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# Organotin(IV) derivatives of acylpyrazol-5-ones

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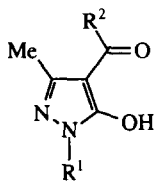
**Abstract**

The synthesis and characterization of triorganotin(IV) derivatives of two 4-acylpyrazol-5-ones(4-acetyl-5-one (HPMAP) and 4-benzoyl-5-one (HPMBP)) and of four 1-acylpyrazol-5-ones (1-acetyl-5-one (APzH), 1-(4'-nitrobenzoyl)-5-one (NPzH) and 1-salicyloyl-5-one (SPzH)) as well as those of diorganotin(IV) derivatives of the three 1-acylpyrazol-5-ones are reported. The X-ray crystal structure of tributyl(4-benzoylpyrazol-5-onato)tin(IV) monohydrate is also described.

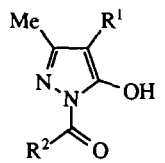
*Keywords:* Tin; Pyrazolone; Crystal structure; Mössbauer spectroscopy; X-ray diffraction

## 1. Introduction

Despite the fact that β-diketones have played a central role in the development of coordination chemistry, more exotic variants incorporating the same central coordination sphere are relatively uncommon. The acylpyrazol-5-ones (**I** and **II**) are an attractive ligand set in this respect, in that they have in themselves a rich chemistry embracing a wide variety of applications both as dyes [1] and as a result of their biological activity [2–5].



**I**



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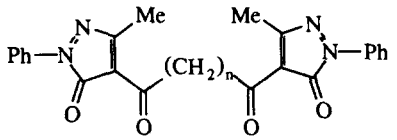

$n = 0, 2, 3, 4$

**III**

From the structural point of view, these ligands can exist in one of several tautomeric forms and it is thus surprising that the coordination chemistry of these ligands has been largely restricted to inorganic systems [6–8]. Indeed, only recently have the first organometallic derivatives of 4-acylpyrazolones (**I**) been reported and these incorporate (olefine)M (M = Rh, Ir) [9] or diorganotin ($R_2Sn$) moieties [10–13]. Of particular relevance to the current work are the structures of the dimethyltin, [12,13] di(*n*-butyl)tin [10] and di(tert-butyl)tin [11] derivatives of various 4-benzoylpyrazol-5-onates which are all six-coordinate, and also the isolation of polymeric organotin derivatives of bis[4-(1-phenyl-3-methyl pyrazol-5-one)dioxoalkanes] (**III**) [14].

Surprisingly, attempts to prepare simple triorganotin derivatives of the 4-acylpyrazol-5-ones (**I**) from $R_3SnCl$ and either the potassium or thallium salts of (**I**) yielded only diorganotin products, a fact attributed to the result of the following disproportionation [12]:

$$R_3SnCl \rightleftharpoons R_4Sn + R_2SnCl_2$$

As the first in a series of papers dealing with organometallic derivatives of acylpyrazol-5-ones, we now report the first syntheses of such triorganotin compounds, and report also the organotin derivatives of the related 1-acylpyrazol-5-ones (**II**), a ligand type for which, as far as we are aware, there is no known organometallic chemistry.

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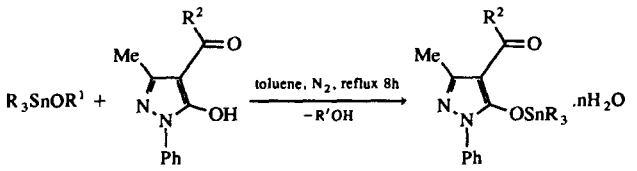
## 2. Results and discussion

The triorganotin(IV) derivatives (R = Bu or Ph) of 1-phenyl-3-methyl-4-acylpyrazolone (PMAP) and 4-benzoylpyrazol-5-one (PMBP) have been isolated from reaction of the free ligand and either tributyltin methoxide or triphenyltin ethoxide in 1 : 1 molar ratio in dry toluene:



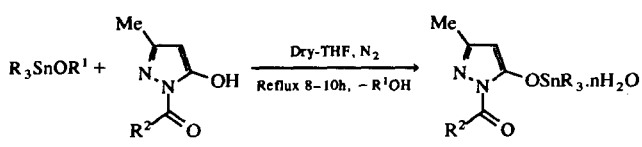

R = Bu, $R^1$ = Me
R = Ph, $R^1$ = Et

R = Bu, $R^2$ = Me (PMAP), n = 0 (1)
= Ph (PMBP), n = 1 (2)
R = Ph, $R^2$ = Me (PMAP), n = 0 (3)
= Ph (PMBP), n = 0 (4)

The products were obtained as the toluene-soluble (but hexane-insoluble) portion of the material produced by solvent evaporation at the end of reaction. A hexane soluble portion, usually extracted first, analyses for the analogous diorganotin(IV) derivative (about 15% of crude product), whose synthesis and properties have been previously published [10,11]. The new triorganotin(IV) derivatives **1–4** are air stable and are readily recrystallised from a dry toluene : ether (1 : 1) mixture, except **1** which was obtained as an dense brown oil. The remaining compounds are bright yellow (**2** and **4**) or colourless (**3**). Compound **2** was isolated only as a stable monohydrate.

Although recrystallization from toluene–ether of the tributyl(4-benzoylpyrazol-5-onato)tin(IV) (**2**) yielded the product as a monohydrate in crystalline form suitable for X-ray diffraction studies, attempts to crystallize triphenyl(4-acetylpyrazol-5-onato)tin(IV) (**3**) from a dilute toluene solution produced crystals of $Ph_4Sn$ after several days in solution. This suggests that the triorganotin(IV) derivatives disproportionate, probably slowly in some solvents, to the diorganotin(IV) derivative and the respective tetraorganotin(IV) moiety, as well as $R_3SnCl$ disproportionating in the presence of the ligand as previously reported [12].

The anerobic reaction between a series of 1-acylpyrazol-5-ones and tributyltin(IV) methoxide or triphenyltin(IV) ethoxide in 1 : 1 molar ratio in dry tetrahydrofuran (THF) over 8–10 h readily produces organotin(IV) derivatives of 1-acylpyrazol-5-ones (**5–9**):

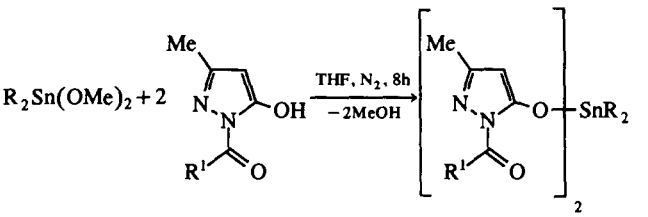



R = Bu, $R^1$ = Me
R = Ph, $R^1$ = Et

R = Bu, $R^2$ = Me (APz), n = 0 (5)
= 4-$NO_2C_6H_4$ (NPz), n = 0 (6)
= 2-$HOC_6H_4$ (SPz), n = 0 (7)
R = Ph, $R^2$ = Me (APz), n = 1 (8)
= 2$HOC_6H_4$ (SPz), n = 1 (9)

The free 1-acylpyrazolones themselves are poorly soluble in dry THF, and so the progress of the reaction could be monitored by the complete dissolution of the ligand followed by a colour change, usually to bright yellow ($R^2$ = NPz or SPz) or red ($R^2$ = APz) after refluxing for about 20 min. The products obtained on removing the solvent at the end of reaction are usually analytically pure. They are poorly soluble in water and in common organic solvents but could be recrystallized over several days from cooled (−5°C) saturated toluene : THF (1 : 1) mixtures. All the triorganotin(IV) derivatives of 1-acylpyrazol-5-ones isolated (**5–9**) are unstable on prolonged standing in ether, dichloromethane or mixtures of THF with alcohols.

