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FULL PAPER

The interaction of organotin(IV) acceptors with a benzoic acid containing two pyrazolone groups †

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A new polydentate ligand, namely 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoic acid (H_2QBz), has been prepared and characterized. The structure of the ligand H_2QBz consists of discrete molecules linked to one another by an extensive H-bonding network. The reactivity of H_2QBz towards $[R_3Sn]_2O$ (R = Ph or Bu^n) and R_nSnCl_{4-n} (R = Me, Bu^n, Bu^t, Ph, $n = 2$; R = Me, $n = 3$) has been investigated. Mono- and di-nuclear derivatives have been obtained depending on the nature of the starting acceptor and reaction conditions. $[Ph_3Sn(HQBz)]$ **1** contains the HQBz ligand coordinated to Ph_3Sn through the deprotonated carboxylic group. In the complex $[(H_2O)Ph_3Sn(HQBz)]$ **2**, obtained by hydration of **1**, the coordination sphere of tin is completed by bonding to a water molecule. The compounds $[(R_3Sn)_2(QBz)]$ (R = Me, **3**; Bu^n, **4**) contain the dianionic ligand bridged to two triorganotin(IV) fragments. In solution the mononuclear triorganotin(IV) aqua complexes $[(H_2O)R_3Sn(HQBz)]$ (R = Ph, **2**; Bu^n, **5**) loose the molecule of water and slowly decompose, yielding the free ligand and the R_3SnOH species. The diorganotin(IV) derivatives $[R_2Sn(QBz)]_2$ (R = Me, **6**; Bu^t, **7**; Bu^n, **8**; Ph, **9**) are dinuclear both in the solid state and in solution. In the structure of $[Me_2Sn(QBz)]_2$ **6** both acidic H atoms of the ligand are substituted by tin: a dimeric centrosymmetric structure forms, involving two $[QBz]^{2-}$ ligands acting as bridges between two tin atoms through both pyrazolone and benzoate moieties. Sn centers in the dimer are five-coordinated in a strongly distorted trigonal bypiramidal environment.

Introduction

Current knowledge of the molecular architecture of oligonuclear metal complexes is basic in terms of understanding the nature of cooperative effects and in the investigation of the reactivity of multimetallic systems.[1] The increasing interest in this field is due to the potential relevance of such compounds in catalysis.[2] An important objective is also the synthesis of new highly soluble metal complexes useful for testing the distinctive reactivity patterns of the multimetallic systems.[3] In recent years organotin(IV) derivatives have received attention, both in academic and applied research, because of the ability of tin to afford stable bonds with carbon as well as with heteroatoms: a wide range of compounds employed in organic synthesis and catalysis (synthesis of polyesters, polyurethanes, cross-linking of silicones, esterification, transesterification, polymerization, *etc.*) have been reported.[4] Organotin(IV) compounds are also used as PVC heat stabilizers, as a component of aquatic antifouling paints, wood preservatives and biocides.[4b,5] It has recently been proposed that polystyrene derivatives bearing side-chain organotin moieties could be produced either by functionalization of suitable polymeric substrates with organometallic reagents or by polymerization of tin containing monomers, thus directly obtaining the desired organotin functionalized polymers.[6] Substituted triphenyltin benzoates were shown to exhibit exceptionally high antitumor activity against several forms of a human tumor and a colon carcinoma.[7]

Pyrazolone-based chelating ligands form a variety of coordination complexes with a number of metal ions, providing varying geometry and nuclearity.[8] In the last few years considerable effort has been directed towards the design of various pyrazolone-based ligands and the study of the relationship between the structural properties and the specific stereochemical requirements of a particular metal-binding site.[9]

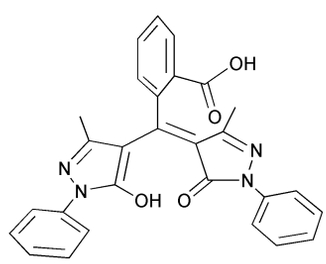

Fig. 1 The pro-ligand H_2QBz.

We have recently reported on the chemical, structural and spectroscopic properties of a series organotin(IV) complexes with 4-acylpyrazolones, characterized by different coordinating properties.[10] As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin compounds with heterocyclic ligands, here we present the synthesis and characterization of a new donor, namely 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)-(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl] benzoic acid (H_2QBz) (Fig. 1) and its chelating behavior towards organotin complexes. The preparation of the ligand H_2QBz, a coordinating agent derived from benzenedicarbonyl dichlorides showing the properties of both pyrazolones and benzoates, is of special interest since the use of oxygen atoms for chelation to a single cation is directly related to the situation

† Coordination chemistry of bis(pyrazolones): a rational design of nuclearity tailored polynuclear complexes. Part 1.

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of carbonyls in *ortho*, *meta* or *para* positions on the aromatic ring.

Experimental

Materials and methods

1-Phenyl-3-methylpyrazolin-5-one, phthaloyl chloride, triethylamine and organotin(IV) halides were purchased from Aldrich (Milwaukee) and used as received. Removal of solvent was always carried out under vacuum using a rotavaporator. The samples for microanalysis were dried *in vacuo* to constant weight (20 °C, *ca*. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium; dichloromethane was distilled from calcium hydride. All solvents were degassed with dry nitrogen prior to use.

Elemental analyses (C,H,N) were performed in-house with a Fisons Instruments 1108 CHNS-O elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian instrument and on a Bruker AC 200 spectrometer operating at room temperature (respectively at 300 and 200 MHz for ^{1}H, 75 and 50 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^{1}H and ^{13}C calibration by internal deuterium solvent lock) and $SnMe_4$ (external). The spectral width is 900 ppm (from +200 to −700 ppm). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. UV-VIS spectra were recorded on a Hewlett-Packard HP-8453 spectrometer. Melting points are uncorrected and were recorded on an SMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_m, reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane solution of complexes **1–9** were measured with a Crison CDTM 522 conductimeter at room temperature. Molecular weight determinations (M.W.) were performed at 40 °C with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil. The solvent was Baker Analysed Spectrophotometric grade chloroform. The results were reproducible to ±2%.

Syntheses

2-[(5-Hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoic acid (H_2QBz). To a solution of 1-phenyl-3-methylpyrazol-5-one (30 g, 0.17 mol) in hot dioxane, $Ca(OH)_2$ (24 g, 0.324 mol) was added. Then by the slow dropwise addition of phthaloyl chloride (17.86 g, 0.088 mol) a yellow precipitate formed. The suspension was stirred overnight under reflux and then neutralized by addition of 2 N HCl giving an oil which was re-crystallized from methanol to yield 12 g of red crystalline product which has been identified as H_2QBz. Yield 90%; mp: 94–97 °C. Anal. calc. for $C_{28}H_{22}N_4O_4$: C, 70.28; H, 4.63; N, 11.71. Found: C, 70.00; H, 4.93; N, 11.56%. Λ_m (CH_2Cl_2, 1×10^{-3} M): 0.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (s, 6H, CH_3), 7.26 (t, 2H, CH_{arom}), 7.43 (t, 4H, CH_{arom}), 7.65 (m, 2H, CH_{arom}), 7.92 (d, 4H, CH_{arom}), 8.0 (m, 2H, CH_{arom}), 8.2–9.5 (br, 2H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.94 (s, CH_3), 112.6 (s, C_{pyr}), 118.47 (s, C_{pyr}), 121.27, 126.49, 128.87 (3s, CH_{arom}), 130.38, 131.18, 131.27, 132.35 (4s, $CH_{benzoic}$), 131.49, 137.69, 141.17, 151.02 (4s, C_{ipso}), 161.49 (CO_{pyr}), 167.93 (s, $CO_{benzoic}$). IR (cm^{-1}): 3400–1800 s br [ν(O–H)], 1720 s [ν(C=O)], 1680 sh, 1650 sh, 1640 s, 1630 s, 1613 s, 1590 s, 1556 s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 504 s, 399 m [ν(Ph)]. UV-VIS (nm, $CHCl_3$, 1.91×10^{-5} M): 252, 397.

