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Novel triorganotin(IV) complexes of β -diketonates bearing two heterocycles in their structures

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ABSTRACT

Novel triorganotin(IV) derivatives of β -diketonate Q ligands (HQ in general, in detail HQ^{fur} = 1-phenyl-3-methyl-4-(2-furancarbonyl)-pyrazol-5-one, HQ^{thi} = 1-phenyl-3-methyl-4-(2-thienylcarbonyl)-pyrazol-5-one) of general formula (Q)SnR₃·xH₂O (R = Ph, *x* = 0; R = Buⁿ or Me, *x* = 1) have been synthesized and spectroscopically and thermally characterized. Triphenyltin(IV) complexes have been isolated as anhydrous compounds while trialkyltin(IV) are always monohydrated. The structures of (Q^{fur})SnPh₃ and (Q^{thi})SnMe₃(OH₂) are recorded. The tin atoms are five-coordinate in both. In the first, the pyrazolonate ligand behaves as an 0,0'-bidentate; there are two similar but independent molecules in the structure. In the *quasi*-trigonal-bipyramidal environments, Sn–O(acyl) are 2.478(3), 2.364(3), Sn–O(pyrazolonate) 2.050(2), 2.079(2), Sn–C 2.123(4)–2.162(3) Å with the longer O(acyl) and a phenyl group *quasi*-trans (O–Sn–C 162.5(1), 160.8(1)°). In (Q^{thi})SnMe₃(OH₂), the three methyl groups are equatorial (Sn–C 2.1259(9)–2.1380(8) Å); Sn–O(Q^{thi},OH₂) are 2.2143(5), 2.3350(6) Å, O–Sn–O 175.36(2)°. Trimethyltin(IV) derivatives decompose on heating with release of H₂O and SnMe₄ and formation of (Q)₂SnMe₂. Decomposition occurs also within two days after dissolution of (Q)SnMe₃(OH₂) in chloroform.

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1. Introduction

Among organometallic compounds, those of tin(IV) play a special role, due to their wide application in industry as wood preservatives, stabilizers for PVC, marine antifouling agents, and in agriculture as fungicides and biocides [1]. In addition, many organotin(IV) compounds have been tested for their *in vitro* activity against a large variety of tumor lines and have been found to be as effective or better than traditional heavy metal anticancer drugs such as *cis*-platin [2].

The rapid rise in the industrial, agricultural and biological applications of organotin(IV) compounds during the last few decades has led to their accumulation in the environment and in biological systems [3]. In particular, the trialkyltin(IV) $[R_3Sn(IV)]^+$ and triaryl-tin(IV) $[Ar_3Sn(IV)]^+$ derivatives exert powerful toxic actions on the central nervous system. Within series of $[R_3Sn(IV)]^+$ compounds, the lower homologues (R = methyl, Me; ethyl, Et) are the most toxic when administrated orally; the toxicity diminishes progressively from tri-*n*-propyl to tri-*n*-octyl, the latter tending not to be toxic at all [4].



Our long interest in organotin(IV) chemistry has been particularly concerned with their coordination and structural chemistry with chelating N- and O-donor ligands such as tris(pyrazolyl)borates [5], bis- and tris-(pyrazolyl)alkanes [6] and 4-acyl-5pyrazolonates [7]. The latter are well known β -diketonate-type donors, widely used as extractants and sequestering agents toward heavy metals [8]. Previous reports on tin(IV) acylpyrazolonates have shown interesting structural features [9] and some of them



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have also displayed interesting anti-proliferative effects on some human melanoma cell lines, particularly toward SK-MEL-5, which is intrinsically resistant to all conventional treatment modalities [10].

Here we extend our studies on different acylpyrazolones containing a heterocycle with an additional donor atom in the acyl pendant, in particular 2-substituted furan and thiophene rings (Chart 1), and on their interaction toward triorganotin(IV) acceptors, where the organic group is methyl, *n*-butyl or phenyl. These proligands are potentially polydentate donors and could be useful in the design and construction of inorganic polynuclear materials.

2. Experimental

2.1. General comments

The tin(IV) and organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The proligands HQ^{fur} and HQ^{thi} were prepared according to the literature [7]. The reactions were carried out under an N_2 stream using Schlenk techniques. Solvents were dried by standard techniques and distilled prior to use.

The samples for microanalyses were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyzer. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin-Elmer System 2000 FT-IR instrument. ¹H and ¹¹⁹Sn NMR spectra were recorded on a Mercury Plus Varian 400 spectrometer operating at room temperature (400 MHz for ¹H and 149.3 MHz for ¹¹⁹Sn). The ¹¹⁹Sn NMR experiments were carried out aliasing by varying the centre of the window, to avoid falling-out resonances, with a spectral width of 900 ppm. Melting points were taken on an IA 8100 Electrothermal Instrument. The electrical conductivity measurements ($\Lambda_{\rm M}$, reported as S cm² mol⁻¹) of the dichloromethane solutions were measured with a Crison CDTM 522 conductimeter at room temperature. TGA-DTA spectra were obtained with a STA 6000 Simultaneous Thermal Analyzer Perkin-Elmer by conducting the thermal studies under an inert atmosphere of dry nitrogen.

2.2. Syntheses

2.2.1. Ligands

The proligands HQ^{fur} and HQ^{thi} were synthesized using the procedure reported by Jensen [11].

2.2.1.1. 1-Phenyl-3-methyl-4-(2-furancarbonyl)-pyrazol-5-one (HQ^{fur}). Yield 71%. M.p. 103–105 °C. Elemental analyses: Anal. Calc. for C₁₅H₁₂N₂O₃: C, 67.16; H, 4.51; N, 10.44. Found: C, 66.91; H, 4.67; N, 10.40%. IR (nujol) data: 3350br v(N–H···O), 3095w v(C–H_{arom}), 2700br v(O–H···O), 1630vs v(C=O), 1580s, 1528s v(C=N + C=C), 689s, 651m, 604m, 585m, 510m, 391m, 291w. ¹H (CDCl₃) NMR: δ 2.63s, (3H, C3–CH₃), 6.66q, 7.32t, 7.72t (3H, C(=O)C₄H₃O), 7.38t, 7.43t, 7.29d (5H, N–C₆H₅), 11.5br, (1 H, OH···O).

