

Organotin(IV) Derivatives of the Ambidentate Ligand 2-Thiouracil. Infrared, Mössbauer, ^1H and ^{13}C NMR Studies

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Complexes $\text{Bu}_2^n\text{Sn}(s^2\text{UraH}_{-2})$ and $[\text{Me}_2\text{SnOH}]_2(s^2\text{UraH}_{-2})$ have been synthesized. Comparison of infrared spectra of the solid complexes with spectra of $s^2\text{Ura}$ and $(\text{PhHg})_2(s^2\text{UraH}_{-2})$ complex and point charge calculations (Mössbauer spectra) allow assignment of structures for the complexes of this ambivalent ligand. Polymeric structures are proposed for the complexes in the solid state, where the organometallic moieties are bonded to exocyclic S and N(3) atoms of the dianionic base, with formation of a four-membered chelate ring for $\text{Bu}_2^n\text{Sn}(s^2\text{UraH}_{-2})$. For $[\text{Me}_2\text{SnOH}]_2(s^2\text{UraH}_{-2})$, ^1H and ^{13}C NMR data suggest retention of penta-coordination in trifluoroacetic acid solution and indicate rapid exchange of Me_2SnOH^+ between the binding sites.

Introduction

In a previous communication [1a] we reported a solid state and solution study on the binding of organomercury(II) cations to the thiolated base 2-thiouracil. The organometallic moiety was essentially used to probe the binding sites of the ambivalent base towards heavy metal ions. The infrared spectra confirmed the existence of various tautomer complexes in the solid and these findings parallel those of glycosylation reactions [2, 3] where substitution reactions may occur at N(1), N(3) and exocyclic S and O. The reaction of 2-thiouracil with dialkyltin(IV) cations is of interest for two reasons. First, organometallic derivatives such as diorga-

notin(IV) compounds have shown antineoplastic (mainly antileukemic) activity and their mode of action has been linked to that of *cis*-diammineplatinum(II) derivatives [4]. Secondly, since in this experiment (*vide infra*, under Experimental) it has been found that $\text{Bu}_2^n\text{Sn}^{2+}$ is acting as a divalent ion, while $\text{Me}_2\text{Sn}^{2+}$ is effectively converted into the univalent Me_2SnOH^+ species, the possibility of investigating analogies and/or differences in binding between uni- and divalent (organo)metallic ions hence arises. In this context it is worth noting that triorganotins (some of which are toxic, at comparable dose levels) do not yield identifiable products when allowed to react under similar conditions (boiling ethanol) with 2-thiouracil [5]. Both mercury(II) and triorganotin(IV) derivatives of substituted pyrimidines have been used as intermediates for the synthesis of pyrimidine nucleosides [3, 5].

Biological properties of organotin derivatives, however, have been studied mostly in connection with their toxicity as compared with analogous organolead compounds [6], although a report suggesting that tin might be a hitherto-unrecognized essential trace element has been presented [7].

Experimental

Di-n-butyltin(IV) dimethoxide, dimethyltin(IV) oxide [kind gift from Schering A.G. (Bergkamen)] and 2-thiouracil were used without further purifica-

tion. Anhydrous methanol and N₂ atmosphere were used throughout all operations.

Preparation of the Complexes

Bu₂ⁿSn(s²UraH₋₂)

5.0 mmol of Bu₂ⁿSn(OMe)₂ (1.085 ml) were added under stirring to a suspension of an equimolar amount of 2-thiouracil in dry methanol (60 ml) and refluxed for 4 hrs. The white solid was filtered, washed with THF and dried over P₄O₁₀ under vacuum.

Anal., calcd. for C₁₂H₂₀N₂OSSn: C, 40.14; H, 5.61; N, 7.80. Found: C, 40.10; H, 5.35; N, 8.40%. The Bu₂ⁿSn(s²UraH₋₂) complex was also obtained by reaction of Bu₂ⁿSn(OMe)₂ and s²Ura in the ratio of 1:2, operating under the same experimental conditions as reported above.

