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TETRAMETHYLDITIN COMPLEXES: A GENERAL METHOD FOR THE PREPARATION OF A CLASS OF COMPOUNDS WITH AN UNUSUAL TIN—TIN BOND

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Summary

The preparation and physical and spectroscopic properties of eight compounds of the type $Me_4Sn_2X_2$ ($X = O_2CR$, S_2CNR_2, $S_2P(OR)_2$) are described, starting from $Me_4Sn_2Cl_2$. The spectroscopic data indicate that X functions as an isobidentate ligand. The tin—tin coupling constants are extremely large (ca. 11—15 kHz), and can be correlated with the pK_a values of the corresponding acids HX.

Introduction

The 1,1,2,2-tetramethylditin group is particularly suitable for obtaining spectroscopic data pertaining to the tin—tin bond. A method for the preparation of tetramethylditindicarboxylates involving the elimination of methane from hexamethylditin on treatment with α-fluoro and α-chloroacetic acids has recently been described [1]. This has prompted us to publish details of a simpler and more general route to compounds of this type, which can readily be extended to weaker acids and which does not lead to side reactions of the type observed when the hydride method [2] is used.

Results and discussion

Since 1,1,2,2-tetramethyl-1,2-dichloroditin [3] is extremely soluble in water (by which it is hydrolysed), the preparation of the compounds $Me_4Sn_2X_2$, where X is a monobasic, bidentate acid residue, can be carried out according to eq. 1 in

TABLE 1

PREPARATIVE DETAILS AND ELEMENTAL ANALYSES FOR COMPOUNDS $Me_4Sn_2X_2$

Compound	X	Crude yield (%)	Recryst. from: [a]	M.p. (K)	C found (calcd.) (%)	H found (calcd.) (%)	Sn [b] found (calcd.) (%)
I	HCO_2	95	CH_2Cl_2	406(dec.)	18.5(18.6)	3.64(3.64)	60.6(61.3)
II	CH_3CO_2	75	PE(40/60)	400(dec.)	23.4(23.1)	4.46(4.36)	57.0(57.1)
III [c]	$ClCH_2CO_2$	81	$CHCl_3$	440(dec.)	19.6(19.8)	3.29(3.33)	48.8(49.0)
IV [c]	Cl_2CHCO_2	99	PE(40/60)	392(dec.)	17.6(17.4)	2.60(2.55)	40.0(42.9)
V [c]	Cl_3CCO_2	88	PE(80/100)	420(dec.)	15.4(15.4)	1.85(1.99)	39.1(38.1)
VI [c]	F_3CCO_2	92	PE (40/60)	420(dec.)	18.4(18.4)	2.28(2.31)	45.4(45.3)
VII	Me_2NCS_2	99	$CHCl_3$	440(dec.)	22.5(22.3)	4.53(4.50)	[d] (44.1)
VIII	$(MeO)_2PS_2$	99	$CHCl_3$	386	15.9(15.7)	4.09(3.95)	[d] (38.8)

[a] PE denotes petroleum ether (boiling range); [b] by X-ray fluorescence (see text); [c] preparation previously described (Ref. 1); [d] not determined.

an aqueous medium; a necessary precondition is that the compounds are only slightly dissociated in water.

$$Me_4Sn_2^{2+} + 2\,X^- \rightarrow Me_4Sn_2X_2 \qquad (1)$$

The products are obtained in very good to nearly quantitative yields as microcrystalline (crystalline when the precipitation is slow) colourless solids: though insoluble in water, they are readily soluble in organic solvents, the solution being insensitive to air. Table 1 gives details of their preparations and elemental analyses.

Birchall and Johnson [1] showed on the basis of spectroscopic data (IR and Raman) that the tin atoms have a coordination number of 5; they suggested that the ligands RCO_2 function as more or less anisobidentate intramolecular bridging groups. Our results confirm the observed symmetry of the tetramethylditin group, as can be seen from Table 2. Consideration of the intensities of the five stretching frequencies due to the Me_4Sn_2 unit show it to have the point group C_{2h}, the inversion element of which leads to the consequence that bands cannot be simultaneously IR- and Raman-active. The Sn—Sn stretching band ν(Sn—Sn), A_g mode, while very weak in the IR spectrum, is of medium intensity in the Raman spectrum. The same is true for the methyl—tin vibrations of the g-modes, and the reverse for the u-modes.

