Journal of Organometallic Chemistry, 436 (1992) 287–298 Elsevier Sequoia S.A., Lausanne JOM 22747

Preparation, IR, ¹³C and ^{119m}Sn Mössbauer spectral studies of organotin(IV) derivatives of ethylenediaminetetraacetic acid

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Abstract

New diorganotin(IV) and triorganotin(IV) derivatives $(R_2Sn)_nEDTA$ (R = Me, Et, "Pr, "Bu, "Oct; n = 1, 2); $(R_2Sn)_3(EDTAH)_2$ ($R = ^nBu$, "Oct); and $(R_3Sn)_3EDTAH$ (R = ME, "Bu, Ph, Cyh) have been prepared by reacting diorganotindichloride and triorganothinchloride with di-, tri- and tetra-silver salts of ethylenediaminetetraacetic acid (EDTAH₄) in 1:1, 2:1, 3:2 and 3:1 (metal/ligand) molar ratio, respectively. The 3:2 diorganotin(IV) compounds possess an octahedral geometry around the Sn atom whereas the diorganotin (1:1, 2:1) and triorganotin (3:1) have five coordinate trigonal bipyramidal geometry around the Sn atom. One of the organotin moieties in $(R_2Sn)_3(EDTAH)_2$ acts as a bridge between two EDTA molecules, resulting in a novel type of complex.

Introduction

Disodiumethylenediaminetetraacetic acid (EDTAH₂Na₂) is one of the most versatile analytical and chelating reagents [1,2]. Only a few diorganotin [3] and triorganotin [4] compounds with EDTA have been reported. In continuation of our earlier work with triorganotin(IV) derivatives of EDTA [5], we report here on some new diorganotin(IV) and triorganotin(IV) complexes with EDTA prepared in different stoichiometries and with interesting bonding sites available to tin(IV).



EDTAH₂Na₂

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Results and discussion

Diorganotin(IV) and triorganotin(IV) chlorides react with di-, tri- and tetra-silver salts of ethylenediaminetetraacetic acid in 1:1, 2:1, 3:2 (diorganotin) and 3:1 (triorganotin) molar ratios, respectively.

$$R_{2}SnCl_{2} + EDTAH_{2}Ag_{2} \rightarrow R_{2}SnEDTAH_{2} + 2AgCl (1:1)$$

$$2R_{2}SnCl_{2} + EDTAAg_{4} \rightarrow (R_{2}Sn)_{2}EDTA + 4AgCl (2:1)$$

$$3R_{2}SnCl_{2} + 2EDTAHAg_{3} \rightarrow (R_{2}Sn)_{3}(EDTAH)_{2} + 6AgCl (3:2)$$

$$3R_{3}SnCl + EDTAHAg_{3} \rightarrow (R_{3}Sn)_{3}EDTAH + 3AgCl (3:1)$$

$$O$$

$$AgO - C^{d} - CH_{2}$$

$$CH_{2} - CH_{2}$$

$$AgO - C - CH_2 - CH_2 - CH_2 - N CH_2 - C - OAg$$

$$(EDTAAg_4)$$

and characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR and Mössbauer spectroscopy. Ethylenediaminetetraacetic acid has six binding sites, four carboxylates (a, b, c, d) and two nitrogens (e, f) available for bonding to tin(IV). All the complexes are white, insoluble in common organic solvents such as chloroform, benzene, methanol, carbontetrachloride and are soluble in ethanol. Physical and analytical data are given in Table 1.

Infrared data

Infrared spectra of the silver, sodium salts and complexes of ethylenediaminetetraacetic acid were recorded in KBr discs in the range 4000-200 cm⁻¹. The stretching frequencies of interest are ν (N-H), ν (COO), ν (Sn-C), ν (Sn-O) (Table 2). In complexes 1-4 the ν (N-H) shifts to a higher value compared to the sodium salt of ethylenediaminetetraacetic acid (EDTAH₂Na₂), which reveals the non-participation of nitrogen atoms in coordination to tin(IV) [5]. In complexes 10-15 the lowering of ν (N–H) compared to EDTAHNa₃ is due to intramolecular hydrogen bonding NH...O=C-; the coordination of nitrogen to tin is ruled out because nitrogen atoms bind to metal only when nitrogen is deprotonated on complex formation. Absence of a ν (N-H) band in complexes 5-9 shows complete deprotonation of all the carboxylate groups. In 1:1 complexes 1-4, a medium-intensity band in the region 1745-1730 cm⁻¹ is due to one of the free C=O of the carboxylate group bonded to tin(IV). The second tin(IV)-bonded carboxylate C=O, which is intermolecularly bonded to tin(IV), C=O \rightarrow Sn, falls in the range 1670– 1645, which is also the region of the hydrogen-bonded two free carboxylates ... H-O-C=O... H-O... present in these complexes. Similarly, in the 1:2 complexes 5-9 free C=O of carboxylate bonded to tin(IV) appears in the range 1740-1730 cm⁻¹, whereas the intermolecularly bonded carboxylate C=O, (C=O \rightarrow Sn) absorbs in the region 1650-1630 cm⁻¹. In the remaining 3:2 and 3:1 Table 1 Physical and analytical data of diorganotin and triorganotin(IV) complexes of EDTA

