DALTON

Symmetry of the co-ordination sphere of di-*n*-butyltin(IV) in complexes with sulfanylcarboxylic acids

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Four di-*n*-butyltin(IV) complexes have been prepared with sulfanylacetic, 2-sulfanylpropionic, sulfanylsuccinic and 2,3-disulfanylsuccinic acid, using two different procedures. The compounds were characterised by elemental analysis, Fourier-transform, Raman, ^{119}Sn Mössbauer, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The IR and Raman data indicate the presence of bidentate carboxylate groups, non-linear C–Sn–C bonds, and Sn–S bonds. The results of Mössbauer spectroscopic measurements, based on point-charge model calculations, have shown the general occurrence of trigonal-bipyramidal environments at tin(IV). The multinuclear NMR studies also suggested the {O,S} co-ordination of the di-*n*-butyltin(IV) fragment, within the cyclic oligomeric complexes.

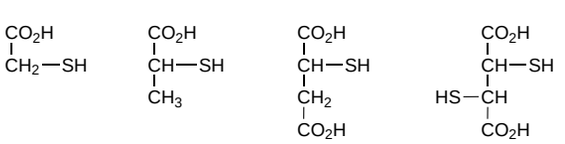
The investigation of the interactions between organotin(IV) mono- and di-cations and biologically active ligands (among them carboxylates and polyhydroxy compounds[1,2]) is of considerable importance due to the possible modification of the biological properties of the organotin(IV) group in the presence of these ligands. Therefore, efforts have been made to elaborate simple procedures for the preparation of complexes,[3,4] as well as to understand the antitumour activity of the organotin(IV) cations.[5] The importance of the organotin(IV) complexes is confirmed by their wide range of possible applications, particularly of those containing sulfur.

Until now only few papers have been published on the structure of organotin(IV)–carboxylate compounds containing {O,S} donor sites.[6–9] Continuing our work on the synthesis, equilibrium and structural characterisation of organotin(IV) complexes with carbohydrates,[4,10–12] as well as carbohydrate derivatives of thiazolidine-4-carboxylic acids[13] and *N*-D-gluconylamino acids[14] containing {O,O} and {O,N} donors, respectively, we have synthesized four di-*n*-butyltin(IV) complexes with four different ligands containing {O,S} donor atoms. The symmetry of the co-ordination sphere of organotin(IV) was determined on the basis of Mössbauer spectroscopy and FTIR, Raman and ^{1}H, ^{13}C and ^{119}Sn NMR measurements were performed to determine the possible binding sites.

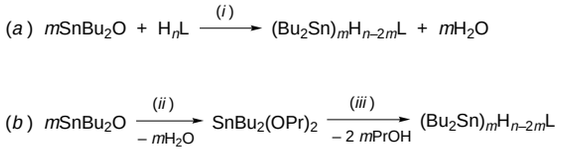
Experimental

Materials

Compounds L^1 and L^2 were from Aldrich, L^3 from Sigma and L^4 from Fluka. Di-*n*-butyltin(IV) oxide was from Fluka. Other reagents and solvents were from Reanal (Hungary).



L^1 L^2 L^3 L^4



Scheme 1 $m = 1$ for L^1–L^3, 2 for L^4. (*i*) MeOH, 2 h reflux; (*ii*) Pr^{n}OH–MeOH (1:4), 5 h reflux; (*iii*) H_nL, 1 h stirring

Preparation of the complexes

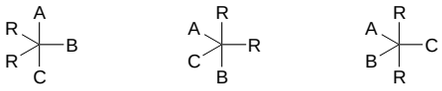
Method a. The complexes were obtained by refluxing equimolar quantities of L^1–L^4 and di-*n*-butyltin(IV) oxide in methanol for 2 h [Scheme 1(*a*)]. Compound **1a** precipitated from the mixture, while the others (**2a**, **3a**, **4a**) were obtained after removal of the solvent by rotary evaporation, then washed and/or recrystallised from methanol or chloroform.