2.2.1.2. 1-Phenyl-3-methyl-4-(2-thienylcarbonyl)-pyrazol-5-one (**HQ**^{thi}). Yield 65%. M.p. 152–155 °C. Elemental analyses: Anal. Calc. for C₁₅H₁₂N₂O₂S: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 63.49; H, 4.29; N, 9.57; S, 11.04%. IR (nujol) data: 3400br v(N–H···O), 2600br v(O–H···O), 3089w v(C–H_{arom}), 1626vs v(C=O) 1601s, 1515m v(C=N + C=C), 688m, 670m, 635m, 608w, 595m, 563w, 514w, 490m, 432w, 408m, 383s, 369s, 314m, 296w, 277s. ¹H (CDCl₃) NMR: δ 2.45s, (3H, C3-CH₃), 7.17t, 7.27t, 7.74d (3H, C(=O)C₄H₃S), 7.47t, 7.72t, 7.85d (5H, N–C₆H₅), 10.5br, (1 H, OH···O).

2.2.2. Metal complexes

2.2.2.1. $(Q^{fur})SnPh_3$ (1). A benzene solution (30 cm^3) of $(Ph_3Sn)_2O$ (1.0 mmol) was added to a benzene solution (30 cm^3) of the ligand HQ^{fur} (2.0 mmol), and the reaction mixture was refluxed for about 2 h. After removing the solvent under reduced pressure on a rotary evaporator, a thick oil was obtained. This was treated with diethyl ether and petroleum ether, and a solid formed, which was re-crystallized from a benzene/petroleum ether mixture. It is soluble in chloroform, benzene, methanol, acetone, acetonitrile and dmso. Yield 64%. M.p. 119-122 °C. Elemental analyses: Anal. Calc. for C33H26N2O3Sn: C, 64.21; H, 4.25; N, 4.54. Found: C, 64.48; H, 4.32; N, 4.68%. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. 10⁻³ M): 0.7 S cm² mol⁻¹. IR (nujol) data: 3129w v(C-H_{arom}), 1603vs v(C=O), 1592s, 1555s, 1523s v(C=N+C=C), 273s, 257vs, 236s v(Sn-C), 454s, 444vs, 369s v(Sn–O), 689s, 658m, 629s, 607m, 592m, 509m, 391w, 291m. ¹H (CDCl₃) NMR (293K): δ. 2.22s. 2.44s (3H, C3–CH₃), 6.53br, 6.61br, 7.40m, 7.64m, 7.76m (23H, Sn-C₆H₅, C(=0)C₄H₃O and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ, 17.5s (C3-CH₃), 127.5-129.5vbr, 135.7s (²J_(Sn-C): 58.4 Hz) 137.1s (²J_(Sn-C): 61.3 Hz), 145.9s, 146.4s (Carom of Sn-Ph), 118.7s, 119.5s, 121.2br, 122.7br, 126.2br, 126.6s, 127.5-129.5vbr, 129.7s, 148.3s, 149.1s, 151.3s (Caromatic of Q^{fur}), 112.7s, 112.9 (C4), 137.9s, 138.1s (C3), 163.9s, 165.2 (C5), 175.0s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ, -176, -180br. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; at 122.0 °C onset of fusion (ΔH_{fusion} = 7.0 kJ/mol), then at 178.6 °C another endothermal event ($\Delta H = 23.7 \text{ kJ/mol}$), from 180 to 500 °C progressive decomposition, with a final residue of 41% weight. Derivatives **2–4** were synthesised in a similar way.

2.2.2.2. (Q^{thi})SnPh₃ (2). Yield 67%. M.p. 130–132 °C. Elemental analyses: Anal. Calc. for C33H26N2O2SSn: C, 62.58; H, 4.14; N, 4.42; S, 5.06. Found: C, 62.31; H, 4.23; N, 4.53; S, 4.83%. Am (CH₂Cl₂, conc. 10^{-3} M): 0.6 S cm² mol⁻¹. IR (nujol) data: 3097w, 3066w v(C-H_{ar-} om), 1600s v(C=O), 1593sh, 1569vs, 1558s, 1515s v(C=N+C=C), 259s, 247s, 233m v(Sn-C), 447vs, 427s, 347s, 327m v(Sn-O), 692s, 670m, 649s, 624m, 571m, 538m, 510m, 485m, 405w, 393w, 294w, 276s, ¹H (CDCl₃) NMR (293 K): δ, 2.06br, 2.23s (3H, C3-CH₃), 7.05br, 7.10t, 7.30-7.50m, 7.60m 7.70t, 7.87br (23H, Sn-C₆H₅, C(=O)C₄H₃S and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ , 16.9s, 17.1s (C3-CH₃), 128.0-130.0vbr, 135.7s (²J_(Sn-C): 59.1 Hz) 137.0s (²*J*_(Sn-C): 64.7 Hz), 148.2s, (*C*_{arom} of Sn-Ph), 120.5br, 121.1br, 122.8s, 126.3s, 127.3s, 127.9s, 128.0-130.0vbr, 138.0s, 148.7s ($C_{aromatic}$ of Q^{thi}), 104.2s, 105.5 (C4), 135.4s, 136.8s (C3), 163.3s, 164.7 (C5), 182.1s, 183.3s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ, +188, -131. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; from 140 to 500 °C progressive decomposition, with a final residue of 42% weight.

2.2.2.3. (Q^{fur})SnBuⁿ₃·H₂O (**3**). Yield 64%. M.p. 120–123 °C. Elemental analyses: Anal. Calc. for C₂₇H₄₀N₂O₄Sn: C, 56.37; H, 7.01; N, 4.87. Found: C, 56.17; H, 7.14; N, 4.91%. A_m (CH₂Cl₂, conc. 10⁻³ M): 0.9 S cm² mol⁻¹. IR (nujol) data: 3156vbr v(H₂O), 3091w v(C-H_{ar}om), 1587s v(C=O), 1564s, 1528vs, 1514s v(C=N+C=C), 608vs, 532 m v(Sn-C), 441s, 386s, 349s v(Sn-O), 692s, 677s, 660s, 647m, 593m, 499m, 392w, 290m, 251m. ¹H (CDCl₃) NMR (293 K): δ, 0.82t, 0.90t, 1.13m, 1.24m, 1.40-1.70m br (27H, Sn-C₄H₉), 2.04s, 2.33s (3H, C3-CH₃), 2.65br (2H, H₂O), 6.56dbr, 7.21br, 7.26t, 7.42t, 7.63br, 7.78d (8H, C(=0)C₄ H_3 O and N-C₆ H_5). ¹³C (CDCl₃) NMR (293 K): δ , 19.1s, 27.0s, 27.3s, 27.8s (¹J_(Sn-C): 356 Hz; ²J_(Sn-C): 19 Hz, ³J_(Sn-C): 74 Hz) (Sn-CH₂CH₂CH₂CH₃), 13.8s (C3-CH₃), 117.6s, 122.7s, 126.3s, 128.8s, 145.5s, 150.4s (Caromatic of Q^{fur}), 111.9s (C4), 138.9s (C3), 163.2s (C5), 172.4s (C0). ¹¹ (CDCl₃) NMR (293 K): δ , +140, -175. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; from 80 to 100 °C loss of one water molecule (weight loss found 3.08%, calcd. 3.12%, ΔH = 12.3 kJ/mol), from 140 to 500 °C progressive decomposition,