The dibutyl and dimethyl derivatives of 1-acylpyrazol-5-ones have also been been prepared, by reaction of $R_2Sn(OMe)_2$ with two molar equivalents of the free ligand:




R = Me, $R^1$ = Me (Apz) (**10**)
$R^1$ = 2-$HOC_6H_4$ (SPz) (**11**)
R = Bu, $R^1$ = Me (APz) (**12**)
$R^1$ = 4-$NO_2C_6H_4$ (NPz) (**13**)
$R^1$ = 2-$HOC_6H_4$ (SPz) (**14**)

### 2.1. IR spectra

The absence of an absorption band due to $\nu$(OH · · · O) suggests coordination to the tin atom through the deprotonated oxygen of the enol tautomer. The $\nu$(C=O) absorption bands are observed between 1675 and 1630 $cm^{-1}$ in the free ligands and have shifted to 1630–1590 $cm^{-1}$ in the anhydrous compounds **1**, **3–7** and **10–14**, indicating that the two oxygen atoms of the β-diketonate fragment of the ligand are involved in coordination to the tin. This signal experiences only minor shifts from about 1675–1630 $cm^{-1}$ in the spectra of the monohydrated compounds **2**, **8** and **9**, which in turn include a band at 3250 $cm^{-1}$ with a weak shoulder at about 3600 $cm^{-1}$ arising from the coordinated water molecule. This suggests that in these hydrates the carbonyl group of the respective

pyrazol-5-one is not coordinated or has only weak interactions with a neighbouring atom, possibly by hydrogen bonding. The vibrations of the azomethine bond in the pyrazole ring are observed between 1580 and 1605 $cm^{-1}$ in the complexes, while bands at around 450 $cm^{-1}$ have been assigned to $\nu$(Sn–O) by analogy with earlier assignments for bis(4-benzoylpyrazol-5-onato)diorganotin(IV) compounds [12]. The two dimethyltin compounds also show $\nu$(Sn–C) at about 550 and 510 $cm^{-1}$, suggesting non-linearity of the C–Sn–C unit and in keeping with the inferences made below from Mössbauer data.

### 2.2. Nuclear magnetic resonance

The $^{1}H$ and $^{13}C$ NMR of **1–14** resemble those of their respective ligands except for the disappearance of the broad OH band of the enol form of the ligand at 9.72–11.38 ppm [8,11–14] in the $^{1}H$ NMR spectrum, consistent with coordination of oxygen to tin after deprotonation. The protons of a coordinated water molecule appear as broad bands at $\delta \approx 3.50$ ppm in the $^{1}H$ NMR spectra of monohydrated compounds **2**, **8** and **9**. The $^{1}H$ NMR spectra of the dimethyltin(IV) derivatives **10** and **11** contain satellites about the methyltin signals with $^{2}J(^{119}Sn–C–^{1}H)$ coupling of 93.6 Hz and 97.0 Hz (Table 1) which reflect the six-coordinated nature of these species, and parallel data for other $R_2SnL_2$ (L = PMBP or PMAP) ($^{2}J \approx 90–130$ Hz) [11,12].

The $^{13}C$ NMR spectra of the complexes show a small but significant shift (up to 8 ppm) in the position of carbon resonances of the methyl carbon attached to C(3) upon coordination as a consequence of reduced shielding in the tin derivatives. This is similar to the previously reported observations for the diorganotin(IV) derivatives of 4-benzoylpyrazol-5-one [12,13]. The position of resonances of the coordinating carbonyl groups have experienced only small shifts from their position in the ligands (about 0–4.5 ppm), although this is consistent both with previous studies of organotin acylpyrazolones [8,11–14] and with chelation of the enol form of the ligand, as indicated by the IR spectra.

The values of $^{1}J(^{13}C–^{119}Sn)$ couplings are also reported in Table 1. The $^{1}J(^{13}C–^{119}Sn)$ value of 362.6 Hz for the monohydrate **2** is lower than might be expected for a five-coordinate geometry around the central tin atom; however, the values of $^{1}J(^{13}C–^{119}Sn)$ coupling for the other triorganotin(IV) derivatives **1–9** are between 448 and 485 Hz and are consistent with such a coordination number. The $^{1}J(^{13}C–^{119}Sn)$ values of 880–980 Hz observed for diorganotin(IV) derivatives **10–14** are markedly higher than the values in the triorganotin derivatives, suggesting that these species, like related diorganotin bis(4-acylpyrazolones) reported previously [8,10–13], have an octahedral coordination about the metal.

From the values of $\delta(^{119}Sn)$ for **1–14** reported in Table 1 the solution behaviour of the compounds can be classified into five groups with respect to the type of coordination around the tin atom.

Firstly, the $\delta(^{119}Sn)$ chemical shifts from −102 to −238 ppm for **1**, **3** and **4** support a five-coordinate geometry around the tin atom, and, together with with the quadrupole splitting (QS) values of about 2.5 mm $s^{-1}$ in the Mössbauer spectra of these species, are consistent with a *cis*-$R_3SnO_2$ coordination (**IV**) in which the 4-acylpyrazol-5-onate ligands are chelating.

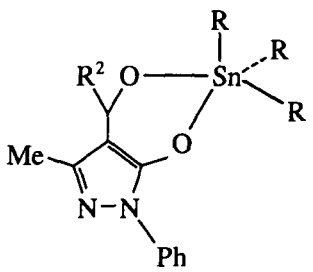
Secondly, the $\delta(^{119}Sn)$ chemical shifts for the tributytin(IV) derivatives of 1-acylpyrazol-5-onates **5–7** appear between −21 and −48 ppm, having experienced an upfield shift from +83 ppm reported earlier for $Bu_3SnOMe$ from which they were made and which is reported to exist as a tetrahedral monomer at room

Table 1
Comparative $^{2}J(^{1}H–^{119}Sn)$, $^{1}J(^{13}C–^{119}Sn)$ and $\delta$ ($^{119}Sn$) data for **1–14** and related organotin compounds

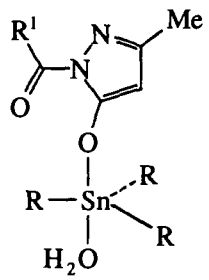
| Compound | $\delta$ ($^{119}Sn$) (ppm) | $^{2}J(^{1}H–^{119}Sn)$ (Hz) | $^{1}J(^{13}C–^{119}Sn)$ (Hz) | CN [a] |
|---|---|---|---|---|
| $Bu_3Sn$(PMAP) | −102.0 | — | 470.0 | 5 |
| $Bu_3Sn$(PMBP)($H_2O$) | −126.0 | — | 362.6 | 5 |
| $Ph_3Sn$(PMAP) | −237.7 | — | — | 5 |
| $Ph_3Sn$(PMBP) | −207.8 | — | — | 5 |
| $Bu_3SnAPz$ | −47.8 | — | 461.4 | 5 |
| $Bu_3SnNPz$ | −21.2 | — | 485.0 | 5 |
| $Bu_3SnSpz$ | −21.0 | — | 449.6 | 5 |
| $Ph_3Sn$(APz)($H_2O$) | −49.2 | — | — | 5 |
| $Ph_3Sn$(SPz)($H_2O$) | −47.3 | — | — | 5 |
| $Me_2Sn(APz)_2$ | −361.3 | 93.6 | 897.9 | 6 |
| $Me_2Sn(SPz)_2$ | −329.7 | 97.0 | 980.2 | 6 |
| $Bu_2Sn(APz)_2$ | −333.2 | — | 879.7 | 6 |
| $Bu_2Sn(NPz)_2$ | −367.0 | — | 896.4 | 6 |
| $Bu_2Sn(SPz)_2$ | −342.4 | — | 925.3 | 6 |

[a] CN, coordination number around tin atom.

temperature [15]. Compounds **5–7** are thus also considered to have a five-coordinate *cis*-$R_3SnO_2$-type geometry around tin, analogous to **IV**. The $^1J(^{13}C-^{119}Sn)$ data for **5–7** are in the region of 450–485 Hz (Table 1) and support this assertion. However, the relatively low field $\delta(^{119}Sn)$ shift values from −21 to −48 ppm (cf. −102 ppm for **1**) appear to indicate greater asymmetry in the two C–O distances of the β-diketonate moiety of the 1-acylpyrazol-5-ones than in their 4-acyl isomers.