| | Compound ^a | | Yield | ш.р. | Analysis (%) fou | ind (calc.) | | |
|--------------|---|-----|-------|---------|------------------|-------------|--------|---------|
| | | | (%) | (C) | C | Н | Z | Sn |
| - | (C ₂ H ₅) ₂ Sn EDTAH ₂ | 1:1 | 88 | 103-104 | 35.89 | 4.87 | 4.82 | 27.02 |
| | 1 | | | | (36.00) | (5.15) | (00) | (25.40) |
| 7 | (n-C ₃ H ₇) ₂ Sn EDTAH ₂ | 1:1 | 87 | 113-115 | 37.89 | 5.93 | 4.59 | 23.03 |
| | 1 | | | | (38.80) | (5.65) | (2.65) | (23.99) |
| د | (n-C ₄ H ₉) ₂ Sn EDTAH ₂ | 1:1 | 92 | 117-120 | 41.17 | 6.54 | 4.11 | 25.07 |
| | a a | | | | (41.32) | (6.12) | (5.35) | (22.70) |
| 4 | (n-C ₈ H ₁₇) ₂ Sn EDTAH ₂ | 1:1 | 89 | 103-105 | 48.94 | 7.12 | 4.12 | 19.43 |
| |) ; ; | | | | (47.08) | (7.56) | (4.41) | (18.62) |
| ŝ | [(CH ₃) ₂ Sn] ₂ EDTA | 2:1 | 69 | 143-145 | 27.90 | 4.10 | 4.39 | 41.27 |
| | 1 . 2 | | | | (28.60) | (4.09) | (4.49) | (40.55) |
| 9 | [(C ₂ H ₅) ₂ Sn] ₂ EDTA | 2:1 | 87 | 120-121 | 34.3 | 5.10 | 4.05 | 35.98 |
| | 1 | | | | (33.15) | (4.91) | (4.29) | (36.44) |
| 7 | [(n-C ₃ H ₇) ₂ Sn] ₂ EDTA | 2:1 | 75 | 116-118 | 37.80 | 6.00 | 3.81 | 37.98 |
| | 1 | | | | (37.80) | (5.79) | (4.01) | (34.03) |
| | [(n-C4H9)2Sn]2EDTA | 2:1 | 92 | 98-100 | 40.64 | 6.59 | 2.78 | 32.48 |
| | | | | | (41.40) | (6.39) | (3.71) | (31.51) |
| 6 | [(n-C ₈ H ₁₇) ₂ Sn] ₂ EDTA | 2:1 | 65 | 137-139 | 50.60 | 7.28 | 1.99 | 23.89 |
| | | | | | (51.04) | (8.17) | (2.86) | (24.28) |
| 10 | [(n-C4H9)2Sn]3[EDTAH]2 | 3:2 | 73 | 147-150 | 40.60 | 6.61 | 3.73 | 27.92 |
| | • | | | | (40.50) | (5.63) | (4.50) | (28.66) |
| 11 | [n-(C ₈ H ₁₇) ₂ Sn] ₃ [EDTAH] ₂ | 3:2 | 76 | 134-137 | 50.06 | 8.75 | 2.47 | 22.90 |
| | | | | | (20.60) | (2.93) | (3.47) | (22.08) |
| 12 | [(CH ₃) ₃ Sn] ₃ EDTAH | 3:1 | 71 | 195196 | 28.30 | 4.92 | 2.11 | 49.76 |
| | 1 | | | | (29.20) | (5.12) | (3.58) | (50.36) |
| 13 | [(n-C4H9)3Sn]3EDTAH | 3:1 | 67 | 1 | I | I | 1 | 31.23 |
| | | | | | | | | (30.74) |
| 14 | [(C ₆ H ₅) ₃ Sn] ₃ EDTAH | 3:1 | 75 | 173-175 | 56.24 | 4.05 | 1.86 | 28.02 |
| | | | | | (57.30) | (4.30) | (2.00) | (26.60) |
| 15 | [(C ₆ H ₁₁) ₃ Sn] ₃ EDTAH | 3:1 | 73 | 115-117 | 54.80 | 7.87 | 1.43 | 24.82 |
| | | | | | (55.16) | (8.04) | (2.01) | (25.58) |

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^a All complexes are white.

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| | | i | | | | | |
|---|---|--------|------------------------|-----------------------|-----|---------|---------|
| | Compound | ∿(N−H) | ν(COO) _{asym} | µ(COO) _{sym} | Δν | ν(Sn−C) | ₽(Sn-O) |
| | EDTANa ₄ | 1 | 1605s | 1400s | 205 | 1 | 1 |
| | | | 1660sh | 1370m | | | |
| | EDTAAg4 | I | 1580bs | 1400s | 180 | 1 | 1 |
| | EDTAH Na, | 3395m | 1630s | 1390s | 240 | I | I |
| | 3 | | 1680sh | 1320s | 360 | | |
| | EDTAHAg ₃ | 3420m | 1580s | 1410s | 170 | 1 | I |
| | EDTAH, Na, | 3260m | 1610s | 1410s | 200 | I | 1 |
| | 9 | | 1680s | 1300s | 380 | | |
| | EDTAH, Ag, | 3400m | 1620s | 1400s | 220 | ŧ | I |
| | a a | | 1660s | 1350s | 310 | | |
| 1 | (C,H,),SnEDTAH, | 3440m | 1660sb | 1400s | 260 | 610m | 360m |
| | 1 | | 1730m | 1300s | 430 | 540m | |
| 7 | (n-C ₄ H ₇),SnEDTAH, | 3420m | 1645sb | 1380s | 265 | 590m | 440w |
| | 1 | | 1730m | 1300s | 430 | | |
| 3 | (n-C ₄ H ₉) ₂ Sn EDTAH ₂ | 3440m | 1660sb | 1385s | 275 | 605m | 490w |
| | 1 | | 1740m | 1300s | 440 | 550w | |
| 4 | (n-C ₈ H ₁₇) ₂ SnEDTAH ₂ | 3440m | 1670sb | 1385s | 285 | 610m | 480w |
| | | | 1745m | 1300s | 445 | 540m | |

Infrared spectral data (4000-200 cm⁻¹) of diorgano and triorganotin(IV) complexes of EDTA.