2-[(5-Hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate triphenyltin(IV), [Ph_3Sn(HQBz)] (1). To a benzene solution (10 ml) of H_2QBz (0.239 g, 0.5 mmol), $(Ph_3Sn)_2O$ was added (0.358 g, 0.5 mmol) under a nitrogen atmosphere. Immediately a clear red-orange solution was obtained which was refluxed overnight. The binary azeotrope water–benzene was distilled off with a Dean–Stark funnel, then the benzene solution obtained was evaporated under reduced pressure. The addition of diethyl ether gave a red-orange precipitate of **1** which was filtered off and washed with diethyl ether. Yield 236 mg, 57%; mp: 176–179 °C. Anal. calc. for $C_{46}H_{36}N_4O_4Sn$: C, 66.77; H, 4.39; N, 6.77. Found: C, 66.81; H, 4.51; N, 6.39%. Λ_m (CH_2Cl_2, 1.2×10^{-3} M): 0.2. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 6H, CH_3), 4.7 (br, 1H, OH), 7.2–7.7 (m, 25H, CH_{arom}), 7.82 (t, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 16.14 (s, CH_3), 112.6 (s, C_{pyr}), 119.0 (s, C_{pyr}), 121.15, 126.29 (2s, CH_{arom}), 128.67 [s, Sn–C_6H_5, $J(^{119}Sn–^{13}C$: 62 Hz)], 130.22, 130.76, 131.16, 133.39 (4s, $CH_{benzoic}$), 136.62 [s, Sn–C_6H_5, $J(^{119}Sn–^{13}C$: 48.5 Hz)], 137.35, 137.88, 141.18, 151.17 (4s, C_{ipso}), 159.13 (CO_{pyr}), 171.52 (s, $CO_{benzoic}$). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ −84.0. IR (cm^{-1}): 3300 sbr [ν(O–H)], 1631 s, 1618 s, 1591 s, 1568 m, 1553 sh [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 504 s, 456 m, 446 m, 399 m [ν(Ph), ν(Sn–O)], 283 s, 266 s, 231 s [ν(Sn–C), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 1.44×10^{-5} M): 252, 397.

2-[(5-Hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate (aqua)triphenyltin(IV), [(H_2O)Ph_3Sn(HQBz)] (2). To a benzene solution (10 ml) of H_2QBz (0.239 g, 0.5 mmol), $(Ph_3Sn)_2O$ was added (0.358 g, 0.5 mmol) under a nitrogen atmosphere. A red-orange solution formed which was refluxed overnight. Then, the solvent was removed under reduced pressure and methanol (30 ml) and water (10 ml) were added until an orange precipitate of **2** formed, which was filtered off and washed with diethyl ether. Yield 310 mg, 73%; mp: 125 °C decomp. Anal. calc. for $C_{46}H_{38}N_4O_5Sn$: C, 65.35; H, 4.53; N, 6.63. Found: C, 65.75; H, 4.80; N, 6.51%. Λ_m (CH_2Cl_2, 0.9 $\times 10^{-3}$ M): 0.2. M.W. ($CHCl_3$, 0.52×10^{-2} M) = 500 (r = M.W./F.W. = 0.59). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 6H, CH_3), 4.7 (br, 1H, OH), 7.2–7.7 (m, 25H, CH_{arom}), 7.82 (t, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.1 (s, CH_3), 112.6 (s, C_{pyr}), 121.1, 126.2, 128.7 (3s, CH_{arom}), 128.8 [s, Sn–C_6H_5, $J(^{119}Sn–^{13}C$: 63.5 Hz)], 130.1, 130.2, 130.3, 130.8, 131.5, 131.6 (6s, $CH_{benzoic}$ + Sn–C_6H_5), 136.6 [s, $J(^{119}Sn–^{13}C$: 47.2 Hz)], 137.3, 137.8, 141.2, 151.2 (4s, C_{ipso}), 161.3 (s, CO). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ −95.4. IR (cm^{-1}): 3300 s br [ν(O–H)], 1631 s, 1618 s, 1591 s, 1568 m, 1553 sh [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 504 s, 456 m, 446 m, 399 m [ν(Ph), ν(Sn–O)], 283 s, 266 s, 231 s [ν(Sn–C), δ(C-Sn–C)]. UV-VIS (nm, $CHCl_3$, 1.91×10^{-5} M): 253, 397.

2-[(5-Oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate bis[trimethyltin(IV)], [(Me_3Sn)$_2$(QBz)] (3). To a benzene solution (10 ml) of H_2QBz (0.239 g, 0.5 mmol), Me_3SnCl (0.358 g, 0.5 mmol) and NaOMe were added. The clear red-orange solution formed was refluxed overnight. The solvent was removed under reduced pressure and diethyl ether was added to obtain a red precipitate of **3** which was filtered off and washed with diethyl ether. Yield 256 mg, 63%; mp: 161–166 °C decomp. Anal. calc. for $C_{34}H_{38}N_4O_4Sn_2$: C, 50.79; H, 4.76; N, 6.97. Found: C, 50.6; H, 4.80; N, 6.97%. Λ_m (CH_2Cl_2, 0.9 $\times 10^{-3}$ M): 0.3. M.W. ($CHCl_3$, 0.32×10^{-2} M) = 780 (r = M.W./F.W. = 0.97). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (s, 6H, CH_3), 4.7 (br, 1H, OH), 7.2–7.7 (m, 25H, CH_{arom}), 7.82 (t, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ −1.95 [s, Sn–CH_3, $^{1}J(^{119}Sn–^{13}C$: 418 Hz)], 15.93 (s, CH_3), 112.67, 118.96 (2s, C_{pyr}), 121.3, 126.4, 128.3 (3s, CH_{arom}), 128.4 130.19, 130.77, 130.96 (4s, $CH_{benzoic}$), 135.22, 137.84, 141.2, 151.48 (4s, C_{ipso}), 160.2, 161.38 (2s, CO_{pyr}), 167.13 (s, $CO_{benzoic}$). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ 150.4. IR (cm^{-1}): 3300 s br [ν(O–H)], 1618 sh, 1593 s, 1562 m, 1520m [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 593m, 552 m [ν(Sn–C)],

508 m, 448 m [ν(Ph), ν(Sn–O)], 399 w, 351 w. UV-VIS (nm, $CHCl_3$, 1.32×10^{-5} M): 255, 395.

