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GROUP IV ORGANOMETALLIC COMPOUNDS

X *. SYNTHESSES AND MÖSSBAUER STUDIES OF SOME MIXED CHELATE DIORGANOTIN(IV) COMPLEXES

V.G. KUMAR DAS *, NG SEIK WENG, JOGINDER SINGH,

Department of Chemistry, University of Malaya, Kuala Lumpur 22-11 (Malaysia)

PETER J. SMITH and ROBIN HILL

International Tin Research Institute, Greenford, Middlesex UB6 7AQ (Great Britain)

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Summary

Novel mixed chelate complexes of diorganotin(IV) of formula $[\text{SnR}_2\text{L}'\text{L}'']$ involving the chelate ligands *N,N*-dialkyldithiocarbamate ($\text{S}_2\text{CNR}'_2$), 8-quinolinolate (oxin), 2-methyl-8-quinolinolate (quin) and the anion of bis(*p*-fluorobenzoyl)methane (fbm) have been synthesised together with the symmetrical bischelates $[\text{SnR}_2(\text{quin})_2]$ ($\text{R} = \text{Me}, \text{Ph}$), and the cationic complex, $[\text{SnMe}_2(\text{PPh}_3\text{O})_2(\text{AsPh}_3\text{O})_2][\text{BPh}_4]_2$, containing mixed monodentate ligands. Configurational assignments of the Sn—C bonds in the octahedral structures of these complexes have been made using Mössbauer spectroscopy.

Introduction

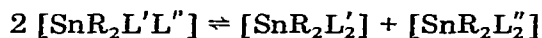
The stereochemical preference for *trans*- $[\text{SnC}_2]$ configuration in octahedral dimethyltin bischelates, $[\text{SnMe}_2\text{L}'_2]$, and for *cis* configuration in the corresponding diphenyltin compounds, although well established, is not fully understood. While theoretical studies based on the ligand-repulsion model indicate that the *cis* structure is more stable than *trans* in this class of compounds [1,2], it is probable that for many $[\text{SnMe}_2\text{L}'_2]$ complexes the *cis*—*trans* repulsive energy differences may be slight and the electronic effect of the two methyl groups forces the *trans* stereochemistry. The methyl group is a very good σ -donor and in *trans* array tends to acquire most of the tin 5s character (Bent's

* Part IX is ref. 13.

rule [3]), thereby favouring a linear C—Sn—C structure. If one or both the methyl groups are replaced by poorer σ -donors (for example, Ph), the *cis* structure is favoured for both steric and electronic reasons [4]. Recent studies [4,5] on mixed alkylphenyltin compounds have largely substantiated this, and it has been suggested [4] that the *cis* preference increases in the order,



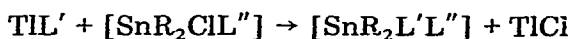
To prove these trends further, we considered it worthwhile to study mixed chelate complexes of formula $[\text{SnR}_2\text{L}'\text{L}'']$. In the literature, however, there is sparse documentation of such compounds, being limited to $[\text{SnMe}_2(\text{oxin})(\text{trop})]$ [6] (trop = tropolonate), $[\text{SnPh}_2(\text{oxin})(\text{PhCOCHCOPh})]$ [7] and the mixed chelates of dimethyltin containing combinations of *N,N*-dimethylmonothio-, -monoseleno-, -dithio-, -thioseleno- and -diselenocarbamates [8]. The difficulties in the synthesis of mixed chelate compounds have been discussed recently by Tanaka and coworkers [8], who have pointed out that large differences in coordinating ability between the ligands tend to favour the formation of the symmetrical bischelates:



Accordingly, we have chosen ligands which, as shown in Table 1, have allowed the successful isolation of the mixed chelate complexes listed therein. Table 1 also includes two symmetrical bischelates and a novel dimethyltin cationic complex containing mixed monodentate ligands not previously reported. The stereochemistry of the Sn—C bonds in these compounds has been investigated using Mössbauer spectroscopy.

Experimental

The mixed chelate complexes were prepared according to the reaction scheme,



where $\text{R}_2 = \text{Me}_2, \text{Bu}_2, \text{Ph}_2$ and BuPh , and L', L'' are chelating ligands such as $\text{S}_2\text{CNR}'_2$, 8-quinolinolate (oxin), 2-methyl-8-quinolinolate (quin) and the anion of bis(*p*-fluorobenzoyl)methane (fbm). $\text{Tl}(\text{fbm})$ was synthesised by the general method described for thallos salts of β -diketonates [9], while $\text{Tl}(\text{quin})$ was prepared duplicating the literature method for $\text{Tl}(\text{oxin})$ [10]. The thallos salts of the *N,N*-dialkyldithiocarbamates were obtained according to established procedures [11,12], as also the diorganotinchloro-oxinates and -dithiocarbamates [5].