Table 2

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| 6 $(C_2H_3)_5 Sh_j EDTA$ - 1730m 1300s 430 540m 7 $((n-C_3H_1)_2 Sh_j EDTA$ - 1650s 1370s 270 665m 400 8 $((n-C_3H_1)_2 Sh_j EDTA$ - 1630s 1370s 230 60m 400m 9 $((n-C_3H_1)_2 Sh_j EDTA$ - 1640s 1370s 230 540m 400m 9 $((n-C_4H_9)_2 Sh_j EDTAH_1$ 3340m 1640s 1370s 230 540m 40m 10 $((n-C_4H_9)_2 Sh_j EDTAH_1$ 3340m 1640sb 1400s 230 540m 40m 11 $((n-C_4H_9)_2 Sh_j EDTAH_1$ 3340m 1640sb 1400s 230 540m 40m 12 $((n-C_4H_9)_2 Sh_j EDTAH_1$ 3340m 1640sb 1400s 230 540m 40m 13 $((n-C_4H_9)_5 Sh_3 EDTAH_1$ 3340m 1640sb 1400s 230 540m 40m 14 $((n-C_4H_9)_5 Sh_3 EDTAH_1$ 3340m 1640sb <td< th=""><th>5</th><th>I(CH₃),Snl,EDTA</th><th>ł</th><th>1630sb</th><th>1380s</th><th>250</th><th>600m</th><th>400w</th></td<> | 5 | I(CH ₃),Snl,EDTA | ł | 1630sb | 1380s | 250 | 600m | 400w |
|--|----|---|-------|--------|--------|----------|------|------|
| 6 $[(C_1H_j)_2Sn]_2EDTA$ - 1650s 1380s 270 605n 40w 7 $[(n-C_3H_j)_2Sn]_2EDTA$ - 1650s 1370s 200 600m 490 8 $[(n-C_4H_j)_2Sn]_2EDTA$ - 1630s 1370s 270 605m 40m 9 $[(n-C_4H_j)_2Sn]_2EDTA$ - 1640s 1370s 270 620m 40m 9 $[(n-C_4H_j)_2Sn]_3EDTAH]_2$ - 1640s 1370s 270 620m 40m 9 $[(n-C_4H_j)_2Sn]_3EDTAH]_2$ - 1620s 1370s 270 620m 40m 10 $[(n-C_4H_j)_2Sn]_3EDTAH]_2$ 3340m 1620s 1370s 230 540m 40m 11 $((n-C_4H_j)_2Sn]_3EDTAH]_3 3340m 1600s 230s 240s 540m 480m 12 [(n-C_4H_j)_5Sn]_3EDTAH]_3 3340m 1600s 230s 230s 240m 240m 13 [(n-C_4H_j)_5Sn]_3EDTAH]_3 3340m 1600s <$ | | 4 | | 1730m | 1300s. | 430 | 540m | |
| 7 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1740m 1310s 430 530m 8 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1630s 1370s 226 600m 490w 9 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1640s 1370s 270 520m 40m 9 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1640s 1370s 250 540m 40m 9 $[(n-C_4H_3)_2Sn]_3EDTAH_3$ 3340m 1640s 1370s 250 540m 40m 10 $[(n-C_4H_3)_2Sn]_3EDTAH_3$ 3340m 1640s 1370s 250 540m 480m 11 $((n-C_8H_{17})_2Sn]_3EDTAH_3$ 3340m 1640s 1410s 230 540m 480m 12 $((n-C_4H_3)_5Sn]_3EDTAH_3$ 3340m 1640s 130s 230 540m 480m 13 $((n-C_4H_3)_5Sn]_3EDTAH_3$ 3340m 1640s 130s 230 540m 480m 14 $((n-C_4H_3)_5Sn]_3EDTAH_3$ 3340m 1600s 130s </th <th>9</th> <th>[(C,H,),Sn],EDTA</th> <th>1</th> <th>1650s</th> <th>1380s</th> <th>270</th> <th>605m</th> <th>400w</th> | 9 | [(C,H,),Sn],EDTA | 1 | 1650s | 1380s | 270 | 605m | 400w |
| 7 $(i-C_3H_j)_5 Sn_j_E EDTA$ - 1630s 1370s 260 600n 490w 8 $(i-C_4H_g)_2 Sn_j_E EDTA$ - 1640s 1370s 270 620m 490w 9 $(i-C_4H_g)_2 Sn_j_E EDTA$ - 1730m 1370s 270 620m 490m 9 $(i-C_4H_g)_2 Sn_j_E EDTAH$ - 1730m 1370s 270 620m 400m 9 $(i-C_4H_g)_2 Sn_j_E EDTAH_j$ 3340m 1640sb 1370s 270 540m 490m 10 $(i-C_4H_g)_2 Sn_j_E EDTAH_j$ 3340m 1640sb 1300s 240 540w 490m 11 $(i-C_4H_g)_2 Sn_j_E EDTAH_j$ 3340m 1640sb 1410s 2.20 540w 480m 12 $((i-C_4H_g)_5 Sn_j_E EDTAH_j$ 3340m 1660s 130ls 2.20 540w 480m 13 $(i-C_4H_g)_5 Sn_j_E EDTAH_j$ 3340m 1660s 1280s 2.10 550w 470m 13 $(i-C_4H_g)_5 Sn_j_E EDTAH_j$ | | | | 1740m | 1310s | 430 | 530m | |
| 8 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1730m 1300s 540m 540m 400m 9 $[(n-C_4H_3)_2Sn]_2EDTA$ - 1640s 1370s 270 540m 400m 9 $[(n-C_6H_{17})_2Sn]_2EDTA$ - 1630s 1370s 270 540m 400m 10 $[(n-C_6H_{17})_2Sn]_3[EDTAH]_2$ 3340m 1620s 1370s 240 540m 480m 11 $[(n-C_6H_{17})_2Sn]_3[EDTAH]_2$ 3330m 1670s 1300s 240 540m 480m 12 $[(n-C_6H_{17})_5Sn]_3[EDTAH]_2$ 3330m 1660s 1300s 230 540m 480m 13 $[(n-C_6H_{17})_5Sn]_3EDTAH$ 3340m 1660s 1310s 230 540m 470m 13 $[(n-C_4H_9)_5Sn]_3EDTAH$ 3345m 1660s 1330s 210 550s 475m 14 $[(C_6H_{11})_5Sn]_3EDTAH$ 3345m 1660s 1330s 210 550s 475m 16 $[(C_6H_{11})_5Sn]_3EDTAH$ 334 | 7 | [(n-C ₃ H ₂),Sn],EDTA | ł | 1630s | 1370s | 260 | 600m | 490w |