**IV**



**V**

Thirdly, the $\delta(^{119}Sn)$ chemical shift of −126 ppm for **2**, $Bu_3Sn(PMBP)(H_2O)$, has experienced a significant upfield shift from the value of +83 ppm for its precursor, $Bu_3SnOMe$. This indicates increased coordination around the tin atom and a five-coordinate tin centre is proposed for this compound. The analytical data support a monohydrate, and $\nu$(C=O) (1675 $cm^{-1}$) shows that the ligand is not bidentate in this compound. X-ray data (see below) confirms a *trans*-$R_3SnLL'$ geometry around tin (**V**), which involves coordinated water as well as the 5-enol oxygen.

Fourthly, and in contrast, $^{119}Sn$ NMR chemical shifts of the two monohydrated triphenyltin(IV) derivatives of the 1-acylpyrazol-5-onates **8** and **9** appear at about −48 ppm and support a four-coordinate environment around tin in solution. However, the Mössbauer parameters for these species (QS values of about 3.5 mm $s^{-1}$) suggests five-coordination in the solid state. One explanation of the data is that the pyrazolone ligand is bridging in the solid state, and this interaction is broken upon dissolution. Such a situation is not uncommon in organotin chemistry, but there is no precedent for such behaviour with β-diketonate ligands or in previous reports on the coordination chemistry of acylpyrazolones. Moreover, the $\nu$(C=O) stretching frequency (1630 and 1645 $cm^{-1}$) suggests that any secondary bonding involving this functionality is at best weak. An alternative rationale lies in the positioning of the water molecule in these species. The IR data suggest that the water molecule is associated with the free C=O group of the 1-acylpyrazol-5-onate by hydrogen bonding, since the shift in $\nu$(C=O) is insufficient to suggest that it is coordinated to tin in these compounds. In addition, the water molecule would be directly coordinated to tin in the solid state as in the structure of $Bu_3Sn(PMBP)(H_2O)$ (**2**) described in Section 2.4, such that the Mössbauer data are consistent with a similar five-coordinated structure for **8** and **9**. In this scenario, the $^{119}Sn$ NMR data imply that in solution the coordinated water molecule is labile with respect to the metal, allowing it to become four coordinated.

Table 2
78 K $^{119}Sn$ Mössbauer data for organotin acylpyrazol-5-onates **1–14**

| Compound | IS (mm $s^{-1}$) | QS (mm $s^{-1}$) |
|---|---|---|
| **1** | 1.18 | 2.49 |
| **2** | 1.45 | 3.80 |
| **3** | 1.14 | 2.53 |
| **4** | 1.26 | 2.64 |
| **5** | 1.14 | 2.58 |
| **6** | 1.08 | 2.51 |
| **7** | 1.03 | 2.43 |
| **8** | 0.95 | 3.34 |
| **9** | 1.42 | 3.57 |
| **10** | 1.25 | 3.76 |
| **11** | 1.21 | 3.88 |
| **12** | 1.27 | 3.60 |
| **13** | 1.28 | 3.55 |
| **14** | 1.31 | 3.63 |

Finally, the $^{119}Sn$ chemical shifts for diorganotin complexes **10–14** have experienced stronger upfield shifts (about −350 ppm), and which are close to the values reported for analogous diorganotin(IV) derivatives of 4-acylpyrazol-5-ones (from −300 to −500 ppm) [11,12].

### 2.3. $^{119}Sn$-Mössbauer spectra

Mössbauer data on QS and isomer shift (IS) values for all the compounds prepared are given in Table 2. The magnitude of the QS values for the anhydrous triorganotin(IV) compounds **1**, **3–7** (2.11–2.58 mm $s^{-1}$) could arise from either tetrahedral or *cis*-trigonal bipyramidal geometries about tin [16], but in the light of the $^{119}Sn$ NMR data discussed earlier the latter assignment is more reasonable. Data for the monohydrated compounds **2**, **8** and **9** (3.34–3.80 mm $s^{-1}$) all relate to a *trans*-$R_3SnO_2$ isomer **V**, in which a monodentate acylpyrazol-5-onate and a water molecule are coordinated to the tin atom through their oxygen atoms.

The Mössbauer QS values for the diorganotin(IV) derivatives **10–14** can be correlated with the C–Sn–C angles in these species using a point charge model reported some years ago by Sham and Bancroft [17]. The angles calculated for QS values in the range 3.55–3.88 mm $s^{-1}$ are 144–157°, consistent with distorted six-coordinate geometries for tin.

These results are further supported by NMR coupling constants $^1J$ and $^2J$. For the dimethyltin(IV) derivatives **10** and **11** the C–Sn–C bond angles were calculated to be 150.9° (**10**) and 156.9° (**11**), respectively from

$^2J(^{119}Sn–C–^1H)$ values of 93.6 Hz and 97.0 Hz, according to the relationship [18]

$$\theta = 0.0161\,|^2J|^2 - 1.32\,|^2J| + 133.4 \quad (1)$$

Similar values (153.9° (**10**) and 162.7° (**11**)) are computed from the $^1J(^{119}Sn–^{13}C)$ couplings using [19],

$$^1J = 11.4\theta - 875 \quad (2)$$

and for the series of butyl compounds (162.7° (**12**), 164.4° (**13**) and 167.3° (**14**)) using [20]

$$^1J = 9.99\theta - 746 \quad (3)$$

Overall, these results compare very well with the C–Sn–C angles of between 150.0 and 154.7° in the crystal structures of dimethyltin, di(*n*-butyl)tin and di(tert-butyl)tin(IV) derivatives of 4-benzoylpyrazol-5-one [10–13] which are reported as distorted octahedral (or skew trapezoidal bipyramidal) species.

### 2.4. Crystal and molecular structure of tributyl(1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)tin(IV) monohydrate, $[SnBu_3(PMBP)\cdot H_2O]$ (2)

Fig. 1 shows the numbering scheme of the asymmetric unit of $SnBu_3PMBP\cdot H_2O$ (**2**). The unit cell viewed perpendicular to the *a*–*c* plane is shown in Fig. 2. Table 3 lists the fractional atomic coordinates, and Table 4 contains the most important bond lengths and angles.

The crystal structure consists of a discrete molecular unit in which one molecule of water (O(3)) is coordinated to tin along with the deprotonated oxygen of a monodentate pyrazolone ligand (O(1)). The molecule exhibits no crystallographic symmetry and all atoms occupy general positions. The coordination environment around tin atom is a distorted trigonal bipyramid with the three butyl groups occupying the equatorial sites and

