Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STRUCTURAL ORGANOTIN CHEMISTRY
I. SOME DIORGANOTIN(IV) SCHIFF BASE COMPLEXES

PETER J. SMITH
Chemistry Department, City of London Polytechnic, 31 Jewry Street, London EC3N 2EY (Great Britain)
D. DODD
Christopher Ingold Laboratories, University College, 20 Gordon Street, London WC1H OAJ (Great Britain)

(Received April 19th, 1971)

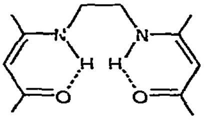
SUMMARY

Diorganotin(IV) dichlorides R_2SnCl_2 (R=Me, Et, Bu and Ph) form 1/1 complexes with the potentially quadridentate Schiff base ligand, bis(acetylacetone)ethylenediimine (H_2Acacen). The ^{119}Sn Mössbauer spectra of these complexes show that the tin atom is occupying a *trans*-R_2SnX_4 octahedral configuration; conductivity measurements in nitrobenzene show that the species in solution are non-ionic and NMR spectra suggest that the adducts are largely dissociated, even in non-coordinating solvents.

INTRODUCTION

There has been considerable interest recently in the structure of diorganotin(IV) dihalide complexes with potentially quadridentate Schiff base ligands[1-5].

Complexes of the neutral ligands were prepared by Barbieri and co-workers[1] who found that both dimethyl- and diphenyltin dichloride readily formed 1/1 adducts with bis(acetylacetone)ethylenediimine [H_2Acacen(I), shown in the keto-amine form].



(I)

Molecular weight measurements in methanol suggested the complexes were ionic of the type $[R_2Sn(H_2Acacen)]^{2+}\ 2Cl^-$, with the ligand functioning as a quadridentate chelate. Nelson and Martin[2] prepared a complex of a similar ligand, H_2Bzacen (with phenyl instead of methyl groups α to the carbonyl groups) containing two Ph_2SnCl_2 moieties per ligand molecule.

Complexes of the dianionic ligands have recently been prepared by Murray and co-workers[3], and by Dey[4]. Bis(salicylaldehyde)ethylenediimino complexes (neutral ligand = H_2Salen) of both dimethyl- and diphenyltin(IV) were characterised, and Murray *et al.*[3] concluded that these possessed the *cis*-octahedral structure, R_2Sn(Salen), on the basis of NMR studies. An Acacen analogue of diphenyltin(IV) was earlier reported[5] where the ligand carried a methyl substituent in the ethylene bridge. There can be little doubt that the ligands are quadridentate chelates in these latter examples.

^{119m}Sn Mössbauer spectroscopy is now well established as a valuable technique for the elucidation of structure in organotin(IV) chemistry. We had already prepared some diorganotin(IV) dichloride complexes of the neutral ligands, including two described by Barbieri *et al.*[1], and tin-119 Mössbauer spectra were recorded in order to investigate the configuration about the tin atom. Conductivity measurements, infrared and NMR spectra were used to further clarify the nature of the species involved.

RESULTS AND DISCUSSION

The analytical data and melting points of the four complexes studied are shown in Table 1. During the course of this work, Barbieri *et al.*[1] reported the preparation of the methyl and phenyl adducts; the melting point of their methyl compound, however, was markedly different from ours, and we repeated the preparation using each of their three solvents (*viz.* acetone, benzene and dioxane) in the hope of obtaining a different isomer of the complex: no successful isolation of a *cis*, *trans*-octahedral pair of isomers, R_2SnX_4, has yet been achieved. However, the melting points of the products were all found to be the same as that of our original compound, which was prepared from ethanol.

TABLE 1

YIELDS, MELTING POINTS AND ANALYTICAL DATA FOR $R_2SnCl_2 \cdot H_2$Acacen COMPLEXES

R	Yield (%)	M.p. (°C)	Analyses, found (calcd.) (%)			
			C	H	N	Cl
Me	60[a]	190–192[b]	37.64 (37.83)	6.00 (5.85)	6.10 (6.31)	15.49 (15.99)
Et	82	164–166	39.84 (40.68)	6.79 (6.36)	5.39 (5.93)	15.34 (15.04)
Bu	36	114	44.84 (45.46)	7.26 (7.20)	5.23 (5.30)	12.49 (13.45)
Ph	92	182–184[c]	49.67 (50.70)	5.34 (5.28)	4.67 (4.93)	12.01 (12.50)

[a] From acetone, 71%; benzene, 88%; dioxane, 30%. [b] Lit.[1], 158–60. [c] Lit.[1], 182–3.

Mössbauer parameters for the complexes are shown in Table 2. The quadrupole splitting values are in the range $\Delta E_Q = 3.66$–4.37 mm/sec. Comparison with similar data on many organotin(IV) compounds whose structures have been determined by X-ray crystallography shows that this range is indicative of a *trans*-octahedral R_2SnX_4 geometry[6–8]. There are indeed a very large number of compounds with ΔE_Q values within the above range[9].