| 8 $(n-C_4H_9)_2 Snl_2 EDTA$ - 1640s 1370s 270 620m 400m 9 $(n-C_4H_9)_2 Snl_2 EDTA$ - 1640s 1370s 270 620m 400m 10 $(n-C_8H_{17})_2 Snl_3 EDTAH_2$ - 1620s 1370s 270 540m 400m 10 $(n-C_8H_{17})_2 Snl_3 EDTAH_2$ 3340m 16640sb 1370s 236 540m 400m 11 $(n-C_8H_{17})_2 Snl_3 EDTAH_2$ 3330m 16640sb 1310s 236 540w 490w 13 $(n-C_8H_{17})_5 Snl_3 EDTAH_2$ 3340m 1660sb 1310s 270 540w 480w 13 $(n-C_4H_9)_5 Snl_3 EDTAH_2$ 3340m 1600sb 1310s 375 540w 470 550s 470m 13 $(n-C_4H_9)_5 Snl_3 EDTAH_2$ 3345m 1600sb 1310s 370s 270 540w 450w 14 $(n-C_4H_9)_5 Snl_3 EDTAH_2$ 3345m 1600sb 1390s 220 540w 450w <tr< th=""><th></th><th>4</th><th></th><th>1730m</th><th>1300s</th><th>430</th><th>540m</th><th></th></tr<> | | 4 | | 1730m | 1300s | 430 | 540m | |
| 9 $[(n-C_8H_{17})_2Sn]_2EDTA$ 1730m 1300s 430 540m 10 $[(n-C_8H_{17})_2Sn]_3EDTAH_1$ 3340m 1620s 1370s 250 550m 480m 10 $[(n-C_8H_{17})_2Sn]_3EDTAH_1$ 3340m 1640sb 1300s 430 545m 480m 10 $[(n-C_8H_{17})_2Sn]_3EDTAH_1$ 3330m 1640sb 1400s 240 540m 490m 11 $[(n-C_8H_{17})_2Sn]_3EDTAH_1$ 3330m 1640sb 1410s 230 540m 490m 12 $[(n-C_8H_{17})_5Sn]_3EDTAH_1$ 3340m 1660sb 1310s 270 550s 470 13 $[(n-C_4H_9)_5Sn]_3EDTAH_1$ 3340m 1660sb 1330s 210 550s 470 13 $[(n-C_4H_9)_5Sn]_3EDTAH_1$ 3340m 1660sb 1380s 220 550s 475m 14 $[(n-C_4H_9)_5Sn]_3EDTAH_1$ 3340m 1650s 1380s 220 550s 470m 16 $[(n-C_4H_{11})_3Sn]_3EDTAH_1$ 3340m | 80 | [(n-C ₄ H _a),Sn],EDTA | I | 1640s | 1370s | 270 | 620m | 400m |
| 9 $[(n-C_8H_{17})_2Sn]_2EDTA$ - $1620s$ $1370s$ 250 $595m$ $480m$ 10 $[(n-C_4H_9)_2Sn]_3[EDTAH]_2$ $3340m$ $1640sb$ $1400s$ 240 $540w$ $490w$ 11 $[(n-C_8H_{17})_2Sn]_3[EDTAH]_2$ $3350m$ $1640sb$ $1400s$ 240 $540w$ $490w$ 11 $[(n-C_8H_{17})_2Sn]_3[EDTAH]_2$ $3350m$ $1640sb$ $1410s$ 230 $540w$ $490w$ 12 $[(n-C_8H_{17})_2Sn]_3EDTAH$ $3340m$ $1640sb$ $1410s$ 230 $540w$ $480w$ 13 $[(n-C_8H_{17})_5Sn]_3EDTAH$ $3340m$ $1660sb$ $1310s$ 230 $540w$ $480w$ 13 $[(n-C_4H_9)_3Sn]_3EDTAH$ $3340m$ $1600sb$ $1390s$ 210 $550s$ 470 14 $[(n-C_4H_9)_3Sn]_3EDTAH$ $3345m$ $1600sb$ $1380s$ 220 $530w$ $450w$ 13 $[(n-C_4H_9)_3Sn]_3EDTAH$ $3345m$ $1600sb$ $1380s$ 220 $530w$ $450w$ 14 $[(C_6H_{11})_3Sn]_3EDTAH$ $3340m$ $1650sb$ $1430m$ 200 $370w$ $230w$ 15 $[(C_6H_{11})_3Sn]_3EDTAH$ $3340m$ $1650sb$ $1380s$ 245 $500w$ $230w$ 15 $[(C_6H_{11})_3Sn]_3EDTAH$ $3340m$ $1650sb$ $1380s$ 245 $200w$ $230w$ 16 $(C_6H_{11})_3Sn]_3EDTAH$ $3340m$ $1650sb$ $1380s$ 245 $200w$ $200w$ 15 $(C_6H_{11})_3Sn_3EDTAH$ $3340m$ $1650sb$ $1280s$ 240 | | a a i i | | 1730m | 1300s | 430 | 540m | |
| 1730m 1730m 1300s 430 545m 10 $(n-C_4H_9_2Sn]_3[EDTAH]_2$ 3340m 1640sb 1400s 240 540w 490w 11 $(n-C_4H_9_2Sn]_3[EDTAH]_2$ 3350m 1640sb 1410s 240 540w 490w 12 $(n-C_4H_9_2Sn]_3[EDTAH]_2$ 3350m 1640sb 1410s 230 540w 480w 12 $(CH_3)_3Sn]_3EDTAH$ 3340m 1660sb 1310s 375 540w 480w 13 $(C_4H_9)_3Sn]_3EDTAH$ 3340m 1660sb 1330s 210 550s 470m 13 $(C_6H_1)_3Sn]_3EDTAH$ 3340m 1660sb 1330s 220 530w 450m 14 $(C_6H_1)_3Sn]_3EDTAH$ 3340m 1660sb 1330s 220 550s 470 16 $(C_6H_{1,1})_3Sn]_3EDTAH$ 3340m 1660sb 1330s 220 550m 470m 17 $(C_6H_{1,1})_3Sn]_3EDTAH$ 3340m 1660sb 1330m 200 370w 230w 18 $(C_6H_{1,1})_3Sn]_3EDTAH$ 3340m 1670sh <th>6</th> <th>[(n-C₈H₁₇),Sn],EDTA</th> <th>I</th> <th>1620s</th> <th>1370s</th> <th>250</th> <th>595m</th> <th>480m</th> | 6 | [(n-C ₈ H ₁₇),Sn],EDTA | I | 1620s | 1370s | 250 | 595m | 480m |
| 10 $[(n-C_4H_9)_2Sn]_3[EDTAH]_2$ 3340m1640sb1400s240540w490w11 $[(n-C_8H_{17})_2Sn]_3[EDTAH]_2$ 3350m1640sb1410s230540w490w12 $[(n-C_8H_{17})_2Sn]_3[EDTAH]_2$ 3350m1640sb1310s375480w480w13 $[(cH_3)_3Sn]_3EDTAH$ 3340m1660sb1310s375410550s470m13 $[(n-C_4H_9)_3Sn]_3EDTAH$ 3345m1660sb1390s210550s470555n14 $[(C_6H_3)_3Sn]_3EDTAH$ 3340m1660sb1380s220550s470555n450w14 $[(C_6H_1)_3Sn]_3EDTAH$ 3340m1660sb1430m200370w230w230w15 $[(C_6H_{11})_3Sn]_3EDTAH$ 3340m1650sb1430m200370w230w260w15 $[(C_6H_{11})_3Sn]_3EDTAH$ 3340m1650sb1380s245500w240w15 $[(C_6H_{11})_3Sn]_3EDTAH$ 3340m1650sb1260s245500w240w16 $[(C_6H_{11})_3Sn]_3EDTAH$ 3340m1650sb1260s245500w240w16 $[(C_6H_{11})_3Sn]_3EDTAH$ 3340m1670sh1270s245500w240w1670sh $[1670sh]_1$ $[1670sh]_1$ $[1670sh]_1$ 270s245500w240w1670sh]_1 $[1670sh]_1$ $[1670sh]_1$ $[1670sh]_1$ 270s240240w1670sh]_1 $[1670sh]_1$ $[1670sh]_1$ </th <th></th> <td></td> <td></td> <td>1730m</td> <td>1300s</td> <td>430</td> <td>545m</td> <td></td> | | | | 1730m | 1300s | 430 | 545m | |
