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Tin(IV) and organotin(IV) derivatives of novel β-diketones Part IV. Triorganotin(IV) complexes of fluorinated 4-acyl-5-pyrazolones. Crystal structure of (1-(4-trifluoromethylphenyl)-3-methyl-4-acetylpyrazolon-5-ato)-triphenyltin(IV)

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Abstract

The synthesis of three 1-(4-trifluoromethylphenyl)-3-methyl-4-R^1(C=O)-5-pyrazolone proligands LH (L^1H; $R^1 = C_6H_5$: L^2H; $R^1 = CH_3$: L^3H; $R^1 = CF_3$) and their interaction with R_3Sn(IV) acceptors (R = Me, Bu^n, Ph) are reported. When R = Me or Bu^n, aquo (4-acylpyrazolonate)$SnR_3(H_2O)$ derivatives are obtained and the anionic donors 4-acylpyrazolonate (L^-) act in the O–monodentate form. These triorganotin complexes are not stable in chlorohydrocarbon solvents and decompose to R_4Sn and bis(4-acyl-5-pyrazolonate)$_2SnR_2$. When R = Ph, stable (4-acyl-5-pyrazolonate)$SnPh_3$ derivatives, both in solution and in the solid state, are obtained. The crystal structure of (1-(4-trifluoromethylphenyl)-3-methyl-4-acetylpyrazolon-5-ato)triphenyltin(IV) shows a five-coordinate tin atom in a strongly distorted *cis*-bipyramidal trigonal environment (axial angle = 161.2(2)°) with the acylpyrazolonate donor acting as an asymmetric O_2–bidentate species (Sn–O(1) = 2.081(6) Å: Sn–O(2) = 2.424(5) Å). Electronic effects are responsible for the different behavior shown by these trialkyl and triphenyl derivatives.

Keywords: 4-Acyl-5-pyrazolones; Crystal structure; IR; NMR; Triorganotin(IV) complex

1. Introduction

Triorganotin compounds are widely used as biocides. For example, triphenyltin (TPT) derivatives are especially effective against two major plant diseases, late blight on potatoes and leaf spot on sugar beet [1]. Tributyltin (TBT) compounds probably have their greatest use as boat bottom antifouling paints. Fouling is caused by the growth of aquatic organisms on the hull of vessels, which creates roughness and so reduces speed per unit fuel and increases travel time. TBT-based paints control fouling effectively by slow release of the TBT moiety into the aqueous solution: TBT is very toxic, even at small concentrations, to marine organisms. Despite the effectiveness of these compounds, this heavy tin use unfortunately leaves its mark on the environment. As a consequence of organotin sea-pollution, some countries [2,3] have severely re-

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stricted their use with promising results; the concentration of organotins in sea water has decreased, although in sediments the decrease is less pronounced [3]. Ultimately, scientists are then faced with a two-fold research problem; that of designing effective and environmentally friendly organotin compounds and that of developing specific extractants for tin to clean organotins from harbor areas [3].

Tin toxicity to marine organisms usually occurs in species such as marine bivalves that accumulate triorganotins since they cannot efficiently metabolize them [4]. For example, a recent study showed mollusks on the Spanish mediterranean coast have elevated amounts of TBT derivatives [5]. In contrast, no organotins were detected in fish muscle and the organotins found in fish liver (red mullet) were TPTs [5]. Structure-activity studies on alkyltins have shown that increasing the alkyl length induces stronger toxicity in aquatic life and milder toxicity in mammals. In mammals, organotin toxicity appears related to the liposolubility of these compounds [6].

Recent studies performed on aquatic organisms show that TPTs induce low enzymatic activity [7]. Unusual enzymatic levels were also observed in mammals (rabbits and lambs), specifically in the liver and kidneys [8], whereas the total prevention of implantation in the early stages of pregnancy was observed in rats [9].

Additional interest in organotins arose recently as some triorganotin containing O_2–bidentate donors (aryl acetates) showed strong antitumor activity, greater than that of cisplatin and of the same order as that of mitomycin C [10,11]. The same study showed that triorganotin(IV) perfluorobenzoates are more active than the non-fluorinated compounds against two breast cancer cell lines (MCF-7, EVSA-T), a colon cancer (WiDr), an ovarian cancer (IGROV), a melanoma (M19 MEL) and a renal cancer (A498).

Because of the interest in organotin compounds, some years ago, we started a systematic study on the chemical, spectroscopic and structural properties of diorganotin derivatives of 4-acyl-5-pyrazolone ligands. These species provide the same framework of the classical β-diketones and are used as dyes [12] and metal extractants [13–16]. The coordination chemistry of these donors towards a variety of metal acceptors has been studied recently. It is possible to find 4-acyl-5-pyrazolonates in a quasi-symmetric O_2–bidentate form [17–22], in a strongly asymmetric O_2–bidentate form [23–33] and also in a O_2,N–exotridentate form [34].

More recently a different coordination pattern was found in aquotriorganotins, $(H_2O)SnR_3(L)$, R = butyl, L = 1-phenyl-3-methyl-4-benzoylpyrazolon-5-ato [35]: R = methyl, L = 1-phenyl-3-methyl-4-methoxybenzoylpyrazolon-5-ato [36]. In these trigonal bipyramidal complexes a water molecule is bound to tin and the acylpyrazolonato binds the tin center in a monodentate fashion through one carbonyl group. The other carbonyl is involved in an intermolecular H-bond network with a nitrogen atom of another ligand. These complexes are not stable and they easily disproportionate in the solid phase and in solution Eq. (1).

$$2(L)SnR_3(H_2O) \underset{-2H_2O}{\rightleftharpoons} 2(L)SnR_3 \rightleftharpoons (L)_2SnR_2 + SnR_4 \quad (1)$$

On the other hand, the triaryltin(IV) complexes are more stable to moisture as suggested by spectroscopic methods [36].

The ligands reported here (Fig. 1) contain fluorine substituents on the N1 phenyl and so resemble the aryl moieties that proved effective in the antitumor study mentioned above. We report the structural properties and behavior in solution of triorganotin(IV) derivatives of these ligands. The crystal structure of the title compound provides an explanation for the different chemical behavior of TBT and TPT species.

