26.47)	White	85	80–83
$\text{Bu}_2\text{Sn(cupf)}_2$ (2)/ Bu_2SnCl_2	47.36 (47.93)	5.53 (5.58)	11.05 (11.12)	23.43 (23.68)	Yellowish-white	68	50–52
$\{[\text{Bu}_2\text{Sn(cupf)}]_2\text{O}\}_2$ (3)/ Bu_2SnO	44.48 (43.93)	6.09 (5.85)	7.41 (7.18)	31.43 (31.29)	Yellowish-white	56	90–93
<i>t</i> - $\text{Bu}_2\text{Sn(cupf)}_2$ (4)/ <i>t</i> - Bu_2SnCl_2	47.36 (47.48)	5.53 (5.55)	11.05 (11.08)	23.43 (23.50)	Yellow	74	107–110
$\text{Oc}_2\text{Sn(cupf)}_2$ (5)/ Oc_2SnCl_2	54.31 (53.97)	7.11 (7.03)	9.05 (9.26)	19.19 (18.94)	Colourless	64	>300
$\text{Oc}_2\text{Sn(cupf)}_2$ (6)/ Oc_2SnO	54.31 (54.44)	7.11 (7.25)	9.05 (9.14)	19.19 (19.33)	Colourless	71	>300

standard for ^1H and ^{13}C , and SnEt_4 for ^{119}Sn as external reference.

2.4. X-ray crystallography

Crystal data for $t\text{-Bu}_2\text{Sn}(\text{cupf})_2$ (**4**): $\text{C}_{20}\text{H}_{28}\text{N}_4\text{O}_4\text{Sn}$, $M_r = 507.15$, monoclinic, space group $C2/c$ (No. 15), with $a = 23.636(3)$ Å, $b = 6.123(1)$ Å, $c = 16.235(2)$ Å, $\beta = 111.487(9)^\circ$, $V = 2186.3(5)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.541$ Mg/m³, $F(000) = 1032$, $\lambda = 0.71073$ Å, $T = 295(2)$ K, μ (Mo $K\alpha$) = 1.201 mm⁻¹, crystal size $0.15 \times 0.25 \times 0.35$ mm. Intensity data of 8205 reflections were measured ($2.65 \leq \theta \leq 31.92^\circ$) on an Enraf-Nonius CAD-4 diffractometer ($\omega - 2\theta$ scans) of which 3770 were independent ($R_{\text{int}} = 0.020$). The intensities of the standard reflections indicated a crystal decay of 2%, which was corrected. A semi-empirical (psi-scan) absorption correction was also applied (min/max transmission: 0.6785/0.8404). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) [12]. 3770 reflections were employed in the structure refinement (135 parameters, 0 restraints). The final R values were $R_1 = 0.0297$ ($I > 2\sigma(I)$) and $wR_2 = 0.0758$ (all data); the goodness of fit was $S = 1.01$; min/max residual electron density $-0.89/0.81$ e Å⁻³. All non-hydrogen atoms were refined anisotropically. Hydrogen atomic positions were generated from assumed geometries. A riding model refinement was applied for the hydrogen atoms.

3. Results and discussion

3.1. X-ray structural study

The molecular structure of **4** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The X-ray analysis established that the cupferronato anions in **4** are coordinated to the tin centre in a bidentate chelating fashion leading to five-membered SnO_2N_2 chelate rings with an $\text{O}(1)\text{--Sn}(1)\text{--O}(2)$ bite angle of $68.76(5)^\circ$. The tin centre is in a skew-trapezoidal geometry defined by four donors derived from the cupferronato ligands and two carbon atoms from the t -butyl substituents. Several dialkyltin(IV) complexes are neither in regular *cis* nor in regular *trans*

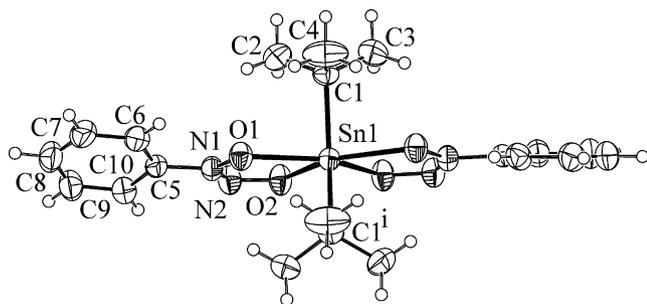


Fig. 1. ORTEP diagram of the molecular structure of complex **4**, with atom labelling scheme. Non-hydrogen atoms are shown as 50% probability ellipsoids and hydrogen atoms are shown as open circles.