| 11 $(n-C_8H_{17})_2 Snl_3 [EDTAH]_2$ 3350m 1680s 1280s 400 600w 12 $((n-C_8H_{17})_2 Snl_3 [EDTAH]_2$ 3350m 1640sb 1410s 230 540w 480w 13 $((cH_3)_3 Snl_3 EDTAH)_3$ 3350m 1660sb 1310s 375 410 550s 475m 13 $((c-4H_9)_3 Snl_3 EDTAH)_3$ 3340m 1600sb 1390s 210 550s 470 550s 475m 14 $[(c-4H_9)_3 Snl_3 EDTAH)_3$ 3340m 1660sb 1380s 220 530w 455m 455m 14 $[(C_6H_{1,1})_3 Snl_3 EDTAH)_3$ 3340m 1650s 1430m 200 370w 230w 260w 260w 240m 200w 260w 240m 200w | 10 | [(n-C ₄ H ₆),Sn] ₃ [EDTAH], | 3340m | 1640sb | 1400s | 240 | 540w | 490w |
| I1 $(n-C_6H_{17})_2 Snl_3 [EDTAH]_2$ 3350m 1640sb 1410s 230 540w 480w 12 $(CH_3)_3 Snl_3 EDTAH$ 3340m 1685m 1310s 375 480w 480w 13 $(CH_3)_3 Snl_3 EDTAH$ 3340m 1660sb 1390s 210 550s 475m 13 $(n-C_4H_9)_3 Snl_3 EDTAH$ 3345m 1660sb 1380s 220 530w 455m 14 $(C_6H_3)_3 Snl_3 EDTAH$ 3340m 1670m 1200s 470 555m 470 14 $(C_6H_{1,1})_3 Snl_3 EDTAH$ 3340m 1650sb 1430m 200 370w 230w 250m 15 $(C_6H_{1,1})_3 Snl_3 EDTAH$ 3340m 1650sb 1380s 245 500w 230w 260w 16 $(C_6H_{1,1})_3 Snl_3 EDTAH$ 3340m 1650sb 1380s 245 500w 260w 16 $(C_6H_{1,1})_3 Snl_3 EDTAH$ 3340m 1670sb 1270s 245 500w 260w 1670sh $1270s$ 245 500w 2400 200w 200w | | 4 5 4 5 | | 1680s | 1280s | 400 | 600w | |
| 12 $[(CH_3)_3 Sn]_3 EDTAH$ 3340m 1685m 1310s 375 13 $[(C-4H_3)_3 Sn]_3 EDTAH$ 3340m 1600sb 1390s 210 550s 475m 13 $[(n-C_4H_9)_3 Sn]_3 EDTAH$ 3340m 1660sb 1390s 210 550s 470 14 $[(C_6H_3)_3 Sn]_3 EDTAH$ 3340m 1650s 1430m 200 370w 230w 14 $[(C_6H_{1,1})_3 Sn]_3 EDTAH$ 3340m 1650s 1430m 200 370w 230w 230w 15 $[(C_6H_{1,1})_3 Sn]_3 EDTAH$ 3340m 1650s 1380s 245 500w 400w 15 $[(C_6H_{1,1})_3 Sn]_3 EDTAH$ 3340m 1650sh 1380s 245 500w 400w | 11 | [(n-C _a H _{1,7}),Sn] ₂ [EDTAH], | 3350m | 1640sb | 1410s | 230 | 540w | 480w |
| 12 $(CH_3)_3 Sn_3 EDTAH$ 3340m 1600eb 1390s 210 550s 475m 13 $(n-C_4H_9)_3 Sn_3 EDTAH$ 3345m 1660s 1250s 410 410 455m 14 $(C_6H_3)_3 Sn_3 EDTAH$ 3345m 1670m 1200s 470 555m 450w 14 $(C_6H_4)_3 Sn_3 EDTAH$ 3340m 1630sb 1430m 200 370w 230w 230w 15 $(C_6H_{11})_3 Sn_3 EDTAH$ 3340m 1650s 1430m 200 370w 230w 260w 15 $(C_6H_{11})_3 Sn_3 EDTAH$ 3340m 1650s 1380s 245 500w 260w 1670sh 1270s 245 500w 260w 240 500w 260w | | | | 1685m | 1310s | 375 | | |
| 13 [(n-C_4H_9)_3Sn]_3EDTAH 3345m 1660s 1250s 410 14 [(n-C_4H_9)_3Sn]_3EDTAH 3345m 1670m 1200s 470 555m 455w 14 [(C_6H_3)_3Sn]_3EDTAH 3340m 1630sb 1430m 200 370w 230w 230w 15 [(C_6H_{11})_3Sn]_3EDTAH 3340m 1660s 1260s 400 330w 260w 16 [(C_6H_{11})_3Sn]_3EDTAH 3340m 1650s 1380s 245 500w 400w | 12 | [(CH ₁) ₁ Sn] ₁ EDTAH | 3340m | 1600sb | 1390s | 210 | 550s | 475m |
| [(n-C₄H₉)₃Sn]₃EDTAH 3345m 1600sb 1380s 220 530w 455w [(C₆H₃)₃Sn]₃EDTAH 3340m 1670m 1200s 470 555m [(C₆H₁₁)₃Sn]₃EDTAH 3340m 1660s 1260s 400 330w [(C₆H₁₁)₃Sn]₃EDTAH 3340m 1655b 1380s 245 500w (C₆H₁₁)₃Sn]₃EDTAH 3340m 1670s 400 | | | | 1660s | 1250s | 410 | | |
| 14 [(C_6H_3)_3Sh]_3EDTAH 3340m 1670m 1200s 470 555m 14 [(C_6H_1)_3Sh]_3EDTAH 3340m 1630sb 1430m 200 370w 230w 15 [(C_6H_{11})_3Sh]_3EDTAH 3340m 1660s 1260s 400 330w 260w 16 [(C_6H_{11})_3Sh]_3EDTAH 3340m 1625sb 1380s 245 500w 400 16 [(C_6H_{11})_3Sh]_3EDTAH 3340m 1670sh 1270s 245 500w 400w | 13 | [(n-C ₄ H ₆) ₁ Sn] ₁ EDTAH | 3345m | 1600sb | 1380s | 220 | 530w | 455w |
| 14 [(C ₆ H ₃) ₃ Sh] ₃ EDTAH 3340m 1630sb 1430m 200 370w 230w 230w 230w 230w 230w 260w 310w 260w 30w 260w 400 330w 260w 400w 310w 260w 400w 310w 260w 400w 310w 260w 400w 300w 3 | | | | 1670m | 1200s | 470 | 555m | |
| 15 [(C ₆ H ₁₁) ₃ Sn] ₃ EDTAH 3340m 1660s 1260s 400 330w 260w 16 [(C ₆ H ₁₁) ₃ Sn] ₃ EDTAH 3340m 1625sb 1380s 245 500w 400w 1670sh 1270s 400 310w 260w 400w | 14 | [(C,H,),Sn],EDTAH | 3340m | 1630sb | 1430m | 200 | 370w | 230w |
| 15 [(C ₆ H ₁₁) ₃ Sn] ₃ EDTAH 3340m 1625sb 1380s 245 500w 400w 1570sh 1270s 400 | | | | 1660s | 1260s | 400 | 330w | 260w |
| 1670sh 1270s 400 | 15 | [(C,H,,),Sn],EDTAH | 3340m | 1625sb | 1380s | 245 | 500w | 400w |
| | | | | 1670sh | 1270s | 400 4 | | |