2. Results and discussion

2.1. Synthesis of the triorganotin(IV)derivatives **1-9**

The triorganotin(IV) derivatives have been obtained, as anhydrous or aquo species, from the metathesis reaction of LH, $NaOCH_3$ and R_3SnCl (R = Me, Bu^n or Ph) in 1:1 molar ratio in benzene:

$$LH + NaOCH_3 + R_3SnCl \xrightarrow[-CH_3OH]{benzene/H_2O_{(v)}} (L)SnR_3(H_2O)_x + NaCl \quad (2)$$

where LH = L^1H, L^2H or L^3H; R = Me or Bu^n $x = 1$; R = Ph $x = 0$.

The tributyl- and triphenyltin(IV) compounds can be more readily obtained in higher yields by reacting $(R_3Sn)_2O$ with the neutral ligands LH in 1:2 molar ratio in refluxing benzene:

$$2LH + (Ph_3Sn)_2O \xrightarrow[-H_2O]{benzene} 2(L)SnR_3 \quad (3)$$

$$2LH + (Bu^n_3Sn)_2O \xrightarrow[-H_2O]{benzene} 2(L)SnBu^n_3 \xrightarrow{+2H_2O_{(v)}} 2(L)SnBu^n_3(H_2O) \quad (4)$$

where LH = L^1H, L^2H or L^3H.

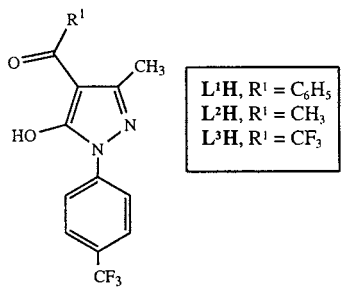

Fig. 1. LH proligands used in this work.

The tributyl and trimethyltin(IV) derivatives rapidly absorb water on exposure to the atmosphere, whereas the triphenyltin(IV) complexes are air and moisture stable. All the compounds are generally low melting solids, very soluble in acetone, acetonitrile, DMSO, alcohol and chlorohydrocarbons, sparingly soluble in diethyl ether and insoluble in hydrocarbons and water.

Conductivity values in dichloromethane are null. This seems to indicate the existence in solution of neutral species or of ion pairing effects. All the complexes show conductivity in DMSO due to a partial dissociation of about 30–50%. This suggest loss of an anionic L^- species, which is confirmed in Section 2.3.

Molecular-weight determinations carried out in chloroform solution on selected triorganotin(IV) complexes confirm a weak metal–donor interaction; the experimental molecular-weight values are less than the theoretical ones. The ratio r ($r = MW/FW$) is on the order of 0.7–0.9 and generally increases with the increase of concentration: this seems to indicate partial dissociation of the anionic (L^-) donor and/or of H_2O. We cannot exclude the possibility of a decomposition process such as (**1**), however, it could be accelerated at the experimental temperature of 40°C. In the case of the triphenyltin(IV) derivative **6** the ratio r is 0.93 in accordance with a negligible dissociation.

2.2. IR data

In the solid state, the donors L^1H, L^2H and L^3H are likely to exist in the amino–diketonic form, exhibiting a broad band at ca. 3400 cm^{-1} due to intermolecular (N–H···O) hydrogen bonds [37]. Upon coordination these absorptions disappear and the ν(C=O) at 1680–1620 cm^{-1} undergoes a red shift (1630–1595 cm^{-1}), thus indicating loss of the acidic proton and involvement of both the carbonyls in bonding with the metal or, at least, in weak interactions with a neighbouring H atom, as previously observed [35,36].

Between 1500 and 1600 cm^{-1} the vibrations of the azomethine bond in the pyrazole and those of Ph rings are observed. In the range 400–500 cm^{-1} some bands due to ν(Sn–O) have been found [23,33]. In the Bu^n_3Sn(IV) and Me_3Sn(IV) derivatives the absorptions assignable to ν_{as}(Sn–C) and ν_s(Sn–C) are observed [38–40] in the range 500–620 cm^{-1} whereas in the Ph_3Sn(IV) complexes the ν_{as}(Sn–C) and ν_s(Sn–C) are in the 200–300 cm^{-1} region [41–44]. The presence of ν_s(Sn–C) in the spectra of aquo derivatives suggests (for a TBP *trans*-O–SnR_3–O system) a deviation from planarity of the SnR_3 moiety which lowers the local symmetry from D_{3h} to C_{3v}. In the spectra of aquo derivatives the band at 3100–3200 cm^{-1} is attributed to intermolecular H-bonded water [35,36].

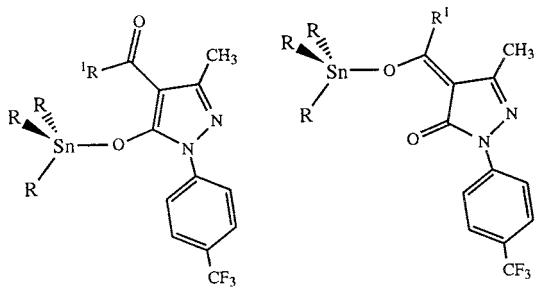

Fig. 2. Isomers present in solution after dissolving $(alkyl)_3Sn(L)(H_2O)$ in chlorohydrocarbon solvents.

2.3. ^1H- and ^{19}F-NMR data

The donors L^1H, L^2H and L^3H exist in chloroform in the amino–diketo tautomeric form. In fact, in the ^1H-NMR spectrum the acidic proton signal is found between 2.50 and 4.50 ppm, a range typical of N–H group: it has been observed that the 4-acylpyrazolones previously investigated always showed a resonance up to 10.0 ppm due to (O–H···O) systems [23–33]. Coordination of the donors in anionic form is confirmed by the disappearance of the above signal. A slight shielding of C^3–CH_3 (compounds **1**–**9**) and of O=CCH_3 signals (compounds **4**–**6**) is generally observed, while aromatics undergo a more complex pattern upon chelation.

In the trimethyl and tri-*n*-butyltin(IV) derivatives we have found two different sets of signals for the R group bound to tin and the tin-proton coupling constant ^2J(Sn–H) in the range 55–58 Hz, which is typical of tetracoordinate species [45]. We have also observed that these complexes are non electrolytes in chlorohydrocarbon solvents, even if they are largely dissociated. We therefore suggest that in solution these compounds lose the molecule of coordinated water and that they exist in both of the isomeric non-fluxional forms shown in Fig. 2.