Table 2

Selected interatomic bond distances (Å) and bond angles (°) for complex 4	
Sn(1)–O(1)	2.347(2)
Sn(1)–O(2)	2.172(2)
Sn(1)–C(1)	2.199(2)
O(1)–N(1)	1.301(2)
O(2)–N(2)	1.305(2)
N(1)–N(2)	1.285(3)
N(1)–C(5)	1.445(3)
C(1)–Sn(1)–C(1) ⁱ	151.3(2)
O(2)–Sn(1)–O(1)	68.76(5)
O(1)–Sn(1)–C(1)	86.4(1)
O(2)–Sn(1)–C(1)	101.5(1)

Equivalent atom generated by (i) $-x, y, 1/2 - z$.

geometry, as they exhibit an intermediate skew-trapezoidal geometry, where the C–Sn–C angle varies from 135 to 155° [13]. In complex **4**, this C–Sn–C angle is $151.3(2)^\circ$. The SnO_2N_2 chelate ring is planar, with an r.m.s. deviation of fitted atoms of 0.0065 Å; the $\text{O}(1)\text{--N}(1)\text{--N}(2)\text{--O}(2)$ torsion angle is $1.7(3)^\circ$. The chelating cupferronato ligand exhibits different Sn–O bond lengths, thus the Sn(1)–O(1) bond is longer (by 0.175 Å) than the Sn(1)–O(2) bond. The N(1)–N(2) bond length of $1.285(3)$ Å is intermediate to that of the corresponding single (1.45 Å) and double bond (1.21 Å) lengths. The average N–O bond length of $1.303(2)$ Å is between that of a single (1.40 Å) and double bond (1.21 Å). These structural features suggest significant electron delocalisation along the N(O)NO moiety, which is typical for organotin(IV) cupferronates [5–7]. The plane defined by the cupferronato $\text{O}(1)\text{--N}(1)\text{--N}(2)\text{--O}(2)$ atoms forms an angle of $18.7(1)^\circ$ with the plane of the phenyl group. In the crystal, C–H $\cdots\pi$ and $\pi\text{--}\pi$ interactions play a major role in the molecular self-assembly.

3.2. FT-IR spectroscopic characterisation

The coordination sites of the ligand were determined by means of FT-IR spectroscopy. For comparison, the FT-IR spectra of the starting diorganotin(IV) compounds and their cupferronato complexes were recorded. The assignment of the characteristic bands of the ligand is based mainly on data published in [14]. On the ligand spectrum, the most important bands from coordination chemistry point of view are following: $\nu(\text{NH}_4^+)$ 3160 cm⁻¹; $\nu(\text{=CH})_{\text{Ph}}$ $3050\text{--}2852$ cm⁻¹; $\nu(\text{C=C})_{\text{Ph}}$ 1483 and 1460 cm⁻¹; $\nu(\text{N--N})$ 1331 and 1314 cm⁻¹; $\nu(\text{N=O})$ 1264 and 1221 cm⁻¹; $\delta(\text{ONNO})$ 907 cm⁻¹; $\gamma(\text{CH})_{\text{Ph}}$ 755 and 689 cm⁻¹; $\delta(\text{NNO})$ 581 cm⁻¹. The characteristic FT-IR bands, which are observed for the **1–6** complexes together with vibrational assignments, are detailed in Table 3.

A comparison of IR spectra of the investigated complexes **1–6** with that of cupferron reveals significant changes in the position of the above-mentioned bands due to electron delocalisation over the coordinated ONNO unit. The stretching vibration (3160 cm⁻¹) related to the ammonium salt of the ligand is absent from the spectra of the complexes, indicating formation of the Sn–O bonds.