with a final residue of 24% weight corresponding to SnO (calcd. 23.41%).

2.2.2.4. (Q^{thi})SnBu₃ⁿ·H₂O (**4**). Yield 73%. M.p. 121–122 °C. Elemental analyses: Anal. Calc. for C₂₇H₄₀N₂O₃SSn: C, 54.84; H, 6.82; N, 4.74; S, 5.42. Found: C, 54.96; H, 6.95; N, 4.85; S, 5.22%. A_m (CH₂Cl₂, conc. 10^{-3} M): 0.7 S cm² mol⁻¹. IR (nujol) data: 3257vbr v(H₂O), 3094w v(C-H_{arom}), 1661 m δ(H₂O), 1571s v(C=O), 1536vs, 1510s v(C=N+C=C), 617m, 604s, 519m v(Sn-C), 444m, 439m, 369m, 344s v(Sn-O), 691s, 676m, 652m, 640m, 562m, 496m, 408w, 392w, 290m, 252m. ¹H (CDCl₃) NMR (293 K): δ, 0.81t, 1.02t, 1.18m, 1.42m, 1.80m br (27H, Sn-C₄H₉), 2.10br (2H, H₂O), 2.18br, 2.31br (3H, C3–CH₃), 7.11t, 7.25t, 7.39t, 7.59d, 7.73t (8H, C(=O)C₄H₃S and N–C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ , 18.5s, 26.9s, 27.3s, 27.7s (¹*J*_(Sn-C): 342 Hz; ²*J*_(Sn-C): 18 Hz, ³*J*_(Sn-C): 72 Hz) (Sn-CH₂CH₂CH₂CH₃), 13.8s (C3-CH₃), 122.9s, 126.5s, 127.5s, 128.3s, 132.1s, 132.7s, 149.2s, 150.1s ($C_{aromatic}$ of Q^{thi}), 103.5s (C4), 138.2s (C3), 163.0s (C5), 182.2s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ , +154, -176. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; from 80 to 100 °C loss of one water molecule (weight loss found 2.98%, calcd. 3.04%, ΔH = 63.8 kJ/mol), from 140 to 500 °C progressive decomposition, with a final residue of 25% weight corresponding to SnS (calcd. 25.49%).

2.2.2.5. $(Q^{fur})SnMe_3 H_2O(5)$. A benzene solution (30 cm³) of the ligand HQ^{fur} (1.0 mmol) was added to a methanolic solution (10 cm³) of sodium methoxide (1.0 mmol) and refluxed for 1 h. A benzene solution (20 cm³) of Me₃SnCl (1.0 mmol) was then added to the above solution dropwise and the reaction mixture was stirred at room temperature for about 3 h. Sodium chloride was filtered off and the solvent removed under reduced pressure on a rotary evaporator until a thick oil was obtained. This was treated with diethyl ether and light petroleum, and a brown solid afforded. It was re-crystallized from benzene/petroleum ether mixture and shown to be compound 5. Yield 66%. M.p. 130-132 °C. Elemental analyses: Anal. Calc. for C18H22N2O4Sn: C, 48.14; H, 4.94; N, 6.24. Found: C, 47.87; H, 4.90; N, 6.09%. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. 10⁻³ M): 1.1 S cm² mol⁻¹. IR (nujol) data: 3105vbr $v(H_2O)$, 1577s v(C=O), 1521vs, 1501s v(C=N + C=C), 558vs, 545s, 534sh v(Sn-C), 430m, 389m, 340s v(Sn-O), 689s, 661s, 649m, 621m, 608m, 590m, 502m, 401w, 305m, 299m, 251m. ¹H (CDCl₃) NMR (293 K): δ, 0.49s (²J_(Sn-H): 56.4 Hz) (9H, Sn-CH₃), 1.25s (2H, H₂O), 2.36s (3H, C3-CH₃), 6.57br, 6.61br, 7.19br, 7.27t, 7.41t, 7.62br, 7.67br, 7.79d, 7.93d (8H, C(=O)C₄H₃O and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ , -0.5s (¹ $J_{(Sn-C)}$: 387 Hz) (Sn-CH₃), 14.7s (C3-CH₃), 117.2s, 122.6s, 126.5s, 128.7s, 132.3s, 145.8s, 150.5s (Caromatic of Q^{fur}), 110.9s (C4), 138.6s (C3), 163.3s (C5), 172.6s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ , +149br. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; from 80 to 140 °C $(\Delta H = 11.23 \text{ kJ/mol})$ loss of one water molecule and one-half of SnMe₄ (total weight loss found 25.0%, calcd. 23.9%), at 141.3-160.8 °C onset of fusion ($\Delta H_{\text{fusion}} = 8.98 \text{ kJ/mol}$), from 170 to 500 °C progressive decomposition, with a final residue of 31% weight corresponding to SnO (calcd. 30.00%). Derivative 6 was synthesised in a similar way.

