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Synthesis, characterization and spectroscopic investigations of tin(IV) and organotin(IV) derivatives of 4-aroyl-5-pyrazolones. Crystal structure of *trans*-dimethylbis[1-phenyl-3-methyl-4-(4-bromobenzoyl)-pyrazolon-5-ato]tin(IV)

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Abstract

Stable six-coordinate derivatives [$(Q)_2SnRX$] [QH is 1-phenyl-3-methyl-4-R′C(=O)-pyrazol-5-one (R′ = 4-BrC_6H_4 {$Q_{Br}H$}, 4-FC_6H_4 {Q_FH}, 4-ClC_6H_4 {$Q_{Cl}H$}, 4-IC_6H_4{Q_IH}, or 4-C_7H_{15}-C_6H_4 {Q_RH}), X = Cl or R, and R = Cl, Me, ^{n}Bu, ^{t}Bu, Ph, vinyl or benzyl] and 1:1 adducts [$(QH)SnR_nX_{4-n}$]$\cdot x$S [QH = 1-phenyl-3-methyl-4-R′C(=O)-pyrazol-5-one (R′ = 4-BrC_6H_4, 4-FC_6H_4 or 4-C_7H_{15}-C_6H_4; X = Cl or R and R = Cl, Me, or Ph; x = 0, 1/2, or 1; S = CH_2Cl_2, H_2O, or Et_2O] have been synthesized and characterized by analysis and spectral (IR, and ^1H, ^{13}C, and ^{119}Sn NMR) data. The diffraction study of the complex [$(Q_{Br})_2SnMe_2$] shows the metal to be six-coordinate in a skewed trapezoidal bipyramidal (STB-6) geometry; Sn–O distances are 2.104(4) and 2.099(4) Å, and 2.385(5) and 2.436(5) Å and the Me–Sn–Me bond angle is 154.5(3)°. In Q_{Br}, 4-bromophenyl and the pyrazolone rings are nearly coplanar. This co-planarity is opposed by an intramolecular repulsive force between one *ortho* H atom of the bromophenyl moiety and one O atom of the chelate ring. This feature appears related to the small bite of the ligand Q_{Br} (O–Sn–O bond angles of 78.5(2)° and 79.5(2)°) which may be responsible for the STB-6 geometry.

Keywords: Tin; X-ray structure; Pyrazolonates; NMR; Group IV; Infrared spectroscopy

1. Introduction

4-Acyl-5-pyrazolones are a class of versatile bidentate pro ligands widely used as extractants [1] for several metal ions, because of their donor ability and their relatively low cost.

According to Pearson [2], these molecules are hard bases which give stable chelate complexes with hard acids such as the alkaline earth metal ions and also with cations such as Al^{3+}, Cr^{3+}, Fe^{3+}, Si^{4+}, and UO^{2+} [3]. Recently we have been investigating the synthesis, infrared and NMR spectra of tin(IV) and organotin(IV) derivatives of several members of this family [4]. The X-ray crystal structures of two derivatives of the series have also been determined; the tin atom in these six-coordinate compounds is in a distorted octahedral environment. Because of our interest in tin chemistry [5] and in view of the potential industrial and biological applications of these types of complex [6], we decided to synthesize and characterize other tin(IV) and organotin(IV) derivatives of 4-aroyl-5-pyrazolones, specifically, proligands containing electron-withdrawing substituents and bulky groups in the 4-aroyl moiety. These enhance the acidity of the compounds and increase their solubilities in organic solvents. An X-ray diffraction study of the structure of *trans*-dimethylbis[1-phenyl-3-methyl-4(4-bromobenzoyl)pyrazolon-5-ato)tin(IV) {$(Q_{Br})_2Sn(CH_3)_2$} is reported.

2. Results and discussion

From the reaction in methanol and alkali between various 1-phenyl-3-methyl-4-(R-C=O)-5-pyrazolones

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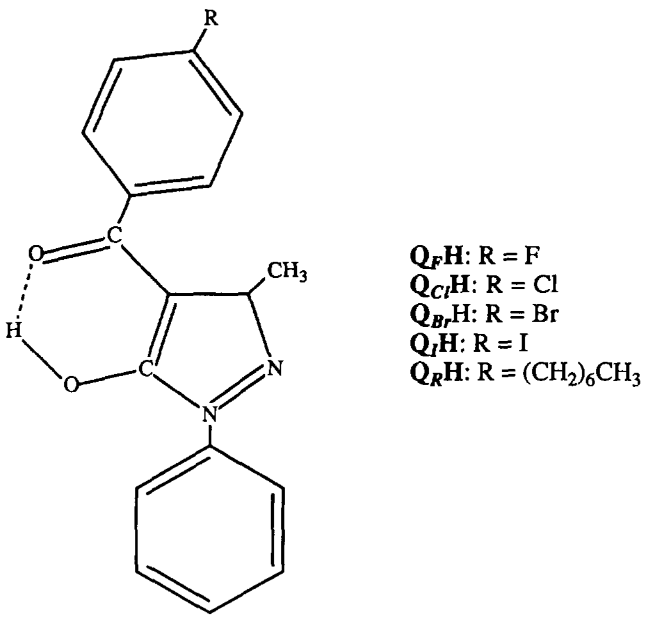


Fig. 1. Schematic representation of the proligands.