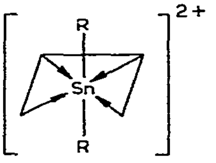
TABLE 2

MÖSSBAUER PARAMETERS AND CONDUCTIVITY DATA FOR $R_2SnCl_2 \cdot H_2Acacen$ COMPLEXES

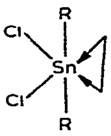
R	δ^a (mm/sec)	ΔE_Q (mm/sec)	$\Lambda_m{}^b$ ($ohm^{-1} \cdot cm^2 \cdot mole^{-1}$)
Me	1.57	4.30	1.31^c
Et	1.67	4.37	0.95
Bu	1.66	4.32	0.64
Ph	1.34	3.66	2.09
$Et_4N^+I^-$			16.1

[a] Relative to SnO_2 at 77°K. [b] 10^{-3} *M* solutions in nitrobenzene at 25°. [c] In methanol, $\Lambda_m = 7.1$ $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$

Two possible configurations may now be written for these complexes: structure (II), containing an ionic $[R_2Sn(H_2Acacen)]^{2+}$ species, or the covalent structure (III), in which the ligand is acting as a bidentate group.



(II)



(III)

A decision between these two structures may be made on the basis of conductivity measurements. Nitrobenzene was the solvent of choice since it had previously been successfully used in assigning structures to complexes of organotin(IV) halides with pyridine chelates[10]. With solvents such as DMF (used by Murray *et al.*[3]) and DMSO, which are themselves good ligands at tin(IV), there is a danger of ionisation by displacement. For a 10^{-3} *M* solution in nitrobenzene, structure (II) should have a molar conductance, Λ_m, within the range 35–55 $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$; a 1/1 electrolyte should have a value of 15–25 $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$. It is apparent from the results, shown in Table 2, that all the complexes are non-electrolytes in nitrobenzene solution. The conductivity of the methyl adduct was also determined in methanol (the solvent used by Barbieri *et al.* in molecular weight measurements[1]) and again the value of Λ_m was less than 10% of that expected for the simplest electrolyte. Thus the ionic structure (II) is ruled out, and structure (III) is proposed for the complexes in the solid state.

The infrared spectra of the solid complexes suggest that the ligand is in the keto-amine form. The ligand absorptions are similar to those reported[11] for the ionic complexes $LnCl_3 \cdot H_2Acacen$, where the Schiff base is probably quadridentate and deduced to be in the keto-amine form. The only major difference is that the tin adducts show the probable ν(N–H) at lower frequency (3150 cm^{-1} rather than[11] 3230, 3400 cm^{-1}), similar to that found for the free ligand (3120 cm^{-1}) which appears to be a "frozen out" equilibrium mixture of keto-amine and enol-imine tautomers in the solid state[12]. Though the latter tautomer is lost in forming the complexes, the strong hydrogen bonding seems to be carried over, and the complexed ligand may be represented by structure (I). Whether the bidentate chelation occurs through the nitrogen or oxygen donors (or both) is unresolved, although donation through the amine nitrogens would be expected to be more effective. Presumably, in the binuclear complex, $(Ph_2SnCl_2)_2 \cdot H_2Bzacen$[2], all four donor atoms are bonded to tin, although an ionic formulation, $[Ph_2Sn(H_2Bzacen)]^{2+}[Ph_2SnCl_4]^{2-}$, is still possible.

The NMR spectra of the adducts in dichloromethane and deuteriochloroform cast light on the species present in solution. Within experimental error, the ligand absorptions are in each case the same as those of the free ligand, which, in most common solvents, is very largely the keto-amine[13]. Similarly, for the methyl adduct, the single tin-methyl resonance is found at the same frequency as that in dimethyltin dichloride (even in the presence of a large excess of added ligand), although the tin–methyl proton coupling constant in a saturated dichloromethane solution of the complex at 35°, $J(^{119}Sn-^{1}H)=78$ Hz, is higher than that found[14] for dimethyltin dichloride itself, $J(^{119}Sn-^{1}H)=$ca. 69 Hz. These results, together with the absence of any tin–ligand proton coupling, suggest that there is some degree of dissociation, with the ligand rapidly exchanging.

Two methods were used in an attempt to determine the extent of this dissociation. On addition of further ligand to a saturated solution of the adduct, the coupling constant rose to 88 Hz before the decreased solubility precluded further measurement. This increase is in itself sufficient to show that, without added ligand, the complex is largely dissociated in solution.

Since the tin-119 chemical shift is often diagnostic of coordination number in solution[15,16], attempts were made to obtain this by heteronuclear double magnetic resonance. However, in non-coordinating solvents, the methyl and ethyl adducts were insufficiently soluble for the determination to be carried out, and, while the butyl compound was quite soluble in dichloromethane, the tin-119 satellites were either not detectable or were obscured by the ligand absorptions.