Table 3
Characteristic vibration bands for 1–6 complexes

Assignment	1	2	3	4	5 and 6
$\nu(\text{CH}_x)$ ($x = 1-3$)	2975 w – 2687 w	2960 m – 2858 m	2955 vs – 2855 m	2975 w – 2846 m	2955 – 2853 m
$\nu(\text{N-N})$	1338 m, 1293 vs	1334 m, 1288 vs	1341 s, 1300 s	1342 vs, 1303 s	1345 m, 1291 vs
$\delta(\text{ONNO})$	918 s	921 s	925 vs	917 s	928 m
$\gamma(\text{CH})_{\text{Ph}}$	754 s, 692 s	750 m, 692 s	758 vs, 693 s	755 s, 691 s	757 s, 693 m
$\nu(\text{Sn-O-Sn})$	–	–	591 s	–	–
$\delta(\text{O-Sn-O})$	681 s	682 s	–	684 m	685 m
$\nu_a(\text{Sn-C})$	541 m	544 m	556 s	595 m	592 m
$\nu_s(\text{Sn-C})$	489 w	488 w	489 w	526 w	494 w
$\nu(\text{Sn-O})$	399 m	400 m	389 s	388 s	400 m

Abbreviations: s = strong; m = medium; w = weak; vs = very strong, sh = shoulder.

The $\nu(\text{N-N})$ and $\delta(\text{ONNO})$ modes are shifted to higher/lower by 3–15/14–26 and to higher by 10–26 cm^{-1} , respectively (see Table 3). In the case of complexes **1**, **2** and **4–6**, the wave numbers of the bands appeared in the 1350–400 cm^{-1} spectral region do not differ as much, indicating the formation of similar structures for the mentioned complexes.

The sharp and strong bands characteristic of the different dialkyltin(IV) cations (νCH_3 and νCH_2) in the interval 2900–2700 cm^{-1} were not significantly affected by the coordination. The presence of two (asymmetric and symmetric) Sn–C absorption bands between 600 and 480 cm^{-1} in the spectra of all compounds strongly suggests that the C–Sn–C bond angle is less than 180°. This is in accord with the ^{119}Sn Mössbauer spectroscopic and X-ray diffraction results.

The wave number of the Sn–O stretching is one of the most important data relating to the bonding mode of the ligand. It was observed that, if the cupferronato anion is coordinated to the tin centre in common bidentate chelating mode, the $\nu(\text{Sn-O})$ a band appears at 399–406 cm^{-1} , while, for the bridging coordination pattern, the $\nu(\text{Sn-O})$ band is centered around 389 cm^{-1} [14]. In our compounds, this band can be assigned in 399–403 cm^{-1} spectral region, except for complexes **3** and **4**. In the case of **3**, the analytical data suggest 1:1 metal to ligand molar ratio. A strong band, characteristic of the tetraorganodistannoxanes and attributed to the $(\text{Sn-O})_2$ ring vibration, is present in the spectrum of **3** at 591 cm^{-1} . It is very interesting that, in the case of dioctyltin(IV)-compounds, the FT-IR spectra of the two $\text{Oc}_2\text{Sn(IV)}$ complexes (**5** and **6**) are quite similar. This, and the absence of the characteristic $\nu(\text{Sn-O-Sn})$ band suggested that, in this case, the distannoxane ring formation did not take place. This observation is in good agreement with the results of Mössbauer spectroscopic investigations.

The molecular geometry of compound **4** was investigated by X-ray diffraction analysis. These results showed that, in this complex, the anion is coordinated to the tin centre in a bidentate chelating mode. Therefore, we could not explain why the Sn–O stretching appears 12 cm^{-1} lower than we expected.

3.3. Mössbauer spectroscopic characterisation

In order to gain further structural information on the solid complexes, the Mössbauer spectra of the compounds were recorded and analysed. The spectra of compounds **1**, **2** and **4–6** comprised only one, well developed doublet (the narrowness of the full width at half the maximum of the observed of the resonance line being average), which suggests the presence of completely equivalent Sn environments in these compounds. An unsymmetric doublet with the line width greater than 1.0 was observed in the spectrum of compound **3**, indicating the presence of Sn in two different coordination environments. This doublet was decomposed into two doublets. The ^{119}Sn Mössbauer spectroscopic parameters are listed in Table 4, together with the suggested configurations according to the pqs concept. The magnitudes of the isomer shift (δ) indicate an oxidation state of Sn(IV) for all the complexes. For Sn(IV) complexes containing the $\text{R}_2\text{Sn(IV)}$ moiety, the quadrupole splitting is dominated by highly covalent Sn–C bonds and if the contributions of the other donor atoms are ignored, it can be shown that Δ is given by

$$\Delta = -4[R][1 - (3/4)\sin^2\theta]^{1/2},$$

where $[R]$ denotes the pqs value of group R , and θ is the C–Sn–C bond angle [15]. This equation has been satisfactory applied to penta- and hexacoordinated Sn(IV) compounds, with the use of appropriate values of $[R]$ for each coordination number [11,16–19]. The model assumes that quadrupole splitting (Δ) arises from point-charge hydrocarbon groups separated by a C–Sn–C angle of $(180 - 2\theta)^\circ$, with contributions from other coordinated ligands being ignored. The quadrupole splitting has been used to estimate the C–Sn–C angle, and they are listed in Table 4.

