Inorganica Chimica Acta, 49 (1981) 149–152
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Group IV Organometallic Compounds.
IX*. Preparation and Spectroscopic Studies of Complexes of Bis(β-carbomethoxyethyl)tin Dichloride

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

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

and P. J. SMITH

International Tin Research Institute, Perivale, Greenford, Middlesex UB6 7AQ, U.K.

Received November 3, 1980

Bis(β-carbomethoxyethyl)tin dichloride forms coordination complexes of formula $R_2SnCl_2L_2$, $R_2SnL'_2$ *and* $R_2SnCl(oxin)$ *where* $L_2 = 2Ph_3AsO$, *phen, bipy and* $L' =$ *oxin,* $-S\underset{\underset{S}{\|}}{C}NR''_2$. *However, it exhibits weaker acceptor properties towards other ligands including phosphine oxides. Structural features of the isolated complexes both in the solid state and in solution are discussed based on spectral (IR, UV, NMR, Mössbauer) evidence.*

Introduction

The title compound is one of several β-carbonylalkyltin chlorides that has received recent attention for its novel synthesis by the AKZO methods [1, 2], but apart from the evidence for intramolecular coordination through its carbonyl functions [2–4], both in the solid state and in solution, there has been no report to-date on its acceptor properties. This paper describes the results of our preliminary investigations in this area.

Experimental

The complexes with 1,10-phenanthroline and Ph_3AsO were prepared by reacting stoichiometric quanti-

TABLE I. Analytical and Physical Data for $(MeOCOCH_2CH_2)_2Sn(IV)$ Complexes.

Complex[a]	Dec. pt. (°C)	Analyses %[b]	
		C	H
$R_2SnCl_2 \cdot phen$	138–9	44.19(44.14)	4.16(4.05)
$R_2SnCl_2 \cdot bipy$[c]	97–8	41.40(41.57)	4.15(4.23)
$R_2SnCl_2 \cdot 2Ph_3AsO$	164–5	52.65(52.81)	4.47(4.40)
$R_2SnCl_2 \cdot 2Ph_3PO$[d]	78–9	56.72(57.41)	4.73(4.78)
$R_2SnCl_2 \cdot opo$[e]	79–80	50.67(50.79)	4.68(4.62)
$R_2Sn(oxin)_2$	152–3	53.39(53.72)	4.53(4.48)
$R_2Sn(S_2CNMe_2)_2$[f]	116–7	31.40(31.54)	4.75(4.88)
$R_2Sn(S_2CNEt_2)_2$	69–70	36.47(36.69)	6.08(5.78)
$R_2SnCl(oxin)$	87–8	43.31(43.20)	4.30(4.24)

[a] $R = MeOCOCH_2CH_2$–. [b] Calcd. values in parentheses. [c] %N: 5.27(5.38). [d] %Cl: 7.7(7.7). [e] opo = $Ph_2P(O)CH_2P(O)Ph_2$. [f] %N: 5.04(5.25).

---

*Part VIII: See Ref. [8].

**Author to whom correspondence should be addressed.

TABLE II. Infra-red Assignments in the 600–250 cm^{-1} Range and of Other Selected Bands (Nujol Mulls).

Complex[a]	$\nu_{C=O}$	ν_{Sn-C}	ν_{Sn-O}	ν_{Sn-N}	Other
R_2SnCl_2	1675vs	584w, 542vw, 516vw	370s (?)		285s, 270s(Sn–Cl)
$R_2SnCl_2 \cdot 2Ph_3AsO$	1725vs	562w	392w, 356s		879vs (As–O); 320m; 294w
$R_2SnCl_2 \cdot 2Ph_3PO$	1685vs	585vw, 537s, 500w	396vw, 380sh, 372m (?)		1195s, 1130vs, 1110w, 1080m (P–O)[b]; 454w; 440vw; 274s
$R_2SnCl_2 \cdot phen$	1750m, 1730vs, 1725vs	592w, 560vw, 545vw		417m, 346w	468vw; 392vw; 268w
$R_2SnCl_2 \cdot bipy$	1728vs	560w, 552sh		402vw, 346w	372vw; 316vw; 292m; 272w
$R_2SnCl_2 \cdot opo$	1684vs	584vw, 560w[c], 544vw	372m (?)		1184m, 1164w, 1116m (P–O)[b]; 276m
$R_2Sn(oxin)_2$	1731vs, 1720sh	580w, 560w	512s	388m	488w; 460vw; 442vw; 422w; 363vw; 346vw; 292w
$R_2SnCl(oxin)$	1735vs, 1712s	578w, 564w	524s	394m	465vw; 428w; 356w; 292vw; 256s (Sn–Cl)
$R_2Sn(S_2CNMe_2)_2$	1730vs, 1696s	564w			1508vs (C⋯N); 976, 968vs,d (C⋯S); 442w; 426w; 344m (Sn–S)
$R_2Sn(S_2CNEt_2)_2$	1734vs, 1701vs	562w			1484s (C⋯N); 988s (C⋯S); 426w; 392w; 350w (Sn–S)