Table 3 ¹H NMR data of diorgano and triorganotin(IV) complexes of EDTA

| 00 | $DC - CH_2$ 1 2 | CH ₂ -COC |) | | | |
|----|---|---|---|--|---------------------------------|--------------------------------|
| 0 | $OC - CH_2$ | ² -N CH ₂ -COC |) | | | |
| | Compound | CH ₂ and CH ₂ | + | $C\dot{H}_2, C\dot{H}_2, C\dot{H}_2, C\dot{H}_2, C\dot{H}_2$ | Sn–alkyl/ –CH ₂ – | phenyl/cyh -CH ₃ |
| | EDTANa4 ^a | 5.02 (s, 4H) | | 5.59–5.54 (m, 8H) | | - |
| | EDTAHNa ₃ ^a | 3.85-3.76 (m, 4H) | | 6.05-5.89 (m, 8H) | - | - |
| | EDTAH ₂ Na ₂ ^a | 3.91-3.69 (m, 4H) | | 5.24-4.12 (m, 8H) | - | |
| 1 | $(C_2H_5)_2$ Sn EDTAH ₂ ^b | 2.78-2.20 | | | 1.95-0.63 | |
| | | (bm, 14H, | | | (m, 10H) | |
| | | $CH_2 = 12H,$ | | | | |
| | | NH = 2H) | | | | |
| 2 | $(n-C_3H_7)_2$ Sn EDTAH ₂ ^b | 3.90-3.10 | | | 1.80-1.10 | 1.00-0.60 |
| | | (m, 14H, | | | (m, 8H) | (t, 6H) |
| | | $CH_2 = 12H,$ | | | | |
| • | | $\mathbf{NH} = \mathbf{ZH}$ | | | 1 (0 1 10 | 1 05 0 55 |
| 3 | $(n-C_4H_9)_2$ Sn EDIAH ₂ | 2.05-2.39 | | | 1.08-1.19 | 1.05-0.55 |
| | | $(m, 14\pi, 1211)$ | | | (m, 12 m) | (11, 01) |
| | | $CH_2 = 12H,$ NU - 2U) | | | | |
| A | (n C H) So EDTAH ^b | 300_340 | | | 1 80-1 10 | 1.00-0.60 |
| • | (I-C ₈ II ₁₇) ₂ SI EDIAI ₂ | (m 14H) | | | (m 28H) | (t 6H) |
| | | $CH_{a} = 12H_{a}$ | | | (111, 2011) | (1, 011) |
| | | NH = 2H | | | | |
| 5 | $[(CH_1)_2 Sn]_2 EDTA^b$ | 1.99–1.45 | | | _ | 0.90 |
| | | (bm, 12H) | | | | (s, 12H) |
| 6 | $[(C_2H_5)_2Sn]_2EDTA^b$ | 2.80-2.53 | | н. | 2.03-1.30 | 1.20-0.98 |
| | | (bm, 12H) | | | (m, 8H) | (t, 12H) |
| 7 | $[(n-C_3H_7)_2Sn]_2EDTA^b$ | 4.15-3.65 | | | 2.60-2.00 | 1.91-1.60 |
| | | (bm, 12H) | | | (m, 16H) | (t, 12H) |
| 8 | $[(n-C_4H_9)_2Sn]_2EDTA^b$ | 3.19-2.80 | | | 2.00-1.20 | 1.10-0.55 |
| | <i></i> | (m, 12H) | | | (m, 24H) | (m, 12H) |
| 9 | $[(n-C_8H_{17})_2Sn]_2EDTA^{b}$ | 2.49-2.12 | | | 1.51-1.10 | |
| | | (m, 12H) | | | (bm, 68H) | 1 00 0 67 |
| 10 | $[(n-C_4H_9)_2Sn]_3$ - | 2.62-2.36 | | | 1.73 - 1.10 | 1.09-0.0/ |
| | [EDIAH] ₂ [°] | (m, 26H, | | | (m, 30H) | (0, 1811) |
| | | $CH_2 = 24H,$ NH = 2H) | | | | |
| 11 | (n-C H -) Sola | $N \Pi = 2 \Pi$ | | | 1 60-1 28 | 1 00_0 89 |
| ** | $[EDT \Delta H]_{b}$ | (m 26H | | | (m 84H) | (m. 18H) |
| | | $CH_{2} = 24H_{2}$ | | | (111) 0 12 1) | (,, |
| | | NH = 2H | | | | |
| 12 | $[(n-C_4H_9)_3Sn]_3EDTAH^{b}$ | 2.90-2.09 | | | 2.00-0.80 | - |
| | , | (m, 13H, | | | (bm, 81H) | |
| | | $CH_2 = 12H$, | | | | |
| | _ | NH = 1H) | | | | |
| 14 | $[(C_6H_5)_3Sn]_3EDTAH^b$ | 3.62-3.55 | | | 7.76-7.16 | - |
| | | (m, 12H) | | | (m, 46H, | |
| | | | | | Ph = 45H | |
| | | 2.54. 2.00 | | | NH = 1H | 1 |
| 15 | ((C ₆ H ₁₁) ₃ Sn] ₃ EDTAH ^b | 5.54-2.90 | | | 4.20-0.08 | _ |
| | | (III, 1511, CH - 1712 | | | (011, 990) | , |
| | | NH = 1H) | | | | |