2-[(5-Oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate bis[tributyltin(IV)], [(Bu^n_3Sn)$_2$(QBz)] (4). This compound has been obtained as for **1** by using 0.5 mmol of H_2QBz and 0.5 mmol of (Bu^n_3Sn)$_2$O. Re-crystallization from $CHCl_3$ gave 350 mg of **4**. Yield 66.1%; mp: 111–112 °C. Anal. calc. for $C_{52}H_{74}N_4O_4Sn_2$: C, 59.11; H, 7.06; N, 5.30. Found: C, 59.15; H, 7.35; N, 5.50%. Λ_m (CH_2Cl_2, 1.3×10^{-3} M): 0.4. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.7 (t, 9H, CH_3), 0.95 (t, 9H, CH_3), 1.07 (m, 6H, CH_2), 1.1 (m, 6H, CH_2), 1.5 (m br, 24H, CH_2), 1.43 (s, 6H, CH_3), 7.28 (t, 2H, CH_{arom}), 7.49 (t, 4H, CH_{arom}), 7.62 (d, 2H, CH_{arom}), 8.01 (m, 6H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 13.52, 16.33, 26.88, 27.60 [4s, Sn–C_4H_9, ^1J(^{119}Sn–^{13}C: 390 Hz)], 16.43 (s, CH_3), 112.64 (s, C_{pyr}), 121.04, 126.3, 128.8 (3s, CH_{arom}), 130.1, 130.8, 130.9 (3s, $CH_{benzoic}$), 135.15, 137.9, 140.5, 151.45 (4s, C_{ipso}), 161.39 (s, CO_{pyr}). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ 106.1. IR (cm^{-1}): 1645 s, 1610 sh, 1599 s, 1548 m br [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 633 s, 591 s [ν(Sn–C)], 508 s, 472 m, 450 w, 409 w, 386 w, 357 w, 343 w, 334 w, 296 w, 262 w [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.81×10^{-5} M): 252, 397.

2-[(5-Hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate (aqua)tributyltin(IV), [(H_2O)Bu^n_3Sn(HQBz)] (5). This compound has been obtained as for **1** by using 0.5 mmol of H_2QBz and 0.25 mmol of (Bu^n_3Sn)$_2$O. Re-crystallization from $CHCl_3$ gave 360 mg of **5**. Yield 92%; mp: 85–88 °C. Anal. calc. for $C_{40}H_{50}N_4O_5Sn$: C, 61.60; H, 6.42; N, 7.13. Found: C, 61.31; H, 6.75; N, 7.00%. Λ_m (CH_2Cl_2, 1×10^{-3} M): 0.05. M.W. ($CHCl_3$, 0.4×10^{-2} M) = 439 (r = M.W./F.W. = 0.56). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.7 (t, 9H, CH_3), 0.95 (t, 9H, CH_3), 1.07 (m, 6H, CH_2), 1.1 (m, 6H, CH_2), 1.5 (m br, 24H, CH_2), 1.43 (s, 6H, CH_3), 7.28 (t, 2H, CH_{arom}), 7.49 (t, 4H, CH_{arom}), 7.62 (d, 2H, CH_{arom}), 8.01 (m, 6H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 13.52, 16.42, 26.88, 27.63 [4s, Sn–C_4H_9, ^1J(^{119}Sn–^{13}C: 392 Hz)], 15.64 (s, CH_3), 112.0 (br, C_{pyr}), 120.9, 125.9 (br, CH_{arom}), 128.7 (s, CH_{arom}), 129.8, 130.6 (2s, $CH_{benzoic}$), 138.0, 140.4 (2s, C_{ipso}). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ 127.3. IR (cm^{-1}): 3000 br [ν(O–H)], 1700 br, 1600 sh, 1599 s, 1563 m, 1548 m br, 1510 m [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 628 s, 592 s, 563 sh [ν(Sn–C)], 508 s, 444 m, 425 w, 407 w, 386 w, 336 m, 293 m [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.88×10^{-5} M): 252, 397.

Bis{2-[(5-oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate dimethyltin(IV)}, [Me_2Sn(QBz)]$_2$ (6). To an acetonitrile solution of 0.5 mmol of H_2QBz, triethylamine was added and a clear solution obtained. Further addition of 0.5 mmol of Me_2SnCl_2, followed by 10 min of stirring under reflux, gave a yellow precipitate of **6**, which was filtered off, washed with ether and re-crystallized from $CHCl_3$–Et_2O. Yield 225 mg, 71%; mp: 296–298 °C. Anal. calc. for $C_{30}H_{26}N_4O_4Sn$: C, 57.63; H, 4.19; N, 8.96. Found: C, 57.38; H, 4.25; N, 8.74%. Λ_m (CH_2Cl_2, 1.2×10^{-3} M): 0.3. M.W. ($CHCl_3$, 0.41×10^{-2} M) = 1200 (r = M.W./F.W. = 1.92). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.01 (s, 6H, Sn–CH_3), 0.55 (s, 6H, Sn–CH_3), 1.26 (s, 6H, CH_3), 1.73 (s, 6H, CH_3), 7.2–7.4 (m, 15H, CH_{arom}), 7.6–7.8 (m, 11H, CH_{arom}), 8.0 (d, 2H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 5.6, 7.2 [2s, Sn–CH_3, ^1J(^{119}Sn–^{13}C: 695 Hz)], 15.92, 17.78 (2s, CH_3), 112.3, 118.0 (2s br, C_{pyr}), 120.43, 121.22, 122.36, 126.54 (4s, CH_{arom}), 128.89, 130.88, 131.51 (3s, $CH_{benzoic}$), 134.45, 137.58, 138.21, 140.83, 149.99, 151.12, 151.54 (6s, C_{ipso}), 159.52, 161.32 (2s, CO_{pyr}), 174.11 (s, $CO_{benzoic}$). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ −118.0. IR (cm^{-1}): 1610 s, 1599 s, 1551 s, 1521 s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 575 m, 563 sh, 520 m [ν(Sn–C)], 507 s, 458 m, 409 w, 398 w, 384 w, 375 w, 352 m, 326 m, 303 m, 280 m, 253 m, 247 m, 224 m [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.86×10^{-5} M): 250, 402.

Bis{2-[(5-oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate di-*tert*-butyltin(IV)}, [Bu^t_2Sn(QBz)]$_2$ (7). This compound was obtained by a similar method to that used for **6**. Re-crystallization from CH_3OH gave 0.370 mg of **7**. Yield 96%; mp: 195 °C. Anal. calc. for $C_{36}H_{38}N_4O_4Sn$: C, 60.95; H, 5.40; N, 7.90. Found: C, 61.03; H, 5.50; N, 8.01%. Λ_m (Acetone, 1×10^{-3} M): 7.4. M.W. ($CHCl_3$, 0.2×10^{-2} M) = 1347 (r = M.W./F.W. = 0.95). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.98 (s, 18H, Sn–C_4H_9), 1.20 (s, 6H, CH_3), 1.34 (s, 18H, Sn–C_4H_9), 1.38 (s, 6H, CH_3), 7.2–7.5 (m, 12H, CH_{arom}), 7.5–7.8 (m, 6H, CH_{arom}), 8.0 (m, 8H, CH_{arom}), 8.2 (d, 2H, CH_{arom}). ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): −96 s br; −196 s br. IR (cm^{-1}): 1600 s, 1581 s, 1539 s, 1514 s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 468 m [ν(Sn–C)], 507 s, 458 m, 384 w, 353 w, 326 w, 316 w, 280 m, 253 m, 247 m, 227 m [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.5×10^{-5} M): 250, 397.