[Me₂SnOH]₂(s²UraH₋₂)

5.0 mmol of Me₂SnO (0.823 g) suspended in 60 ml of dry methanol were treated under reflux for 4 hrs with 2.5 mmol of 2-thiouracil. The white solid was filtered, washed with three portions of hot THF (30 ml each) and dried over P₄O₁₀ under vacuum.

Anal., Calcd. for C₈H₁₆N₂O₃SSn₂: C, 21.00; H, 3.52; N, 6.12. Found: C, 21.30; H, 3.17; N, 6.65. The complex was also obtained by reaction of Me₂SnO with an equimolar amount of 2-thiouracil (*i.e.* excess of ligand) under the same experimental conditions outlined above.

The complexes appear to be stable in the solid state.

Microanalyses were performed by Laboratorio di Microanalisi, Istituto di Chimica Organica dell'Università, Milano, Italy.

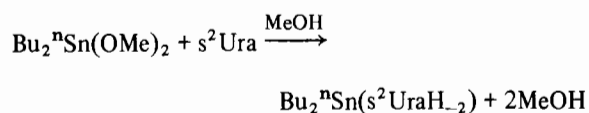
Infrared spectra (4000–180 cm⁻¹) were obtained with a Perkin-Elmer 580 Spectrophotometer as split mulls using CsI windows. ¹H and ¹³C NMR spectra of the complexes were measured with a Jeol-PFT-100 FT spectrometer relative to internal TMS; temperature of the probe being *ca.* 32 °C. Natural-abundance proton-decoupled ¹³C and partially coupled NMR spectra were recorded.

The solubility of the complexes in most organic solvents is very poor. Hydrolysis occurs when heating the complexes in DMSO-d₆, giving back the starting 2-thiouracil, although this is not as severe as in the case of the trialkyltin derivatives [5]. Solutions in trifluoroacetic acid are stable; however, saturated solutions had to be used in order to obtain suitable concentrations. The Mössbauer spectra at liquid nitrogen temperature were registered in a Laben 8001 multichannel analyzer with a Ca¹¹⁹SnO₃ source (10 mCi from Radiochemicals, Amersham) held at room temperature, moving with constant acceleration in a triangular waveform.

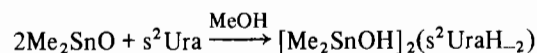
Source motion was measured by MWE (Munich) FG 2 function generator, MR 250 driving unit and velocity transducer. The reduction of data and calculation of Mössbauer Quadrupole Splittings (ΔE) were performed according to procedures described elsewhere [8, 9].

Results and Discussion

The synthesis of Bu₂ⁿSn(s²UraH₋₂) was accomplished by a simple metathetical reaction:



In contrast, when one mole of dimethyltin(IV) oxide was reacted with 2-thiouracil, which possesses two acidic hydrogens, only a partial neutralization could be achieved, the oxide being converted into a Me₂SnOH⁺ moiety:



It is worth noting that while in the case of RHg⁺ complexes, the electrophilic attack on the thiolated base could be accomplished in two steps, yielding both RHg(s²UraH₋₁) [1a] and (RHg)₂(s²UraH₋₂) derivatives [10], as for the R₂Sn²⁺ complexes, the base is acting in both cases as a dianionic species regardless of the stoichiometry of reactants employed. While a chelate effect could be invoked for Bu₂ⁿSn(s²UraH₋₂), it appears that also in the case of [Me₂SnOH]₂(s²UraH₋₂) the reaction leading to the 2:1 complex is favored. Under different experimental conditions it has been found that the stoichiometry of the platinum base complexes depends both on the Pt: base ratio and on the pH. For instance, the *cis*-diaquo species reacts with adenine, adenosine and AMP to give 1:1, 1:2 and 2:1 (Pt: base) complexes and in the formation of platinum-uridine 'blues' [11] *cis*-(H₃N)₂Pt²⁺ acts as a bifunctional electrophile toward cytidine in acidic solutions, while acting as a unifunctional electrophile at pH 7.