 \overline{a} D₂O. \overline{b} CDCl₃ + DMSO- d_6 (4:1).

Table 4

¹³C NMR spectra data of diorgano and triorganotin(IV) complexes of EDTA

| ЮОН | c-čH ₂ _b | ČH ₂ -O | НОС | - | 2 3 | 4 | e e | ٢ | 80 | | | |
|-----|---|--------------------|------------|---------------------|-----------------------------------|----------------|---------------------|---------------------------------|-------|-------|-------|-------|
| | | | S | n-CH ₂ - | CH ₂ – CH ₂ | $-CH_2 - CH_2$ | CH ₂ -CH | ₂ -CH ₂ - | ĆH, | | | |
| ЮОН | $c - cH_2$ | CH2-C | НОО | | | | | 1.1.10 T | | | | |
| | Compound | a, b | c, d, e, f | C00 | Sn-R | | | | | | | |
| | | | ÷ | | 1 | 2 | e | 4 | S | 6 | 7 | 8 |
| | EDTANa4 d | 54.42 | 61.32 | 182.22 | 1 | ł | I | 1 | I | 1 | I | I |
| | EDTAHNa, " | 53.75 | 60.12 | 178.99 | ł | ı | ł | ı | ı | I | 1 | I |
| | EDTAH, Na, a | 52.40 | 58.90 | 171.50 | I | I | 1 | ı | I | I | I | I |
| 2 | $(n-C_3H_7)_2Sn$ EDTAH ₂ ^b | 48.88 | 59.36 | 169.63 | 17.64 | 16.45 | 12.51 | I | 1 | I | I | ł |
| | 1 | | | 168.40 | | | | | | | | |
| 3 | (n-C ₄ H ₉) ₂ SnEDTAH ₂ ^b | 48.61 | 57.71 | 168.39 | 26.76 | 26.43 | 25.08 | 13.44 | I | I | I | I |
| | | | | 166.58 | | | | | | | | |
| 11 | [(n-C ₈ H ₁₇) ₂ Sn] ₃ [EDTAH] ₂ | 58.39 | 61.73 | 167.89 | 33.85 | 31.83 | 29.33 | 25.67 | 27.74 | 22.63 | 21.96 | 14.03 |
| | | | | 170.81 | | | | | | | | |
| 14 | [(C ₆ H ₅) ₃ Sn] ₃ EDTAH ^b | 50.43 | 58.42 | 171.85 | 137.19 | ı | I | I | I | I | ı | 1 |
| | 1 5 5 | | | 172.69 | 128.41 | | | | | | | |
| 15 | [(C ₆ H ₁₁) ₃ Sn] ₃ EDTAH ^b | 49.02 | 58.09 | 166.98 | 36.88 | 31.16 | 30.01 | 30.69 | 28.73 | 26.68 | ı | I |
| | | | | 194.98 | | | | | | | | |
| | | | | | | | | | | | | |

^{*a*} D_2O . ^{*b*} $CDCl_3 + DMSO-d_6$ (4:1).

complexes 10–15, a strong absorption in the region 1685–1660 cm⁻¹ is assigned to the free hydrogen bonded carboxylates ... H–O–C=O... H–O, and another strong band in the range 1645–1600 cm⁻¹ is due to the bidentately bonded carboxylate [5]. The magnitude of separation $\Delta \nu$, $[\Delta \nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}]$, of the COO group is very useful for drawing structural inferences. In complexes 1–9, the $\Delta \nu$ values in the range 445–430 are clearly from the unidentately bonded carboxylates [6], and the second set of $\Delta \nu$ values 285–250 for the same compounds are from the intermolecularly bonded carboxylate C=O (as C=O \rightarrow Sn) as well as from the free-hydrogen-bonded carboxylate groups, which also absorb in the same region. For complexes 10–15, $\Delta \nu$ values in the range 245–200 are from the bidentately bonded carboxylated [7] and are comparable to the sodium salts whereas $\Delta \nu$ values in the range 470–375 are from the hydrogen-bonded free carboxylate groups. Sn–C stretching frequencies appear at 600–500 cm⁻¹ for alkyl derivatives and 330–250 cm⁻¹ for the phenyl compounds [5]. Bands in the region 500–400 cm⁻¹ are assigned to Sn–O stretching, as reported earlier [8].

¹H NMR data

The spectra of the di-, tri- and tetra-sodium salts of ethylenediaminetetraacetic acid (EDTA) were recorded in D_2O and those of the soluble complexes in a mixture of CDCl₃ and DMSO-d₆ (4:1) (Table 3). In the spectra of EDTAH₂Na₂ and EDTAHNa₃, the signals due to NH protons appear at 7.23 and 7.28 ppm, respectively, whereas in complexes 1-4, 10-13 and 15, the NH protons move upfield and appear along with all the CH₂ protons of EDTA as a multiplet; in complex 14, the protons move downfield and appear along with the phenyl protons as a complex multiplet. All the CH₂ protons of EDTA undergo a high field shift, to differing extent, after complex formation. All the alkyl/phenyl/cyclohexyl protons calculated from the integration curves for all the complexes agrees with the total number of protons calculated from the expected molecular formula, thus confirming complex formation.