Bis{2-[(5-oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate di-*n*-butyltin(IV)}, [Bu^n_2Sn(QBz)]$_2$ (8). This compound has been obtained by the same method used for **6**. Re-crystallization from CH_3OH gave 0.22 g of the analytical sample **8**. mp ($CHCl_3$–CH_3OH) 293–294 °C. Anal. calc. for $C_{36}H_{38}N_4O_4Sn$: C, 60.95; H, 5.40; N, 7.90. Found: C, 60.81; H, 5.70; N, 7.71%. Λ_m (CH_2Cl_2, 1.2×10^{-3} M): 0.8. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.5–1.5 (m, 36H, Sn–C_4H_9), 1.25 (s, 6H, CH_3), 1.38 (s, 6H, CH_3), 7.2–7.5 (m, 12H, CH_{arom}), 7.5–7.8 (m, 6H, CH_{arom}), 7.8–8.1 (m, 10H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 12.97, 13.58, 16.2, 17.89, 26.01, 26.54, 27.11, 28.07 (8s, Sn–C_4H_9), 15.88 (br, CH_3), 119.84, 121.01, 122.47 (3s, CH_{arom}), 125.71, 126.22, 128.80 (3s, $CH_{benzoic}$), 130.38, 130.90, 132.02, 137.85, 151.05 (5s, C_{ipso}), CO_{pyr} and $CO_{benzoic}$ not observed. ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): δ −155.5 s. IR (cm^{-1}): 1606 s, 1590 s, 1558 s, 1514 s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 628 s, 613 s, 597 s m [ν(Sn–C)], 520 s, 505 s, 456 m, 410 m, 384 w, 366 w, 351 w, 342 w, 322 m, 310 s, 277 w, 265 m [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.8×10^{-5} M): 255, 403.

Bis{2-[(5-oxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoate diphenyltin(IV)}, [Ph_2Sn(QBz)]$_2$ (9). This compound has been obtained by the same method used for **6**. Re-crystallization from CH_3OH gave 0.33 g (88% yield) of the analytical sample **9**. mp ($CHCl_3$–CH_3OH) 293–294 °C. Anal. calc. for $C_{40}H_{30}N_4O_4Sn$: C, 64.11; H, 4.04; N, 7.48. Found: C, 64.32; H, 3.91; N, 7.17%. Λ_m (Acetone, 1×10^{-3} M): 6.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.5–1.5 (m, 36H, Sn–C_4H_9), 1.25 (s, 6H, CH_3), 1.38 (s, 6H, CH_3), 7.2–7.5 (m, 12H, CH_{arom}), 7.5–7.8 (m, 6H, CH_{arom}), 7.8–8.1 (m, 10H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 16.11 (br, CH_3), 112.5, 118.0 (2s br, C_{pyr}), 121.27, 126.26 (3s, CH_{arom}), 129.0, 129.9, 130.1 (3s br, $CH_{benzoic}$ + Sn–C_6H_5), 135.0 (3s br, $CH_{benzoic}$ + Sn–C_6H_5), 137.78, 151.12 (5s, C_{ipso}), 161.14 (s, CO_{pyr}), $CO_{benzoic}$ not observed. ^{119}Sn NMR ($CDCl_3$, 121.4 MHz): −250 br, 254 sh. IR (cm^{-1}): 1600 s, 1581 s, 1539 s, 1514 s [ν(C⋯O), ν(C⋯C), ν(C⋯N)], 468 m [ν(Sn–C)], 507 s, 458 m, 384 w, 353 w, 326 w, 316 w, 280 m, 253 m, 247 m, 227 m [ν(Ph), ν(Sn–O), δ(C–Sn–C)]. UV-VIS (nm, $CHCl_3$, 0.9×10^{-5} M): 249, 400.

X-Ray crystallography

Crystals of the ligand H_2QBz, for X-ray crystallographic studies were isolated by re-crystallization from methanol. In the case of derivative **1** crystals suitable for X-ray diffraction studies were obtained by slow evaporation of mother liquids after the main portion of the complex had been removed by

Table 1 Crystallographic data, details of data collection and refinement for H_2QBz, **1**, **2** and **6**

	H_2QBz	**1**	**2**·0.5$(CH_3)_2CO$	**6**·$CHCl_3$
Molecular formula	$C_{28}H_{22}N_4O_4$	$C_{46}H_{36}N_4O_4Sn$	$C_{47.5}H_{41}N_4O_{5.5}Sn$	$C_{31}H_{27}Cl_3N_4O_4Sn$
M	478.50	827.48	874.53	743.60
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.835(2)	16.572(3)	10.944(2)	10.554(2)
b/Å	10.012(2)	9.972(2)	12.883(3)	13.143(3)
c/Å	13.487(3)	23.699(6)	16.213(3)	13.759(3)
α/°	108.97(3)		84.27(3)	110.67(3)
β/°	101.97(3)	97.06(3)	75.58(3)	105.15(3)
γ/°	98.40(3)		68.90(3)	103.15(3)
Volume/Å^3	1195.4(4)	3887.4(14)	2065.3(7)	1610.4(6)
Z	2	4	2	2
D_c/Mg m^{-3}	1.329	1.414	1.406	1.533
Absorption coefficient/mm^{-1}	0.091	0.707	0.672	1.084
Crystal size/mm	0.8 × 0.3 × 0.2	0.5 × 0.4 × 0.4	0.6 × 0.4 × 0.2	0.6 × 0.4 × 0.2
Temperature/K	180	180	170	170
Data collection range, *θ*/°	3.1–27.4	2.5–27.0	2.7–25.7	2.8–26.8
Reflections collected	3768	31957	11677	9112
Independent reflections (R_{int})	3768 (0.086)	8371 (0.040)	7203 (0.063)	6083(0.055)
Data/parameters	2072/334	6327/502	6076/543	4901/415
Goodness of fit on F^2	1.109	1.137	1.014	1.045
wR_2	0.0860	0.0927	0.1012	0.1137
R_1	0.0511	0.0361	0.0449	0.0480
Largest diff. peak and hole/e Å^{-3}	0.152; −0.145	1.189; −0.558	1.014; −0.913	1.338; −1.065

filtration. By re-crystallization of **1** in CH_3OH–acetone we obtained single crystals which were shown to contain a hydrated compound **2**. Single crystals of **6** have been isolated by evaporation of a $CHCl_3$–CH_3OH solution of the complex.

The data for H_2QBz and complexes **1**, **2** and **6** were collected on an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo-Kα radiation. Absorption correction was not applied. The structures were solved by direct methods (SHELXS-86)[11] and refined anisotropically for all non-hydrogen atoms using the crystallographic program package SHELXL-93.[12] The acid hydrogen atom of $HQBz^-$ in the structures **1** and **2** and those of water molecules in **2** were localized from the Δ*F* syntheses and refined isotropically. All other H atoms were included in the calculated positions and refined in a riding mode. The acetone molecule in **2** is strongly disordered between two positions around an inversion centre and the chloroform molecule in **6** is partially disordered between two positions.