[a] R = $MeOCOCH_2CH_2$–. [b] β-carbomethoxyethyl bands overlaid. [c] Overlaps with ligand band.

ties of the reactants in $CHCl_3$; for the phosphine oxide adducts the solvent medium used was benzene. In the case of the bipyridyl complex, the ligand was dissolved in ethanol and added to a hot benzene solution of the Lewis acid, and the whole concentrated and cooled to obtain the crystalline product. The bis(oxinate) was synthesised by the method of Westlake and Martin [5] and the chlorooxinate was obtained from this by reaction with an equivalent amount of the diorganotin dichloride in benzene. The bis(N,N-dialkyldithiocarbamato) complexes were prepared by reacting $(MeOCOCH_2CH_2)_2SnCl_2$ with stoichiometric amounts of the appropriate Tl(I) salts [6, 7] of the dithiocarbamates in $CHCl_3$.

The complexes are listed in Table I together with their analytical and physical data. Mössbauer spectra of the complexes were obtained at 80 K using a constant acceleration microprocessor Mössbauer spectrometer as described previously [8]. The experimental error in the measured values of centre shift (C.S.) and quadrupole splitting (Q.S.) parameters is ±0.05 mm s^{-1}.

Results and Discussion

Infra-red data on the complexes are assembled in Table II. All compounds show that the carbonyl stretching frequency in the parent Lewis acid at 1675 cm^{-1} is significantly displaced to higher wave numbers, with the exception of the phosphine oxide complexes. This suggests that intramolecular coordination of the carbonyl groups to tin is still dominant in the latter complexes. For the N,N-diethyldithiocarbamato complex, the observation of a single strong band at 988 cm^{-1} ($\nu_{C\cdots S}$) is strongly indicative of a chelating ligand [9] and, therefore, of six-coordinate tin in the compound. The band for the analogous N,N-dimethyldithiocarbamato complex appears as a sharp doublet at 976, 968 cm^{-1}, probably on account of solid state splitting. The spectra of the oxinates show in addition to the Sn–C stretching modes, one other strong absorption in the 500–600 cm^{-1} region. This band which is absent in the spectrum of the uncomplexed ligand is reasonably assigned to Sn–O vibration [10]. The location also of Sn–N stretching modes in the 380–400 cm^{-1} region [10] attests to the chelating nature of the oxin ligand in these complexes. These conclusions are supported by Mössbauer spectroscopic data on the complexes which are listed in Table III, together with the calculated quadrupole splitting values for the complexes based on our previously reported additivity expressions for octahedral [11] and trigonal bipyramidal [12] coordination. Again, except for the phosphine oxide complexes, the agreement between observed Q.S. values and those calculated for octahedral *trans-* or *cis-*

TABLE III. ^{119m}Sn Mössbauer Parameters (mm s^{-1}) for $(MeOCOCH_2CH_2)_2Sn(IV)$ Compounds.

Compound[a]	C.S.[b,c]	Obs. Q.S.[c]	Calc. Q.S.[d]
R_2SnCl_2	1.50 (1.50)[e]	3.55 (3.45)[e]	
R_2SnCl_2•phen	1.48	3.97	4.04[f]
R_2SnCl_2•bipy	1.46	4.03	3.96[f]
R_2SnCl_2•$2Ph_3AsO$	1.34	4.11	4.08[f]
R_2SnCl_2•$2Ph_3PO$	1.46	3.62	4.44[f]
R_2SnCl_2•opo	1.36	3.57	4.32[f]
$R_2Sn(oxin)_2$	0.90	2.05	1.96[g]
$R_2Sn(S_2CNMe_2)_2$	1.50	3.30	3.62[f]
$R_2Sn(S_2CNEt_2)_2$	1.56	3.32	3.62[f]
$R_2SnCl(oxin)$	1.27	3.09	3.21[h]

[a] $R = MeOCOCH_2CH_2$–. [b] Relative to Ba $^{119m}SnO_3$. [c] ±0.05 mm s^{-1}. [d] Using the additivity expressions and p.q.s. values in references 11 and 12. [e] P. G. Harrison, T. J. King and M. A. Healy, *J. Organometal Chem.*, *182*, 17 (1979). [f] For octahedral *trans*-R_2Sn and *cis*-L_2Sn moieties. For the all-*trans* isomers in $R_2SnCl_2L_2$, the predicted values would be very slightly larger ($\eta \neq 0$). [g] For *cis*-R_2Sn octahedral geometry. [h] For trigonal bipyramidal geometry with *equatorial* disposition of R groups.