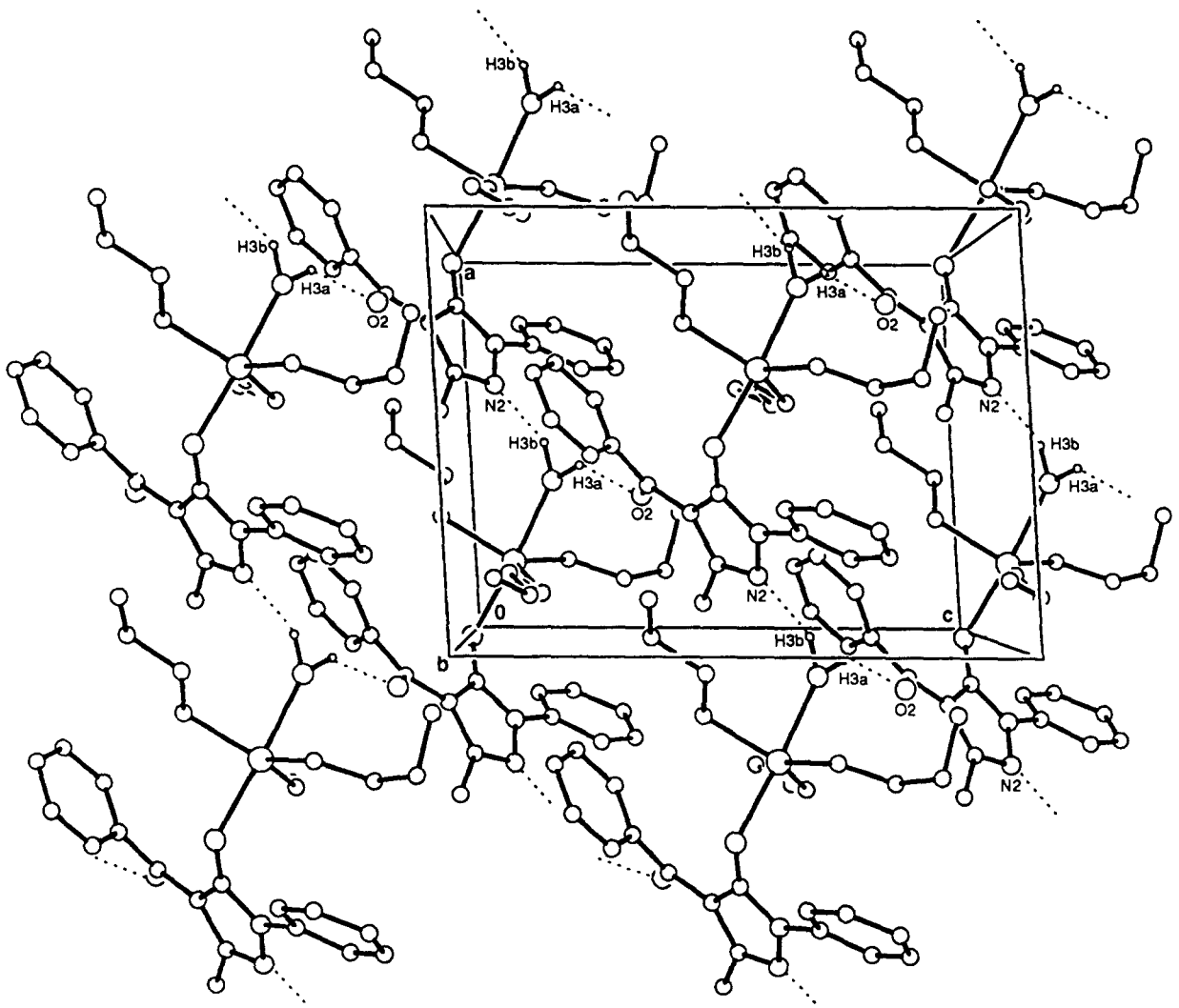



Fig. 2. A view of the lattice structure of **2** along *b*. Hydrogen bonds are shown as dotted lines.

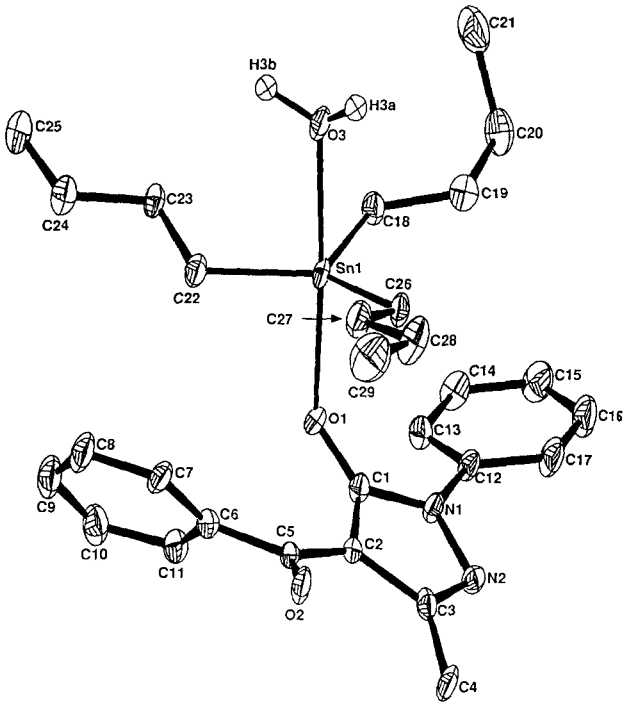



Fig. 1. The asymmetric unit of **2** showing the numbering scheme used in the text and tables.

the oxygen atoms of a water and of the monodentate pyrazolone ligand occuping the apical positions. The Sn atom is displaced from the $C_3$ plane of the butyl α-carbon atoms by only 0.16 Å, reflecting the strength of the bond between the metal and the solvate. Related $H_2O$..Sn interactions are given in Table 5 for comparison. The near-linearity of the angle O(1)–Sn(1)–O(3) (174.9(2)°) also reflects the strength of coordination of the solvate molecule.

The two Sn–O bonds, Sn(1)–O(1) (2.224(6) Å) and Sn(1)–O(3) (2.345(7) Å), are typical of their type (see Table 5). In related diorganotin(IV) systems, the C–O distance usually increases upon coordination of the oxygen atom to tin atom [10–12]. In **2** however, the unique monodentate nature of the pyrazolone ligand means that the C(5)–O(2) distance of 1.243(9) Å has the lowest value yet observed among the relevant analogues, and this value is identical with the distance of 1.233(8) Å in the ligand, HPMBP [21].

The 4-benzoyl carbonyl oxygen atom O(2) is thus not involved in any intramolecular interactions involving tin. This is unusual for this ligand which in previous reports has always been chelated to a metal centre. The supramolecular structure of **2** does, however, incorporate a hydrogen-bonding network involving the hydrogens of the water molecule along with N(2) and O(2) atoms of neighbouring molecules (Fig. 2). Typically, H(3b) of the molecule as shown interacts with N(2) of the molecule generated by the operator $1+x$, $y$, $z$ (1.90 Å), while H(3a) interacts with the O(2) of the lattice neighbour generated via the operator $0.5+x$, $0.5-y$, $0.5+z$ (1.77 Å). Lattice propogation of these two hydrogen bonds serves to generate infinite two-dimensional sheets of molecules which stack along *b*.

## 3. Experimental details

The triphenyltin(IV) chloride, triphenyltin(IV) methoxide, tributyltin(IV) methoxide, dimethyltin(IV) methoxide and diphenyltin(IV) dichloride were obtained commercially from Aldrich (UK). 1- and 4-acylpyrazolones were prepared by literature methods [6,23]. The solvents were obtained commercially and used without further purification, except for toluene and for THF, which were dried using benzophenone and distilled under a nitrogen atmosphere.

Spectra were recorded on the following instruments: JEOL GX270 ($^1$H and $^{13}$C NMR), GX400 ($^{119}$ NMR) and Perkin–Elmer 599B (IR). NMR spectra were recorded in $CDCl_3$ unless indicated otherwise. Details

Table 3
Fractional atomic co-ordinates for **2**

| | $x$ ($\times 10^{-4}$) | $y$ ($\times 10^{-4}$) | $z$ ($\times 10^{-4}$) |
|---|---|---|---|
| Sn(1) | 1847.8(5) | 1412.0(2) | 840.8(3) |
| N(1) | −2322(5) | 1340(2) | 688(4) |
| N(2) | −3442(5) | 1705(2) | 638(4) |
| O(1) | −148(5) | 1204(2) | −92(3) |
| O(2) | −1387(5) | 2715(2) | −1521(4) |
| O(3) | 3993(5) | 1686(2) | 1702(4) |
| C(1) | −1312(7) | 1465(3) | −45(5) |
| C(2) | −1828(6) | 1922(3) | −579(5) |
| C(3) | −3153(7) | 2049(3) | −111(5) |
| C(4) | −4166(7) | 2479(3) | −435(5) |
| C(5) | −1131(6) | 2233(3) | −1383(5) |
| C(6) | −98(7) | 1961(3) | −2076(5) |
| C(7) | 1096(7) | 2243(3) | −2372(6) |
| C(8) | 2028(8) | 2020(3) | −3067(6) |
| C(9) | 1738(8) | 1514(3) | −3490(6) |
| C(10) | 543(8) | 1240(3) | −3221(5) |
| C(11) | −359(7) | 1462(3) | −2497(5) |
| C(12) | −2315(7) | 912(3) | 1419(5) |
| C(13) | −1693(7) | 427(3) | 1160(5) |
| C(14) | −1672(7) | 16(3) | 1873(6) |
| C(15) | −2294(8) | 66(3) | 2855(6) |
| C(16) | −2934(8) | 544(3) | 3095(6) |
| C(17) | −2943(7) | 977(3) | 2396(5) |
| C(18) | 1890(7) | 763(3) | 1937(5) |
| C(19) | 1327(8) | 900(3) | 3042(6) |
| C(20) | 1584(9) | 465(4) | 3883(6) |
| C(21) | 3139(9) | 396(4) | 4234(6) |
| C(22) | 3027(7) | 1341(3) | −559(5) |
| C(23) | 4094(7) | 889(3) | −523(5) |
| C(24) | 5003(8) | 892(3) | −1513(6) |
| C(25) | 6003(8) | 415(4) | −1547(6) |
| C(26) | 1030(7) | 2155(3) | 1392(5) |
| C(27) | 1539(7) | 2636(3) | 771(6) |
| C(28) | 1033(8) | 3166(3) | 1179(7) |
| C(29) | 1453(9) | 3634(4) | 517(7) |