The symmetrical bischelates, $[\text{SnR}_2(\text{quin})_2]$ ($\text{R} = \text{Me}, \text{Ph}$), were prepared by the method described by Westlake and Martin [7] for the corresponding bis-oxinates. The complex, $[\text{SnMe}_2(\text{PPh}_3\text{O})_2(\text{AsPh}_3\text{O})_2][\text{BPh}_4]_2$, was obtained immediately upon adding an ethanolic solution containing the two oxygen-donor ligands to an ethanolic solution containing dimethyltin dichloride and sodium tetraphenylborate. The reactants were kept in the stoichiometric ratio indicated below in parenthesis:

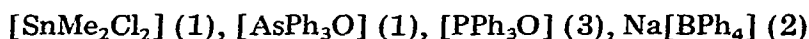


TABLE 1
CHARACTERISATION OF $[\text{SnMe}_2(\text{PPh}_3\text{O})_2(\text{AsPh}_3\text{O})_2][\text{BPh}_4]_2$ AND OTHER DIORGANOTIN BISCHELATE COMPLEXES

Complex	Decomp. Pt. (°C)	Analyses (%) ^a			UV (nm) ^{b, c}
		C	H	N	
$[\text{SnMe}_2(\text{quin})_2]$	289-290	57.10(56.82)	4.91(4.73)	6.16(6.02)	360(3.72), 333(3.62), 317(3.53)
$[\text{SnPh}_2(\text{quin})_2]$	287-289	65.67(65.24)	4.61(4.41)	4.65(4.75)	360(3.50), 336(sh)(3.47), 318(3.46)
$[\text{SnPh}_2(\text{quin})(\text{oxin})]$	259-261	64.44(64.74)	4.37(4.35)	4.83(4.87)	374(3.54), 334(3.38), 318(sh)(3.33)
$[\text{SnBuPh}(\text{quin})(\text{oxin})]$	137-138	62.64(62.70)	5.21(5.04)	4.99(5.04)	345(4.27), 260(4.40)
$[\text{SnPh}_2(\text{oxin})(\text{fbrm})]$	224-226	63.70(63.94)	3.86(3.70)	2.17(2.07)	383(3.41) ^d , 332(3.30) ^d
$[\text{SnPh}_2(\text{oxin})(\text{S}_2\text{CNMe}_2)]$	192-193	50.87(53.63)	4.08(4.10)	4.90(5.21)	
$[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$	125-127	29.41(28.80)	5.26(5.28)	6.57(6.72)	
$[\text{SnBu}_2(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{CNBu}_2)]$ ^e	liq.	44.98(45.16)	7.90(7.87)	5.11(4.79)	
$[\text{SnMe}_2(\text{PPh}_3\text{O})_2(\text{AsPh}_3\text{O})_2][\text{BPh}_4]_2$ ^f	165-167	73.02(73.71)	5.41(5.38)		

^a Calcd. values are given in parentheses. ^b Spectral data refer to oxin and quin. bands in CHCl_3 unless stated otherwise (log ϵ values are given in parentheses). ^c For uncomplexed Hoxin and Hquin, λ_{max} values are resp. 313 and 305 nm. ^d In benzene. ^e % S: 21.9(21.9). ^f % As: 7.2(7.5).

In the IR (Nujol mull), the complex showed bands (principal bands in italics) due to $\nu(\text{P}-\text{O})$ at 1132, 1120vs, doublet, 1082s, 1064m cm^{-1} and due to $\nu(\text{As}-\text{O})$ at 890w, 874, 866s, doublet, 842w cm^{-1} .

The mixed chelate complexes were prepared using benzene as the solvent medium except in the case of the mixed dithiocarbamates where chloroform was used. After filtering off the thallos chloride using a Kieselguhr filter-cake, the solutions were concentrated to low volumes with minimal application of heat. Cooling, followed by addition of a small amount of petroleum ether, yielded crystalline solids in all cases except $[\text{SnBu}_2(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{CNBu}_2)]$, which was obtained as a pale yellow oil.