Infrared and Mössbauer Spectra

The relevant infrared data, reported in Table I, illustrate the changes following the metallation. All vibrations which in the free ligand are present at frequencies higher than 3000 cm⁻¹, where ν(NH) are to be expected, are absent in Bu₂ⁿSn(s²UraH₋₂) while in the dimethyltin(IV) complex they are extremely weak.

Vibrations Associated with the Organometallic Moiety

In the latter complex, however, the most striking feature in this region is the appearance of a medium

TABLE I. Relevant Infrared Absorptions.^a

Compound ^b	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{SnC}_2)$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{S})$
$s^2\text{Ura}$	1702s 1682s	1560s,bd 1172m 1155m			
$[\text{Me}_2\text{SnOH}]_2(s^2\text{UraH}_{-2})^c$	1572s	1524s 1240w 1215w	565s 515m	580s,bd 430s,bd	370w 255w
$\text{Bu}_2^{\text{n}}\text{Sn}(s^2\text{UraH}_{-2})$	1568s	1520s 1210w	605m 575s		395w 370m 245w

^aWavenumbers, cm^{-1} . Abbreviations: s = strong, m = medium, w = weak, bd = broad, sh = shoulder. The band assignments are commented in the text. ^bThe IUPAC-IUB abbreviations are employed, see Biochemistry, 9, 4022 (1970). Since $s^2\text{Ura}$ is the normal abbreviation for 2-thiouracil, we have used $s^2\text{UraH}_{-2}$ for the dianion. ^cA medium intensity band at 3465 cm^{-1} is assigned as $\nu(\text{O}-\text{H})$ of a coordinate hydroxide group.

intensity band at 3465 cm^{-1} , which is assigned as $\nu(\text{O}-\text{H})$ of a coordinated hydroxide group on the basis of the frequencies reported [12] for $\nu(\text{O}-\text{H})$ in a series of dialkyltin nitrate hydroxides ($\text{R} = \text{CH}_3$, 3390 cm^{-1} ; $\text{R} = n\text{-C}_3\text{H}_7$, 3430 cm^{-1} ; $\text{R} = n\text{-C}_4\text{H}_9$, 3460 cm^{-1}). The corresponding Sn-O stretching vibrations are reported at 530 and 403 cm^{-1} , at 597 and 530 cm^{-1} and at 586 and 520 cm^{-1} for those dimeric $\text{R}_2\text{Sn}(\text{OH})\text{NO}_3$ derivatives for which hydroxo bridged structures have been found [13]. 2-Thiouracil exhibits strong bands at 548 and 522 cm^{-1} which appear to be unshifted in the dimethyltin(IV) complex, with the addition of absorptions at $580(\text{s},\text{bd})$, $565(\text{s})$, $515\text{ cm}^{-1}(\text{m})$ and a broad band between 500 and 410 cm^{-1} , which also envelopes some ligand vibrations. The broad bands at 580 cm^{-1} and *ca.* 430 cm^{-1} are tentatively assigned to $\nu(\text{Sn}-\text{O})$ vibrations, while the 565 and 515 cm^{-1} absorptions may be due to $\nu_{\text{as}}(\text{SnC}_2)$ and $\nu_{\text{s}}(\text{SnC}_2)$, respectively. For polymeric $(\text{Me}_2\text{SnO})_n$ the latter vibrations are reported at 550 and 517 cm^{-1} [14]. The corresponding skeletal vibrational modes ($\nu_{\text{s}} + \nu_{\text{as}}(\text{SnC}_2)$) in $\text{Bu}_2^{\text{n}}\text{Sn}(s^2\text{UraH}_{-2})$ are present at $605(\text{m})$ and $575\text{ cm}^{-1}(\text{s})$.