2.2.2.6. $(Q^{thi})SnMe_3 \cdot H_2O$ (**6**). Yield 80%. M.p. 134–136 °C. Elemental analyses: *Anal.* Calc. for C₁₈H₂₂N₂O₃SSn: C, 46.48; H, 4.77; N, 6.02; S, 6.89. Found: C, 46.28; H, 4.86; N, 5.92; S, 6.65%. Λ_m (CH₂Cl₂, conc. 10⁻³ M): 0.9 S cm² mol⁻¹. IR (nujol) data: 3105vbr ν (H₂O), 1681mbr δ (H₂O), 1561s ν (C=O), 1538vs, 1508vs ν (C=N + C=C), 553vs, 542s ν (Sn–C), 442sh, 430 m, 373 m, 348 m ν (Sn–O), 689s, 675m, 650m, 616w, 602m, 519w, 497w, 402w, 306m, 251m. ¹H (CDCl₃) NMR (293 K): δ , 0.37s (²_{J(Sn–H)}: 53.2 Hz) (9H, Sn–CH₃), 1.24s (2H, H₂O), 2.30s (3H, C3–CH₃), 7.12t, 7.25t, 7.40 m, 7.60d,

7.68d, 7.77d (8H, C(=O)C₄H₃S and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ, -0.8s (¹*J*_(Sn-C): 365 Hz) (Sn-CH₃), 16.0s (C3-CH₃), 122.5s, 126.4s, 127.4s, 128.9s, 131.9s, 132.5s, 149.0s, 150.3s (*C*_{aromatic} of Q^{thi}), 103.7s (C4), 138.5s (C3), 163.1s (C5), 182.8s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ, +173, -175. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; from 80 to 140 °C loss (Δ*H* = 92.5 kJ/mol) of one water molecule and one-half of SnMe₄ (total weight loss found 24.0%, calcd. 23.1%), at 142.9 °C onset of fusion (Δ*H*_{fusion} = 12.3 kJ/mol), from 160 to 500 °C progressive decomposition, with a final residue of 32% weight corresponding to SnS (calcd. 32.41%).

2.2.2.7. $(Q^{fur})_2 SnMe_2$ (7). To a methanol solution (30 ml) of Q_SH (2 mmol) were added KOH (2 mmol) and (CH₃)₂SnCl₂ (1 mmol). A precipitate formed immediately. The mixture was stirred overnight and the precipitate was then filtered off, washed with methanol (10 ml) and dried under reduced pressure at room temperature. This was recrystallised from chloroform/methanol and shown to be compound 7. Yield 86%. M.p. 170–174 °C. Elemental analyses: Anal. Calc. for C32H28N4O6Sn: C, 56.25; H, 4.13; N, 8.20. Found: C, 56.14; H, 4.20; N, 8.03%. $\Lambda_{\rm m}$ (CH₂Cl₂, conc. 10⁻³ M): $0.5 \text{ S cm}^2 \text{ mol}^{-1}$. IR (nujol) data: 3050w v(C-H_{arom}), 1601m, 1591s v(C=0), 1574s, 1542s, 1524s v(C=N+C=C), 593m, 583s, 532m v(Sn-C), 476s, 437m, 396m, 374s v(Sn-O), 684s, 661s, 646m, 625vs, 615m, 508s, 405w, 335w, 296m, 280m, 254w. 246w. ¹H (CDCl₃) NMR (293 K): δ, 0.96s (²J_(Sn-H): 98.8 Hz) (6H, Sn-CH₃), 2.31s (6H, C3-CH₃), 6.62d, 7.25m, 7.67d, 7.93d (16H, C(=O)C₄H₃O and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ , 9.6s (¹J_{(Sn-} C: 928 Hz) (Sn-CH₃), 17.2s (C3-CH₃), 118.8s, 121.5s, 125.9s, 129.1s, 146.1s, 148.8s, 151.8s (*C*_{aromatic} of Q^{fur}), 112.6s (*C*4), 138.4s (*C*3), 163.4s (*C*5), 176.1s (*C*0). ¹¹⁹Sn (*C*DCl₃) NMR (293 K): δ , -323. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; at 141.3–160.8 °C onset of fusion ($\Delta H_{\rm fu-}$ sion = 8.9 kJ/mol), from 170 to 500 °C progressive decomposition, with a final residue of 31% weight corresponding to SnO (calcd. 30.00%). Derivative 8 was synthesised in a similar way.

2.2.2.8. (Q^{thi})₂SnMe₂ (8). Yield 81%. M.p. 165–166 °C. Elemental analyses: Anal. Calc. for C₃₂H₂₈N₄O₄S₂Sn: C, 53.72; H, 3.94; N. 7.83; S, 8.96. Found: C, 53.46; H, 4.05; N, 7.82; S, 8.64%. Am $(CH_2Cl_2, \text{ conc. } 10^{-3} \text{ M})$: 0.6 S cm² mol⁻¹. IR (nujol) data: 3097w v(C-H_{arom}), 1593s v(C=O), 1548vs, 1520s v(C=N+C=C), 589m, 572s, 542m v(Sn-C), 456m, 428s br, 375m, 356s v(Sn-O), 694s, 646s, 640sh, 622s, 509m, 491w, 404w, 301w, 289w, 274w, 251w, 247w. ¹H (CDCl₃) NMR (293K): δ , 0.97s (²J_(Sn-H): 98.0 Hz) (6H, Sn-CH₃), 2.15s (6H, C3-CH₃), 7.13t, 7.25m, 7.54d, 7.65d, 7.96d (16H, C(=0)C₄H₃S and N-C₆H₅). ¹³C (CDCl₃) NMR (293 K): δ , 9.6s (¹J_(Sn-C): 901 Hz) (Sn-CH₃), 16.9s (C3-CH₃), 121.4s, 125.9s, 127.5s, 129.2s, 132.3s, 133.0s, 148.6s ($C_{\rm aromatic}$ of $Q^{\rm thi}$), 104.9s (C4), 138.4s (C3), 162.7s (C5), 182.6s (CO). ¹¹⁹Sn (CDCl₃) NMR (293 K): δ , -315. TGA-DTA (mg% vs. °C): heating from 30 to 500 °C with a speed of 5 °C/min; at 142.9 °C onset of fusion (ΔH_{fusion} = 12.3 kJ/ mol), from 160 to 500 °C progressive decomposition, with a final residue of 32% weight corresponding to SnS (calcd. 32.41%).

2.3. Structure determinations

Full sphere of 'low'-temperature CCD/area detector diffractometer data were measured (monochromatic Mo K α radiation ($\lambda = 0.7107_3$ Å), ω -scans) yielding N_{total} reflections, these merging to N unique (R_{int} cited) after absorption correction, these being used in the full matrix least squares refinements on F^2 , refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Reflection weights were ($\sigma^2(F_o^2) + (aP)^2$ (+ bP))⁻¹ ($P = (F_o^2 + 2F_c^2)/3$). N_o reflections with I > 2(I) were considered 'observed'. Results are given below and in the tables and figures, the latter showing nonhydrogen atom ellipsoids at the 50% probability amplitude level, hydrogen atoms having arbitrary radii of 0.1 Å. Neutral atom complex scattering factors were used within the SHELXL 97 program [12].