In the spectra of triphenyltin(IV) complexes it is not possible to distinguish between signals due to aromatic protons of the ligand and those linked to tin, but integration takes their presence into account.

We have also carried out ^1H-NMR spectroscopy of compound **4** in DMSO; two sets of signals have been found, of which the more intense is likely due to a tetracoordinate triorganotin species, whereas the other is assigned to a bis(acylpyrazolonate)diorganotin(IV) complex which arises from the decomposition reaction (**1**).

In a coordinating solvent such as DMSO the ^2J(Sn–H) coupling constants due to triorganotin(IV)-acylpyrazolonates, as well as those for the starting triorganotin(IV) halide, are of the same order (60–70 Hz). This suggests that DMSO can displace the anionic ligand (L^-) from the coordination sphere.

Derivatives **1**–**9** were also studied with ^{19}F-NMR spectroscopy. The donors L^1H and L^2H absorb at +62.3 ppm whereas L^3H shows two resonances; at +63.0 ppm, which is due to CF_3 at the same position in L^1H and L^2H, and at +75.3 ppm that belongs to the CF_3 in R^1 position. The latter is similar to the signal shown by another 4-acylpyrazolone donor previously used [25]. Only very small shifts have been detected among the free neutral ligands (L^1H, L^2H and L^3H) and their triorganotin derivatives. In the spectra of **3**, **4** and **5** several signals appeared in accordance with isomers and/or species arising from the reaction (**1**).

2.4. ^{119}Sn-NMR data

The alkyl complexes generally show two resonance bands in the range (+80)–(+155) ppm typical of R_3SnO tetrahedral species [46,47], and in agreement with breaking of the Sn–OH_2 bond and formation in solution of both the isomers shown in Fig. 2. Instead, the triphenyltin(IV) derivatives give a unique resonance between −132 and −181 ppm implying a five-coordinate *cis*-O_2SnR_3 TBP geometry [48].

As previously observed [35,36] the aquo derivatives undergo a decomposition reaction; in two days, R_4Sn and $(L)_2SnR_2$ compounds are always recovered from the solutions. The stability of the complexes has been monitored by using ^{119}Sn-NMR spectroscopy. We have recorded the spectra with a different number of cycles acquired and have found that $(L)SnPh_3$ are always more stable than the $(L)SnMe_3$ and $(L)SnBu^n_3$, however they are somewhat less stable than all the previously reported (4-acyl-5-pyrazolonate)triphenyltin(IV) species [36].

2.5. X-ray crystallography

The crystal structure of (1-(4-trifluoromethylphenyl)-3-methyl-4-acetylpyrazolon-5-ato)triphenyltin(IV), **6**, is made up of discrete molecules and no crystallographic imposed symmetry is found. A view of the molecular structure is shown in Fig. 3. Table 1 and Table 2 show relevant geometrical parameters. The metal coordination number is five as three C atoms, from the phenyl groups, and two O atoms, from the chelating ligand, are coordinated to the tin. This species resembles Ph_3Sn(bzbz), (bzbz = 1,3-diphenylpropane-1,3-dionato or benzoylbenzoate), which has a TBP configuration [49], with the chelating β-diketonate ligand bzbz forming a 6-membered ring C–C–O–Sn–O–C as in our case. In the bzbz complex one oxygen occupies an axial position (Sn–O2 = 2.267(6) Å) and the other an equatorial site (Sn–O1 = 2.094(7) Å); two phenyls are in the trigonal plane and the third is apical. Both Sn–O bonds differ more in our complex (Sn–O2 = 2.424(5) and Sn–O1 = 2.081(6)Å) than in the bzbz species. Our axial

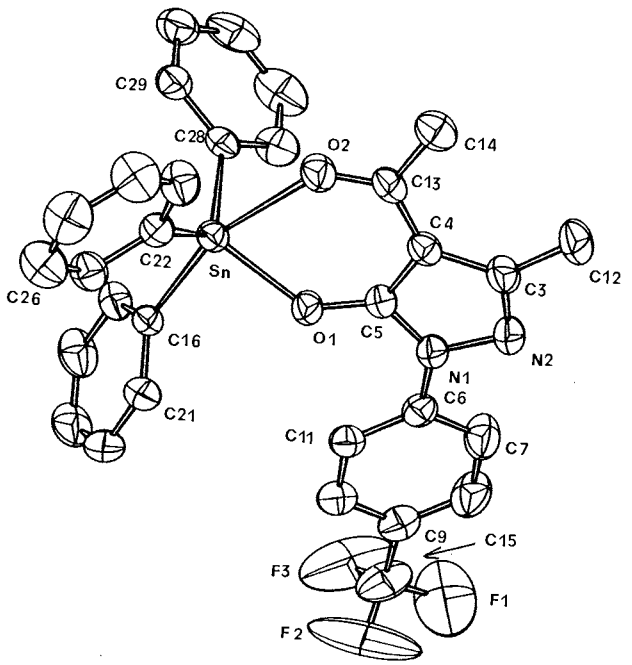

Fig. 3. An ORTEP diagram of compound **6**. Displacement ellipsoids are shown at the 30% probability level.

bond angle (O2–Sn–C16) is 161.2(2)° and is similar for the bzbz species (163.7(2)°) showing that both compounds have large distortion from a regular TBP geometry of 180°. The equatorial angles (O1–Sn–C22, O1–Sn–C28 and C22–Sn–C28) add to 353.3° (355° for the bzbz complex) confirming the departure from the TBP configuration that is characterized by a value of 360°. In addition, the metal appears 0.32 Å out of the trigonal plane (defined by O1, C22 and C28) towards C16 and resembles a system approaching tetrahedral geometry.