Method b. Di-*n*-butyltin(IV) oxide (1 g) was refluxed in methanol–*n*-propanol (4:1, 250 cm^3) for 5 h. The oxide reacted with *n*-propanol, giving di-*n*-butyltin(IV) propoxide and water [Scheme 1(*b*)]. From the solvent mixture the water distils off as an azeotrope. After its removal and cooling, an equimolar quantity of L^1–L^4, dissolved in methanol, was added to the solution of di-*n*-butyltin propoxide with vigorous stirring. Compound **1b** precipitated during the stirring, **2b** crystallised out,while **3b** and **4b** were obtained after evaporation of the solvent at room temperature and then washed or recrystallised from methanol or chloroform.

Elemental analyses (C, H, S) were carried out by Ilse Beetz Microanalytical Laboratory, Kronach, Germany. The analytical data are presented in Table 1 together with other characteristic physical constants.

Measurements

The ^{119}Sn Mössbauer spectra were recorded at 77 K on a conventional RANGER spectrometer in constant-acceleration mode with a source activity of 0.4 GBq. Computer evaluation was used to determine isomer shift (i.s.) and quadrupole splitting (q.s.) values. The spectra were analysed as Lorentzian lines by least-squares fitting. The reproducibility of the Mössbauer



I **II** **III**

Scheme 2

parameters was found to be ±0.02 (i.s.) and 0.04 mm s^{-1} (q.s.), respectively, in each measurement. The i.s. values are referred to that of $CaSnO_3$.

The Fourier-transform IR spectra of L^1–L^4 and the complexes as KBr pellets were measured on Bio-Rad Digilab Division FTS-40 and FTS-65A instruments. Liquid samples were examined as thin films on KBr plates in the range 4000–200 cm^{-1}. Fourier-transform Raman spectra were recorded using a Bio-Rad Digilab Division spectrometer from liquid and solid samples contained in glass cuvettes. Relevant vibration bands are reported in Table 2. The ^{119}Sn (134.29), ^{13}C (90.56) and ^{1}H (360.13 MHz) NMR spectra of complexes containing {O,S} donor atoms were recorded on a Bruker AMX 360 spectrometer equipped with a 5 mm multinuclear tuneable probe and an X32 computer using UXNMR software. The compounds were measured in $CDCl_3$ or $(CD_3)_2SO$ in a standard manner. The ^{13}C chemical shifts were referred to appropriate signals of the solvents and recalculated to the δ scale {δ(^{13}C) 77.00 ($CDCl_3$), 39.60 [$(CD_3)_2SO$]}. The ^{119}Sn chemical shifts were referred to external neat $SnMe_4$ (δ 0.0) placed in a coaxial capillary. The ^{119}Sn and ^{13}C chemical shifts are collected in Table 4.

Calculations

For the determination of the steric arrangement around tin(IV) in these compounds, q.s. values were calculated on the basis of a simple but general molecular orbital model, according to the partial quadrupole splitting (p.q.s.) concept,[15,16] for the possible symmetries of five-co-ordinated tin(IV) given in Fig. 3 involving binding by two butyl groups and negatively charged (deprotonated) sulfur and carboxylate oxygen atoms. It was also taken into account that the carboxylate group can co-ordinate either in a mono- or bi-dentate manner. Equations (1)–(3) were used in

$$\text{q.s.}_1 = (-7R^{\text{tbe}} + 4A^{\text{tba}} + 4C^{\text{tba}} + B^{\text{tbe}})/7^{-\frac{1}{2}} \quad (1)$$

$$\text{q.s.}_2 = (-2R^{\text{tba}} - 5R^{\text{tbe}} + 4A^{\text{tbe}} + 4C^{\text{tbe}} - 2B^{\text{tba}})/13^{-\frac{1}{2}} \quad (2)$$

$$\text{q.s.}_3 = -4R^{\text{tba}} + A^{\text{tbe}} + B^{\text{tbe}} + C^{\text{tbe}} \quad (3)$$

the calculation, for the general structures **I**–**III** shown in Scheme 2. The p.q.s. values of the different functional groups used in our calculations, and the calculated q.s. values for tin(IV) in different stereochemical arrangements, are given in Table 6 and Fig. 3, respectively.