2.3.1. Crystal/refinement data

2.3.1.1. $(Q^{fur})SnPh_3$ (1). $C_{33}H_{26}N_2O_3Sn$, M = 617.3. Triclinic, space group $P\bar{1}$ (C_i^1 , No. 2), a = 11.802(2), b = 13.937(3), c = 18.225(4) Å, $\alpha = 108.913(4)$, $\beta = 101.353(5)$, $\gamma = 97.104(5)^\circ$, V = 2723(1) Å³ (*T ca.* 153 K). D_c (Z = 4) = 1.506 g cm⁻³. $\mu_{Mo} = 0.98$ mm⁻¹; specimen: 0.36 × 0.36 × 0.15 mm; ' $T_{min/max} = 0.90$ ('empirical'/multiscan correction). $2\theta_{max} = 70^\circ$; $N_t = 45928$, N = 22950 ($R_{int} = 0.034$), $N_o = 14725$; $R_1 = 0.049$, $wR_2 = 0.16$ (a = 0.062, b = 4.9); S = 1.09.

2.3.1.2. $(Q^{thi})SnMe_3(OH_2)$ (**6**). $C_{18}H_{22}N_2O_3SSn$, M = 465.1. Monoclinic, space group P_{21}/c $(C_{2h}^5$, No. 14), a = 11.7698(1), b = 10.2815(1), c = 16.2938(2) Å, $\beta = 98.608(1)^\circ$, V = 1949.52(3) Å³ (*T* ca. 100 K). D_c (Z = 4) = 1.585 g cm⁻³. $\mu_{Mo} = 1.44$ mm⁻¹; specimen: 0.44 × 0.27 × 0.23 mm; ' $T_{min}/max = 0.87$. $2\theta_{max} = 112^\circ$; $N_t = 214648$, N = 25798 ($R_{int} = 0.039$), $N_o = 17174$; $R_1 = 0.029$, $wR_2 = 0.074$ (a = 0.038); S = 0.97.

Variata. Water molecule hydrogen atoms were located and refined.

3. Results and discussion

3.1. Synthesis of derivatives 1-8

Derivatives **1–4** have been synthesized by direct interaction between HQ (HQ = HQ^{fur} or HQ^{thi}) proligands and $(R_3Sn)_2O$ (R = Ph or Buⁿ) in benzene at reflux. By contrast, trimethyltin(IV) derivatives **5** and **6** have been synthesized from interaction between the sodium salts of 4-acyl-5-pyrazolones and Me₃SnCl in benzene at room temperature. While triphenyltin(IV) derivatives **1** and **2** are air and moisture stable, all of the others (**3–6**) absorb water when exposed to atmosphere, and have been characterized as monohydrated compounds (Q)SnR₃(OH₂) (R = Me or Buⁿ) (Scheme 1). They are very soluble in all common organic solvents, such as chloroform, benzene, methanol, acetone, acetonitrile and dmso, but insoluble in saturated hydrocarbons and water. Conductivity measurements in acetonitrile and acetone have confirmed their nonelectrolyte nature.

The dimethyltin(IV) derivatives **7** and **8** have been synthesized from dimethyltin(IV) dichloride in methanol and sodium methoxide by using a 1:2 metal to ligand ratio (Scheme 2). They are air and moisture stable, highly soluble in chlorohydrocarbon solvents, dmso and acetone, where they are non-electrolytes, and insoluble in diethyl ether, alcohols, hydrocarbons and water.



3.2. Infrared Spectroscopy

In the solid state, the proligands HQ are likely to exist as a mixture of both the amino-diketonic form, exhibiting a broad absorption due to an intermolecular v(N-H···O) mode in the range 3350-3400 cm⁻¹, and of the keto-enol form with an intramolecular *v*(O– H…O) mode that affords a very broad band at $2600-2700 \text{ cm}^{-1}$ [13]. Upon coordination these absorptions disappear and the v(C=0) at 1626–1630 cm⁻¹ undergoes a red shift in the range 1603–1561 cm⁻¹, in accordance with deprotonation of HQ and involvement of both carbonyl groups in bonding with the metal, particularly in the case of derivatives 1 and 2; in the monohydrate derivatives **3–6** we find weak interactions with neighbouring hydrogen atoms of a water molecule resulting in a broad band between 3100 and 3250 cm⁻¹, as previously observed for similar compounds [9d]. Below the v(C=0) band down to 1500 cm⁻¹ we have assigned the vibrations of the azomethine bond in the pyrazole and the v(C=C) of Ph and heteroaromatic rings. By careful comparison of the far-IR of the proligands and their tin derivatives, we have also tentatively assigned as v(Sn-O) modes some new strong bands in the range $400-500 \text{ cm}^{-1}$ [14].

In the far-IR spectra of triphenyltin(IV) derivatives **1** and **2** the $v_{as}(Sn-C)$ and $v_s(Sn-C)$ have been observed in the range 200–300 cm⁻¹ [15], whereas for tributyl- and trimethyl-tin(IV) derivatives **3–6** novel absorptions in the range 500–620 cm⁻¹ due to $v_{as}(Sn-C)$ and $v_s(Sn-C)$ modes have been assigned thus [16]. The presence of $v_s(Sn-C)$ in the far-IR of the monohydrate derivatives **3–6** seems to indicate (for a TBP *trans*-O–SnR₃-O system) a deviation from planarity of the SnR₃ moiety, with a lowering of the local symmetry from D_{3h} to C_{3v} . Moreover, the band at 3100–3200 cm⁻¹ in the IR spectra of **3–6** can be attributed to intermolecular H-bonded water [9d,17].

In the IR spectra of **7** and **8** the broad band of the neutral HQ proligands has disappeared upon coordination and the v(C=O) band is shifted to lower frequencies. In the far-IR region new absorptions due to Sn–C and Sn–O stretching modes have been







assigned, on the basis also of infrared studies on analogous compounds previously reported [9]. The presence of more than one v(Sn-C) mode seems indicative of some distortion from regular octahedral geometry.