Table 4
Selected geometric data for **2**: bond lengths (Å) and bond angles (°)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| O(1)–Sn(1) | 2.224(6) | O(3)–Sn(1) | 2.345(7) |
| C(18)–Sn(1) | 2.126(8) | C(22)–Sn(1) | 2.127(8) |
| C(26)–Sn(1) | 2.145(9) | N(2)–N(1) | 1.398(8) |
| C(1)–N(1) | 1.391(9) | C(12)–N(1) | 1.410(9) |
| C(3)–N(2) | 1.311(9) | C(1)–O(1) | 1.283(9) |
| C(5)–O(2) | 1.243(9) | C(2)–C(1) | 1.401(10) |
| C(3)–C(2) | 1.443(9) | C(5)–C(2) | 1.456(9) |
| C(4)–C(3) | 1.485(10) | C(6)–C(5) | 1.500(11) |
| *Bond angles* | | | |
| O(3)–Sn(1)–O(1) | 174.9(2) | C(18)–Sn(1)–O(1) | 98.3(3) |
| C(18)–Sn(1)–O(3) | 86.7(3) | C(22)–Sn(1)–O(1) | 90.9(3) |
| C(22)–Sn(1)–O(3) | 85.7(3) | C(22)–Sn(1)–C(18) | 118.1(3) |
| C(26)–Sn(1)–O(1) | 93.6(3) | C(26)–Sn(1)–O(3) | 85.1(3) |
| C(26)–Sn(1)–C(18) | 117.0(3) | C(26)–Sn(1)–C(22) | 123.3(4) |
| C(1)–N(1)–N(2) | 111.4(6) | C(12)–N(1)–N(2) | 120.5(6) |
| C(12)–N(1)–C(1) | 128.1(6) | C(3)–N(2)–N(1) | 106.2(6) |
| C(1)–O(1)–Sn(1) | 124.0(5) | O(1)–C(1)–N(1) | 122.2(7) |
| C(2)–C(1)–N(1) | 105.4(6) | C(2)–C(1)–O(1) | 132.3(6) |
| C(3)–C(2)–C(1) | 105.9(6) | C(5)–C(2)–C(1) | 127.5(7) |
| C(5)–C(2)–C(3) | 126.4(7) | C(2)–C(3)–N(2) | 111.1(7) |
| C(4)–C(3)–N(2) | 121.2(7) | C(4)–C(3)–C(2) | 127.5(7) |
| C(2)–C(5)–O(2) | 121.7(7) | C(6)–C(5)–O(2) | 119.4(6) |
| C(6)–C(5)–C(2) | 118.9(7) | | |

of our Mössbauer spectrometer and related procedures have been given elsewhere [24].

### 3.1. Synthesis of tributyl(1-phenyl-3-methyl-4-acetylpyrazol-5-onato)tin(IV) ($SnBu_3$(PMAP)) (1)

To a toluene solution (80 ml) of HPMAP (0.43 g, 0.002 mol) in a 500 ml two-neck quick-fit flask, set up with a refluxing condenser, and sustained under nitrogen flow, was added an equimolar quantity of tributyltin methoxide (0.57 ml, 0.002 mol), using a syringe, at room temperature. The mixture was then refluxed with stirring for 8 h. The solvent was evaporated under vacuum on a rotary evaporator at 60°C. A light-brown viscous oil was obtained on evaporating to dryness and was in an analytically pure form (yield, 0.93 g (92%)) Anal. Found: C, 56.8; H, 7.8; N, 5.4. $C_{24}H_{38}N_2O_2Sn$. Calc.: C, 57.0; H, 7.5; N, 5.6%. IR: $\nu$(C=O) 1590 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 0.79–1.49 (m, 27H, $C_4H_9Sn$), 2.45 (s, 3H, 3-Me); 2.40 (s, 3H, 4-acetyl Me); 7.10–7.70 (m, 5H, phenyl groups) ppm. $^{13}C$, NMR: $\delta$ 17.6 (3-Me), 27.8 (4-acetyl, Me), 104.7 (C-4),

Table 5
Comparative structural data for **2** and related compounds

| Compound | Bond distance (Å) | | | C–Sn–C angle (°) | Reference |
|---|---|---|---|---|---|
| | Sn–$OH_2$ | O–Sn, C=O · · · Sn | C=O | | |
| HPMBP [a] | | | 1.233(8) | | [21] |
| $Me_2Sn(PMBP)_2$ [a,b] | | 2.103, 2.375 | 1.295 | 153.3 | [12] |
| $Me_2Sn(PMBP\text{-}Br)_2$ [b,c] | | 2.057, 2.411 | 1.253 | 154.5 | [13] |
| $Bu^n_2Sn(PMBP)_2$ [a,b] | | 2.115, 2.365 | 1.335 | 154.7 | [10] |
| $Bu^t_2Sn(PMBP)_2$ [a,b] | | 2.140, 2.421 | 1.289 | 150.0 | [11] |
| $Bu_3Sn(PMBP)(H_2O)$ (2) [a] | 2.345(7) | 2.224(6) [e] | 1.243(9) | 119.5 | This work |
| $(Me_3Sn)_2SO_4 \cdot H_2O$ [d] | 2.335(4) | 2.239(4) [e] | | | |
| $Me_3Sn(PhSO_3) \cdot H_2O$ [d] | 2.300(1) | 2.370(1) [e] | | | |
| $Me_3Sn(NO_3) \cdot H_2O$ [d] | 2.470(2) | 2.220(3) [e] | | | |
| $Me_3Sn(O_2CC_5H_4N\text{-}2) \cdot H_2O$ [d] | 2.430 | 2.185 [e] | | | |

[a] PMBP = 4-benzoylpyrazol-5-onate.
[b] Average data for two ligands in the molecule.
[c] MMBP-Br = p-bromobenzoylpyrazol-5-onate.
[d] [22] and references cited therein.
[e] Sn–O.

148.0 (C-3), 160.7 (4-acetyl, CO), 192.8 (C-5), 122.2, 125.8, 128.8, 138.3 ($C_{i,o,m,p}H_5$(N-1)) ppm. $^1J$(Sn–C) = 470 Hz. $^{119}$Sn NMR: $\delta$ −102 ppm. Mössbauer: IS 1.18 mm s$^{-1}$; QS 2.49 mm s$^{-1}$.

### 3.2. Synthesis of tributyl(1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)tin(IV)monohydrate ($SnBu_3(PMBP)\cdot(H_2O)$) (2)

This compound was prepared in a manner analogous to that described for **1** by refluxing equimolar quantities of tributyltin methoxide (0.56 g, 0.002 mol) and HPMBP (0.64 g) in toluene, under nitrogen flow, for 8 h. The yellow solid obtained on evaporating the contents of the flask to dryness was washed with *n*-hexane (100 ml) to remove unreacted ligand, tributyltin methoxide and $Bu_2Sn(PMBP)_2$. The product was then extracted from the flask into dry toluene (30 ml), evaporated to dryness and recrystallized from toluene hexane (1 : 1) mixture (yield, 0.59 g, (50%); melting point (m.p.), 110°C). Anal. Found: C, 59.6; H, 7.2; N, 4.7. $C_{19}H_{42}N_2O_3Sn$. Calc.: C, 59.5; H, 7.2; N, 4.8%. IR: $\nu$(C=O) 1675 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 0.84–1.51 (m, 27H, $C_4H_9Sn$); 2.45 (s, 3H, 3-Me); 7.22–7.80 (m, 10H, phenyl groups) ppm. $^{13}$C NMR: $\delta$ 16.0 (3-Me); 13.6, 19.3, 27.3, 27.7, 27.8 ($C_4H_9Sn$), 127.8, 128.2, 130.7, 128.6 (4-benzoyl, $C_{i,o,m,p}H_5$), 104.7(C-4), 149.0 (C-3), 160.6 (4-benzoyl, CO), 191.7 (C-5), 122.2, 126.0, 128.6, 138.3 ($C_{i,o,m,p}H_5$(N-1)) ppm. $^1J$(Sn–C) = 362.6 Hz; $^{119}$Sn NMR: $\delta$ −126.9 ppm. Mössbauer: IS 1.45 mm s$^{-1}$; QS 3.80 mm s$^{-1}$.