Crystallographic data and some details of data collection and structure refinement are given in Table 1. The most relevant bond distances and angles in the structures of **1**, **2** and **6** are listed in Table 2 (later).

CCDC reference numbers 158774–158777.

See http://www.rsc.org/suppdata/dt/b1/b100988p/ for crystallographic data in CIF or other electronic format.

Results and discussion

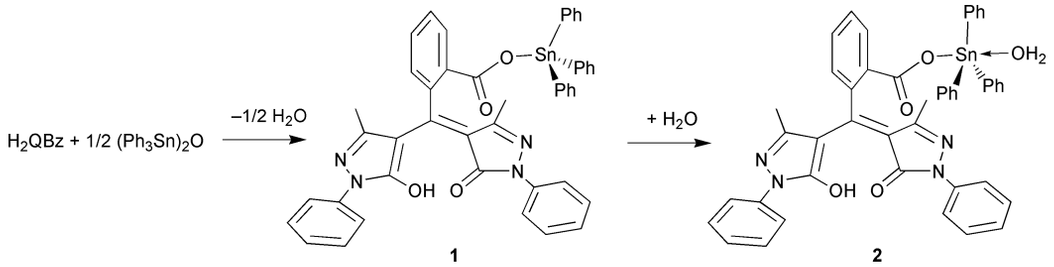
Synthesis

The ligand 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]-benzoic acid H_2QBz has been prepared from phthaloyl chloride and 1-phenyl-3-methylpyrazol-5-one in anhydrous dioxane following the procedure developed by Jensen for the synthesis of 4-acylpyrazol-5-ones.[13] Obviously, the use of phthaloyl chloride prevents bis(acylpyrazolone) from being obtained, due to the formation of the stable lactone intermediate, analogous to that reported for the condensation of phenol with phthaloyl chloride,[14] which hydrolyses in alkali media giving H_2QBz in high yield. The preparation of H_2QBz presented here seems to be much more convenient with respect to that reported for the substituted bis(1-phenyl-3-methyl-5-hydroxypyrazol-4-yl)arylmethanes by the condensation of 1-phenyl-3-methylpyrazol-5-one with aryl dialdehydes.[15] The reaction between pyrazolone and isophthaloyl- or terephthaloyl-chloride under the same conditions, according to the general procedure,[13] results in the formation of the 1,3-[16] and 1,4-bis[4-(1-phenyl-3-methylpyrazol-5-one)carbonyl]benzene[17] respectively. Even if pyridine or a proton-sponge were employed instead of calcium hydroxide, as used in the method of Jensen,[13] H_2QBz was the only reaction product. So, to date no synthetic procedure has been found for 1,2-bis[4-(1-phenyl-3-methylpyrazol-5-one)carbonyl]-benzene, although this compound has been erroneously reported by Yoshikuni.[18]

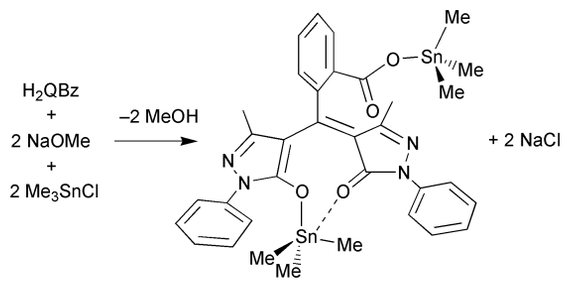
The reaction between equimolar quantities of the ligand H_2QBz and $(Ph_3Sn)_2O$ in benzene under nitrogen gave the red-orange complex $[Ph_3Sn(HQBz)]$ **1** containing the ligand in the monanionic form bonded to the tin center only through the benzoate arm. This compound was also obtained when a strong excess of $(Ph_3Sn)_2O$ was employed. Complex **1**, being left in air for more than 2 hours, reacts with moisture yielding the orange derivative $[(H_2O)Ph_3Sn(HQBz)]$ **2** in which a water molecule is also bonded to tin. Alternatively **2** can be prepared by addition of H_2O to a solution of **1** in CH_3OH (Scheme 1).

When two moles of Me_3SnCl react with one mole of H_2QBz in the presence of an equivalent amount of NaOMe the red compound $[(Me_3Sn)_2(QBz)]$ **3** forms in which the ligand is coordinated to two tin(IV) moieties through both benzoate and pyrazolonate arms (Scheme 2). The reaction between H_2QBz and $(Bu^n_3Sn)_2O$ produces two different products depending on the stoichiometric ratios employed. When equimolar quantities of reactants were employed the red 2 : 1 complex $[(Bu^n_3Sn)_2(QBz)]$ **4** was obtained (Scheme 3), whereas an excess of H_2QBz [$H_2QBz/(Bu^n_3Sn)_2O$ ratio > 2 : 1] afforded the red 1 : 1 complex $[(H_2O)Bu^n_3Sn(HQBz)]$ **5**, analogous to **2**. Surprisingly, it was not possible to obtain the analogous 2 : 1 complex with $(Ph_3Sn)_2O$ even in more drastic conditions as well as a complex containing the ligand $[HQBz]^-$ bonded to only one Me_3Sn(IV) moiety. No reaction has been observed between H_2QBz and Et_3SnBr or Cy_3SnCl, the starting materials being quantitatively recovered.

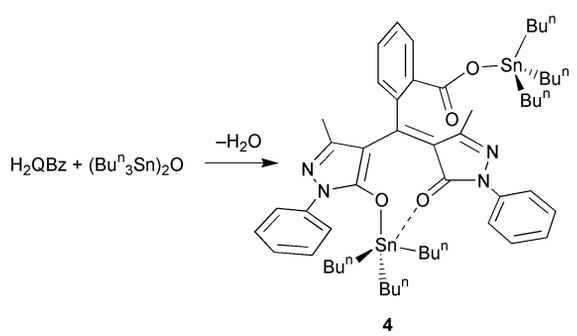
From the interaction between diorganotin halides R_2SnCl_2 (R = Me, Bu^n, Bu^t or Ph) and H_2QBz in the presence of base (NEt_3, KOH or NaOMe) the dinuclear yellow complexes $[R_2Sn(QBz)]_2$ (**6–9**) (Scheme 4) were always obtained (see below). No other stoichiometries have been found under our conditions.