It is not possible to decide solely on the basis of the frequency difference $\nu_{as} - \nu_s(CO_2)$ whether the group RCO_2 functions in solution as an iso- or anisobidentate ligand, since apart from the O—C—O angle the bond strength is also involved; in the isobidentate case the latter leads to varying differences. More important are the observations that (a) the frequencies in the solid state and in solution do not differ significantly, (b) that these frequencies are lower than those of the sodium or ammonium salts of the corresponding acids (in which the residues are certainly isobidentate), and (c) that the band due to $\nu_{as}(CX_2)$ is ca. 200 cm^{-1} lower than ν(C=X) in comparable esters [4]. In compound VIII, $Me_4Sn_2(S_2P(OMe)_2)_2$, the coupling between tin and phosphorus leads to a ^{119}Sn spectrum in which the main and satellite signals occur as regular triplets with $^2J(^{119}Sn—S—^{31}P)$ 30 Hz; this also suggests that the P—S—Sn bonds are equivalent. The NMR data are presented in Table 3: the direct tin—tin and tin—carbon coupling constants are of particular interest. According to Pople and Santry, the direct coupling constant between two elements is given by the following equation:

$$^1J(X—Y) = \frac{16\beta^2}{9\gamma_X\gamma_Y h} \cdot \psi^2_{ns(x)}(0) \cdot \psi^2_{ns(y)}(0) \cdot \alpha^2(x) \cdot \alpha^2(y) \cdot (\Delta E)^{-1}$$

α^2 and $\psi^2(0)$ are respectively the s-character of the X—Y hybrid orbital and the valence-electron density at the nucleus; ΔE is the mean electronic excitation energy [5]. Thus ^1J(Sn—C) is proportional to $\alpha^2(5s)\alpha^2(2s)$. If we make the further assumption that the s-character of carbon varies little in a series of related compounds (see for example [6]), the coupling should be proportional to $\alpha^2(5s)$. According to Drago [7], pentacoordinate tin compounds which have a trigonal bipyramidal arrangement of the bonds around tin undergo rehybridisation so that the equatorial bonds are of sp^2 type. Thus the quotient of ^1J(Sn—C)

TABLE 2

SOME VIBRATIONAL FREQUENCIES FROM THE IR AND RAMAN (Ra) SPECTRA OF COMPOUNDS I—VIII

		I		II		III		IV
		IR	Ra	IR	Ra	IR	Ra	IR
CX_2	ν_{as}	1548vs		1565vs		1580vs		1600vs
	ν_s	1360s		1405s		1387s		1385s
Me_4Sn_2	A_u	550vs	—	551vs	—	553cs	—	554vs
	A_g	—	546m	—	543m	—	546m	—
	B_g	—	525m	—	532va	—	537vs	—
	B_u	527vs	—	527vs	—	535s	—	525vs
SnSn	A_g	212vw	212m	216w	216m	216m	216m	213vw
SnX	ν_{as}	477w	—	—	—	490s	485w	499s
Me_4Sn_2	ν_s	304s	300w	284m	—	303vs	306w	341vs
	δ_{as}	156vs	156w	150vs	—	148vs	—	148vs
	δ_s	145s	146m	—	145m	—	143m	142(sh)

[a] PS_2 fragment.

for four- and five-coordinate species should be ca. 0.33/0.25, i.e. ca. 1.32. The same argument suggests that the corresponding quotient for ^1J(Sn—Sn) should be $(0.33/0.25)^2$, i.e. ca. 1.74. Typical four-coordinate compounds $Me_4Sn_2X_2$, X = Me [8], H, Cl, Br, I [9] have ^1J(Sn—C) 240—280 Hz, while the compounds described here give values of 340—370 Hz. The quotient of these values is of the expected magnitude. A different situation applies for the tin—tin coupling: while the value for Me_6Sn_2 is 4404 Hz [10], the pentacoordinate compounds have values between 11 and 15 kHz, so that the quotient is 2.5 to 3.4. This indicates that (perhaps because of considerable variations in ΔE) the equation given above must be used in the modified form [5] in which the $\alpha^2 . \Delta E$ term is replaced by π_{XY}, the mutual polarisability of X and Y, which in its turn depends on $\beta(XY)$, the s-overlap integral between X and Y.