Ligand Vibrations

The 4-oxo-2-thione structure of solid 2-thiouracil is confirmed by the X-ray spectra* [15]. We have previously shown that changes in the vibrations occurring in the double-bond stretching frequencies region may be conveniently used to probe the site(s) of metallation. A multiplicity of absorptions was observed in this region, which could be rationalized in terms of the occurrence of various tautomer complexes $\text{RHg}(s^2\text{UraH}_{-1})$. For the dialkyltin(IV) complexes (this work) a much simpler picture is observed since we have in both instances a single strong absorp-

tion at 1568 and 1572 cm^{-1} , respectively, (Table I) with a hint of a shoulder at *ca.* 1560 cm^{-1} . For uracil and thymine two frequencies have been assigned [16] in this region, the higher frequencies band to $\nu(\text{C}=\text{O})$ and the lower frequency band to phase $\nu(\text{C}_4=\text{O}) + \nu(\text{C}_5=\text{C}_6)$. Changes in these vibrational modes have been used to differentiate between N(1) and N(3) tautomers in Pt-uracil complexes [1b, 17].

Moreover, the 1560 cm^{-1} band of free 2-thiouracil (thioamide band I [18]) also shows marked changes (1520 cm^{-1} in $\text{Bu}_2^{\text{n}}\text{Sn}(s^2\text{UraH}_{-2})$ and 1524 cm^{-1} in $[\text{Me}_2\text{SnOH}]_2(s^2\text{UraH}_{-2})$) which are similar to those observed in $\text{RHg}(s^2\text{UraH}_{-1})$ complexes, where binding to the exocyclic sulfur is also involved. Since, on the basis of the stoichiometry of the complexes, the ligand is acting as a dianionic moiety, no contribution from a N-H deformation mode is expected in this region. It has been suggested, on the basis of UV-visible spectrophotometric data, that in the dianionic form the negative charges are localized on O and S [19]. A (O,S) diglucoside is obtained by reaction of the chloromercury(II), silver(I) and thallium(I) salts of 2-thiouracil with acetobromoglucose [3] and the easily-hydrolyzed crude product [5] $[\text{Bu}_3^{\text{n}}\text{Sn}]_2(s^2\text{UraH}_{-2})$ (not isolated), which is also formulated as O and S bonded in a similar reaction, has been proposed as an intermediate, although the final product is the N(1) substituted pyrimidine nucleoside. No infrared data are reported in either case.

In order to discriminate between O and S *versus* N and S binding the newly-synthesized compound [10] $[\text{PhHg}]_2(s^2\text{UraH}_{-2})$ was chosen as a comparison. If the site of binding of (organo)mercury(II) ions to 2-thiouracil may tentatively be inferred by the nature of the glycosylation products, the two

TABLE II. Isomer Shift, Experimental and Calculated Nuclear Quadrupole Splitting.

Compound	δ^a	ΔE_{exp}^b	Proposed Structure	$\Delta E_{\text{calcd}}^c$	η^d
$[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$	1.28	1.74	I	-1.89	1.00
			II (L = OH or O, or N)	-1.74 ÷ -2.01	0.70-0.43
	1.22	2.88	III (L ₁ = O, N; L ₂ = OH, N)	2.71 ÷ 2.83	0.20-0.29
			IV (L ₁ = OH; L ₂ = O, N)	-2.56, -2.99	0.83, 1.00
$\text{Bu}_2^{\text{n}}\text{Sn}(\text{s}^2\text{UraH}_{-2})$	1.40	2.99	IV (L ₁ = N, L ₂ = O)	-2.99	1.00
			V	-2.84	0.59