3.3. NMR Spectroscopy

The proligands HQ exist in chloroform in the keto-enol tautomeric form as confirmed by the broad resonance up to 10.0 ppm in their ¹H NMR spectra, originating in (O-H…O) systems as previously observed in examples of other 4-acylpyrazolones [9]. The disappearance of such signals in the proton spectra of 1-6 indicates coordination of the donors in anionic form. Moreover, a slight shielding of C3–CH₃ in Q ligands is generally observed, while aromatic protons present a more complex pattern upon chelation. In the ¹H NMR of the triphenyltin(IV) adducts **1–2** it has not been possible to distinguish between signals due to aromatic protons of the ligand and those linked to tin, but integration takes their presence into account. By contrast, in the ¹H NMR of tributyland trimethyl tin(IV) derivatives 3-6 multiplets for butyl and singlets for methyl groups bound to tin have been found between 0 and 2 ppm, with tin-proton coupling constants ${}^{2}J_{(Sn-H)}$ in the range 55– 58 Hz for **5** and **6**, which is typical of tetracoordinate species [18].

We have observed that in solution derivatives **3–6** progressively decompose to tetraorganotin(IV) and diorganotin(IV) acylpyrazolonates. As an example here we describe the decomposition process of **5** as followed by the ¹H NMR technique over two days after dissolution of the sample in chloroform. Apart the set of proton resonances due to the starting species (Q^{fur})SnMe₃(OH₂), two new Sn–CH₃ resonances appear in the ¹H NMR spectrum at 0.06 ppm (${}^{2}J_{(Sn-H)}$: 53.0 Hz) and 0.96 ppm (${}^{2}J_{(Sn-H)}$: 100.4 Hz), together with an additional peak at 2.31 ppm (Fig. 1). This may be explained by a progressive decomposition of triorganotin(IV)

into tetraorganotin(IV) and diorganotin(IV) derivatives. In fact the resonance at 0.06 ppm is due to $Sn(CH_3)_4$ [19], while those at 0.96 and at 2.31 ppm can be attributed respectively to $Sn-CH_3$ and $C3-CH_3$ in the Q^{fur} component of $(Q^{fur})_2Sn(CH_3)_2$ [20].

An analogous behaviour has been previously observed in the case of $(acac)SnMe_3$ (acac = 2,4-pentanedionate) [21] and (oxin)SnMe₃ (oxin = 8-hydroxyquinolinato) [22]. By contrast, triphenyltin(IV) derivatives **1** and **2** are stable in solution for several days.

¹³C NMR spectra are in good agreement with previous observations. In detail, the values of the ¹*J*_(Sn-C) coupling constants of trimethyltin(IV) derivatives **5** and **6** are 387 and 365 Hz, respectively, and by applying the empirical relationship between ¹*J*_(Sn-C) and the angle θ (C-Sn-C) proposed by Holecek and Lycka (¹*J*_(Sn-C) = 9.99 θ (C-Sn-C) –746 [23]), values of 113 and 111° are calculated for θ (C-Sn-C), in accordance with all methyl groups in the equatorial plane of a trigonal bipyramidal environment on tin, and in good agreement with the structural results of derivative **6** (see below).

We have also performed ¹¹⁹Sn NMR studies at room temperature for derivatives **1–6** which absorb between –180 and +190 ppm. In particular, derivative **1** shows close resonances around –180 ppm, in a range typical of a five-coordinate *cis*-O₂SnR₃ TBP geometry [23], for which, in principle, the three isomers (a–c) shown in Scheme 3 are possible. Clearly, however, the isomer (c) is not feasible due to the steric limitations of the acylpyrazolonate ligand, so that only the former two isomers are likely, one with both carbonyl arms of Q^{fur} in equatorial positions and the other with one equatorial and one axial position occupied by the two oxygen atoms of Q^{fur} (Scheme 3).

By contrast, derivatives **2–4** and **6** display two well-separated resonances, one at negative values (in the range from -122 to -176 ppm) and the other at positive values (in the range from +140 to +188 ppm). In the case of **2** the value at +188 ppm can



be ascribed to the presence of a tetrahedral OSnPh₃ species arising from rupture of an Sn–O bond in the five-coordinate cis-O₂SnR₃ TBP geometry (Scheme 4). By contrast, for **3**, **4** and **6** the positive value arises from tetrahedral OSnR₃ species after breaking of the Sn–OH₂ bond in solution (Scheme 4) [24], while the negative value can be attributed to the aquo trialkyltin(IV) species having *trans*-O₂SnR₃ TBP geometry. An additional possibility is that the apical position of the water molecule is occupied by a sulfur or oxygen donor atom of the heterocycle (thiophene of furan) of a neighbouring complex molecule. However, ¹¹⁹Sn NMR studies carried out at different molar concentrations of the sample didn't afford any detectable shift in these resonances, as expected for the case of intermolecular interactions.

Finally, derivative **5** shows a unique resonance at +149 ppm, in accordance with fast and complete breaking of the Sn–OH₂ bond after dissolution of the sample in deuterochloroform and the presence of only the tetrahedral OSnMe₃ species.

¹H NMR spectra of **7** and **8** indicate a skewed *trans*-octahedral geometry about the tin atom, that has been inferred from the ${}^{2}J_{(Sn-H)}$, which are 98.8 and 98.0 Hz for **7** and **8**, respectively. By applying the Lockhart relationship between the C–Sn–C angle and tin-proton ${}^{2}J$ coupling constant [19a], angles of 160.1° and 158.6° have been calculated for **7** and **8**, respectively.



Scheme 4.







Fig. 3. IR spectra of derivative **5** and its intermediates recovered after heating to 100 °C and 170 °C respectively, compared with the IR of derivative **7**.

Further support comes from the ¹³C NMR spectra of **7** and **8**, values of ¹*J*_(Sn-C) being 925 and 901 Hz, respectively. In fact, on the basis of the empirical relation θ (C–Sn–C) = 0.178 × [¹*J*(¹³C–¹¹⁹Sn)] + 14.74, derived by Howard for octahedral dialkyltin complexes of type R₂SnCh₂ (R = alkyl, Ch = bidentate ligand) [25], the calculated C–Sn–C angles for **7** and **8** are 180 and 175° (angles calculated from this relationship have a standard error calculated as ±l2°).

In addition, ¹¹⁹Sn NMR spectra of **7** and **8** show unique resonances at -323 and -315 ppm, respectively, in close agreement with those of bis(acylpyrazolonate)dimethyltin(IV) derivatives previously reported and structurally characterized [9].