Results and Discussion

The analytical data and the characteristic physical constants for the complexes are reported in Table 1. Results refer to the formation of compounds with 1:1 metal-to-ligand ratio, with the exception of di-*n*-butyltin(IV)–2,3-disulfanylsuccinic acid (**4a**, **4b**) where a 2:1 metal-to-ligand ratio was found, reflecting the four accessible binding sites. All the complexes are soluble in Me_2SO. Compounds **1a**, **1b**, **2a** and **2b** are soluble also in $CHCl_3$, CCl_4 and C_6H_6. Complexes **2b**, **3a**, **3b**, **4a** and **4b** are soluble in methanol, too.

Fourier-transform IR and Raman spectroscopy

The vibration spectroscopic data (Table 2) suggest that the two kinds of preparation methods used resulted in complexes with the same structure. In the spectra of free L^1–L^4 a characteristic absorption band for S–H vibrations, between 2550 and 2575 cm^{-1}, and for the CO_2H group, between 1690 and 1715 cm^{-1}, are present. These bands cannot be found in the spectra of the complexes, indicating co-ordination of deprotonated thiol and carboxylate group(s) to the tin. Fig. 1 shows the IR and Raman spectra of 2,3-disulfanylsuccinic acid and its di-*n*-butyltin(IV) complex, as an example. It is clear that all of the four possible donor groups are deprotonated and co-ordinated in the complex, which is possible only in the case of a 2:1 metal-to-ligand ratio. In spite of this, in the case of **3a** and **3b**, one of the two carboxylate groups (probably that which is far from the thiol group) remains protonated (non-co-ordinated), as evidenced by the IR bands characteristic for the ν(C=O) stretching vibrations, slightly shifted to higher wavenumbers, compared to the free L. Thus only one extra donor group in the molecule cannot promote the formation of a higher metal-to-ligand ratio in the complex, as in the case of compounds **4a** and **4b**. The difference (Δν) between $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ compared with that for sodium salts of L^1–L^4 (Table 3), reflects the bridging bidentate co-ordination mode of the CO_2^- group. In the case of compounds **1a**, **1b**, **4a** and **4b** these bands are doublets due to the asymmetrical (different C–O bond lengths) co-ordination to the tin. The presence of an Sn–S absorption band in the 380–400 cm^{-1} region of the Raman spectra of the complexes pro-

Table 1 Physical and analytic data for di-*n*-butyltin(IV) complexes of ligands containing {O,S} donor atoms

		Analysis (%)[a]				
Ligand	Compound	C	H	S	Colour	M.p./°C
L^1	**1a**[b]	37.25	6.25	9.9	White	178–181
	1b[c]	37.25	6.25	9.9	White	179–182
		(37.2)	(6.25)	(9.95)		
L^2	**2a**[b]	38.4	6.4	9.55	Yellow	—
	2b[c]	39.25	6.55	9.5	White	99–102
		(39.20)	(6.6)	(9.5)		
L^3	**3a**[b]	37.8	5.75	8.45	White	111–113
	3b[c]	37.75	5.8	8.45	White	110–114
		(37.85)	(5.8)	(8.4)		
L^4	**4a**[b]	34.95	5.45	14.6	White	250–252
	4b[c]	34.85	5.5	14.65	White	247–250
		(34.9)	(5.35)	(15.5)		

[a] Calculated values in parentheses. [b] Prepared under reflux. [c] Propoxide method.