^aMössbauer Isomer Shift at 77.3 K with respect to R. T. CaSnO₃, mm s⁻¹. ^bExperimental nuclear quadrupole splitting at 77.3 K, mm s⁻¹. ^cCalculated Nuclear quadrupole splitting. Partial quadrupole splitting (p.q.s.) values, mm s⁻¹, for the proposed idealized configurations are literature values or calculated according to reported procedures (8, 23-25): in particular, Structure I: $([\text{R}] - [\text{hal}])^{\text{tet}} = -1.37$ [8] $([\text{S}] - [\text{hal}])^{\text{tet}} = -0.55$ [24]; $([\text{OH}] - [\text{hal}])^{\text{tet}} = ([\text{OCH}_2\text{CH}_2] - [\text{hal}])^{\text{tet}} = -0.55$ [24]. $([\text{O}] - [\text{hal}])^{\text{tet}} = -0.079$ (calcd. according to Reference [8]); $([\text{N}] - [\text{hal}])^{\text{tet}} = ([\text{N}] - [\text{hal}])_{\text{pyr}}^{\text{tet}} = -0.075$ [8]. Structure II-IV: $\{\text{R}\}^{\text{tbe}} = -1.13$ [8]; $\{\text{R}\}^{\text{tba}} = -0.94$ [8]; $\{\text{OH}\}_{\text{bridg}}^{\text{tba}} = -0.13$ [8]; $\{\text{OH}\}_{\text{bridg}}^{\text{tbe}} = +0.02$ [8]; $\{\text{S}\}^{\text{tbe}} = -0.6$ [25]; $\{\text{O}\}^{\text{tba}} = \{\text{8-hydroxyquinoline}\}^{\text{tba}} = -0.05$ [25] $\{\text{O}\}^{\text{tbe}} = +0.13$ (calcd according to Ref. [8]); $\{\text{N}\}^{\text{tba}} = \{\text{N}\}_{\text{pyr}}^{\text{tba}} = -0.035$ [8] $\{\text{N}\}^{\text{tbe}} = +0.15$ (calcd. according to Ref. [8]). ^d $(V_{xx} - V_{yy})/V_{zz}$ (the asymmetry parameter).

organomercury(II) ions in $[\text{PhHg}]_2(\text{s}^2\text{UraH}_{-2})$ are expected to be bonded to O and S. The infrared spectrum shows two strong absorptions at 1610 and 1580 cm⁻¹, which is in sharp contrast with the single absorption exhibited both by $\text{Bu}_2^{\text{n}}\text{Sn}(\text{s}^2\text{UraH}_{-2})$ and $[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$. The close similarity of the latter spectra suggests that binding occurs at the same base sites, S and presumably N(3). Since these bands are the only absorptions present in this region, no evidence of the existence of different tautomer complexes is found. In view of the expected intermolecular interactions in the solid, mostly due to OH groups, involvement of exocyclic oxygen is also possible, which also might affect vibrational modes containing $\nu(\text{C}=\text{O})$ character.

Apart from the double-bond stretching region, in the infrared spectrum the 800-1200 cm⁻¹ region also appears to be somewhat influenced by metallation. Indeed, Tobias *et al.* [20] interpreted Raman spectroscopic changes of nucleobase vibrations at *ca.* 1200 and 800 cm⁻¹ to probe the metal binding sites. Differences in the infrared spectra between the individual tautomers can also be observed [21], although they are of limited diagnostic value since absorptions are, in general, weak.

As for the 2-thiouracil complexes, they exhibit a series of bands which are somewhat shifted with respect to the free ligand in this region: $\text{Bu}_2^{\text{n}}\text{Sn}(\text{s}^2\text{UraH}_{-2})$, 1210(w), 1184 cm⁻¹ (m); $[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$, 1240(w), 1215(w), 1170 cm⁻¹(m) these vibrational modes are thought to contain some $\nu(\text{C}=\text{S})$ character [1a, 18], but their diagnostic value appears to be poor, since, for instance, no clearcut difference between 1:1 ($\text{MeHg}(\text{s}^2\text{UraH}_{-1})$) and 2:1

($[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$) complexes is observed in this region. Moreover the more intense bands might be the result of a superimposition with alkyl deformation frequencies. The most noticeable change in the 800-900 cm⁻¹ region is the disappearance of the medium intensity band at 890 cm⁻¹. In the lower frequency region, vibrations occur at 203, 245, 370, 395 cm⁻¹ for $\text{Bu}_2^{\text{n}}\text{Sn}(\text{s}^2\text{UraH}_{-2})$ and at 222, 250 and 370 cm⁻¹ for $[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$ which are absent in the spectrum of free 2-thiouracil. The bands near 400 cm⁻¹ may reasonably [22] be assigned to $\nu(\text{Sn}-\text{S})$ though we recognize the approximate nature of such designation for a mode which will probably have only partial $\nu(\text{Sn}-\text{S})$ character. Furthermore, the environment of tin in the complexes has been investigated by Mössbauer spectroscopy (Table I) in the solid state.