3.4. Thermal studies

Derivatives **1–6** display low apparent melting/decomposition points, within the range 118–136 °C. However thermal studies carried out with TGA-DTA techniques have shown a more complex behaviour on heating. In particular derivatives **3–6** undergo decomposition with the formation of different substances.

Detailed thermal studies have been performed for all derivatives 1-6 in the temperature range 30–500 °C under an inert atmosphere of dry nitrogen. The data indicate that anhydrous triphenyltin(IV) derivatives **1** and **2** are stable to decomposition







Fig. 5. Projection of molecule 1 of compound **1** quasi-normal to the acylpyrazolonate coordination plane (molecule 2 is similar). Non-hydrogen atoms are shown with 50% probability amplitude displacement envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

up to 180 and 140 °C, respectively, derivative **1** showing at 122.0 °C and 178.6 °C endothermic events assignable to fusion (the former) and decomposition (the latter), whereas derivative **2** seems to progressively decompose without a real fusion. Final black residues of more than 40% weight are probably a mixture of SnO (or SnS for **2**) and organic uncombusted material. By contrast, thermal runs of derivatives **3** and **5** containing the Q^{fur} ligand leave a residue corresponding to SnO, whereas for **4** and **6** with the sulfur-containing Q^{thi} ligand, the final residue is SnS, as confirmed by the good

Table 1

Metal atom environments, $\mathbf{1}$, (the two values in each entry are for molecules n = 1 and 2).

Atoms	Parameter	Atoms	Parameter			
Distances (Å)						
Sn(n)-O(n41)	2.478(3),	Sn(n)-C(n51)	2.141(3),			
	2.364(3)		2.149(3)			
Sn(n)-O(n5)	2.058(2),	Sn(n)-O(n61)	2.162(3),			
	2.079(2)		2.145(3)			
O(n41)-C(n41)	1.255(4),	Sn(n)-C(n71)	2.123(4),			
	1.273(4)		2.133(3)			
O(n5)-C(n5)	1.298(4),					
	1.298(4)					
Angles (°)						
O(n41)-Sn(n)-	76.19(9),	O(n5)-Sn(n)-	118.8(1),			
O(n5)	77.24(9)	C(n51)	123.0(1)			
O(n41)-Sn(n)-	81.1(1), 82.2(1)	O(n5)-Sn(n)-	86.4(1), 84.4(1)			
C(n51)		C(n61)				
O(n41)-Sn(n)-	162.5(1),	O(n5)-Sn(n)-	108.1(1),			
C(n61)	160.8(1)	C(n71)	109.7(1)			
O(n41)-Sn(n)-	81.0(1), 85.4(1)	C(n51)-Sn(n)-	106.1(1,			
C(n71)		C(n61)	103.9(1)			
Sn(n)-O(n41)-	129.5(2),	C(n51)-Sn(n)-	123.3(1),			
C(n41)	135.1(2)	C(n71)	121.0(1)			
Sn(1) = O(n5) =	125.4(2),	C(n61) - Sn(n) - Sn(106.8(1),			
C(n5)	132.9(2)	C(n71)	106.0(1)			
Interplanar dihedral angles (°) and atom deviations ($\delta Å$)						
C_3O_2/C_3N_2	9.0(1), 5.0(2)	C_3N_2/C_6	31.0(2), 21.6(2)			
Sn/C_3O_2	0.790(4),	C_3N_2/C_4O	39.7(2), 28.0(2)			
	0.002(5)					
Torsion angles (°) (carbon atoms denoted by number only)						
O(n41)-Sn(n)-	-152.6(3),	O(n5)-Sn(n)-	-83.8(3),			
n51-n52	-165.7(3)	n51-n52	-96.4(3)			
O(n41)-Sn(n)-	39.1(6), 40.2(5)	O(n5)-Sn(n)-	45.6(3), 56.2(3)			
n61-n62		n61-n62				
O(n41)-Sn(n)-	-68.4(3),	O(n5)-Sn(n)-	-140.5(3),			
n71-n72	-63.0(3)	n71-n72	-137.7(3)			

Table	2		
Metal	atom	environment,	6

Atoms	Parameter	Atoms	Parameter	
Distances (Å)				
Sn-C(10)	2.1380(8)	Sn-O(1)	2.3350(6)	
Sn-C(20)	2.1227(8)	Sn-O(5)	2.2143(5)	
Sn-C(30)	2.1259(9)			
Angles (°)				
O(1)-Sn-C(10)	85.57(3)	O(5)-Sn-C(10)	93.17(3)	
O(1)-Sn-C(20)	86.96(3)	O(5)-Sn-C(20)	90.15(3)	
O(1)-Sn-C(30)	90.06(3)	O(5)-Sn-C(30)	94.48(3)	
C(10)-Sn-C(20)	125.34(4)	O(1)-Sn-O(5)	175.36(2)	
C(10)-Sn-C(30)	116.96(4)	C(20)-Sn-C(30)	117.11(4)	
Sn-O(5)-C(5)	119.72(4)			
Torsion angles (°) (carbon atoms denoted by number only)				
5-N(1)-11-12	-44.3(1)	5-4-41-42	19.6(1)	
		4-41-42-46	16.3(1)	

O(1), H(1A)···O(41)(\bar{x} , 1 - y, 1-z) 2.6626(9), 1.86(1) (O-H 0.82(1) Å); O(1), H(1B)···N(2)(x, 3/2 - y, z - ½) 2.7645(9), 1.91(2) (O-H 0.87(2) Å).

correspondence between experimental and calculated weight losses. Such thermal behaviour is typical and well known for alkyltin(IV) complexes with O- or S-containing ligands [26].

The aquo $Bu^n_3 Sn(IV)$ derivatives **3–4** lose their coordinated water, endothermal dehydration taking place in a single step within the range 80–100 °C (see Fig. 2), as confirmed by comparison of theoretical and experimental values of percentage weight reduction. Further support is provided by the close correspondence of the IR spectra of the powders recovered after heating derivatives **3–4** to 100 °C, with those of the starting compounds, the only



Fig. 6. (a) Projection of the molecule of 6; (b) hydrogen-bonding in 6, showing the formation of a polymer of dimers, along c.

difference being the disappearance of the broad absorption due to Sn-coordinated water in the range from 3100 to 3250 cm⁻¹. After dehydration, other endothermic events are observed at higher temperatures, probably due to melting, with decomposition of anhydrous (Q)SnBu₃ substances.