An attempted preparation of $[\text{SnBuPh}(\text{oxin})(\text{fbm})]$ yielded a mixture of $[\text{SnBuPh}(\text{oxin})_2]$ and $[\text{SnBuPh}(\text{fbm})_2]$. Likewise, the reaction of $[\text{SnR}_2\text{Cl}(\text{S}_2\text{CNMe}_2)]$ ($\text{R} = \text{Me}, \text{Ph}$) with $\text{Tl}(\text{oxin})$, in both benzene and ethanol, yielded only the symmetrical bischelates. However, in a variation of the method using $\text{Tl}(\text{S}_2\text{CNMe}_2)$ and $[\text{SnPh}_2\text{Cl}(\text{oxin})]$, it was possible to isolate the complex $[\text{SnPh}_2(\text{oxin})(\text{S}_2\text{CNMe}_2)]$ as the first crop upon concentrating the benzene medium. A completely satisfactory carbon analysis was not obtained for this complex, but in support of its formulation is the identification of the following fragment ion peaks among the tin containing clusters in its mass spectrum. The m/e values given are based on ^{120}Sn and ^{32}S and refer to the most intense peak in the clusters containing tin. Clusters occurring in trace amounts relative to the base peak $[\text{SnSCNMe}_2]$ (m/e 208) are indicated by an asterisk against the m/e value.

$[M - 3]$ (m/e 535 *; $M =$ molecular ion); $\text{SnPh}_2(\text{oxin})(\text{S}_2\text{CN})$, (m/e 508), $\text{SnPh}(\text{oxin})(\text{S}_2\text{CNMe}_2)$, (m/e 461) *; $\text{SnPh}(\text{oxin})(\text{S}_2\text{CNMe})$, (m/e 446) *, $\text{SnPh}(\text{oxin})(\text{SCNMe}_2)$, (m/e 429); $\text{SnPh}(\text{oxin})(\text{SCNMe})$, (m/e 414); $\text{Sn}(\text{oxin})(\text{S}_2\text{CNMe})$, (m/e 369); $\text{Sn}(\text{oxin})(\text{SCSNH})(?)$, (m/e 355).

The complex showed bands in the IR {Nujol mull; 1466vs, $\nu(\text{C}\equiv\text{N})$; 984m, 972w, $\nu(\text{C}\equiv\text{S})$ } and UV (Table 1) which indicate the presence of chelated ligands [13] and, therefore, of six-coordinate tin in the compound.

Mössbauer spectra of the complexes were obtained at 80 K using a constant acceleration microprocessor Mössbauer spectrometer as described previously [5]. Mass spectral data on the mixed dithiocarbamato-oxin complex were obtained on a AEI-MS 3074 double beam mass spectrometer. The following conditions were used: electron energy, 70 eV, pressure, $1-3 \times 10^{-7}$ Torr; current 300 μA ; source temperature, 150°C.

Results and discussion

The Mössbauer parameters for the complexes are given in Table 2 together with literature data on some symmetrical bischelate complexes. The observed quadrupole splittings are also compared in the Table with calculated values based on the additivity model [14,15] for idealized *cis*- or *trans*- $[\text{SnR}_2]$ geometries.

The centre shift (c.s.) and, in particular, the quadrupole splitting (q.s.) values for both $[\text{SnPh}_2(\text{quin})_2]$ and $[\text{SnMe}_2(\text{quin})_2]$ are seen to be higher than those for the corresponding oxin complexes. In the literature [14], a *trans* label has been given to octahedral $[\text{SnR}_2\text{X}_4]$ compounds which show q.s. values in the

TABLE 2
MÖSSBAUER DATA (mm s^{-1}) AT 80 K

Complex	c.s. ^{a, b}	Obs. q.s. ^a	Calc. q.s. ^{c, d}
[SnMe ₂ (quin) ₂]	1.08	3.27	(+) 3.92 ^e
[SnPh ₂ (quin) ₂]	1.04	3.50	(+) 3.70 ^e
[SnMe ₂ (oxin) ₂]	0.88 ^g	2.02 ^g	(-) 1.96 ^f
[SnBuPh(oxin) ₂]	0.86 ^h	1.93 ^h	(-) 1.88 ^f
[SnPh ₂ (oxin) ₂]	0.68 ^g	1.69 ^g	(-) 1.80 ^f
[SnPh ₂ (quin)(oxin)]	0.75	1.65	(-) 1.80 ^f
[SnBuPh(quin)(oxin)]	0.84	2.08	(-) 1.88 ^f
[SnPh ₂ (oxin)(fbm)]	0.65	1.75	(-) 1.84 ^f
[SnPh ₂ (oxin)(S ₂ CNMe ₂)]	0.95	1.65	(-) 1.60 ^f
[SnMe ₂ (S ₂ CNMe ₂)(S ₂ CNEt ₂)]	1.39	2.84	(+) 3.00 ^e
[SnMe ₂ (S ₂ CNMe ₂) ₂]	1.57 ⁱ	3.14 ⁱ	(+) 3.00 ^e
[SnMe ₂ (S ₂ CNEt ₂) ₂]	1.51 ^j	3.04 ^j	(+) 3.00 ^e
[SnPh ₂ (S ₂ CNEt ₂) ₂]	1.17 ^j	1.76 ^j	(-) 1.40 ^f
[SnMe ₂ (PPh ₃ O) ₂ (AsPh ₃ O) ₂][BPh ₄] ₂	1.27	4.56	(+) 4.40 ^e