The tin—tin bond distance in the related $Ph_4Sn_2(OAc)_2$ of 269 pm [11] (compared with 277 pm in Ph_6Sn_2), and the relatively high Sn—Sn frequencies (Table 2) tend to confirm the importance of π_{XY} for ^1J(Sn—Sn).

The variations in the spectral parameters in compounds I to VIII will be affected by the electron-withdrawing power of the ligand X, which can be qualitatively described by the pK_a value of the acid HX. If we consider the carboxylates I to VI, the methyl resonances (^{1}H, ^{13}C) are shifted to lower field with decreasing pK_a, while the $^{13}CO_2$ resonance moves steadily to high field. At the same time the coupling constants ^1J(Sn—C) and ^1J(Sn—Sn) decrease; the latter shows a good linear correlation ($|r| = 0.948$) with the pK_a value of the corresponding acid HX. These variations van be explained in terms of delocalisation of the electron pair of the carboxylate group into the tin—tin bond. Fig. 1 shows the situation for large and small pK_a values.

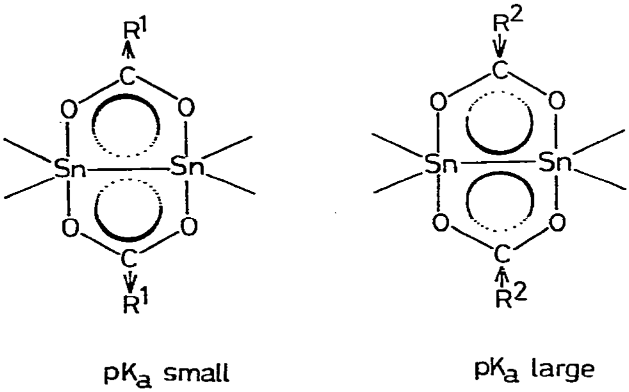
The electronic spectra of compounds I to VI show a regular hypochromic shift of the absorption band from 233 to 218 nm ($\epsilon_\lambda = 4000$); this can again be explained in terms of electron delocalisation.

	V		VI		VII		VIII	
Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra
	1615vs		1655/ 1630vs		970/ 955vs		669/ 662vs	[a]
	1390s		1445s		572— 568s		534m	534m [a]
—	556vs	—	554vs	—	532vs	534vw	544vs	543w
545m	—	546m	—	545m	—	526m	523(sh)	521(sh)
532vs	—	530vs	—	527vs	520vw	520vs	—	517vs
—	526vs	—	525s	—	511vs	513w	514vs	512(sh)
211m	212w	211m	—	206m	—	202m	191vw	194m
450w	449s	451w	446vs	—	369/ 360m	369/ 360w	383m	380w
344v	340vs	344w	319w	—	263w	—	267s	266w
148m	150vs	150s	168vs	168(sh)	164w	164w	164w	—
142(sh)	—	143(sh)	—	140m	—	160s	—	141s

Experimental

(a) Preparation of compounds I to VIII

To a stirred solution of tetramethyldichloroditin in degassed water (typical concentration 2 g/50 cm^3) is slowly added a solution of the sodium or ammonium salt of the corresponding acid HX (50—100% excess). The only slightly water-soluble products (compound VI is somewhat more soluble) are precipitated in microcrystalline form and isolated by filtration. They are washed several times with water and once with a little methanol and dried in vacuo at room temperature to constant weight. Compound IV is light-senstitive. Solution of these ditins are, in contrast to other tetramethylditin compounds, inert to oxidation by oxygen from the air over periods of several days, so that they can be recrystallised from the appropriate solvents (Table 1) without difficulty.



pK$_a$ small

pK$_a$ large

Fig. 1. Schematic representation of the differing delocalisation of the electron pair of the carboxylate group in $Me_4Sn_2(O_2CR)_2$.