### 3.3. Synthesis of triphenyl(1-phenyl-3-methyl-4-acetylpyrazol-5-onato)tin(IV) ($SnPh_3(PMAP)$) (3)

This compound was prepared in a manner analogous to that described for **1**, by refluxing equimolar quantities of triphenyltin ethoxide (0.43 g, 0.002 mol) and HPMAP (0.79 g, 0.002 mol) in toluene, under nitrogen for 8 h. The pure product was extracted in toluene as described for **1** and recrystallized from *n*-hexane (yield, 0.62 g (55%); m.p., 160°C). Anal. Found: C, 63.6; H, 4.6; N, 4.9. $C_{30}H_{26}N_2O_2Sn$ Calc.: C, 63.7; H, 4.6; N, 5.0%. IR: $\nu$(C=O) 1595 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.43 (s, 3H, 3-Me), 2.38 (s, 3H, 4-acetyl Me) 7.26–7.80 (m, 20H, phenyl groups) ppm. $^{13}$C NMR: $\delta$ 17.3 (3-Me), 28.4(4-acetyl, Me), 105.0 (C-4), 149.2 (C-3), 161.5 (4-acetyl, CO), 192.3 (C-5), 122.3, 125.9, 128.3, 139.0 ($C_{i,o,m,p}H_5$(N-1)) ppm. $^{119}$Sn NMR: $\delta$ −237.7 ppm. Mössbauer: IS 1.14 mm s$^{-1}$; QS 2.53 mm s$^{-1}$.

### 3.4. Synthesis of triphenyl(1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)tin(IV) ($SnPh_3PMBP$) (4)

To a toluene solution (80 ml) of NaPMBP (0.60 g, 0.002 mol) in a 500 ml two-neck quick-fit flask, set up with a refluxing condenser and sustained under nitrogen flow, was added triphenyltin chloride (0. 79 g, 0.002 mol) in toluene. A greenish-yellow solution left at the end of the reaction (8 h) was evaporated to dryness on a rotary evaporator at 60°C, yielding a dense greenish-yellow oil. This oil contains a mixture of $SnPh_2(PMBP)_2$ and $SnPh_3PMBP$. The diphenyltin derivative was first collected, together with unreacted ligand, by extraction into *n*-hexane (80 ml). The triphenyltin derivative, insoluble in *n*-hexane, was collected in 50 ml of dry toluene and concentrated to dryness. It was recrystallized from toluene : hexane (1 : 1) mixture (yield, 0.64 g, (57%); m.p., 52°C) Anal. Found: C, 66.8; H, 4.6, N, 4.5. $C_{35}H_{28}N_2O_2Sn$. Calc.: C, 67.0; H, 4.5; N, 4.5%. IR: $\nu$(C=O) 1597 cm$^{-1}$ $^1$H NMR ($CDCl_3$): $\delta$ 1.68 (s, 3H, 3-Me), 7.14-7.78 (m, 30H, phenyl groups) ppm. $^{13}$C NMR: $\delta$ 17.0 (3-Me), 127.0, 128.3, 131.0, 129.2 (4-benzoyl, $C_{i,o,m,p}H_5$) 104.6 (C-4), 149.3 (C-3), 161.8 (4-benzoyl, CO) 191.3 (C-5), 121.6, 125.0, 128.1, 138.0 ($C_{i,o,m,p}H_5$(N-1)); 121.6; 125.0; 128.1; 138.0(Sn-Ph) ppm. $^{119}$Sn NMR: $\delta$ −207.8 ppm. Mössbauer: IS 1.26 mm s$^{-1}$; QS 2.64 mm s$^{-1}$.

Compound **4** may also be prepared from HPMAP and $Ph_3SnOEt$, as described for the synthesis of $SnPh_3(PMAP)$ (**3**).

### 3.5. Synthesis of tributyl(1-acetyl-3-methylpyrazol-5-onato)tin(IV) ($SnBu_3(APz)$) (5)

To a THF (80 ml) suspension of APzH (0.56 g, 0.004 mol) in a Schlenk tube under a nitrogen atmosphere at room temperature was added an equimolar quantity of tributyltin methoxide (1.15 ml). The reaction proceeded under reflux, with the initial suspension disappearing giving a clear brown solution. Refluxing was continued for 8 h, and the solvent was removed under vacuum at room temperature. The crude product was analytically pure but was recrystallized from toluene: THF (1 : 3) mixture (yield, 1.28 g (74%); m.p., 214°C). Anal. Found: C, 49.8, H, 7.7; N. 6.7. $C_{18}H_{34}N_2O_2Sn$. Calc.: C, 50.4; H, 7.9; N, 6.5%. IR: $\nu$(C=O) 1592 cm$^{-1}$. $^1$H NMR (demethylsulphoxide-$d_6$ (DMSO-$d_6$)): $\delta$ 2.05 (s, 3H, 3-Me), 2.08 (s, 3H, 4-acetyl Me), 5.66 (s, 1H, C-4 methine H), 0.95; 1.42 (m, $C_4H_9Sn$) ppm. $^{13}$C, NMR: $\delta$ 16.9 (3H, 3-Me), 11.4 (3H, 1-acetyl, Me), 105.7 (1H, C-4), 140.2 (C-3), 150.4 (C-5), 166.7 (1-acetyl, CO), 13.5, 18.5, 24.9, 26.9 (Bu–Sn) ppm. $^1J$(Sn–H) = 461.4 Hz. $^{119}$Sn NMR: $\delta$ −47.8 ppm. Mössbauer: IS 1.14 mm s$^{-1}$; QS 2.58 mm s$^{-1}$.

### 3.6. Synthesis of tributyl[1-(4'-nitrobenzoyl)-3-methylpyrazol-5-onato]tin(IV) ($SnBu_3(NPz)$) (6)

To a greenish-yellow clear solution of NPzH (0.49 g, 0.002 mol) in a two-neck 500 ml quick-fit flask fitted with a refluxing condenser, obtained by warming gently

(30°C) in *p*-dioxan (150 ml), was added a methanolic solution (100 ml) of sodium methoxide (0.11 g, 0.002 mol). The formation of NaNPz in situ was indicated by the brick-red suspension obtained immediately. Tributyltin chloride (0.65 g, 0.002 mol) dissolved in methanol (50 ml) was then added carefully, yielding a clear red solution, which was then set to reflux for 6 h. After cooling, the solvent was removed under vacuum. The product $SnBu_3(NPz)$ was extracted into 100 ml of chloroform, filtered and evaporated to dryness under vacuum, producing the analytically pure yellow product (yield, 0.41 g (38%); m.p., 152°C (decomposition)). Anal. Found: C, 51.7; H, 6.8; N, 7.9. $C_{23}H_{35}N_3O_4Sn$. Calc.: C, 51.5; H, 6.5; N, 7.8%. IR: $\nu$(C=O) 1610 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 2.43 (s, 3H, 3-Me), 5.77 (s, 1H, C-4 methine H), 8.14–8.40 (m, 4H, $C_6H_4NO_2$), 0.81–1.53 (m, 27H $C_4H_9Sn$) ppm. $^{13}C$ NMR: $\delta$ 18.7 (3-Me), 138.0 (C-3), 106.6 (C-4), 149.2 (C-5), 163.8 [(N-1), CO], 89.8, 122.7, 128.9, 128.3 ($C_{i,o,m,p}H_4NO_2$), 13.5, 19.3, 26.0, 26.6, 27.0, 27.4, 27.8, 28.0 (Bu–Sn) ppm. $^1J$(Sn–C) = 485.0 Hz. $^{119}Sn$ NMR: $\delta$ −21.4 ppm. Mössbauer: IS 1.08 mm $s^{-1}$; QS 2.51 mm $s^{-1}$.