Table 1
Selected bond distances (Å) of **6**

Bond	Distance (Å)
Sn–O1	2.081(6)
Sn–O2	2.424(5)
Sn–C16	2.169(7)
Sn–C22	2.137(6)
Sn–C28	2.121(7)
O1–C5	1.283(9)
O2–C13	1.24(1)
N1–N2	1.403(9)
N1–C5	1.36(1)
N1–C6	1.42(1)
N2–C3	1.32(1)
C3–C4	1.43(1)
C3–C12	1.50(1)
C4–C5	1.41(1)
C4–C13	1.42(1)
F1–C15	1.18(1)
F2–C15	1.28(2)
F3–C15	1.18(2)

Table 2
Selected bond angles (°) of **6**

Bond	Angle (°)
O2–Sn–O1	76.8(2)
C5–N1–N2	111.8(6)
C16–Sn–O1	84.6(2)
C6–N1–N2	118.7(6)
C16–Sn–O2	161.2(2)
C6–N1–C5	129.3(6)
C22–Sn–O1	121.7(2)
C3–N2–N1	104.8(7)
C22–Sn–O2	83.2(2)
C4–C3–N2	112.2(7)
C22–Sn–C16	105.3(2)
C12–C3–N2	118.1(8)
C28–Sn–O1	107.3(2)
C12–C3–C4	129.7(8)
C28–Sn1–O2	83.8(2)
C5–C4–C3	104.4(7)
C28–Sn–C16	104.3(2)
C13–C4–C3	133.6(7)
C28–Sn–C22	124.3(3)
C13–C4–C5	121.9(7)
N1–C5–O1	120.9(6)
C4–C5–O1	132.3(7)
C4–C5–N1	106.7(6)

Such a trend away from TBP geometry can also be observed by examining the bond angles subtended by O2 on the equatorial plane. The angles O2–Sn–O1, O2–Sn–C22 and O2–Sn–C28 are 76.8(2), 83.2(2) and 83.8(2)°, respectively, are all much lower than the expected 90° for a regular TBP geometry. However, at the other apex of the bipyramid, C16 subtends much larger angles; the angles C16–Sn–O1, C16–Sn–C22 and C16–Sn–C28 are 84.6(2), 105.0(3) and 104.3(2)°, respectively. This is coherent with an approximate tetrahedral system. We conclude that the metal coordination geometry can be described as intermediate between a TBP and a tetrahedron: a pure tetrahedral scheme would exclude O2 from the coordination sphere.

A search in the literature [50] on the geometry of 'SnO_2C_3' species shows an overwhelming number (81/94 = 86%) being TBP, as seen in the sum of the equatorial angles being 360°. The *trans* axial angle of the bipyramid is in the range of 167–180°. Many of these species are polymeric with the second oxygen atom, O2, belonging to a different anion. The remaining 13 species are monomeric and represent cases in between TBP and tetrahedral geometries where O2 is not strongly coordinated, as in compound **6**. The *trans* axial angle range is 147.2–163.7° for this second group.

For chelating ligands having lower bite angle such as carboxylates, three geometric categories; TBP (polymeric), pure tetrahedral and intermediate cases are allowed. The factors affecting the structure of triorganotin carboxylates were previously discussed [51,52] and recently reviewed [53].

In 'SnO_2C_3' TBP species, the apical positions are occupied by either two oxygens or one oxygen and one C atom. Interestingly, the literature shows that when both apical positions are occupied by O atoms, the two Sn–O bonds differ, even in some cases with the existence of equivalent environments above and below the trigonal plane. Thus, it is not surprising that a symmetric ligand such as bzbz also shows (as mentioned above) two different Sn–O bonds in a more distorted geometry. Therefore the greater difference between the two Sn–O bonds of our complex can be ascribed to the asymmetry of our ligand.

Complexes more closely related to **6** include some recently described trialkyltin pyrazolonates [$Bu^n_3Sn(Q')(H_2O)$], (Q′ = 1-phenyl-3-methyl-4-benzoylpyrazolon-5-ato) [35] and [$Me_3Sn(Q_A)(H_2O)$] (Q_A = 1-phenyl-3-methyl-4-methoxybenzoyl-pyrazolon-5-ato) [36]: they show the second O of the pyrazolone ligand out of the coordination sphere of the TBP geometry and replaced by a water molecule. However these complexes disproportionate Eq. (1). Instead, the presence of Ph groups in our complex confers more stability to the system and such a reaction is not allowed. Therefore the ligand chelating effect preserves the triphenyl complex since no water enters the coordination sphere.

The different behavior is due to the electron withdrawing effect of the phenyl group which removes electron density from the metal, making it more acidic. This induces an increased donation from an O2 lone-pair such that a balance of charge on the metal is reached. Similar behavior by the Ph group was observed in a bis(pyrazolonato)diphenyltin species, $Ph_2Sn(Q_{Br})_2$, (Q_{Br}) = 1-phenyl-3-methyl-4-(4-bromobenzoyl)pyrazolon-5-ato [18] and results in the shortest Sn–O2 bond distance for the entire family of bis(4-acyl-5-pyrazolonato)diorganotins (Sn–O1 = 2.13 Å, Sn–O2 = 2.24 Å: average values on the two ligands).

Comparison with the antitumor compound Ph_3Sn(benzoate) [11] (Sn–O1 = 2.073(3), Sn–O2 = 2.674(3) Å) shows the same type of structure and equal covalent (primary) bonds (Sn–O1), whereas in **6**, the coordinative (secondary) bond (Sn–O2) is somewhat shorter.

The bite angle of the chelating ligand ranges from 79 to 85° in bis(4–acyl-5-pyrazolonato)diorganotins [18,23–26,28,29,31–33]. The present study shows that such angle bite can be further reduced, as O1–Sn–O2 is 76.8(2)°. Together with a small bite angle, two different Sn–O bonds are found [18,23–26,28,29,31–33] and for **6** this is confirmed as Sn–O1 = 2.081(6) Å and Sn–O2 = 2.424(5) Å. These lengths compare well with 2.094(9) and 2.42(1) Å, respectively, found in $Cy_2Sn(Q_D)_2$ (Q_D) = 1,3-dimethyl-4-acetylpyrazolon-5-ato [32]. All of the other pairs of related Sn–O bonds found in the literature [18,23–26,28,29,31,33] show less difference between them than that seen in **6**, according

to the rule: the smaller the bite, the greater the difference between Sn–O_P and Sn–O_S (O_P/O_S refers to primary/secondary bond).

All chelating 4-acyl-5-pyrazolone-organotins show O1 (the oxygen closer to the N moiety) associated to the primary bond [18,23–29,31–33] and this feature is also confirmed for **6**. Since in a TBP geometry an axial bond is longer than an equatorial bond, O2 is logically found at the apex of the bipyramid.