The full width at half maximum of the peaks (Γ) and the asymmetrical shape of the Mössbauer spectrum of **3** indicate more than one tin coordination environment. Resolution of the spectrum results in adjacent quadrupole splitting values of 3.18 and 3.93 mm s^{-1} , which indicate *mer*-Tbp and *trans*- O_h tin(IV) coordination environments (Fig. 2). In contrast with this, the spectrum of analogous

Table 4
Experimental and calculated Mössbauer parameters and the proposed structures for complexes 1–6

Complex	$\delta_{m1/m2}$	$ A_{m1/m2} $	$A_{calc1/calc2}$	$\Gamma_{1/2}$	I_a	θ	Geometry
1	1.40	4.12	4.23	0.86	–	180	<i>trans</i> -O _h
2	1.41	4.18	4.23	0.86	–	168	<i>trans</i> -O _h
3	1.23	2.99	3.18	0.87	1:1	122	<i>mer</i> -Tbp
	1.27	3.87	3.93	0.87		154	<i>trans</i> -O _h
4	1.56	3.49	3.58	0.91	–	138	<i>trans</i> -O _h
				0.95		(151)	
5	1.41	4.21	4.23	0.82	–	165	<i>trans</i> -O _h
6	1.46	3.99	3.93	0.87	–	162	<i>trans</i> -O _h

m, experimental; calc, calculated; Tbp, trigonal bipyramidal; O_h, octahedral; θ is C–Sn–C bond angle, given in °, value in parentheses was obtained from X-ray diffraction measurement.

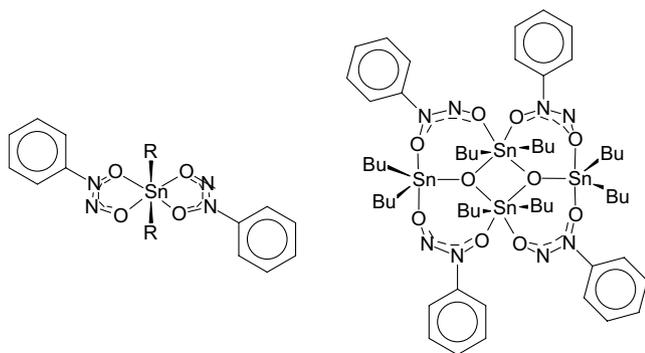


Fig. 2. Proposed solid-state structures for R₂Sn(cupf)₂ [R = Et (1), Bu (2), *t*-Bu (4) and Oc (5, 6)] and {Bu₂Sn(cupf)₂O}₂ (3) complexes.

complexes 1, 2 and 4–6 exhibit only a symmetrical doublet. In these complexes, the experimental δ and $|A|$ values fall in the range of those noted for the *trans*-O_h complexes [16], with the four O donor atoms in equatorial position (Fig. 2). In case of 1, 2 and 5, the Δ_{exp} values are much higher than 4.00 mm s⁻¹, as observed for the earlier studied Bu₂Sn(IV)-complexes of pyridine mono- and dicarboxylic acids [8]. Therefore, it can not be ruled out that in these compounds the central Sn(IV) atoms are in heptacoordinated surroundings, adopting one more ligand which can be one solvent or one water molecule as obtained for the numerous diorganotin(IV) cupferronato complexes [7]. In compound 4 the bulkiness of the *t*-butyl-groups prevents the formation of *trans*-Pbp coordination environment.

3.4. Structure determination by NMR spectroscopy in solution

¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded (in CDCl₃) to gain some insight into the solution structure of the complexes. For proton-containing groups directly attached to the Sn atom (Et, Bu, *t*-Bu, Oc and Ph), proton spectra exhibited ¹¹⁹Sn (and ¹¹⁷Sn) satellite signals due to ²J(¹¹⁹Sn–¹H) or ³J(¹¹⁹Sn–¹H) couplings. In a similar fashion, resonance due to the carbon atoms in groups attached to tin exhibited ¹¹⁹Sn (and ¹¹⁷Sn) satellites arising from one-bond and multiple-bond ⁿJ(¹¹⁹Sn–¹³C) spin–spin couplings. All the ¹H, ¹³C and ¹¹⁹Sn chemical shifts have the

values normally expected and can be found at the end of this chapter with some of the detectable couplings.