Trimethyltin(IV) derivatives **5** and **6** show a different thermal behaviour with respect to the previous. Both display two consecutive plateaus, one starting at ca. 100 °C and the other at ca. 160 °C for **5** and at 150 °C for **6**. After these steps, the percentage loss of weight corresponds to the liberation of H₂O and of one half of an SnMe₄ component, with concomitant formation of intermediate species, which have been characterized by IR and proton NMR as the bis(acylpyrazolonate)dimethyltin(IV) compounds **7** and **8** (Scheme 2). Derivatives **7** and **8** have also been prepared by interaction between two equivalents of HQ^{fur} and

one equivalent of dichlorodimethyltin(IV) in methanol in the presence of sodium methoxide (Scheme 2). Their analytical and spectral data are the same of those of the intermediates of decomposition of **5** and **6** recovered after a thermal run stopped at 170 °C.

We have studied in detail the thermal decomposition of **5** and its rearrangement into the derivative $(Q^{fur})_2 SnMe_2$ (**7**).

By the comparison of the IR spectra of the two intermediates, recovered after heating at 100 and 170 °C, with those of the starting derivative **5** and of derivative **7** (Fig. 3) we observe that the IR of the intermediate recovered after the first step is exactly comparable with the IR of derivative **7** synthesized using Me₂SnCl₂ as reactant. Hence, during this first thermal step the elimination of the water molecule and formation of the dimethyltin(IV) complex is essentially complete.

In the second step we have melting/decomposition in the range 172–176 °C, corresponding to the melting with decomposition observed in the TGA spectrum of derivative **7**. From comparison of the TGA spectra of **5** and **7** we observe the correspondence of the curves after 170 °C, with two typical inflection points at ca. 290 and 330 °C (Fig. 4). An analogous thermal behaviour has been found for derivative **6**, which transforms into the corresponding dimethyltin(IV)bis(acylpyrazolonate) compound **8**. Also in this case we have confirmed the transformation by comparison of IR, proton NMR and TGA-DTA spectra of the intermediate recovered by stopping the thermal run of **6** at 140 °C and those of derivative (Q^{thi})₂SnMe₂ (**8**) synthesized by using Me₂SnCl₂ as reactant.

3.5. Structure determination of $[(Q^{fur})SnPh_3](1)$ and $(Q^{thi})SnMe_3(OH_2)$ (6)

The results of the single crystal X-ray structure determinations of derivatives 1 and 6 are consistent with their formulation as (Q^{fur})SnPh₃ and (Q^{thi})SnMe₃(OH₂), respectively. In **1**, the pyrazolate ligand is 0,0'-bidentate and the complex mononuclear, with fivecoordinate O₂SnC₃ metal atom environments. Two full independent molecules, devoid of crystallographic symmetry, comprise the asymmetric unit of the structure, representative molecule 1 being shown in Fig. 5, with metal atom coordination environments presented comparatively in Table 1. A number of the latter differ rather surprisingly between the two molecules, indicating a rather flexible array, cf. the two similar complexes defined in the studies of refs. [27,28]. (See also Ref. [29] where two such molecular units are linked by a bifunctional ligand). Differences in Sn(n)-O(n41) cf. Sn(n)-O(n5) correlate with differences observed in the associated C-O distances; the dispositions of the three phenyl rings persist across both molecules. The exocyclic angles at C(n42) of the pendant furyl rings are very disparate (C(n41)-C(n42)-C(n46)); O(n43) 132.8(3), 130.8(4), 116.8(3), 119.8(3)°), regardless of whether O(n43) lies *cis* to O(n41), as is the case in molecule 1, or trans (molecule 2). The coordination environments are more nearly trigonal-bipyramidal than square pyramidal, although the large angle (O(n41)-Sn-C(n61), 152.5(1), 160.8(1)°) is well removed from linearity in each case.

On passing to **6**, the more feebly bound carbonyl oxygen atom is detached, being supplanted by a more strongly bound water molecule. In the structure of **6**, a single molecule of $(Q^{thi})SnMe_3(OH_2)$, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The tin atom coordination environment is again quasi-trigonal bipyramidal, with the three methyl groups in the equatorial plane (Table 2, Fig. 6(a)). Such an environment has been defined previously in an earlier determination of a similar complex with a different 'Q' ligand in ref. [9d], the present offering superior precision. Hydrogen-bonds from the water molecule (Table 2) link (A) centrosymmetrically to the ligand carbonyl oxygen atoms, forming a dimer, the other (B) linking to the nitrogen atom of a *c*-glide related unit, forming a polymer of dimers in that direction (Fig. 6(b)).

4. Conclusions

We have synthesized novel triorganotin(IV) derivatives, with acylpyrazolonate Q ligands incorporating oxygen- (Q^{fur}) and sulfur-heterocycles (Q^{thi}) in their acyl fragments, by direct reaction between HQ and $(R_3Sn)_2O$ in benzene (R = Ph or Bu) and between HQ and Me₃SnCl in benzene/methanol in the presence of NaOMe. The triphenyltin(IV) adducts are anhydrous derivatives of formula (Q)SnPh₃ where Q is O,O'-bidentate and tin is five-coordinate in the solid state. By contrast, the tributyl- and trimethyl-tin(IV) adducts are monohydrated aquo compounds with general formula (Q)SnR₃(OH₂), with Q acting in a monodentate fashion through only one carbonyl arm, the other being involved in a hydrogen-bonding network with neighbouring water molecule components. The tin atoms are in trigonal-bipyramidal environments, with the water molecules directly bonded to the tin atoms. Such Sn–OH₂ bonds are broken in solution and tetrahedral OSnC₃ species formed. After some days on standing in solution the trimethyltin(IV) compounds slowly decompose into (Q)₂SnMe₂ derivatives and SnMe₄. Such decomposition can be induced by heating, with release of H₂O and volatile SnMe₄ within the range 80–100 °C. Dimethyltin(IV) derivatives (Q)₂SnMe₂ have been also synthesized from HQ and Me₂SnCl₂ in basic methanol and exist as skewed *trans*-octahedral compounds, both in the solid state and solution.

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Appendix A. Supplementary material

Full cif depositions (excluding structure factor amplitudes) CCDC 779873 and 799085 can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.002.

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