3. Conclusions

A series of triorganotin(IV) species has been obtained with new functionalized 4-acyl-5-pyrazolonates. In the solid state the alkylorganotins exist in a *trans*-TBP geometry with the donor as a monodentate ligand and a molecule of water in an apical position. Instead, triphenyltin complexes adopt a *cis*-TBP configuration, with the ligand acting in the bidentate form. The electron withdrawing effect of the phenyl groups on tin is responsible for the inclusion of the second O atom of the ligand in the metal coordination sphere. A large distortion is present in the structure, however, which can be interpreted as an intermediate stage between a TBP and a tetrahedral configuration. The alkyl derivatives undergo a change from the solid state (*trans*-TBP five-coordinate) to a four-coordinate species in solution, whereas for the phenyl species the *cis*-TBP solid state geometry is retained in solution.

In the literature, there are examples of structural changes upon dissolving triorganotins (R = Ph [51c,52], R = alkyl [51d]). Although available IR and ^{119}Sn-NMR data that can help in describing definite trends are limited, it seems that, in solution, triaryltin(IV) complexes are more stable than trialkyltin(IV) species. In particular, *trans*-TBP species tend to disassociate in solution [51,52]. Since this geometry is more common for alkyl than aryl derivatives, this may explain the greater efficiency of TBT species over triaryltins in antifouling paints. Thus, the chelating effect operating in the *cis*-TBP configuration, commonly found in triaryltin species, provides more stability. These properties are probably related to degradation of organotins and studies of such features are underway by our group.

As mentioned in the Introduction, the effectiveness of TBT antifouling paints is due to slow release of the organotin moiety. Therefore, organotins with tunable half-lives can help in regulating levels of acceptable pollution while still providing excellent properties as biocides. Tin has the unique property that, as an inorganic species, it is harmless. (This feature is not shared by other toxic organometals, Pb, Hg, etc. since the metals themselves are toxic.) The ideal metal biocide should be an organotin that undergoes a fast degradation to mono-organotin or inorganic tin after performing its work. Interesting examples are some tri- and di-phenyltin-trichloroacetates [54] which degrade to di- and mono-organotins. Since mono-organotins and inorganic tin species are non-toxic, such a finding should be desirable for organotin biocides. Commercial TBT paints do not provide such a feature as toxic derivatives are accumulated in the environment. In the title compounds, the presence of a 4-trifluoromethyl-phenyl linked to N^1 position of the pyrazole ring lowers the β-diketonate donor ability, making the tin derivatives less stable to hydrolysis and also increasing decomposition in solution, mainly in the case of alkyltin(IV) derivatives.

This study also shows that:

1. DMSO easily displaces the anionic ligand in the title compounds, a useful feature as a potential additive to organotin antifouling paints.
2. Since the fluorinated beta-diketonate ligands used in this study result in less stable organotin complexes, their potential use as organotin extractants is not as effective as the ones previously described [24–33].
3. The structure of compound **6** is similar to that of a related potent antitumor species [11]; they have equal Sn–O covalent bonds while the secondary bond (Sn–O2) is somewhat shorter than in the antitumor complex.

4. Experimental

4.1. General comments

The reactions were carried out under N_2 stream using Schlenk techniques. Solvents were dried by standard techniques. The samples were dried in vacuo to constant weight (20°C, *ca* 0.1 Torr). ^{1}H-, ^{19}F- and ^{119}Sn-NMR spectra were recorded operating at room temperature (300 for ^{1}H, 282.2 MHz for ^{19}F and 111.9 MHz for ^{119}Sn). H, F and Sn chemical shifts are reported in ppm versus Me_4Si, $CFCl_3$ and Me_4Sn, respectively. The tin spectra were run with a spectral width of 1000 ppm, and the chemical shifts were checked for aliasing by varying the center of the window. Each tin spectrum was acquired in *ca* 30 min (ca 300 transients). All the chemicals were analytical reagent grade from Aldrich.

4.2. Syntheses of the ligands

4.2.1. 1-(4-Trifluoromethylphenyl)-3-methylpyrazol-5-one

Ethyl acetylacetate (0.027 mol, 3.47 g) was added dropwise to a solution (30 cm^3) of 1-(4-trifluoromethylphenyl)hydrazine (0.027 mol, 4.7 g). KOH (1.8 mmol, 0.1 g) was subsequently added. The mixture was heated to reflux and stirred for 1 h, then the solvent

was removed on a rotary evaporator and the crude product washed with diethyl ether (50 ml) and light petroleum (50 ml). After filtration the brown powder was dried in vacuo and shown to be 1-(4-trifluoromethyl-phenyl)-3-methylpyrazol-5-one. Yield 46%. M.p.: 183–185°C. Anal. Calc. for $C_{11}H_9F_3N_2O$: C, 54.5; H, 3.7; N, 11.6. Found: C, 54.4; H, 3.8; N, 11.4%. IR data: 2700 br, ν(O–H···O), 1629 s, ν(C=O). ^{1}H-NMR data ($CDCl_3$): 2.22 s (3C–CH_3), 3.47 s (4CH_2), 7.64 d, 8.06 d (4-$C_6H_4CF_3$). MS: m/z 242 (M^+).

If the synthesis is carried out without the base a dark-red powder is recovered from the solution which has been identified by ^{1}H-NMR as a mixture of 1-(4-trifluoromethylphenyl)-3-methylpyrazol-5-one and of the condensation intermediate ethyl 3-[2-(4-trifluoromethylphenyl) hydrazono]butanoate, which shows the following signals: 1.95 s (N=C–CH_3), 1.27 t,4.18 q (OCH_2CH_3), 3.36 s (4CH_2), 7.08 d, 7.45 d (4-$C_6H_4CF_3$), 8.42 s br (N–H).

The donors L^1H, L^2H and L^3H were then synthesized following the procedure reported by Jensen [55].

4.2.2. 1-(4-Trifluoromethylphenyl)-3-methyl-4-benzoyl-pyrazol-5-one (L^1H)

Yield 92%. M.p.: 150–152°C. Anal. Calc. for $C_{18}H_{13}F_3N_2O_2$: C, 62.4; H, 3.8; N, 8.1. Found: C, 62.2; H, 3.9; N, 8.3%. IR data: 3340 br, ν(N–H···O), 1635 m, ν(C=O). ^{1}H-NMR data ($CDCl_3$): 2.10 s (C^3–CH_3) 7.50–7.70 m, 7.75 d, 8.12 d (O=CC_6H_5, N^1-4-$C_6H_4CF_3$), 3.70 s br (N–H···O). ^{19}F-NMR data ($CDCl_3$): −62.4.