^a $\pm 0.05 \text{ mm s}^{-1}$. ^b Relative to BaSnO₃. ^c Using the electric field gradient expressions and partial quadrupole splitting (p.q.s.) values in refs. 14 and 15, and assuming p.q.s. values for quin and fbm to be identical to the p.q.s. values of their respective unsubstituted parent chelates. ^d Predicted signs are given in parentheses. ^e *trans*-[SnR₂]. ^f *cis*-[SnR₂]. ^g Ref. 30. ^h Ref. 5. ⁱ Ref. 27. ^j Ref. 25.

range 3.37–4.32 mm s^{-1} and a *cis* label to those with q.s. values lying in the range 1.63–2.34 mm s^{-1} . However, in a recent correlation, Bancroft and Sham [16] have shown for the [SnMe₂X₄] system that the C–Sn–C angle decreases smoothly away from 180° as the q.s. value decreases from about 4.00 mm s^{-1} , so that in the case of highly distorted structures a *cis* or *trans* label might be of questionable validity. Nevertheless, for the bisoxinates [SnR₂(oxin)₂], where R₂ = Me₂ [17], (MeOCOCH₂CH₂)₂ [13], Ph₂ [17], MePh [4] and BuPh [5], the Mössbauer data have been reasonably interpreted in favour of distorted *cis* octahedral structures. This is in consonance with the small bite size [2,18] of the oxin ligand. In contrast, the larger q.s. values for the symmetrical [SnR₂(quin)₂] complexes observed in this study appear to be more in accord with *trans* or distorted *trans* structures. Thus, the q.s. value for [SnPh₂(quin)₂] is almost identical to that of [SnPh₂Cl₂(bipy)] [19], which has a C–Sn–C angle of 173.5°, as deduced crystallographically [20]. The observed q.s. value is also seen to be in excellent agreement with the calculated value based on *trans*-[SnPh₂] geometry. This stereochemical result constitutes the first example of its kind among diphenyltin bischelates where the theoretically predicted *cis* structure [1,2] is not experimentally observed. We do not envisage that the introduction of a methyl substituent *ortho* to N in oxin would profoundly alter the bite size of the ligand. On the other hand, the substituent may impose a steric congestion in the *cis* structure which could be relieved in a distorted *trans* arrangement in which one end of the bidentate ligand (in this case, N) is pushed further away from the Sn atom than is the case [21] with unsubstituted oxin. This assumption finds support in recent theoretical calculations [2] which reveal the distorted *trans* structure to be energetically more stable than the undistorted *cis*.

The replacement of one of the quin ligands in [SnPh₂(quin)₂] with oxin,

however, yields a mixed chelate complex with significantly lower c.s. and q.s. values. For this latter complex, as well as for the analogous novel complex with totally mixed ligands, $[\text{SnBuPh}(\text{quin})(\text{oxin})]$, the q.s. values are seen to be in good agreement with the calculated values assuming *cis*- $[\text{SnR}_2]$ stereochemistry. It would thus appear that the preference for distorted *trans* structure in the case of $[\text{SnPh}_2(\text{quin})_2]$ is occasioned by the more acute steric interaction involving two quin ligands in the alternative *cis* structure.

For $[\text{SnMe}_2(\text{quin})_2]$, the observed q.s. is at variance with the calculated values for either *cis* (-1.96 mm s^{-1}) or *trans* ($+3.92 \text{ mm s}^{-1}$) stereochemistries. The C—Sn—C bond angle estimated [16] from the observed q.s. value is about 138° , which is intermediate between the values for regular *cis* and *trans* geometries. In solution, however, a distorted *trans* configuration seems indicated for the complex from its 60 MHz ^1H NMR spectrum. Thus in CDCl_3 , the spectrum reveals a single Sn—Me resonance and $^2J(^{119}\text{Sn—Me})$ value of 88.7 Hz, comparable to that observed for several *trans*- $[\text{SnMe}_2]$ octahedral structures [16,22], and appreciably larger than 71.2 Hz reported [23] for $[\text{SnMe}_2(\text{oxin})_2]$ which, from X-ray structural evidence [21], has a distorted *cis* geometry (C—Sn—C angle = 110.7°).