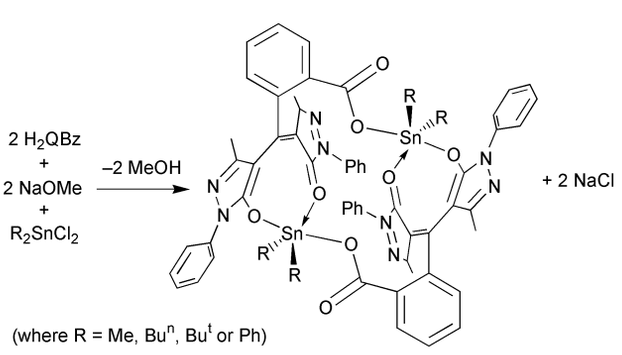
Scheme 1



Scheme 2



Scheme 3



Scheme 4

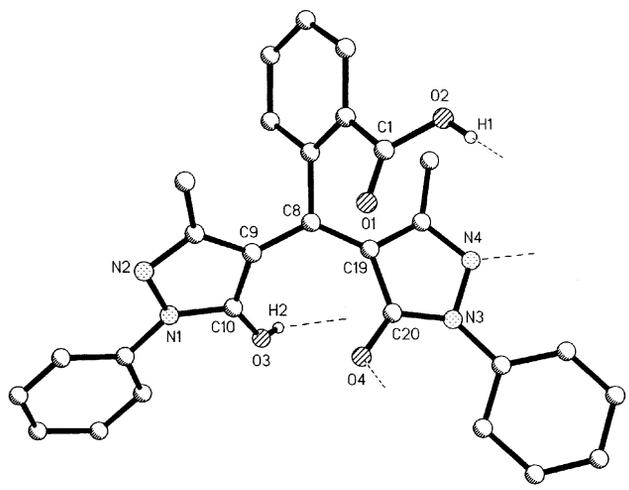


Fig. 2 The molecular structure of H_2QBz. All the hydrogen atoms except those involved in hydrogen bonding are omitted.

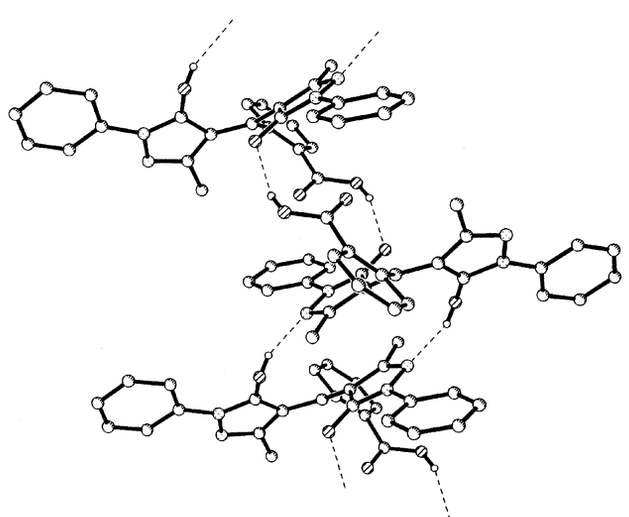


Fig. 3 The H-bond network in the crystal structure of H_2QBz.

The vaporimetric molecular weight measurements show compounds **2** and **5** dissociated in chloroform to a large extent, whereas in the case of the complexes **6** and **7** the empirical molecular weight is very close to that calculated for the dinuclear structure found in the solid state.

All compounds are non-electrolytes both in dichloromethane and acetone solution, suggesting that the dissociation of **2** and **5** is likely due to the breaking of the Sn–OH_2 bond and the subsequent slow hydrolysis reaction (1):

$$[(H_2O)R_3Sn(HQBz)] \rightleftharpoons R_3SnOH + H_2QBz \quad (1)$$

Our hypothesis has been confirmed from spectral data, the ^{1}H NMR spectra of **2** and **5** in $CDCl_3$ after 4 days being similar to that of H_2QBz, whereas both the ^{1}H and ^{119}Sn NMR spectra of **2**, 30 min after dissolution, are similar to those of **1**. In addition, in the ^{119}Sn spectra of **2** and **5** recorded 24 h after the solution had been prepared, the signals due to R_3SnOH species appeared.[19]

Crystal structure description and discussion

The crystal structure of H_2QBz consists of discrete molecules linked to one another by an extensive H-bonding network (Figs. 2 and 3). Both pyrazolone moieties are linked to the benzoate fragment of the molecule *via* the C8 carbon atom, the distances C9–C8 and C19–C8 being similar [1.416 and 1.415(10) Å] and attributed to a bond intermediate between a single and a double bond. One of the two acidic protons is localized on the O2 atom of the carboxylate fragment, with the distance C1–O1 being 1.207(9) Å, typical of C=O in a $–CO_2H$ moiety. Another acidic proton is bonded to the O3 atom and is involved in hydrogen

Table 2 The most relevant bond distances (Å) and angles (°) in the structures of H_2QBz, **1**, **2** and **6**

	H_2QBz	**1**	**2**	**6**
Sn–O(1)		2.075(3)	2.140(3)	2.150(4)
Sn ··· O(2)		2.890(3)	2.806(4)	2.730(3)
Sn–O(3)		—	—	2.066(3)
Sn–O(4)		—	—	2.282(4)
Sn–O(5)		—	2.594(3)	—
Sn–C(29)		2.120(4)	2.128(5)	2.114(5)
Sn–C(30)				2.112(7)
Sn–C(35)		2.123(4)	2.140(5)	
Sn–C(41)		2.126(4)	2.118(4)	
C(1)–O(1)	1.207(9)	1.311(4)	1.315(5)	1.311(6)
C(1)–O(2)	1.343(13)	1.230(5)	1.233(6)	1.235(6)
C(10)–O(3)	1.238(8)	1.274(4)	1.294(6)	1.309(6)
C(20)–O(4)	1.276(8)	1.288(4)	1.284(6)	1.277(7)
N(1)–N(2)	1.390(8)	1.396(4)	1.380(6)	1.393(6)
N(2)–C(11)	1.392(9)	1.299(5)	1.315(6)	1.306(7)
N(3)–N(4)	1.424(7)	1.394(4)	1.411(6)	1.384(7)
N(4)–C(21)	1.361(10)	1.314(5)	1.307(7)	1.321(7)
O(3) ··· O(4)		2.416(4)	2.423(5)	2.767(6)
O(1)–Sn–O(3)		—	—	82.4(1)
O(1)–Sn–O(4)		—	—	161.2(1)
O(1)–Sn–O(5)		—	177.1(1)	—
C(29)–Sn–C(35)		108.75(14)	114.8(2)	
C(29)–Sn–C(41)		110.17(15)	131.4(2)	
C(35)–Sn–C(41)		123.01(15)	108.4(2)	
C(29)–Sn–C(30)				143.7(2)
Dihedral pz1/pz2		28	38	48

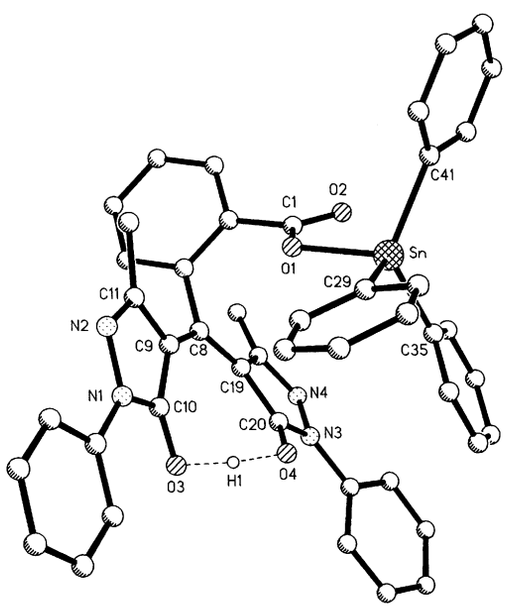


Fig. 4 The molecular structure of **1**. All the hydrogen atoms except those involved in hydrogen bonding are omitted.

bonding with the nitrogen atom of the neighboring molecule [O3 ··· N4 2.690(8) Å], rather than with O4 [the distance O3–H2 ··· O4 is 2.967(8) Å]. The system of intermolecular H-bonds between the enolic OH-groups and nitrogen atoms of the pyrazolone-rings (O3 ··· N4) as well as between OH-fragments of carboxylic and carbonylic oxygens of the pyrazolone moiety [O2–H1 ··· O4 2.630(7) Å] link discrete molecules in the infinite chains.