TABLE 3

NMR PARAMETERS (^1H, ^{13}C, ^{119}Sn) FOR COMPOUNDS $Me_4Sn_2X_2$ IN $CDCl_3$ (δ in ppm with respect to TMS (^1H, ^{13}C) and Me_4Sn (^{119}Sn) as internal standard, J in Hz)

Compound	I	II	III	IV	V	VI	VII	VIII
X	HCO_2	CH_3CO_2	$ClCH_2CO_2$	Cl_2CHCO_2	Cl_3CCO_2	F_3CCO_2	Me_2NCS_2	$(MeO)_2PS_2$
$pK_a(HX)$	3.75 [a]	4.75 [a]	2.85 [a]	1.29 [b]	0.7 [a]	0.23 [c]	2.95 [b, d]	1.55 [b]
$\delta(CH_3)$	0.71	0.66	0.74	0.83	0.89	0.88	0.78	0.97
δ(H) in X	7.58	1.97	3.94	5.83	--	–	3.53	3.73
$\delta(CH_3)$	−2.21	−2.48	−1.83	−1.51	−1.50	−1.31	−0.99	2.26
$\delta(CO_2/CS_2)$	173	182	178	175	171	168	203	—
$\delta(Sn)$ [e]	−135(−122)	−128(−117)	−95(−86)	−57	−15	−44	−72	−22
^2J(Sn—C—H)	61.0	61.0	61.1	60.8	61.0	61.2	55.0	57.0
^3J(Sn—Sn—C—H)	13.1	13.2	13.2	13.2	13.2	13.2	12.5	11.8
^1J(Sn—C)	369	368	353	350	344	347	340	344
^2J(Sn—Sn—C)	80.9	85.3	85.3	80.9	79.4	78.0	57.4	63.4
^1J(Sn—Sn) [e]	(13056)	14980(14549)	[f]	12622	12323	11424	14479	12119

For coupling constants, Sn denotes ^{119}Sn. [a] Ref. 12; [b] Ref. 13; [c] from K_a = 0.588 (25°C), Ref. 14; [d] value for H_2NCS_2H; [e] sat. solns. in C_6D_6 (values in parentheses $CDCl_3$); [f] not observed.

(b) Elemental analysis

Analysis for tin was carried out by means of X-ray fluorescence in chloroform solution with Me_2SnCl_2 as standard.

Excitation: gold tube 35 kV, 10 mA, Ksistalloflex IV (Siemens).

Impulse rate measurement: via LiF goniometer with energy discrimination at SnK_α. An absorption effect of 12% in the specific impulse rate is observed in the concentration range 0.05 to 0.2 mol/l.

(c) Spectral measurements

Raman spectra were obtained using a Coderg T800 spectrometer in conjunction with an argon laser operating at 488 nm (200 mW), with crystalline samples in melting-point tubes.

FIR measurements were made on a Bruker IFS 113 spectrometer (sample as disc in polythene, 10—60 mg), IR measurements on a Leitz IIIG spectrometer.

The following instruments were used for NMR measurements: ^1H, Varian A60 and Bruker WH90; ^{13}C, WH90; ^{119}Sn, Bruker HFX90. Details are given in Table 3. It should be noted that the ^{119}Sn spectra of the isotopomers $Me_2{}^{119}Sn(X)$-$^{117}SnMe_2(X)$ are distinctly second-order, the centre of gravity of the doublet visible being displaced 25—30 Hz from the signal due to isotopomers containing only one magnetic nucleus or two ^{119}Sn nuclei. All NMR spectra were recorded at ca. 308 K; no concentration- or temperature-dependence studies have been carried out.

UV-spectra were recorded using a Leitz-Unicam SP800 spectrometer; sample concn. ca. 2×10^{-3} molar in C_6H_{12}, quartz cuvette, $d = 1$ mm.

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