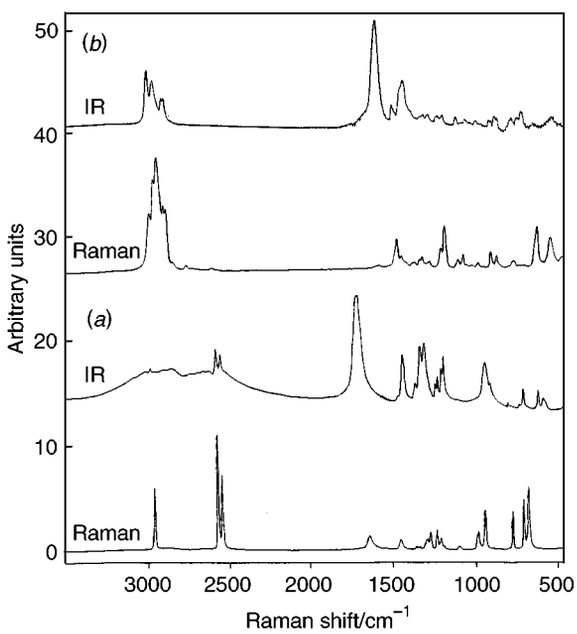


Fig. 1 Infrared and Raman spectra of 2,3-disulfanylsuccinic acid (*a*) and its di-*n*-butyltin(IV) complex (*b*)

Table 2 Infrared and Raman spectral data (cm^{-1}) for free L^1–L^4 and their di-*n*-butyltin(IV) complexes

	IR			Raman			
Compound	ν(C=O)	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	ν(SH)	ν(Sn–S)	ν_{asym}(Sn–C)	ν_{sym}(Sn–C)
L^1	1713.1vs			2576.2vs			
1a		1573.7s	1409.0m		382.4vs	598.4w	516.6w
		1547.9s	1393.5m				
1b		1574.2s	1409.3m		382.5vs	598.6w	548.0vs
		1548.1s	1394.5m				
L^2	1714.2vs			2574.6vs			
2a		1546.9s	1408.0m		397.8ms	597.3m	516.0m
2b		1542.8s	1409.7m		395.5ms	599.3m	515.2m
L^3	1697.0vs			2565.2vs			
				2549.2m			
3a	1745.0w	1552.2s	1416.7m		394.6s		
	1713.2m						
3b	1713.3s	1552.1s	1417.2m		394.5s	596.8m	516.3m
	1713.3 (sh)						
L^4	1693.6s			2564.5s			
				2539.1ms			
4a		1577.8 (sh)	1415.7m		386.7vs	597.4m	517.9m
		1552.6vs	1389.3m				
4b		1561.4 (sh)	1410.9mw		386.2s	597.3m	517.8m
		1553.2s	1389.3mw				

Table 3 The difference between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ for the carboxylates and their complexes

	$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)/cm^{-1}$		
Compound	Sodium salt	*a*	*b*
L^1	156.2, 181.3	138.9, 180.22	138.9, 180.8
L^2	190.7	148.1	148.3
L^3	198.7	144.3	144.1
L^4	203.3	163.4	169.9

[a] Complex prepared under reflux. [b] Complex prepared by the propoxide method.

vides support for co-ordination of sulfur to tin. The presence of two (asymmetric and symmetric) Sn–C absorption bands in the region 600–515 cm^{-1} reveals that the R–Sn–R bond angle is less than 180° in all compounds. Vibration bands (480–450 cm^{-1}) characteristic for Sn–O bonds also appeared. In the spectra of all complexes, bands characteristic for the *n*-butyl skeleton are present.[17]

NMR spectroscopic measurements

The ^{119}Sn and ^{13}C NMR spectroscopic data are shown in Table 4.

For compound **1b** one set of chemical shifts was observed in each of the ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum the SH signal and the coupling constant $^3J(CH_2–SH)$ (observed for the starting L) disappeared. These facts, a *ca*. 6 ppm change of $\delta(^{13}C)$ for the CH_2 group with respect to the starting acid and $^3J(^{119}Sn–^1H)$ 33.1 Hz support the formation of a Sn–S bond.