4.2.3. 1-(4-Trifluoromethylphenyl)-3-methyl-4-acetyl-pyrazol-5-one (L^2H)

Yield 68%. M.p.: 112–114°C. Anal. Calc. for $C_{13}H_{11}F_3N_2O_2$: C, 54.9; H, 3.9; N, 9.9. Found: C, 54.7; H, 4.0; N, 9.6%. IR data: 3420 br, ν(N–H···O), 1645 m, ν(C=O). ^{1}H-NMR data ($CDCl_3$): 2.18 s, 247 s (C^3–CH_3, O=CCH_3), 7.70 d, 8.08 d (N^1-4-$C_6H_4CF_3$), 4.50 s br (N–H···O). ^{19}F-NMR data ($CDCl_3$): −62.4.

4.2.4. 1-(4-Trifluoromethylphenyl)-3-methyl-4-trifluoroacetyl-pyrazol-5-one (L^3H)

Yield 75%. M.p.: 123–124°C. Anal. Calc. for $C_{13}H_8F_6N_2O_2$: C, 46.17; H, 2.38; N, 8.28. Found: C, 45.96; H, 2.53; N, 8.12%. IR data; 3420 br, ν(N–H···O), 1645 m, ν(C=O). ^{1}H-NMR data ($CDCl_3$): 2.48 q (C^3–CH_3), 7.74 d, 8.01 d (N^1-4-$C_6H_4CF_3$), 4.10s br (N–H···O). ^{19}F-NMR data ($CDCl_3$): −63.0, −75.3.

4.3. Syntheses of the complexes

4.3.1. [Aquotrimethyl(1-(4-trifluoromethylphenyl)-4-benzoyl-pyrazolon-5-ato)tin(IV)], [(L^1)Sn(CH_3)$_3$(H_2O)], **1**

A benzene solution (30 cm^3) of the ligand L^1H (1.0 mmol) was added to a methanolic solution (10 cm^3) of sodium methoxide (1.0 mmol) and refluxed for 1 h. A benzene solution (20 cm^3) of Me_3SnCl (1.0 mmol) was then added to the above solution dropwise and the reaction mixture was stirred at room temperature for about 3 h. Sodium chloride was filtered off and the solvent removed under reduced pressure on a rotary evaporator until a thick oil was obtained. This was treated with diethyl ether and light petroleum, and a brown solid afforded. This was recrystallized from benzene/petroleum ether mixture and shown to be compound **1**.

Yield 42%. M.p.:137–138°C. Anal. Calc. for $C_{21}H_{23}F_3N_2O_3Sn$: C, 47.85; H, 4.40; N, 5.31%. Found: C, 47.60; H, 4.54; N, 5.16%. Λ_M (CH_2Cl_2): 0.5 Ω^{-1} cm^2 mol^{-1}, $0.9\cdot10^{-3}$ M: Λ_M (DMSO): 17.9 Ω^{-1} cm^2 mol^{-1}, $0.8\cdot10^{-3}$ M. FW Calc.: 527; MW Found ($CHCl_3$): 365, r: 0.69, 0.9×10^{-2} m; 378, r: 0.72, 1.8×10^{-2} m. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.85 s br; δ(Sn–CH_3), 0.59 s ($^2J_{(Sn-H)}$ = 56.3 Hz): δ(L^1), 1.98 s br (C^3–CH_3), 7.45–7.65m, 7.70 d, 8.10 d (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.3. ^{119}Sn-NMR ($CDCl_3$): +152.2, +148.7. IR (nujol) cm^{-1}: 3180 br, ν(H_2O): 1658 m, δ(H_2O): 1606 m, ν(C=O): 565 m, 552 vs, ν(Sn–C): 440 s, 419 m, 403 w, ν(Sn–O).

Compounds **2–9** were obtained in a similar fashion. For derivatives **2, 3, 5, 6, 8** and **9**, the following alternative synthesis can also be used: a benzene solution (30 cm^3) of (R_3Sn)$_2$O (R = Bu^n or Ph) (1.0 mmol) was added to a benzene solution (30 cm^3) of the ligand LH (2.0 mmol), and the reaction mixture was refluxed for about 2 h. After removing the solvent under reduced pressure on a rotary evaporator, a thick oil was obtained. This was treated with diethyl ether and petroleum ether, and a solid formed, which was recrystallized from benzene/petroleum ether mixture.

4.3.2. [Aquotri-n-butyl(1-(4-trifluoromethylphenyl)-4-benzoyl-pyrazolon-5-ato) tin(IV)], [(L^1)Sn(C_4H_9)$_3$(H_2O)], **2**

Yield 38%. M.p.:249–251°C. Anal. Calc. for $C_{30}H_{41}F_3N_2O_3Sn$: C, 55.15; H, 6.33; N, 4.29%. Found: C, 54.96; H, 6.38; N, 4.12%. Λ_M (CH_2Cl_2): 0.7 Ω^{-1} cm^2 mol^{-1}, 0.8×10^{-3} M. Λ_M (DMSO): 21.6 Ω^{-1} cm^2 mol^{-1}, 0.5×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.80s br: δ(Sn–C_4H_9), 0.93 t, 1.25–1.47 m, 1.58–1.72 m; δ(L^1), 2.11 s (C^3–CH_3), 7.48–7.75 m, 8.05–8.15 m (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.3. ^{119}Sn-NMR ($CDCl_3$): +128.2. IR (nujol) cm^{-1}: 3120 br, ν(H_2O); 1656 m, δ(H_2O); 1616 m, ν(C=O); 592 m, 504 s, ν(Sn–C): 440 m, 420 m, 409 w, ν(Sn–O).