The molecular structures of **1**, **2** and **6** are shown in Figs. 4, 5 and 6 respectively, and selected interatomic parameters are listed in Table 2. All three derivatives are molecular complexes, in which molecular species are separated by van der Waals distances. In **2**, additional H-interactions have been found between hydrogen atoms of the water molecule and the N atom of the ligand's pyrazole ring.

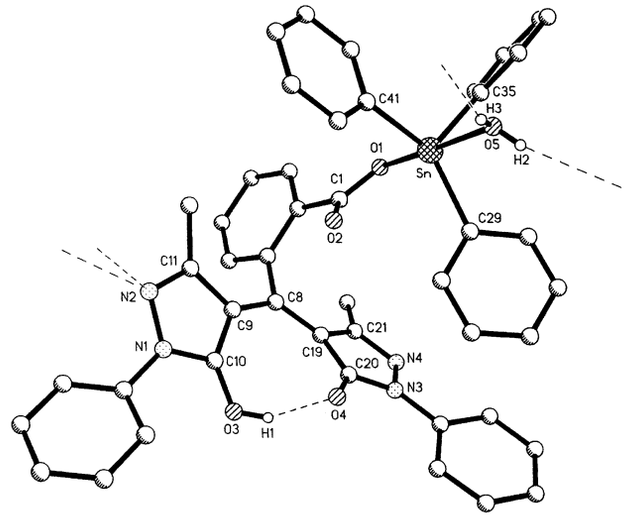


Fig. 5 The molecular structure of **2**. All the hydrogen atoms except those involved in hydrogen bonding are omitted.

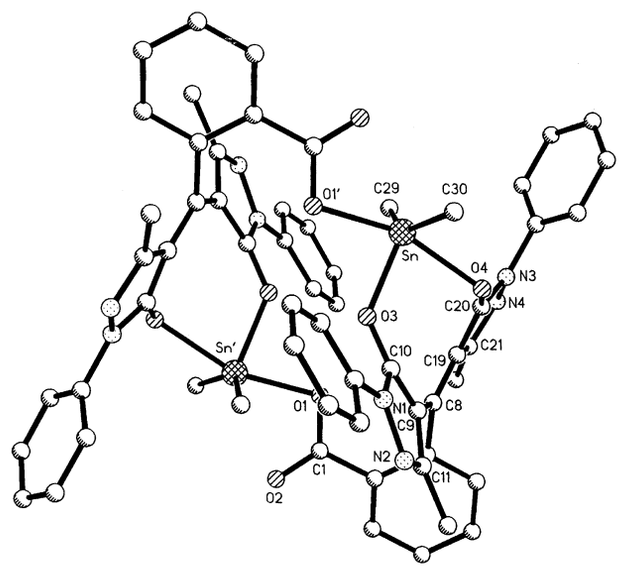


Fig. 6 The molecular structure of **6**. All the hydrogen atoms are omitted.

Structures **1** and **2** contain the $[HQBz]^-$ ligand coordinated to only one tin center through the carboxylic fragment by substitution of the acidic H atom. This is in contrast to the $R_3SnOCOR'$ complexes previously structurally characterized that consist of infinite chains with tin atoms linked by bridging μ-carboxylic groups,[20] in both **1** and **2** only one carboxylic oxygen is directly bonded to tin, with the corresponding C–O showing a normal single (1.31–1.32 Å) and the other a double bond (1.23 Å). In **1**, the coordination number of tin is four with a distorted tetrahedral environment, whereas tin in **2** is five-coordinated in a distorted trigonal bipyramidal geometry, a water molecule being additionally bonded to the metal atom. Nevertheless, the presence of weak interactions between the second oxygen of the carboxylate group and the tin atom (Sn ··· O2 = 2.89 Å in **1** and 2.81 Å in **2**) or even a geometrical arrangement influenced by Coloumbic interactions should be mentioned, regarded by some authors as an additional coordination of tin.[20–22] As a main obstacle to the former interpretation we can see that the Sn ··· O2 distance in hydrated complex **2** is less than in **1**.

The formation of monomeric molecules in the compounds in question may be caused by steric hindrances due to the presence of both bulky phenyl-groups and a hindered carboxylate-ligand that have been already reported for such tetrahedral

triphenyltin carboxylates as benzoate,[23] *p*-chlorobenzoate,[24] *o*-aminobenzoate,[25] *o*-methoxybenzoate,[26] *o*-(2-hydroxynaphthylazo)benzoate[27] and others. The steric effects that prevent the formation of a polynuclear chain structure, at the same time do not protect the tin center of **1** from hydration, which easily occurs resulting in **2** with a five-coordinate tin moiety.

The Sn–C distances in **1** and **2** are nearly the same, surprisingly unaffected by the different coordination number, and are typical for triphenyltin(IV) derivatives.[28] The sum of C–Sn–C angles in **1** (341.9°) is also in the range reported for triphenyltin(IV) benzoates, being quite close to the 340.6° value found in $Ph_3Sn(C_6H_5CO_2)$.[23] However, the Sn–O lengths in compound **2** are influenced by the higher coordination number and also by the presence of a water molecule in a *trans* position, forming a very weak bond with tin [Sn–OH_2, 2.594(3) Å]. In fact, the Sn–O1 distance in **1** is 2.075(3) Å, whereas in **2** it is elongated up to 2.140(3) Å.

The second acidic H atom, in the di-pyrazolone fragment of $[HQBz]^-$, in both **1** and **2** is not substituted by metal, but is involved in strong intramolecular H-bonding (O3–H ··· O4 is 2.416 Å in **1** and 2.423 Å in **2**). In compound **1**, the H atom is effectively centered between O3 and O4, whereas there is an asymmetric H-bond in **2** with O3 acting as H-donor and O4 as H-acceptor. A possible reason for this asymmetry could be the presence of additional H-bonds in **2**. In fact, both H atoms of the water molecule interact with the N2 atom of two other molecular units, which act as H-acceptors. Thus, N2 is involved in two H-bonds (O5–H1 ··· N2 is 3.13 Å and O5–H2 ··· N2 is 2.97 Å), whereas the nitrogen atom of the other pyrazolone ring (N4) isn't involved at all. Accordingly, the N2–C11 distance is slightly elongated in **2**, likely due to an additional H-interaction which destroys the symmetrical arrangement of the two pyrazolyl fragments present in **1**. Apparently, the presence of H-bonds between complexes results in the different orientations of the carboxylic groups in **1** and **2**, as can be clearly seen from comparison of Figs. 4 and 5. The pyrazolone fragments are flat and due to steric reasons are rotated with respect to each other by 29.0° causing a degree of tension in the conjugated system. In the free ligand, due to the absence of an O3 ··· O4 H-bond the dihedral angle between the planes is significantly larger (53.2°).