The ^{13}C NMR chemical shift of the CO_2^- group and the changed value with respect to the starting acid in $CDCl_3$, *i.e.* a considerable downfield shift, indicates the bidentate character of this group.[18] Taking the existence of a Sn–S bond into account, the existence of this bidentate character is only possible *via* co-ordination of the C=O oxygen to another tin atom. The $\delta(^{119}Sn)$ value corresponds to a 4 + 1 type of co-ordination,[19] in a trigonal-bipyramidal arrangement. The value of the coupling constant $^1J(^{119}Sn–^{13}C)$ corresponds to a C–Sn–C angle[20] of *ca*. 130° (trigonal-bipyramidal co-ordination sphere of tin with two butyl groups in the equatorial plane). Since there is only one signal in the ^{119}Sn NMR spectrum, five-co-ordination can be realised only by formation of a cyclic oligomer or a very long linear oligomer (short linear oligomers would require the existence of at least two signals for end and middle structural units, the relative integral intensity being dependent on the length of the chain). Meunier-Piret *et al.*[21] published the crystal structure of di-*n*-butyl(thiosalicylato)-tin(IV), showing that this compound forms a centrosymmetric hexamer. This finding is in line with the above-mentioned existence of only one signal in the ^{119}Sn NMR spectrum.

The ^{119}Sn NMR chemical shift and coupling constant of complex **1b** in Me_2SO have practically the same values as those in $CDCl_3$, but the $\delta(^{13}C)$ of CO_2^- is different. This may be accounted for by the formation of a monomeric unit from a cyclic oligomer, one molecule of solvent being co-ordinated and retaining five-co-ordination of tin [Fig. 4(*d*)]. The asymmetric bidentate character of the CO_2 group is changed to monodentate. Lockhard[22] has observed such a type of monomerisation in an analogous 3-sulfanylpropionic acid derivative, based on molecular-weight determination.

The solubility of product **1a** is much lower than **1b** in $CDCl_3$. We cannot exclude the formation of a linear polymer under the reported experimental conditions.

Compound **2b** has the same character as **1b** as is clear from a comparison of the data in Table 3. Two sets of ^{13}C pairs having non-equivalent abundance have been observed in the ^{13}C NMR spectrum for $Sn–CH_2$ groups. The formation of a pair of signals is due to the presence of a chiral centre in the molecule (C–S carbon). Two sets of pairs can be explained by the existence of two different types of cyclic oligomers: (*i*) two conformational isomers due to stereochemical reasons; (*ii*) two isomers having different ring sizes.

Compounds **3a**, **3b**, **4a** and **4b** are practically insoluble in $CDCl_3$ and as a result they were measured in Me_2SO. The ligand to tin ratio is 1:1 in **3a**, **3b** and 1:2 in **4a**, **4b** according to ^{1}H NMR integrals. The interpretation of the ^{13}C and ^{119}Sn NMR data is the same as for **1b** in Me_2SO.

Mössbauer measurements

Mössbauer parameters determined by computer evaluation of the spectra measured at liquid-nitrogen temperature are presented in Table 5. All spectra exhibit i.s. and q.s. which clearly indicate the presence of tin(IV) species. The spectra, independently of the preparation mode (*a*) and (*b*), with ligands L^1–L^4, comprised only one, well developed doublet (the narrowness of the full width at half of the resonance peaks is average) (Fig. 2), which suggests the presence of completely equivalent tin environments in these compounds.

For structural elucidation based on Mössbauer parameters,

Table 4 Tin-119 and ^{13}C NMR data for the di-*n*-butyltin(IV) complexes in $CDCl_3$ and $(CD_3)_2SO$ [a]