The complex $[\text{SnPh}_2(\text{oxin})(\text{fbm})]$, which contains two dissimilar chelating ligands coordinated to tin, shows a q.s. value compatible with *cis*- $[\text{SnPh}_2]$ stereochemistry and on the basis of comparison UV spectra in chloroform, shows little tendency to disproportionate to $[\text{SnPh}_2(\text{oxin})_2]$ and $[\text{SnPh}_2(\text{fbm})_2]$. In the IR (hexachlorobutadiene mull), the complex showed a broad carbonyl stretching frequency centred at 1532 cm^{-1} .

The complex $[\text{SnPh}_2(\text{quin})(\text{oxin})]$ also showed stability towards disproportionation in chloroform, but the related derivative, $[\text{SnBuPh}(\text{quin})(\text{oxin})]$, which is only sparingly soluble, appears to be quite labile in this medium.

A stereochemical preference for *cis* configuration of the phenyl groups at tin is also strongly indicated from the Mössbauer result for $[\text{SnPh}_2(\text{oxin})-(\text{S}_2\text{CNMe}_2)]$. This complex together with $[\text{SnMe}_2(\text{oxin})(\text{trop})]$ (trop = tropolone) [6] and $[\text{SnPh}_2(\text{oxin})(\text{Ch})]$ (Ch = acac or fbm) formally constitute examples of mixed chelate organotin compounds containing the 5-membered oxin ring in combination respectively with other four-, five- and six-membered chelate rings.

The mixed dithiocarbamate complex, $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$, shows somewhat lower c.s. and q.s. values than the corresponding symmetrical bisdithiocarbamate complexes (Table 2). The tin atom in $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)_2]$ has been shown from a crystal structure study [24] to be in a distorted octahedral *trans*- $[\text{SnR}_2\text{X}_4]$ environment, with the methyl groups lying above and below the plane formed by the four S atoms of the two anisobidentate [25] *N,N*-dimethyldithiocarbamate ligands. The C—Sn—C bond angle in this latter complex is observed to be 136° , while for $[\text{SnPh}_2(\text{S}_2\text{CNEt}_2)_2]$, which has a distorted octahedral *cis*- $[\text{SnR}_2\text{X}_4]$ geometry [26], the observed value is 101.4° . The calculated q.s. for a *cis* octahedral structure for $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$ is -1.56 mm s^{-1} . This is clearly not in agreement with the observed q.s. value for the complex which is more in accord with the calculated value based on *trans* stereochemistry. This prompts us to suggest a highly distorted *trans* octahedral structure for the mixed dithiocarbamate complex. It is instruc-

tive that the c.s. for this complex lies intermediate between the values [27] for $[\text{SnPh}_2(\text{S}_2\text{CNEt}_2)_2]$ and $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)_2]$, suggesting [28] that the C—Sn—C bond angle is probably also intermediate between the “*cis*” and “*trans*” values of the symmetrical bischelates. The ^1H NMR spectrum of $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$ in CDCl_3 shows a single Sn—Me resonance at δ 1.50 ppm and 2J value of 85 Hz. These data compare favourably with those reported for $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)_2]$ [29]. In the IR (Nujol mull), the following bands (cm^{-1}) may be readily assigned for $[\text{SnMe}_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{CNEt}_2)]$: 1488s $\nu(\text{C}\equiv\text{N})$, 984, 976s, doublet $\nu(\text{C}\equiv\text{S})$, 555m $\nu_{\text{as}}(\text{Sn}-\text{C})$, 384w, 368w $\nu(\text{Sn}-\text{S})$. The complex also appears to be stable in chloroform and this contrasts with the lability of mixed chelates of dimethyltin containing combinations of *N,N*-dimethylmonothio-, -monoseleno-, -dithio-, -thioseleno- and -diselenocarbamates reported previously by Tanaka and coworkers [8].

A *trans*- $[\text{SnMe}_2]$ configuration may be unambiguously assigned for the mixed ligand cationic complex, $[\text{SnMe}_2(\text{PPh}_3\text{O})_2(\text{AsPh}_3\text{O})_2][\text{BPh}_4]_2$, for which the observed q.s. value is close to the average of the values 4.75 and 4.03 mm s^{-1} reported [15] for $[\text{SnMe}_2(\text{PPh}_3\text{O})_4][\text{BPh}_4]_2$ and $[\text{SnMe}_2(\text{AsPh}_3\text{O})_4][\text{BPh}_4]_2$, respectively, and also in excellent agreement with the calculated value (Table 2).

Further synthetic studies on an extended range of mixed chelate complexes of diorganotin are currently in progress and these will be reported at a later date

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