Mössbauer Data

The isomer shift, δ , values for the obtained complexes (Table II) fall within the range characteristic for the organotin(IV) complexes [8]. The experimental nuclear quadrupole resonances, ΔE , have been rationalized according to the point charge model formalism [8] to provide informations on the tin(IV) environment in the 2-thiouracil complexes.

In the first instance, the $[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$ complex was examined: the experimental spectrum showed two doublets, the inner with $\Delta E_{\text{exp}} = 1.74$ mm s⁻¹ and the outer with $\Delta E_{\text{exp}} = 2.88$ mm s⁻¹, showing different coordination sites and/or geometries around the two tin(IV) atoms of the two $[\text{Me}_2\text{SnOH}^+]$ groups. In view of the ambivalency of

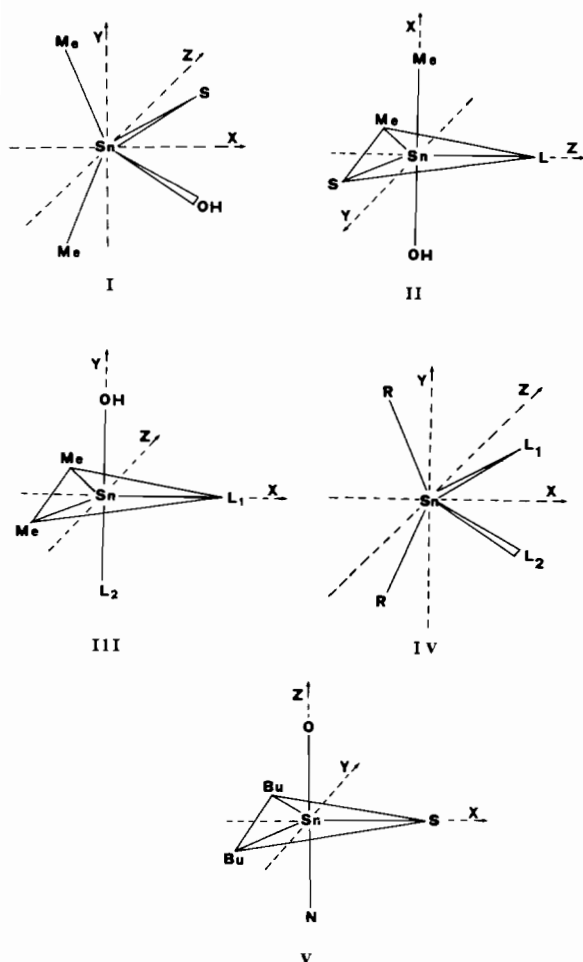


Fig. 1. Idealized structures for the complexes $[\text{Me}_2\text{SnOH}]_2\text{-(s}^2\text{UraH}_{-2})$ (I–IV) and $\text{Bu}_2\text{Sn(s}^2\text{UraH}_{-2})$ (IV, V). X, Y, Z are the directions of the principal components of the electric field gradient ($|V_{zz}| > |V_{yy}| \geq |V_{xx}|$).

2-thiouracil, several structural hypotheses have been advanced and ΔE 's have been calculated by using the appropriate sets of equations and p.q.s. values [8, 23, 24]. In Table II are summarized the calculated ΔE which differ from the experimental ΔE by less than the accepted tolerance limit $\pm 0.4 \text{ mm s}^{-1}$ [23]. Table II clearly shows that structures I ($\Delta E_{\text{calcd}} = -1.89$) and II (ΔE_{calcd} ranging from -2.01 to -1.74) of Fig. 1 could justify the inner doublet and both would have the thiolate ion involved in a binding site, the other three sites in I being occupied by the 2 methyl groups and by the OH of the $\text{Me}_2\text{-SnOH}^+$ unit. As far as the structure II (Fig. 1) was concerned we could not distinguish if the equatorial L was bridging OH of a different CH_3SnOH^+ unit or N(3) or O(4) of the $\text{s}^2\text{UraH}_{-2}$ ligand. Structure III and IV gave ΔE_{calcd} (respectively $2.71 \div 2.83 \text{ mm s}^{-1}$ and -2.56 or -2.99 mm s^{-1}) which agreed with

the experimental ΔE (2.88 mm s^{-1}) of the outer doublet. Also in this case there are several possibilities of coordination through different donor atoms (see Table II).