The available evidence suggests that, in deuteriochloroform and dichloromethane at least, the complexes are largely dissociated, and it is therefore likely that our conductivity measurements in nitrobenzene and methanol also refer to the dissociated species. Similar ready dissociation in solution has previously been observed for the neutral acetylacetone complex, $SnCl_4 \cdot HAcac$[17], and accounts, in part, for the high values of the van 't Hoff '*i*' factor (2.6–2.9) observed by Barbieri *et al.* in methanol[1]. Hydrolysis of the ligand, which occurs fairly readily in aqueous systems[18], might account for the remainder of the discrepancy.

To date, therefore, the only examples of quadridentate chelation at organotin(IV) appear to be the complexes with dianionic Schiff base ligands. Complexes with the neutral ligands thus far examined are only bidentate in the solid and are largely dissociated in solution. Although cationic organotin(IV) species are known, *e.g.*[10,19], $[Me_2SnCl \cdot Terpy]^+$, they are not formed in the present system.

EXPERIMENTAL

Mössbauer spectra were obtained using a constant velocity cam-driven instrument, with both absorber and $^{119m}SnO_2$ source cooled to liquid nitrogen temperature. Samples were sealed in polythene cells, and two scans were performed for each compound. The values of δ and ΔE_Q are considered accurate to within ±0.08 mm/sec.

Conductivity measurements were carried out using a Mullard immersion conductivity cell with bright platinum electrodes (cell constant 1.45) and a Philips conductivity-measuring bridge PR 9500. The nitrobenzene solvent (BDH Analar) was dried with molecular sieve type 4A, previously activated at ca. 180°, and had a specific conductivity, K, of less than 7×10^{-8} $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. The values of Λ_m are considered accurate to within 2%.

Infrared spectra were recorded on a Perkin–Elmer SP 457 instrument, using nujol mulls dispersed as capillary films between potassium bromide plates.

Nuclear magnetic resonance spectra were obtained using Perkin–Elmer R12, Varian HA 100 and Jeol C-60-H instruments.

Bis(acetylacetone)ethylenediimine was prepared by the method of Martell, Belford and Calvin[20].

Dichloro[bis(acetylacetone)ethylenediimine]diorganotin(IV) complexes were precipitated on mixing equimolar quantities of the appropriate diorganotin dichloride and the ligand dissolved in ethanol. Recrystallisation from ethanol gave white crystalline solids; the yields, melting points and analytical data are recorded in Table 1. The adduct of dimethyltin dichloride was similarly prepared using acetone, benzene and dioxane as solvents, and in each case the complex had a melting point which was identical with that of the compound prepared from ethanol.

ACKNOWLEDGEMENTS

We are grateful to Professor Alwyn G. Davies and Dr. M. D. Johnson for helpful discussion and to Mr. John Eley and Mr. Les Smith for assistance with the NMR spectra; we would also like to thank Messrs. Albright and Wilson (Mfg.) Ltd. for the loan of the Mössbauer Spectrometer, and the Science Research Council and the Inner London Education Authority for financial assistance.

REFERENCES

1 G. Faraglia, F. Maggio, R. Cefalù, R. Bosco and R. Barbieri, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 177.
2 W. H. Nelson and D. F. Martin, *J. Organometal. Chem.*, 4 (1965) 67.
3 A. van den Bergen, R. J. Cozens and K. S. Murray, *J. Chem. Soc. A*, (1970) 3060.
4 K. Dey, *J. Inorg. Nucl. Chem.*, 32 (1970) 3125.
5 W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, 27 (1965) 89.
6 B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *J. Chem. Soc. A*, (1969) 143.
7 A. G. Davies, L. Smith and P. J. Smith, *J. Organometal. Chem.*, 23 (1970) 135.
8 B. W. Fitzsimmons, *J. Chem. Soc. A*, (1970) 3235.
9 P. J. Smith, *Organometal. Chem. Rev. Sect. A*, 5 (1970) 373.
10 J. E. Fergusson, W. R. Roper and C. J. Wilkins, *J. Chem. Soc.*, (1965) 3716.
11 N. K. Dutt and K. Nag, *J. Inorg. Nucl. Chem.*, 30 (1968) 3273.
12 K. Ueno and A. E. Martell, *J. Phys. Chem.*, 59 (1955) 998.
13 G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 83 (1960) 2099.
14 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 1566.
15 A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt and W. McFarlane, *J. Chem. Soc. C*, (1969) 1136.
16 A. G. Davies, L. Smith, P. J. Smith and W. McFarlane, *J. Organometal. Chem.*, 29 (1971) 245.
17 A. L. Allred and D. W. Thompson, *Inorg. Chem.*, 7 (1968) 1196.
18 D. F. Martin and F. F. Cantwell, *J. Inorg. Nucl. Chem.*, 26 (1964) 2219; 30 (1968) 1931.
19 F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, (1968) 3019.
20 A. E. Martell, R. L. Belford and M. Calvin, *J. Inorg. Nucl. Chem.*, 5 (1958) 170.