Within a given set of related diorganotin(IV) complexes, the chemical shift of the ¹¹⁹Sn 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 ¹¹⁹Sn resonance to lower frequencies [20]. The ¹¹⁹Sn chemical shift values for the complexes studied, in general follow the expected trends. Thus in 4, the observed –222 ppm, falls in the range typical of hexacoordinated organotin(IV) complexes in chloroform solution. In case of 1 and 2, the magnitude of the δ^{Sn} values (–356 and –376 ppm) reflects also the existence of the distorted octahedral geometry in solution, but it can not be ruled out that in these compounds the central Sn(IV) atoms are in heptacoordinated surroundings, adopting one more ligand which can be one methanol or one water molecule. The measured two δ^{Sn} values for 3 are in accordance with the Mössbauer spectroscopy results for this complex (two quadrupole splitting values of 3.18 and 3.93 mm s⁻¹). The magnitude of δ^{Sn} values (–140 and –68 ppm) indicate *trans*-O_h and *mer*-Tbp tin(IV) coordination environments as obtained in the solid state. These data suggesting that the coordination geometry of this complex remains unaffected by dissolution.

Et₂Sn(cupf)₂ (1): ¹H NMR (CDCl₃, 500.13 MHz, 25 °C) δ = 8.0 (m, Ph-H2, -H6), 7.37 (m, Ph-H3, -H4, -H5), 1.38 (m, 2H, Sn(CH₂CH₃)), 1.38 (m, 3H, Sn(CH₂CH₃)). ¹³C NMR (CDCl₃, 125.76 MHz, 25 °C) δ = 140.5 (s, Ph-C1), 130.63 (s, Ph-C4), 129.22 (s, Ph-C3, -C5), 118.4 (s, Ph-C2, -C6), 18.2 (s, Et-C1 [¹J(¹¹⁹Sn–¹³C) = 812]), 13.2 (s, Et-C2 [²J(¹¹⁹Sn–¹³C) = 27.3]). ¹¹⁹Sn NMR (CDCl₃, 186.36 MHz, 25 °C) δ = –356.

Bu₂Sn(cupf)₂ (2): ¹H NMR (CDCl₃, 500.13 MHz, 25 °C) δ = 7.97 (d, 2H, Ph-H2, -H6) 7.46 (s, 3H, Ph-H3, -H4, -H5) 1.69 (m, 8H, Sn(CH₂)₂CH₂CH₃) 1.35 (m, 4H Sn(CH₂)₂CH₂CH₃) 0.89 (t, 6H, Sn(CH₂)₃CH₃). ¹³C NMR (CDCl₃, 125.76 MHz, 25 °C) δ = 135 (s, Ph-C1 [¹J(¹¹⁹Sn–¹³C) = 808]), 130.1, 129.5 (s, Ph-C4), 129.1, 128.8 (s, Ph-C3, -C5), 120.24, 119.5 (s, Ph-C2, -C6), 29.69, 29.13 (s, C1, [¹J(¹¹⁹Sn–¹³C) = 1028.8]), 28.4, 27.7

(s, C2, [$^2J(^{119}\text{Sn}-^{13}\text{C}) = 24.2$]) 27.05, 26.5 (s, C3, [$^3J(^{119}\text{Sn}-^{13}\text{C}) = 105.6$]) 13.7 (s, C4). ^{119}Sn NMR (CDCl_3 , 186.36 MHz, 25 °C) $\delta = -376$.

{[$\text{Bu}_2\text{Sn}(\text{cupf})_2\text{O}$]}₂ (**3**): ^1H NMR (CDCl_3 , 500.13 MHz, 25 °C) $\delta = 7.69$ (dd, 2H Ph-H2, -H6) 7.45 (m, 3H, Ph-H3, -H4, -H5) 4.72 (s, $(\text{CH}_2)_3\text{CH}_3$). ^{13}C NMR (CDCl_3 , 125.76 MHz, 25 °C) $\delta = 144$ (s, Ph-C1), 130.9 (s, Ph-C4), 130.8 (s, Ph-C3, -C5), 121 (s, Ph-C2, -C6) 29.9 (d, C1, [$^1J(^{119}\text{Sn}-^{13}\text{C}) = 919$]), 27.3 (d, C2, [$^2J(^{119}\text{Sn}-^{13}\text{C}) = 25.6$]) 24 (d, C3, [$^3J(^{119}\text{Sn}-^{13}\text{C}) = 114.3$]), 13.3 (d, C4). ^{119}Sn NMR (CDCl_3 , 186.36 MHz, 25 °C) $\delta = -140, -68$.