¹³C NMR data

The spectra of the di-, tri- and tetra-sodium salts of ethylenediaminetetraacetic acid were recorded in D_2O and those of the complexes in a mixture of $CDCl_3$ and $DMSO-d_6$ (4:1) (Table 4). The number of signals found correspond with the presence of magnetically non-equivalent carbon atoms. In di- [9], tri- and tetra-sodium salts of EDTA, only one type of carboxylate group is present, as shown by the presence of only one signal, whereas in the case of complexes 2, 3, 11, 14 and 15 the appearance of two signals for the carboxyl carbons clearly shows two types of carboxyl groups. The high-field signal is assigned to the free carboxylic acid group and the lower field signal to the carboxylate bonded to tin(IV). In the triphenyl complexes. The identification of the alkyl/phenyl/cyclohexyl carbons in all the complexes confirms complex formation.

Mössbauer data

The ^{119m}Sn Mössbauer spectra (Table 5) are best interpreted on the basis of the quadrupole splitting (QS) values [10]. In diorganotin(IV) complexes, when the

| | Compound | IS (SnO ₂) | $QS \pm 0.06$ | Line v | vidths | $\rho = QS/IS$ |
|---|--|------------------------|---------------|--------|--------|----------------|
| | | ± 0.08 | | 1 | 2 | |
| 5 | $(n-C_4H_9)_2$ Sn EDTAH ₂ (1:1) | 1.30 | 3.14 | 1.22 | 1.49 | 2.41 |
| } | $[(n-C_4H_9)_2Sn]_2EDTA(2:1)$ | 1.28 | 2.98 | 1.04 | 1.42 | 2.33 |
|) | $[(n-C_4H_9)_2Sn]_1[EDTAH]_2(3:2)$ | 1.31 | 3.11 | 1.27 | 1.45 | 2.37 |
| 5 | $[(C_6H_{11})_3Sn]_3EDTAH(3:1)$ | 1.39 | 2.99 | 1.06 | 1.32 | 2.15 |

Table 5 ^{119m}Sn Mössbauer data (80 K, mm s⁻¹)

donor atoms are highly electronegetive, the QS is mainly determined by the C-Sn-C bond angle and distortion from a regular six coordination gives values similar to those for five coordination [6]. The Mössbauer data (IS 1.24–1.55 and QS 3.10–3.70 mm s⁻¹) for diorganotin carboxylates supports a distorted *trans* octahedral geometry around tin(IV) [11]. In the present investigation, the QS values in complexes 3 and 10 fall in the range of five and six coordinated distorted structures. However, the infrared data supports a five coordinate structure for complex 3 and a distorted octahedral structure for complex 10. The isomer shift values in complexes 8 and 15 lie in the range typical of triorganotin(IV) carboxylates [12] while the quadrupole splitting values lie in the range of triorganotin derivatives of amino acids with trans trigonal bipyramidal geometry around the tin atom [13]. Hence five coordinated trigonal bipyramidal geometry around the tin atom has been confirmed for complexes 8 and 15. The ρ value (QS/IS ratio) also supports a coordination number of tin higher than four.

Experimental

Materials

Trimethyl and tributyltinchlorides were obtained from Alfa products. Tricyclohexyltinchloride was obtained from Aldrich. Dibutyl- and dioctyltindichlorides were prepared by the reported method [14]. Di-, tri- and tetra-sodium salts of ethylenediaminetetraacetic acid were obtained from Alfa products.

Preparation of silver salts of ethylenediaminetetraacetic acid (EDTAH₄)

The silver salts of Na_2EDTAH_2 , Na_3EDTAH and Na_4EDTA were prepared by the addition of the required amount of silver nitrate to a solution of sodium salt of $EDTAH_4$ in distilled water. The silver salt of the EDTA precipitated and was separated by filtration, washed several times with hot water and dried under vacuum.

 $EDTAH_{2}Na_{2} + 2AgNO_{3} \rightarrow EDTAH_{2}Ag_{2} + 2NaNO_{3}$ $EDTAHNa_{3} + 3AgNO_{3} \rightarrow EDTAHAg_{3} + 3NaNO_{3}$ $EDTANa_{4} + 4AgNO_{3} \rightarrow EDTAAg_{4} + 4NaNO_{3}$

Preparation of complexes

Di-, tri- and tetra-silver salts of ethylenediaminetetraacetic acid (EDTA) (1.0 mmol for 1:1, 2:1, 3:1 and 2.0 mmol for 3:2 (metal/ligand)) were dissolved in



absolute ethanol (30 cm³). To this solution, was added a solution of diorganotindichloride (1.0 mmol for 1:1, 2.0 mmol for 2:1 and 3.0 mmol for 3:2) and triorganotinchloride (3.0 mmol for 3:1) dissolved in absolute ethanol (10 cm³). The reaction mixture was refluxed on a water bath. The pink-coloured silver chloride started separating out within 10–15 min. The reaction mixture was further refluxed for 4 h until all the silver chloride separated out. This was removed by filtration and washed with absolute ethanol. From the filtrate, the ethanol was removed by distillation leaving a solid or a liquid complex which was dried under vacuum. All the complexes were recrystallized from absolute ethanol.



Fig. 2. R = Me, ⁿPr, ⁿBu, ⁿOct (1:2).



Fig. 3. R = Me, "Bu, Ph, Cyh (1:3).

Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen were carried out by Microanalytical Service R.S.I.C., Panjab University, Chandigarh. Tin was estimated as SnO₂. Infrared spectra were recorded on Pye–Unicam SP3-300 spectrometer as KBr discs. The ¹H and ¹³C NMR spectra were recorded on Brucker AC 200 spectrometer using tetramethylsilane as internal standard. Mössbauer spectra were recorded on a Harwell 6000 series spectrometer with samples at about 80 K and source Pd/Sn at room temperature; isomer shifts are relative to SnO₂ at room temperature.

Conclusions

Interesting structural information has been obtained from IR, NMR and Mössbauer spectral studies. Diorganotin(IV) 1:1 and 1:2 and triorganotin(IV) 1:3 complexes possess a five coordinate distorted trigonal bipyramidal geometry around the Sn atom (Figs. 1–3). The trinuclear 3:2 complexes have six coordinate distorted octahedral geometry around the Sn atom with one bridging R_2 Sn moiety (Fig. 4).



Fig. 4. $R = {}^{n}Bu$, ${}^{n}Oct$ (3:2).

Acknowledgment

Financial assistance from CSIR is gratefully acknowledged.

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