4.3.3. [Triphenyl(1-(4-trifluoromethylphenyl)-4-benzoyl-pyrazolon-5-ato) tin(IV)], [(L^1)Sn(C_6H_5)$_3$], **3**

Yield 56%. M.p.:252–254°C. Anal. Calc. for $C_{36}H_{27}F_3N_2O_2Sn$: C, 62.19; H, 3.91; N, 4.03%. Found:

C, 62.05; H, 3.78; N, 4.20%. Λ_M (CH_2Cl_2): 0.9 Ω^{-1} cm^2 mol^{-1}, 0.6×10^{-3} M. Λ_M (DMSO): 22.1 Ω^{-1} cm^2 mol^{-1}, 0.3×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(Sn–C_6H_5), not distinguishable from aromatics of the ligand: δ(L^1), 1.95 s (C^3–CH_3), 7.40–7.80 m, 8.00–8.16 m (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.5 [1], −62.4 [3], −62.3 [1]. ^{119}Sn-NMR ($CDCl_3$): −168.2. IR (nujol) cm^{-1}: 1610 s, ν(C=O); 251 vs, 233 m, ν(Sn–C); 440 vs, 422 m, 408 m, ν(Sn–O).

4.3.4. [Aquotrimethyl(1-(4-trifluoromethylphenyl)-4-acetyl-pyrazolon-5-ato) tin(IV)], [(L^2)Sn(CH_3)$_3$(H_2O)], **4**

Yield 63%. M.p.:194–195°C. Anal. Calc. for $C_{16}H_{21}F_3N_2O_3Sn$: C, 41.32; H, 4.55; N, 6.02%. Found: C, 41.28; H, 4.68; N, 5.87%. Λ_M (CH_2Cl_2): 0.8 Ω^{-1} cm^2 mol^{-1}, 0.8×10^{-3} M. Λ_M (DMSO): 13.6 Ω^{-1} cm^2 mol^{-1}, 0.9×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.90 s br; δ(Sn–CH_3), 0.66 s br ($^2J_{(Sn-H)} = 56.8$ Hz); δ(L^2), 2.21 s, 2.30 s, 2.55 s, 2.70 s (C^3–CH_3, O=CCH_3), 7.70 d br, 8.08 d br (N^1–$C_6H_4CF_3$). ^{1}H-NMR (DMSO): δ(H_2O), 2.98 s br; δ(Sn–CH_3), 0.81 s [1] ($^2J_{(Sn-H)}$ = 128.6, 123.8 Hz), 0.54 s [3] ($^2J_{(Sn-H)} = 69.0$, 66.4 Hz); δ(L^3), 2.33 s [3], 2.29 s [3], 2.13 s [1], 2.08 s [1] (C^3–CH_3, O=CCH_3), 7.68 d, 7.79 m, 8.08 m, 8.32 d (N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.6 [6], −62.5 [1], −62.3 [1]. ^{119}Sn-NMR ($CDCl_3$): +155.2, +152.0. IR (nujol) cm^{-1}: 3180 br, ν(H_2O); 1657 m, δ(H_2O); 1612 s, ν(C=O); 553 s, 527 m, ν(Sn–C): 443 s, 402 m, ν(Sn–O).

4.3.5. [Aquotri-n-butyl(1-(4-trifluoromethylphenyl)-4-acetyl-pyrazolon-5-ato) tin(IV)], [(L^2)Sn(C_4H_9)$_3$(H_2O)], **5**

Yield 42%. M.p.:208–209°C. Anal. Calc. for $C_{25}H_{39}F_3N_2O_3Sn$: C, 50.78; H, 6.65; N, 4.74%. Found: C, 50.55; H, 6.71; N, 4.48%. Λ_M (CH_2Cl_2): 0.6 Ω^{-1} cm^2 mol^{-1}, 0.9×10^{-3} M. Λ_M (DMSO): 19.3 Ω^{-1} cm^2 mol^{-1}, 0.6×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.95 s br; δ(Sn–C_4H_9), 0.96 t, 1.20–1.54 m, 1.62–1.80 m; δ(L^2), 2.15 s, 2.22 s (C^3–CH_3), 7.38–7.64 m, 8.00–8.12 m (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.6 [1], −62.5 [1], −62.4 [1], −62.3 [4]. ^{119}Sn-NMR ($CDCl_3$): +152.0, +83.8. IR (nujol) cm^{-1}: 3210 br, ν(H_2O); 1645 m, δ(H_2O): 1618 s, ν(C=O); 615 s, 542 m, ν(Sn–C); 443 s, 412 m, ν(Sn–O).

4.3.6. [Triphenyl(1-(4-trifluoromethylphenyl)-4-acetyl-pyrazolon-5-ato)tin(IV)], [(L^2)Sn(C_6H_5)$_3$], **6**

Yield 72%. M.p.:115–118°C. Anal. Calc. for $C_{31}H_{25}F_3N_2O_2Sn$: C, 58.80; H, 3.98; N, 4.42%. Found: C, 58.58; H, 3.75; N, 4.23%. Λ_M (CH_2Cl_2): 0.7 Ω^{-1} cm^2 mol^{-1}, 0.8×10^{-3} M: Λ_M (DMSO): 20.1 Ω^{-1} cm^2 mol^{-1}, 0.8×10^{-3} M. FW Calc.: 633; MW found ($CHCl_3$): 590, r: 0.93, $1.0 \cdot 10^{-2}$ m. ^{1}H-NMR ($CDCl_3$): δ(Sn–C_6H_5), not distinguishable from aromatics of the ligand; δ(L^2), 2.40 s br (C^3–CH_3), 7.40–7.60 m, 7.65–7.90 m, 8.04 d (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.3. ^{119}Sn-NMR ($CDCl_3$): −179.8. IR (nujol) cm^{-1}: 1622 s, ν(C=O); 238 s, ν(Sn–C); 455 sh, 450 vs 442 sh, ν(Sn–O).

4.3.7. [Aquotrimethyl(1-(4-trifluoromethylphenyl)-4-trifluoroacetyl-pyrazolon-5-ato)tin(IV)], [(L^3)Sn(CH_3)$_3$(H_2O),] **7**

Yield 42%. M.p.:173–175°C. Anal. Calc. for $C_{16}H_{18}F_6N_2O_3Sn$: C, 37.03; H, 3.50; N, 5.40%. Found: C, 36.82; H, 3.62; N, 5.27%. Λ_M (CH_2Cl_2): 0.9 Ω^{-1} cm^2 mol^{-1}, 0.7×10^{-3} M. Λ_M (DMSO): 23.5 Ω^{-1} cm^2 mol^{-1}, 0.6×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.75 br: δ(Sn–CH_3), 0.62 s ($^2J_{(Sn-H)} = 58.4$, 56.0 Hz); δ(L^3), 2.45 q (C^3–CH_3), 7.46 d, 8.11 d (N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −63.1, −72.2. ^{119}Sn-NMR ($CDCl_3$): +142.7. IR (nujol) cm^{-1}: 3120 br, ν(H_2O); 1645 sh, δ(H_2O); 1614 s br, ν(C=O): 553 vs, 530 m, ν(Sn–C); 463 m, 441 s, 416 s, 402 m ν(Sn–O).