$\text{Bu}_2\text{Sn(s}^2\text{UraH}_{-2})$ was an easier application of the point charge model formalism. In fact both the structure IV and V of Fig. 1 ($\Delta E_{\text{calcd}} = 2.99 \text{ mm s}^{-1}$ and -2.84 mm s^{-1} , respectively) could represent configurations of the complex, but while in the monomeric structure IV an unlikely coordination arises since the base would act as a chelating ligand through O(4) and N(3), which disagrees with the presence of $\nu(\text{Sn-S})$ vibrations in the infrared, in V the pentacoordination could be more reasonably achieved through bridges of donor atoms (S, N, O) in a polymeric configuration.

^1H and ^{13}C NMR Spectra

Chemical shift changes of H_5 and H_6 protons of the base are observed in the ^1H NMR spectra of the complexes. The $\text{Bu}_2\text{Sn(s}^2\text{UraH}_{-2})$ complex shows a downfield shift which is similar to the trend shown by $\text{RHg(s}^2\text{UraH}_{-1})$ [1a] complexes and by the newly-synthesized $[\text{PhHg}]_2(\text{s}^2\text{UraH}_{-2})$, in DMSO-d_6 solutions, the latter exhibits the largest shift ($\text{H}_5 = 6.25$; $\text{H}_6 = 7.75$) with respect to the free base in the same solvent ($\text{H}_5 = 5.91$; $\text{H}_6 = 7.48$). Downfield shifts are generally observed in the case of S bonded 2-mercaptopyrimidine complexes [26]. No activation of C(5)-H or C(6)-H bonds as a result of metallation has been observed, since no broadening of these signals occur nor spin-spin coupling between the ^{119}Sn ($I = \frac{1}{2}$, natural abundance 8.58%) of ^{117}Sn ($I = \frac{1}{2}$, natural abundance 7.61%) and the H_5 and H_6 protons was observed, as is the case in Pt-uracil complexes [21]. The appearance of a single signal associated with the dimethyltin(IV) moieties in the $[\text{Me}_2\text{SnOH}]_2(\text{s}^2\text{UraH}_{-2})$ complex (flanked by satellites due to $^2\text{J}(\text{H}-^{119/117}\text{Sn})$) is in marked contrast with the solid state Mössbauer spectra. This indicates that a single type of organometallic moiety is present in solution, which might be due either to solvent-induced dissociation of the complex with no concomitant hydrolysis, since the H_5 and H_6 signals differ from those of the free ligand, see Table III), and/or a (organo)metallic ion exchange process of which evidence has been found in the (organo) mercury(II) complexes [1a]. The $^2\text{J}(\text{H}-^{119/117}\text{Sn})$ value is consistent with pentacoordination of the tin atom in solution, as ^2J values have been rationalized in terms of 'the amount of s character' in the Sn-C bond [27], and correlations have been found with the C-Sn-C angle and the size of the chelate ring [28], the number of alkyl groups attached to tin, and their length [29].

As for pentacoordinated, sulfur-bonded dimethyltin(IV) derivatives, complexes with L-cysteine, L-cysteine ethyl ester and DL-penicillamine are

TABLE III. ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR Data for 2-Thiouracil Complexes.^{a,b,c}

Compound	H ₅ ^d	H ₆ ^d	R ₂ Sn	² J(¹ H- ¹¹⁹ Sn)	² J(¹ H- ¹¹⁷ Sn)
s ² Ura	6.42d(1)	7.71d(1)			
[Me ₂ SnOH] ₂ (s ² UraH ₋₂)	6.22d(1)	7.48d(1)	1.42s(12)	80.5	77
Bu ₂ ⁿ Sn(s ² UraH ₋₂)	6.50d(1)	7.78d(1)	1.02-2.2		
Compound	C(2)	C(6)	C(Sn)	¹ J(¹³ C- ¹¹⁹ Sn)	¹ J(¹³ C- ¹¹⁷ Sn)
s ² Ura	178.77	146.67			
[Me ₂ SnOH] ₂ (s ² UraH ₋₂)	178.45	146.87	7.94	610	583
Bu ₂ ⁿ Sn(s ² UraH ₋₂)	178.77	146.74			