TABLE IV. PMR Spectral Data for $(MeOCOCH_2CH_2)_2Sn(IV)$ Compounds.[a]

Compound[b]	Chemical shifts (δ[c])			
	H_α	H_β	H_c	Other
R_2SnCl_2	1.92 1.78[d] 2.10[e] 1.71[f]	2.93 2.47[d] 2.97[e] 2.75[f]	3.82 3.11[d] 3.62[e] 3.65[f]	
R_2SnCl_2•phen	1.74	2.82	3.44	
R_2SnCl_2•$2Ph_3AsO$	1.79	2.82	3.64	
R_2SnCl_2•bipy	1.89	2.90	3.76	
R_2SnCl_2•$2Ph_3PO$	1.92	2.91	3.78	
R_2SnCl_2•opo	1.90	2.91	3.78	
$R_2Sn(oxin)_2$	1.34	2.44	3.52	7.99 (4-Hoxin); 8.42 (2-Hoxin)
$R_2SnCl(oxin)$	1.77 1.75[d]	2.84 2.74[d]	3.63 3.18[d]	8.42 (4-Hoxin); 9.12 (2-Hoxin)
$R_2Sn(S_2CNMe_2)_2$	2.25 2.67[d]	3.04 3.13[d]	3.68 3.28[d]	3.42 (N–Me) 2.84[d] (N–Me)
$R_2Sn(S_2CNEt_2)_2$	2.27 2.70[d]	3.04 3.25[d]	3.68 3.26[d]	1.28 (N–$CH_2\underline{Me}$); 3.76 (N–CH_2) 0.93[d] (N–$CH_2\underline{Me}$); 3.38[d] (N–CH_2)

[a] In $CDCl_3$ at 35 °C unless otherwise indicated. [b] $R = MeOCOCH_2CH_2$–. [c] p.p.m. downfield from TMS. [d] In benzene. [e] In pyridine. [f] In DMSO.
(H_c) (H_β) (H_α)

R_2Sn and trigonal bipyramidal *equatorial*-R_2Sn stereochemistries, as appropriate, is well within the acceptable error margin of ±0.4 mm s^{-1} for the additivity model [13]. For the phosphine oxide complexes, the Mössbauer parameters differ little from that of the parent Lewis acid, which has a distorted octahedral configuration with *cis*- disposition of the halogens and CSnC bond angle of 144° [4]. It is conceivable that the phosphine oxide ligands are located outside the primary coordination sphere of tin in the octahedral crystal lattice, and, perhaps, in proximity to the electron-deficient carbon of the coordinated carbonyl groups. In this respect, an analogy may be drawn with the non-ionic and octahedral complexes of Ph_2SnCl_2 of 1:4 stoichiometry with morpholine, piperidine and β- and γ-picolines [14]. The IR spectra of the complexes in the P–O stretching region which would be particularly diagnostic of complexation are, however, complicated by absorptions due to the β-carbomethoxyethyl groups on tin, thus precluding any firm conclusion. Intramolecular coordination by the carbonyl groups, on the other hand, certainly seems disfavoured for the coordinatively unsaturated chlorooxinate complex.

The weaker acceptor property of $(MeOCOCH_2CH_2)_2SnCl_2$ relative to simple dialkyltin- or diaryltindihalides is further evidenced by the absence of adduct formation upon recrystallising the Lewis acid in pyridine or dimethylsulphoxide, although in solution there appears to be some coordinative interaction based on PMR data (Table IV). Thus the proton H_c and, to some exent, also H_α and H_β of the β-carbomethoxyethyl group resonate at higher magnetic fields in these donor solvents relative to their positions in $CDCl_3$. Upfield shifts have also been observed in benzene [3], but this has been accounted for in terms of anisotropic shielding arising from complex formation of benzene with the electron-deficient carbonyl group. Of the isolable complexes examined in $CDCl_3$, it would seem that only the 1,10-phenanthroline and Ph_3AsO complexes retain their stereochemical integrity. The H_α, H_β and H_c resonances for the bipyridyl and phosphine oxide complexes in $CDCl_3$ are almost identical in value to the parent diorganotin dichloride, suggesting lability for these ligands in solution. For both $(MeOCOCH_2CH_2)_2Sn(oxin)_2$ and the chlorooxinate their UV spectra in $CHCl_3$ reveal weak to medium intensity bands at 320 and 334 nm in addition to the strong band at 381 nm. The 320 nm band of the free ligand suffers displacement to longer wavelengths upon chelation [15], so that the co-presence of this band in the above complexes indicates both chelating and non-chelating ligands in solution. The time-averaged PMR spectrum for the bis(oxinate) shows the 2-H(oxin) and 4-H(oxin) resonances at 8.42 and 7.99 p.p.m. respectively, differing only slightly from the free ligand values of 8.73 and 8.04 p.p.m. [16]. Considerable downfield shifts in these resonances are to be anticipated for strong chelation [17], and, indeed, relative to the bis(oxinate), the chlorooxinate appears to involve a greater extent of chelation in solution.