		δ(^{13}C)[$^n J$(^{119}Sn–^{13}C)/Hz (n = 1–3)]					
Compound	δ(^{119}Sn)	C^1	C^2	C^3	C^4	CO_2^-	Others
L^1 [b]	—	—	—	—	—	176.36	26.06 CH_2
1b [b]	−45.0	22.65 (547.9)	27.58 (23.4)	26.57 (97.8)	13.67	182.02	31.44
1b [c]	−49.8	21.97 (558.9)	27.25 (33.9)	25.94 (86.9)	13.68	174.61	39.60
L^2 [b]	—	—	—	—	—	179.95	35.22 CH 20.33 CH_3
2b [b]	−63.3	23.02 22.25 22.90 22.13	27.66	26.61	13.69	184.68	41.37 CH 24.55 CH_3
L^3 [c]	—	—	—	—	—	172.16 173.88	39.94 CH_2 35.87 CH
3a [c]	−75.0	22.05 (558.9)	27.31 (33.9)	26.03 (86.9)	13.75	176.10 172.54	42.90 42.62
L^4 [c]	—	—	—	—	—	171.87	44.42 CH
4a [c]	−65.9	22.20 (550.1)	27.30 (30.2)	26.13 (88.2)	13.79	174.24	54.11

[a] Atoms C^1–C^4 are the carbon atoms of butyl residues in sequence from the tin atom. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$.

Table 5 Experimental ^{119}Sn Mössbauer parameters (mm s^{-1}) for the di-*n*-butyltin(IV) complexes; proposed structure *TBPY*

Ligand	Method	i.s.	q.s.	Ref.
L^1	*a*	1.49	3.28	This work
	b	1.49	3.28	This work
	a	1.42	3.23	14 [c]
L^2	*a*	1.43	3.18	This work
	b	1.48	3.25	This work
L^3	*a*	1.43	3.18	This work
	b	1.60	3.49	This work
	a	1.33	3.20	14 [c]
L^4	*a*	1.47	3.24	This work
	b	1.43	3.27	This work

[a] Prepared under reflux. [b] Propoxide. [c] Dimethyltin(IV) complex.

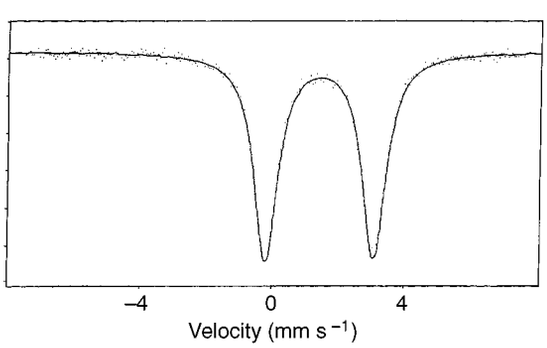


Fig. 2 Mössbauer spectrum of the dibutyltin(IV)–2-sulfanylpropionic acid complex

the p.q.s. concept [15,23,24] was used. The p.q.s. values of the functional groups [15,25,26] used in the calculations are listed in Table 6. All possible arrangements for five-co-ordinated tin(IV) (which was evidenced by the above IR and NMR measurements) are shown in Fig. 3. All of the structures with calculated q.s. values smaller than 2.32 mm s^{-1} can immediately be eliminated because of the great differences from the measured values. Structures in which the R–C–R bond angle is 180 or 90° can also be eliminated on the basis of NMR measurements which had shown the presence of a *ca*. 130° R–C–R bond angle. In this way three structures remained: 1, 6 and 11. According to the IR spectroscopic measurements, there is no monodentate carboxylate co-ordination so the only possible structure must be 1, with the two butyl and the thiol groups in equatorial and

Table 6 Partial quadrupole splitting values (mm s^{-1}) of the functional groups used in the calculations

p.q.s. (R)	p.q.s. (S^-)	p.q.s. (CO_2^-)
−1.37 (t)		0.0 75 $(tba)_b$
−0.94 (tba)	−0.595 (tba)	0.293 $(tbe)_b$
−1.13 (tbe)	−0.6 (tbe)	−0.1 $(tba)_m$
−1.03 (oc)	−0.56 (oc)	0.06 $(tbe)_m$

t = Tetrahedral, oc = octahedral.