^aIn trifluoroacetic acid; chemical shifts δ (ppm) from internal tetramethylsilane. J values in Hz. ^bAbbreviations: d = doublet, s = singlet. ^cNumber of protons from integrated intensities in parenthesis. ^dJ_{H₅-H₆} = 7.5 Hz.

reported [30] for the latter (Me₂SnClpen): ²J(¹H-¹¹⁹Sn) 79.1 Hz and ¹J(¹³C-Sn) = 600.6 Hz.

In principle, ¹³C NMR spectra could also provide information of, *inter alia*, the binding sites of the organometallic moieties on the base. Indeed, ¹³C NMR chemical shifts of the CH₃ groups in methylated uracils and thiouracils provide a very effective way of establishing whether methylation has occurred on O-, S- or N-sites and, in the latter case, whether at N(1) or N(3) [31]. In this study [31], shifts for C(2), C(4) and C(5) are reported to be sometimes small (less than 2 ppm for N-methylation), and in the case of N-methylated-uracil derivatives, invariably shifted to higher field, while for the various thiouracils no consistent pattern is observed as the result of competing electronic and steric strain factors. In our complexes the ¹³C chemical shift changes are very low, even for the C(2) signals, and C(4) and C(5) could not be assigned. On expansion, however, ¹J(¹³C-¹¹⁹Sn) and ¹J(¹³C-¹¹⁷Sn) satellites of the (CH₃)₂SnOH⁺ moiety, in a region which is not obscured by signals due to the solvent, become more visible and they are assigned with confidence also on the basis of their ratio (1.0463) which is in very good agreement with ¹¹⁹Sn/¹¹⁷Sn = 1.0465.

The range of the ¹J values is typical of penta-coordinated organotin(IV) species bonded to S and N ligands [22, 30].

Concluding Remarks

Infrared spectra suggest a similar coordination of the organotins to the dianionic thiolated base. For the dibutyltin(IV) complex there is in principle the possibility of forming a stable four-membered ring chelate by coordinating both to exocyclic sulfur and N(3), as reported [32] in the X-ray structure of

dichlorobis(2-pyridinethiolato)tin(IV). Mössbauer data, however, are consistent both with tetra- and pentacoordinate structures, the 4-coordinate case being rather unlikely since a chelate complex involving binding to O(4) and N(3) only, is at variance with the IR data which suggest binding to sulfur. The 5-coordinate case involves a polymeric structure and suffers from a lack of selectivity since binding to all donor atoms is possible.

As for the [Me₂SnOH]₂(s²UraH₋₂) complex, the Mössbauer spectrum clearly shows the presence of two different tin environments (two doublets are distinctly observed). Once again, point charge calculations are consistent both with tetra- and pentacoordinate tins, however the inner doublet appears, in both structural hypotheses, to be associated with a sulfur-bonded Me₂SnOH⁺ moiety in a monomeric (4 coordination) or polymeric hydroxobridged (5 coordination) form. The outer doublet, on the other hand, may be associated with Me₂SnOH⁺ bonded either to nitrogen or oxygen, both in a monomeric and polymeric form. Solution studies (¹H and ¹³C NMR) indicate that, at least in the case of [Me₂SnOH]₂(s²UraH₋₂), pentacoordinate species are present in TFA solution and the appearance of a single signal due to the organometallic moieties suggests the occurrence of a rapid exchange process between binding sites. The ambivalency of the nucleobase and the extensive electronic delocalization in the dianion may ultimately be responsible for this exchange process in solution, along with the concomitant involvement of several, if not all, of the possible ligating groups in the solid.

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