4.3.8. [Aquotri-n-butyl(1-(4-trifluoromethylphenyl)-4-trifluoroacetyl-pyrazolon-5-ato)tin(IV)], [(L^3)Sn(C_4H_9)$_3$(H_2O)], **8**

Yield 64%. M.p.:95–100°C. Anal. Calc. for $C_{25}H_{36}F_6N_2O_3Sn$: C, 46.54; H, 5.62; N, 4.34%. Found: C, 46.17; H, 5.75; N, 4.40%. Λ_M (CH_2Cl_2): 0.4 Ω^{-1} cm^2 mol^{-1}, 1.0×10^{-3} M. Λ_M (DMSO): 25.1 Ω^{-1} cm^2 mol^{-1}, 1.0×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(H_2O), 1.80 s br; δ(Sn–C_4H_9), 0.85 t, 1.25–1.45 m, 1.60–1.75 m; δ(L^3), 2.36 q (C^3–CH_3), 7.55 d br, 7.80 d br (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.8, −73.2. ^{119}Sn-NMR ($CDCl_3$): +148.7, +128.2. IR (nujol) cm^{-1}: 3370 br, ν(H_2O): 1706 m, δ(H_2O); 1659 s, ν(C=O); 619 s, 528 m, ν(Sn–C); 455 vs, 407 m, ν(Sn–O).

4.3.9. [Triphenyl(1-(4-trifluoromethylphenyl)-4-trifluoroacetyl-pyrazolon-5-ato) tin(IV)], [(L^3)Sn(C_6H_5)$_3$], **9**

Yield 85%. M.p.:120–121°C. Anal. Calc. for $C_{31}H_{22}F_6N_2O_2Sn$: C, 54.18; H, 3.23; N, 4.08%. Found: C, 54.25; H, 3.45; N, 4.26%. Λ_M (CH_2Cl_2): 0.2 Ω^{-1} cm^2 mol^{-1}, 0.5×10^{-3} M. Λ_M (DMSO): 16.1 Ω^{-1} cm^2 mol^{-1}, 1.3×10^{-3} M. ^{1}H-NMR ($CDCl_3$): δ(Sn–C_6H_5), not distinguishable from aromatics of the ligand; δ(L^3), 2.35 q (C^3–CH_3), 7.26–7.44 m, 7.57 d, 7.69 m, 7.87 d (O=CC_6H_5, N^1–$C_6H_4CF_3$). ^{19}F-NMR ($CDCl_3$): −62.8, −74.2. ^{119}Sn-NMR ($CDCl_3$): −119.9. IR (nujol) cm^{-1}: 1636 s, ν(C=O); 278 s, 263 s, 234 vs ν(Sn–C); 453 vs, 444 vs, 403 m, ν(Sn–O).

4.4. Crystallographic study of [(L^2)SnPh_3]

A $P2_1$ Syntex diffractometer was used for the measurements of the cell constants and for the data collection. A summary of crystal data together with details of

data collection and computer resolution is given in Table 3. Monitoring of three check reflections (taken every 100 reflections) indicated no decay. No absorption phenomena were found after a psi-scan on reflection [0, 0, −4]. Data were corrected for Lorentz and polarization. The molecular structure was solved using the heavy atom method in CAOS [56]. A Patterson map showed the position of the tin atom which gave an R value of 0.27. A Fourier map revealed the remaining non-H atoms, although the F atoms showed disorder and their positions were determined later.

Subsequent calculations were performed as follows; refinement, on F, based on the minimization of $\Sigma\, w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/(a + F_o + cF_o^2)$, where a and c are of the order of $2F_o(\min)$ and $2/F_o(\max)$ [57], respectively: anisotropic displacement parameters were refined for non-H atoms. After refinement convergence, an atomic list (C(15) excluded) provided a Fourier analysis which showed 5 peaks of similar intensity corresponding to F atoms and additional areas of diffuse intensity were observed in the map. The 5 peaks were at expected C–F distances from C(15) (they are in the range 1.18–1.35 Å). As a good model for this system was not found, three rational peaks were chosen and assigned to the 3 expected F atoms. These peaks have acceptable F–C(15)–F bond angles. As the real occupational factor could not be estimated, they were assigned a factor of 1. Fig. 3 indicates clearly the rotational disorder for the CF_3 group, and must be considered cautiously because the real displacement parameters for these three atoms are smaller than those shown (shrunk ellipsoids should correspond to these F atoms). At this point, H atoms were introduced at fixed positions with a C–H distance of 0.96 Å. H isotropic displacement parameters were kept fixed until refinement convergence. Atomic scattering factors and anomalous dispersion terms were taken from the literature [58].

Table 3
Summary of crystal data and computer resolution

Emperical formula	$C_{31}H_{25}N_2O_2F_3Sn$
Formula weight	633.24
Temperature (K)	298
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.202(2)
b (Å)	11.960(2)
c (Å)	13.315(3)
α (°)	68.14(1)
β (°)	73.14(1)
γ (°)	75.46(2)
V (Å^3)	1424.2(5)
Z	2
μ (Mo–K$_\alpha$ (mm^{-1}))	9.57
Crystal color	Colorless
Crystal habit	Block
Crystal size (mm)	$0.40 \times 0.20 \times 0.15$
Reflections collected	7532
Reflections refined	3502
Reflections unique	6886
$2\theta_{max}$ (°)	54.1
Scan speed (° min^{-1})	2
Scan range (°)	0.85
Parameters refined	352
$R(F, F>4\sigma(F))$[a]	0.041
R_w	0.053
S[b]	0.999

[a] $R(F) = \Sigma\,|(F_o - F_c)|/\Sigma\, F_o$.

[b] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n-p)]^{0.5}$, n = no. of data and p = no. of refined parameters.

5. Supplementary material available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 110211 for **6**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. F_o/F_c listing is available from F.C.

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