Compound **6** was also prepared as described for the synthesis of $SnBu_3(APz)$ (**5**).

### 3.7. Synthesis of tributyl(1-salicyloyl-3-methylpyrazol-5-onato)tin(IV) ($SnBu_3(SPz)$) (7)

This compound was prepared in a manner analogous to that described for **5**, by reacting equimolar quantities of tributyltin methoxide (0.57 ml, 0.002 mol) and SPzH (0.44 g, 0.002 mol) in THF (150 ml). The initial white suspension dissappeared as the reaction progressed, giving a clear bright yellow solution within 5 min of reaction. The crude bright yellow product was recrystallized from acetonitrile (yield, 0.96 g, (95%); m.p., 78°C (decomposition)). Anal. Found: C, 54.3; H, 7.3; N, 5.4. $C_{23}H_{36}N_2O_3Sn$. Calc.: C, 54.4; H, 7.1; N, 5.5%. IR: $\nu$(C=O) 1595 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.4 s (3H, 3-Me), 5.8 (s, 1H, C-4 methine H), 6.52–7.82 (m, 4H, $C_6H_4OH$), 0.77–1.59 (m, 27H, $C_4H_9Sn$), 11.59 (s, 1H, salicyloyl OH) ppm. $^{13}C$ NMR; $\delta$ 16.8 (3-Me), 138.4 (C-3), 106.0 (C-4), 149.8 (C-5), 165.3 ((N-1), CO), 92.2, 120.3, 128.6, 128.4 ($C_{i,o,m,p}H_4 \cdot OH$), 13.3, 19.3, 26.3, 26.9, 27.3, 27.8, 28.0 (Bu–Sn) ppm. $^1J$(Sn–C) = 449.6 Hz. $^{119}Sn$ NMR: $\delta$ −21.0 ppm. Mössbauer: IS 1.03 mm $s^{-1}$; QS 2.43 mm $s^{-1}$.

### 3.8. Synthesis of triphenyl(1-acetyl-3-methylpyrazol-5-onato)tin(IV)monohydrate ($SnPh_3(APz) \cdot H_2O$) (8)

This compound was prepared in a manner analogous to that for **5**, by refluxing equimolar quantities of triphenyltin ethoxide (0.79 g, 0.002 mol) and APzH (0.28 g) in THF (100 ml). The initial suspension disappeared after 2 h, giving a clear light-brown solution. The crude product was recrystallized from toluene–THF (yield, 0.84 g (82%); m.p., 178°C). Anal. Found: C, 57.0; H, 4.5; N, 5.9. $C_{24}H_{24}N_2O_3Sn$. Calc.; C, 56.8; H, 4.7; N, 5.6%. IR: $\nu$(C=O) 1630 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 1.98 (s, 3H, 3-Me), 2.02 (s, 3H, 1-acetyl Me), 5.24 (s, 1H, C-4 methine H), 7.18–7.76 (m, 18H, phenyl groups) ppm. $^{13}C$ NMR: $\delta$ 11.9 (1-acetyl, Me), 19.7 (3-Me), 139.5 (C-3), 90.4 (C-4), 158.3 (C-5), 168.8 (1-acetyl, CO), 128.3, 128.4, 129.3, 129.5, 130.0, 130.1, 132.2, 132.6, 133.3, 138.6, 139.9, 140.3 (Sn–Ph) ppm. $^{119}Sn$ NMR: $\delta$ −49.2 ppm. Mössbauer: IS 0.95 mm $s^{-1}$; QS 3.34 mm $s^{-1}$.

### 3.9. Synthesis of triphenyl(1-salicyloyl-3-methylpyrazol-5-onato)tin(IV)monohydrate ($SnPh_3SPz \cdot H_2O$) (9)

This compound was prepared in a manner analogous to that for **8**, by refluxing equimolar quantities of triphenyltin ethoxide (0.79 g, 0.002 mol) and SPzH (0.44 g) in THF (150 ml). The initial white suspension of SPzH disappeared after reaction for 20 min, giving a clear bright yellow solution. The crude product was recrystallized from a toluene : THF (1 : 3) mixture (yield, 1.03 g, (88%); m.p., 167°C (decomposition)). Anal. Found: C, 59.4; H, 4.5; N, 4.7. $C_{29}H_{26}N_2O_4Sn$. Calc.: C, 59.5; H, 4.4; N, 4.8%. IR: $\nu$(C=O) 1645 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): 2.48 (s, 3H, 3-Me), 5.83 (s, 1H, C-4 methine H), 7.34–7.87 (m, 19H, phenyl groups), 11.72 (s, 1H, salicyloyl OH) ppm. $^{13}C$ NMR: $\delta$ 18.8 (3-Me), 142.1 (C-3), 107.0 (C-4), 152.7 (C-5), 164.4 ((N-1), CO), 87.2, 117.2, 128.7, 129.4, 29.5, 131.9 and 136.2 ($C_{i,o,m,p}H_4 \cdot OH$), 122.4, 128.1, 128.4, 128.7, 129.6, 129.8, 130.5, 134.4, 135.1 (Bu–Sn) ppm. $^{119}Sn$ NMR: $\delta$ −47.3 ppm. Mössbauer: IS 1.42 mm $s^{-1}$; QS 3.57 mm $s^{-1}$.

### 3.10. Synthesis of dimethyl bis(1-acetyl-3-methylpyrazol-5-onato)tin(IV) ($SnMe_2(APz)_2$) (10)

This compound was prepared in a manner analogous to that described for **12** by refluxing dimethyltin dimethoxide (0.42 g, 0.002 mol) and APzH (0.56 g, 0.004 mol) in toluene for 8 h. The initial light-yellow suspension of APzH disappeared only after refluxing for about 90 min, yielding a light-brown solution. The solvent was removed under vacuum to give a light-brown solid product (yield, 0.56 g (65%); m.p., 159°C). Anal. Found: C, 38.8; H, 4.3; N, 12.8. $C_{14}H_{20}N_4O_4Sn$ Calc.: C, 39.3; H, 4.7; N, 13.1%. IR: $\nu$(C=O) 1594, $\nu$(Sn–C) 551, 510 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.11 (s, 6H, 3-Me), 5.57 (s, 2H, C-4 methine H), 0.90 (s, 6H, Me-Sn) ppm. $^2J(^1H–Sn)$ = 97.0 Hz. $^{13}C$ NMR: $\delta$ 18.7 (3-Me), 105.6 (C-4), 136.4 (C-3), 150.6 (C-5), 12.0 (*N*-acetyl, Me), 165.3 (*N*-acetyl, CO), 8.9 (Me–Sn) ppm. $^1J(^{13}C–Sn)$ = 879.9 Hz. $^{119}Sn$ NMR: $\delta$ = −361.3 ppm. Mössbauer: IS 1.25 mm $s^{-1}$; QS 3.76 mm $s^{-1}$.