t- $\text{Bu}_2\text{Sn}(\text{cupf})_2$ (**4**): ^1H NMR (CDCl_3 , 500.13 MHz, 25 °C) $\delta = 7.97$ (m, 2H, Ph-H2, -H6) 7.46 (m, [$^1J(^{119}\text{Sn}-^1\text{H}) = 99$] 3H, Ph-H3, -H4, -H5), 1.4 (m, 8H, *t*- Bu_2Sn), 1.27 (m, 4H, [$J(^{119}\text{Sn}-^1\text{H}) = 183$, *t*- Bu_2Sn] 1.17 (m, 6H, *t*- Bu_2Sn). ^{13}C NMR (CDCl_3 , 125.76 MHz, 25 °C) $\delta = 140.2$ (s, Ph-C1 [$^3J(^{119}\text{Sn}-^{13}\text{C}) = 1001$]), 129.9 (s, Ph-C4), 129.1 (s, Ph-C3, -C5), 119.6 (s, Ph-C2, -C6), 25.3 (s, C1 [$^1J(^{119}\text{Sn}-^{13}\text{C}) = 1017$]), 30.0 (s, C2 [$^2J(^{119}\text{Sn}-^{13}\text{C}) = \text{NO}$]). ^{119}Sn NMR (CDCl_3 , 186.36 MHz, 25 °C) $\delta = -222$.

$\text{Oc}_2\text{Sn}(\text{cupf})_2$ (**5**): ^1H NMR (CDCl_3 , 500.13 MHz, 25 °C) $\delta = 8.29$ (d, Oc-H1), 8.14 (d, Ph-H2, -H6), 7.61 (t, Oc-H2), 7.55 (q, Oc-H3), 7.49 (t, Ph-H3, -H4, -H5), 7.41 (t, Oc-H4), 7.33 (d, Oc-H5), 3.31 (m, Oc-H6), 1.28 (t, Oc-H7), 0.81 (d, Oc-H8). ^{13}C NMR (CDCl_3 , 125.76 MHz, 25 °C) $\delta = 142.8$ (s, Ph-C1), 130.1 (s, Ph-C4), 129.8 (s, Ph-C3, -C5), 115.6 (s, Ph-C2, -C6), 33.3 (s, C1, [$^1J(^{119}\text{Sn}-^{13}\text{C}) = 737$]), 31.9 (s, C2, [$^2J(^{119}\text{Sn}-^{13}\text{C}) = 31.4$]), 29.7 (s, C3, [$^3J(^{119}\text{Sn}-^{13}\text{C}) = 119.1$]), 29.2 (s, C4), 25.9 (s, C5), 24.1 (s, C6), 22.0 (s, C7), 14.2 (s, C8). ^{119}Sn NMR (CDCl_3 , 186.36 MHz, 25 °C) $\delta = -156$.

The chemical shifts are in ppm, coupling constants in Hz, s = singlet, d = doublet, t = triplet, m = multiplet, NO = not observed.

4. Conclusion

We have shown that the tin center exhibits *trans*- O_h geometry in $\text{R}_2\text{Sn}(\text{cupf})_2$ diorganotin(IV)-cupferronates having longer (R = Et, Bu, Oc) alkyl chains or larger (R = *t*-Bu) organic substituents attached on tin. In these complexes the cupferronato anions are chelated to the tin center. Moreover, in Sn_2O_2 stannoxanic ring containing complex **3**, each of the four cupferronato ligands bridge a pair of tin atoms, thus the tin center have *trans*- O_h and *mer*-Tbp environments. Multi-nuclear solution NMR spectroscopic data of the complexes provide useful complementary information about structures in solution of the solid complexes.

Acknowledgements

This work was supported by the Hungarian Scientific Research Funds (OTKA) T 043551 and F 60496 Projects,

the Ministero dell'Istruzione, dell'Università e della Ricerca (M.I.U.R., CIP 2004059078_003) and the Università di Palermo (ORPA 41443), Italy.

Appendix A. Supplementary material

CCDC 614144 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.04.003](https://doi.org/10.1016/j.jorganchem.2007.04.003).

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