In the structure of **6** both acidic H atoms of the ligand are substituted by tin. However, due to the large distance between carboxylic and pyrazolone donor sites, they could not be coordinated by the same Sn atom, distinguishing this structure from a series of mononuclear diorganotin dicarboxylates.[22] This is the reason why in this case a dimeric centrosymmetric structure forms, involving two $[QBz]^{2-}$ ligands acting as bridges between two tin atoms. Both Sn centers in the dimer are five-coordinated in a strongly distorted trigonal bypiramidal environment, just as in the case of **2**. The Sn–O1 distance is 2.150(4) Å, close to Sn–O in (dimethyltin)dibenzoate [2.128(3) Å and 2.156(3) Å].[29] The Sn–O bond lengths from pyrazolone oxygens are different, being Sn–O3 2.066(3) Å and Sn–O4 2.282(4) Å, apparently, due to the *trans* position of O4 with respect to O1 and, possibly, also as a consequence of some steric hindrance. Accordingly, the corresponding C–O distances are also different [C10–O3 is 1.309(6) Å and C20–O4 is 1.277(7) Å]. Sn–C distances are nearly equal for both methyl groups [2.112(7) Å and 2.114(5) Å] and are close to those in other dimethyltin carboxylates [*e.g.* 2.10(2) Å in $(CH_3)_2Sn(C_6H_5CO_2)_2$[29]]. The angle C–Sn–C in **6** [143.7(2)°] is intermediate between that found in (dimethyltin)diacetate [135.0(5)°][30] and (dimethyltin)dibenzoate [147.2(7)°].[29] As in the triphenyltin derivatives discussed above, the carboxylic O2 atom in **6** is not involved in a direct Sn–O bond, however the distance from tin is 2.730(3) Å, a little bit shorter than in **1** and in **2** and sometimes regarded as a coordination.[22] On going from **1**, to **2** and to **6**, a change in the relative positions of the pyrazole rings (pz) is found, from more parallel to each other (dihedral pz1/pz2 is 29° in **1**) to less parallel (dihedral pz1/pz2 is 37° in **2** and 48° in **6**). Consequently, the distances C8–C9 and C8–C19 differ significantly in **1**, less in **2** and they are equal in **6**, likely indicating disruption of the conjugative effect between chromophore pyrazole rings. In fact, the free H_2Q ligand is red, the compounds **1** and **2** are orange coloured, whereas compound **6**, containing the pz rings in less parallel orientations than the others, is yellow.

Spectral properties

The UV spectra of H_2QBz and its complexes exhibit two bands at *ca*. 250 and 400 nm due to π–π* absorptions of the ligand. In the undissociated dinuclear complexes **6–9** the second band is generally shifted to lower frequencies upon coordination whereas in the triorganotin(IV) derivatives **1–5** both bands remain unchanged.

In the IR spectra of the triorganotin(IV) derivatives the C=O stretching band due to the benzoic moiety is shifted to lower frequencies up to 1640 cm^{-1} with respect to the free ligand. In the diorganotin(IV) species the same absorption falls in the range 1610–1595 cm^{-1}, suggesting a strong interaction between the benzoate arm of the ligand and the tin center, in accordance with X-ray data.

In the 500–400 cm^{-1} region of all the complexes some absorptions, typical of Sn–O stretching vibrations both for benzoate–Sn (in all species) and pyrazolonate–Sn interactions (in the dimers **6–9** and in the triorganotin complexes **3** and **4**), appear. The Sn–C stretching bands characteristic of a four-to-five-coordinate tin center bonded by two or more organic groups can be easily detected. In the case of the dialkyltin(IV) complexes the number of bands suggests R groups occupying the equatorial positions, as confirmed in the crystal structure of **6**.

In the spectra of the triorganotin(IV) derivatives **1**, **2** and **5** the presence of a broad absorption between 3400 and 2800 cm^{-1} provides further support that the ligand acts in the monoanionic form and proves the existence of a H-bond between both pyrazolonate moieties.

The ^1H, ^{13}C and ^{119}Sn NMR spectra of tin derivatives **1–9** together with the spectral data of the pro-ligand H_2QBz are reported in the Experimental section. In the ^1H and ^{13}C NMR spectra of derivatives **2** and **5** only one signal has been found for each equivalent group of protons and carbons respectively. This is strange, as generally the phenyl groups occupy both equatorial and axial positions in a five-coordinate tin environment, so that for the Ph_3Sn moiety at least two different signals are expected. The ^{119}Sn NMR of both **2** and **5** show a single signal which is very close to that reported for four- to-five coordinate tin centers.[19,31] On this basis we propose that breaking of the Sn–OH_2 bond occurs, as confirmed also by M.W. measurements and by the NMR spectra of **1** which are almost identical to those of the hydrate species **2**.

The ^{119}Sn NMR spectra of the compounds **3** and **4**, in which two triorganotin(IV) groups are coordinated by the dianionic $[QBz]^{2-}$ ligand, exhibit a single resonance. The ^1H and ^{13}C NMR spectra of **3** show broad singlets for the 3-CH_3 groups of the ligand and for the Me_3Sn. In this case for a compound stable in solution we should have at least two signals in the ^{119}Sn NMR spectra and two or more signals for the Me_3Sn moieties in the proton and carbon spectra. From the combined M.W. and conductivity data, which indicate the existence of non-ionic species in solution, a fluxional equilibrium can be proposed for **3** and **4**.

In the ^{119}Sn NMR spectra of dimethyl- and di-*n*-butyl-tin(IV) complexes **6** and **8** only one signal, typical of a five-coordinate species, has been found in accordance with the solid state structure.[19,31] However, in the ^1H and ^{13}C NMR spectra of these compounds two signals for the Me_2Sn (**6**) and two set of signals for the $Bu^n{}_2Sn$ (**8**), have been detected with an intensity ratio of

1 : 1. On the basis of ^{119}Sn data we exclude the existence of isomers, whereas the signals in the ^{1}H and ^{13}C spectra should be attributed to two non-equivalent R groups bonded to tin.

In the ^{119}Sn NMR spectrum of the di-*tert*-butyl derivative **7** two signals of the same intensity have been detected, one typical of a four- and another of a five-coordinate tin(IV) center.[19,31] In this compound, for which a dimeric structure in solution has been demonstrated by M.W. measurements, two different tin(IV) environments are likely due to the strong steric hindrance of the *tert*-butyl groups which prevents the existence of two five-coordinate tin centers.

In the ^{119}Sn NMR spectrum of the diphenyltin derivative **9** two signals (relative intensity 1 : 4) have been found likely due to the presence of different isomers, as already reported for the analogous pyrazolonate complexes.[32] All signals in the ^{1}H and ^{13}C NMR spectra are broad, in accordance with a fluxional behavior of this compound in chloroform solution.

Conclusion

The new pro-ligand 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)-methyl]benzoic acid H_2QBz, has been shown to be able to form mononuclear, dinuclear and heterobimetallic complexes. The nuclearity and stoichiometry were found to be a function of the nature of the starting acceptor, $[R_3Sn]^+$ derivatives being completely different from $[R_2Sn]^{2+}$, and also of the different donating ability of benzoate and pyrazolonate arms. Preliminary studies show that H_2QBz has potential for the design of heterobimetallic systems containing both transition and post-transition metals.

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