The H_α and H_β resonances of the dithiocarbamato complexes in $CDCl_3$ occur at somewhat lower magnetic fields than for the uncomplexed Lewis acid. Only one sharp signal is observed in both $CDCl_3$ and benzene for the N-methyl protons in $(MeOCOCH_2CH_2)_2Sn(S_2CNMe_2)_2$, unlike for $Me_2NCSSMe$ [18]. This suggests that the two N-methyl groups become almost equivalent by chelation of the dithiocarbamato group. Further, in benzene, the spectra of both $(MeOCOCH_2CH_2)_2Sn(S_2CNMe)_2$ and $(MeOCOCH_2CH_2)_2Sn(S_2CNEt_2)_2$ show the H_α and H_β resonances displaced further downfield but not H_c, which suffers an upfield shift (Table IV). These trends are explicable in terms of benzene–solute stereospecific interaction at electron-deficient nitrogen which shifts the N–Me and N–Et resonances to higher field relative to their values in $CDCl_3$, as described by Honda *et al.* [19] for $Me_2Sn(S_2CNMe_2)_2$, but with the anisotropic shielding effect in the present cases encompassing as well the carbomethoxyl proton (H_c).

Further studies on the synthesis and structure of coordination complexes of $(MeOCOCH_2CH_2)_2SnCl_2$ and of its functionally modified derivatives are currently underway and will be reported at a later date.

Acknowledgement

We wish to thank the International Tin Research Council, London, for permission to publish this paper and the University of Malaya for a research grant under Vote F.

References

1 J. W. Burley, R. E. Hutton and V. Oakes, *J. Chem. Soc. Chem. Commun.*, 803 (1976).
2 R. E. Hutton, J. W. Burley and V. Oakes, *J. Organometal. Chem.*, *156*, 369 (1978).
3 R. M. Haigh, A. G. Davies and M.-W. Tse, *J. Organometal. Chem.*, *174*, 163 (1979).
4 P. G. Harrison, T. J. King and M. A. Healy, *J. Organometal. Chem.*, *182*, 17 (1979).
5 A. H. Westlake and D. F. Martin, *J. Inorg. Nucl. Chem.*, *27*, 1579 (1965).
6 S. Akerstrom, *Arkiv. Kemi*, *24*, 495 (1965), *Chem. Abstr.*, *63*, 12160 (1965).
7 R. J. Magee and M. J. O'connor, *Inorg. Chem. Acta*, *16*, 107 (1976).
8 V. G. Kumar Das, Ng Seik Weng, P. J. Smith and R. Hill, *J. Chem. Soc. Dalton Trans.*, in press.
9 F. Bonati, S. Cenini and R. Ugo, *J. Organometal. Chem.*, *10*, 257 (1967).
10 K. Kawakami and R. Okawara, *J. Organometal. Chem.*, *6*, 249 (1966).
11 G. M. Bancroft, V. G. Kumar Das and K. D. Butler, *J. Chem. Soc. Dalton Trans.*, 2355 (1974).
12 G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clark, *J. Chem. Soc. Dalton Trans.*, 643 (1976).
13 M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc. Dalton Trans.*, 281 (1972).
14 B. A. Goodman, N. N. Greenwood, K. L. Jaura and K. K. Sharma, *J. Chem. Soc.*, *A*, 1865 (1971).
15 T. Moeller and F. L. Pundsack, *J. Am. Chem. Soc.*, *76*, 617 (1954).
16 L. W. Reeves and K. O. Strømme, *Canad. J. Chem.*, *39*, 2318 (1961).
17 H. A. Meinema, E. Rivarola and J. G. Noltes, *J. Organometal. Chem.*, *17*, 71 (1969).
18 C. E. Holloway and M. H. Gitlitz, *Canad. J. Chem.*, *45*, 2659 (1967).
19 M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, *30*, 3231 (1968).