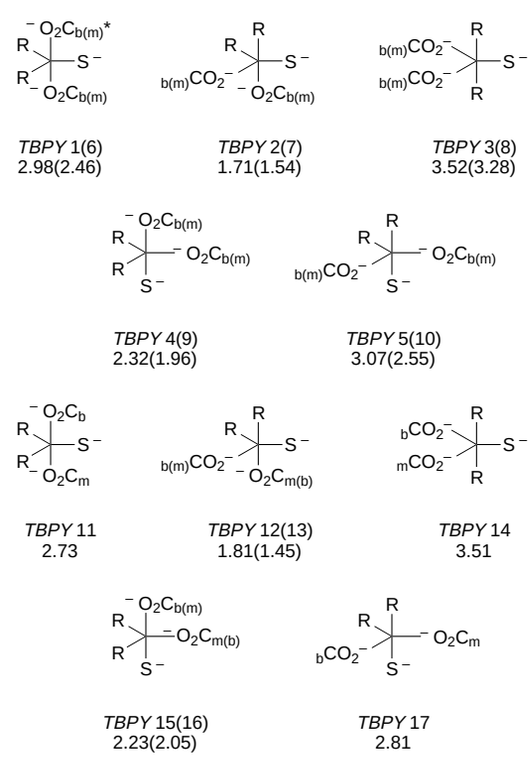


Fig. 3 Calculated quadrupole splitting values for the tin(IV) co-ordination spheres in different stereochemical arrangements with trigonal-bipyramidal (*TBPY*) symmetry of the R_2S^{IV} cation. b = Bidentate, m = monodentate

the bridging bidentate carboxylic groups in axial positions (Fig. 4). However, in some cases the difference between the calculated and measured q.s. values is larger than the experimental error. This can be explained in that the calculated value is given

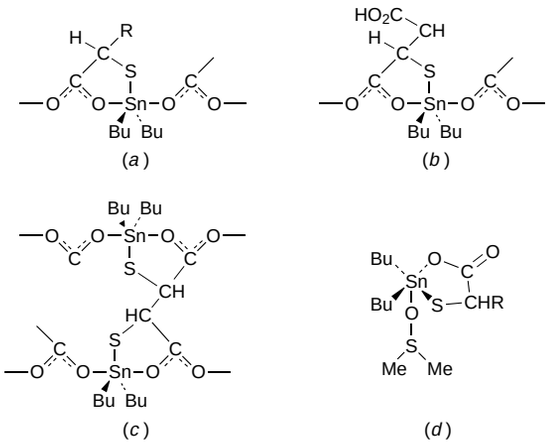


Fig. 4 Proposed structures for the $SnBu_2$ complexes with (*a*) sulfanylacetic and 2-sulfanylpropionic acid, (*b*) sulfanylsuccinic acid, (*c*) 2,3-disulfanylsuccinic and (*d*) supposing co-ordination of solvent

for the ideal structure with a 120° C–Sn–C bond angle. On the basis of equation (3) in ref. 27 the deviation from the ideal structure can be estimated. A distortion of 5–10° results in a 0.2–0.41 mm^{-1} greater measured q.s. value than is that calculated for the ideal structure. In case of our complexes this means a C–Sn–C angle between 125 and 130° which agrees well with the values determined by NMR measurements.

Conclusion

Both synthetic procedures used resulted in the formation of complexes with 1:1 metal-to-ligand ratio, except for **4a** and **4b** where a 2:1 metal-to-ligand ratio was found, reflecting the four accessible binding sites. The IR, Raman and NMR spectral data for the prepared complexes indicate five-co-ordinate trigonal-bipyramidal moieties with equatorial thiol and two butyl groups and axial carboxylate groups, forming cyclic oligomers, in some cases of different sizes, or very long linear oligomers. In compounds **3a** and **3b** one carboxylate group is not involved in co-ordination to tin(IV). The Mössbauer measurements in combination with IR and NMR spectroscopy allowed us to determine the steric arrangement around the tin, among the seventeen theoretically possible structures.

Acknowledgements

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