### 3.11. Synthesis of dimethyl bis(1-salicyloyl-3-methylpyrazol-5-onato)tin(IV) ($SnMe_2(SPz)_2$) (11)

This compound was prepared according to the manner described for **10**, by reacting dimethyltin dimethoxide (0.42 g, 0.002 mol) and SPzH (0.87 g, 0.004 mol) in toluene at room temperature for 8 h. The initial yellow suspension of SPzH gradually disappeared, to yield a brightly coloured golden-yellow solution, after reaction for about 15 min. The solvent was removed under vacuum to give a bright-yellow solid product (yield, 0.70 g (60%); m.p., 135°C (decomposition)). C, 49.7; H, 4.5; N, 9.3. Anal. Found: $C_{24}H_{24}N_4O_6Sn$ Calc.: C, 49.4; H, 4.1; N, 9.6%. IR: $\nu$(C=O) 1615, $\nu$(Sn–C) 545, 510 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.42 (s, 6H, 3-Me), 7.21–7.74 (m, 8H, phenyl groups), 5.82 (s, 2H, C-4 methine H), 11.38 (s, salicyloyl OH), 1.05 (s, Me–Sn) ppm. $^2J(^1H–Sn) = 97.0$ Hz. $^{13}C$ NMR: $\delta$ 18.6 (3-Me), 104.9 (C-4), 138.3 (C-3), 149.8 (C-5), 164.2 (salicyloyl, CO); 116.1, 119.7, 121.8, 126.7 127.3, 131.2 (salicyloyl, phenyl), 7.8 (Me–Sn) ppm. $^1J(^{13}C–Sn) = 980.2$ Hz. $^{119}Sn$ NMR: $\delta$ −329.7 ppm. Mössbauer: IS 1.21 mm $s^{-1}$; QS 3.88 mm $s^{-1}$.

### 3.12. Synthesis of di(n-butyl) bis(1-acetyl-3-methylpyrazol-5-onato)tin(IV) ($SnBu_2(APz)_2$) (12)

To a suspension of APzH (0.56 g, 0.004 mol) in 40 ml of toluene in a Schlenk tube, under nitrogen atmosphere, was added a toluene solution of dibutyltin dimethoxide (0.59 ml, 0.002 mol). The ligand suspension disappeared after gentle refluxing for 90 min, yielding a lightly brown solution. The refluxing was continued for 8 h. The solvent was removed under vacuum to give a brown solid (yield, 0.80 g (78%); m.p., 181°C). Anal. Found: C, 56.2; H, 5.8, N, 8.2. $C_{30}H_{36}N_4O_4Sn$ Calc.: C, 56.7; H, 5.7; N, 8.8%. IR: $\nu$(C=O) 1596 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 2.08 (s, 6H, 3-Me), 2.11 (s, 6H, 1-acetyl Me), 5.56 (s, 2H, C-4 methine H), 0.79–1.54 (m, 18H, $C_4H_9Sn$) ppm. $^{13}C$ NMR: $\delta$ 18.2 (3-Me), 100.5 (C-4), 138.7 (C-3), 155.8 (C-5), 11.9 (*N*-acetyl, Me), 168.2 (N-acetyl, CO), 13.2 19.7, 26.5, 27.7 (Bu–Sn) ppm. $^1J(^{13}C–Sn) = 879.7$ Hz. $^{119}Sn$ NMR: $\delta$ −333.2 ppm. Mössbauer: IS 1.27 mm $s^{-1}$; QS 3.60 mm $s^{-1}$.

### 3.13. Synthesis of di(n-butyl) bis[1-(4'-nitrobenzoyl)-3-methylpyrazol-5-onato]tin(IV) ($SnBu_2(NPz)_2$) (13)

This compound was prepared in a manner analogous to that described for **12**, by refluxing dibutyltin dimethoxide (0.59 ml, 0.002 mol) and NPzH (0.98 g, 0.004 mol) in toluene. The yellow suspension of NPzH gradually disappeared, giving a clear red solution within 20 min of reaction. The solvent was removed under vacuum, yielding a red–orange solid. The product was extracted into 100 ml of chloroform and then evaporated to dryness, giving an analytically pure product (yield, 0.90 g (62%)); m.p., 187°C). Anal. Found: C, 50.0; H, 4.7; N, 12.0. $C_{30}H_{34}N_6O_8Sn$. Calc.: C, 49.7; H, 4.7; N, 11.6%. IR: $\nu$(C=O) 1630 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$): $\delta$ 0.78–1.45 (m, 18H, $C_4H_9Sn$); 2.49 (s, 6H, 3-Me); 5.78 (s, 2H, C-4 methine H); 6.65-7.97 (dd, 8H, phenyl group) ppm. $^{13}C$ NMR: $\delta$ 18.8 (3-Me), 13.5, 23.4, 25.7, 26.6 (Bu–Sn); 107.0 (C-4); 138.7(C-3); 158.3 (C-3); 168.2 (*N*-nitrobenzoyl, CO); 114.8, 115.8, 116.1, 117.2, 128.8, 121.46, 130.1, 133.6, 133.9 (*N*-nitrobenzoyl, phenyl) ppm. $^1J = 896.4$ Hz. $^{119}Sn$ NMR: $\delta$ −367.0 ppm. Mössbauer: IS 1.28 mm $s^{-1}$; QS 3.55 mm $s^{-1}$.

### 3.14. Synthesis of dibutyl bis(1-salicyloyl-3-methylpyrazol-5-onato)tin(IV) ($SnBu_2(SPz)_2$) (14)

This compound was prepared in a manner analogous to that described for **12** by reacting dibutyltin dimethoxide (0.59 ml, 0.002 mol) and SPzH (0.87 g, 0.004 mol) in toluene at room temperature for 8 h. The initial yellow suspension of SPzH gradually disappeared, to yield a brightly coloured, golden-yellow solution after reaction for about 15 min. The solvent was removed under vacuum to give a yellow solid product (yield, 1.04 g (78%); m.p., 216°C). Anal. Found: C, 54.0; H, 5.6; N, 8.2. $C_{30}H_{36}N_4O_6Sn$. Calc.: C, 54.0; H, 5.4; N, 8.4%. IR: $\nu$(C=O) 1620 $cm^{-1}$. H NMR (DMSO-$d_6$): $\delta$ 2.38 (s, 6H, 3-Me), 7.12–7.19 (m, 8H, phenyl protons), 5.69 (s, C-4 methine H), 11.63 (s, 1H, salicyloyl OH), 0.88-1.61 (m, 18H, $C_4H_9Sn$) ppm. $^{13}C$ NMR: $\delta$ 17.8 (3-Me), 106.8 (C-4), 139.7 (C-3), 154.8 (C-5), 166.3 (*N*-salicyloyl, CO), 116.9, 128.6, 129.4, 132.2, 133.9, (*N*-salicyloyl phenyl), 13.7, 20.2, 26.6, 26.9 (Bu–Sn), ppm. $^1J(^{13}C–Sn) = 925.3$ Hz. $^{119}Sn$ NMR: $\delta$ −342.4 ppm. Mössbauer: IS 1.31 mm $s^{-1}$; QS 3.63 mm $s^{-1}$.

### 3.15. X-ray data collection and structure determination for tributyl(1-phenyl-3-methyl-4-benzoylpyrazol-5-onato)tin(IV)

A crystal of approximate dimensions 0.25 × 0.25 × 0.2 mm was used for data collection.

#### 3.15.1. Crystal data

$C_{19}H_{42}N_2O_3Sn$; $M = 585.4$; monoclinic; $a = 9.436(2)$, $b = 25.092(7)$ and $c = 12.481(2)$Å; $\beta = 92.99(2)°$; $U = 2951.1$ Å$^3$; space group, $P2_1/n$; $Z = 4$; $D_c = 1.32$ g $cm^{-3}$; $\mu$(Mo K$\alpha$) = 9.0 $cm^{-1}$; $F(000) = 1216$. Data were measured at 170 K on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$. 5065 reflections were collected of which 3120 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarization but not for absorption effects. The structure was solved by Patterson methods and refined

using the SHELX [25,26] suite of programs. In the final least-squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions (C–H, 0.96 Å) except in the instance of the coordinated water protons (H(3a) and H(3b)) which were located and refined at a distance of 0.96 Å from O(3).

Final residuals after 10 cycles of least squares were $R = 0.0450$, $R_w = 0.0440$, for a weighting scheme of $w = 2.2351/[\sigma^2(F) + 0.001063(F)^2]$. Maximum final shift to estimated standard deviation was less than 0.0005. The maximum and minimum residual densities were 0.49 and −0.47 electrons $Å^{-3}$ respectively. Final fractional atomic coordinates and selected geometric data are given in Tables 3 and 4 respectively. Tables of anisotropic temperature factors, hydrogen atom positions and a complete listing of structural data are available as supplementary data. The asymmetric unit is shown in Fig. 1, together with the labelling scheme used in the text and Tables.

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