(QH in general, in detail: $Q_{Br}H$, R = 4-BrC_6H_4; Q_FH, R = 4-FC_6H_4; $Q_{Cl}H$, R = 4-ClC_6H_4; Q_IH: R = 4-IC_5H_4; Q_RH, R = 4-C_7H_{15}-C_6H_4) (Fig. 1) and several R_nSnX_{4-n} (R = alkyl, aryl or X, X = Cl or Br, $n = 0$, 1, or 2) complexes **1–21** (Eq. 1) with empirical composition $[(Q)_2SnR_nX_{2-n}]$ have been obtained (Table 1).

$$2QH + 2KOH + R_nSnX_{4-n} \longrightarrow \underset{\mathbf{1\text{–}21}}{[(Q)_2SnR_nX_{2-n}]} + 2KX + 2H_2O \quad (1)$$

Alternatively these compounds can be obtained by reaction of R_nSnX_{4-n} with TlQ prepared by addition of QH to $Tl(OC_2H_5)$ (Eq. 2).

$$2TlQ + R_nSnX_{4-n} \longrightarrow \underset{\mathbf{1\text{–}21}}{[(Q)_2SnR_nX_{2-n}]} + 2TlX \quad (2)$$

Interaction under N_2 of Q_FH or $Q_{Br}H$ with $MeSnCl_3$, $PhSnCl_3$ or $SnCl_4$ in diethyl ether or dichloromethane in absence of base, under reflux, gives the 1 : 1 adducts **22–27** $[QHR_nSnX_{4-n}] \cdot xS$ (s = solvent, X = Cl, R = X, Me, or Ph) (Eq. 3).

$$QH + R_nSnX_{4-n} \xrightarrow{S} \underset{\mathbf{22\text{–}28}}{[QHR_nSnX_{4-n}] \cdot xS} \quad (3)$$

No adduct could be isolated when either $Q_{Br}H$ or Q_FH react with Me_2SnCl_2 under the same conditions. This is consistent with the low acidity [7] of these organotin(IV) acceptors and is similar to the earlier

Table 1
Analytical data of the complexes **1–28**

	Compound	Yield (%)	M.p. (°C)	Elemental Analyses (Found(calc.) (%))		
				C	H	N
1	$[(Q_{Br})_2Sn(CH_3)_2]$	67	234–236	49.97 (50.21)	3.44 (3.51)	6.28 (6.50)
2	$[(Q_{Br})_2Sn(C_6H_5)_2]$	74	196–198	55.91 (56.07)	3.44 (3.48)	5.57 (5.68)
3	$[(Q_{Br})_2Sn(n\text{-}C_4H_9)_2]$	64	140–150(dec.)	53.70 (53.36)	4.54 (4.48)	5.77 (5.93)
4	$[(Q_{Br})_2Sn(CH_2C_6H_5)_2]$	54	135–139	55.91 (56.89)	3.77 (3.78)	5.18 (5.53)
5	$[(Q_{Br})_2Sn(C_2H_3)_2]$	86	193–194	51.28 (51.56)	3.37 (3.42)	6.05 (6.33)
6	$[(Q_{Br})_2Sn(t\text{-}C_4H_9)_2]$	82	233–234	53.58 (53.36)	4.46 (4.48)	5.68 (5.93)
7	$[(Q_{Br})_2Sn(CH_3)Cl]$	73	210–212	47.41 (47.68)	3.04 (3.09)	6.48 (6.36)
8	$[(Q_{Br})_2Sn(C_6H_5)Cl]$	76	196–198	51.15 (50.91)	3.12 (3.09)	5.75 (5.93)
9	$[(Q_{Br})_2Sn(n\text{-}C_4H_9)Cl]$	65	214–216	49.80 (49.41)	3.61 (3.60)	5.87 (6.07)
10	$[(Q_{Br})_2SnCl_2]$	54	211–213	45.45 (45.27)	2.73 (2.68)	6.09 (6.21)
11	$[(Q_F)_2Sn(CH_3)_2]$	88	169–170	58.12 (58.48)	4.18 (4.09)	7.43 (7.58)
12	$[(Q_F)_2Sn(CH_3)Cl]$	65	204–206	55.13 (55.33)	3.43 (3.58)	7.58 (7.37)
13	$[(Q_F)_2SnCl_2]$	58	235–237	52.20 (52.34)	3.18 (3.10)	7.30 (7.18)
14	$[(Q_{Cl})_2Sn(CH_3)_2]$	92	220–222	55.72 (55.99)	3.87 (3.92)	7.47 (7.25)
15	$[(Q_{Cl})_2Sn(CH_3)Cl]$	77	208–210	53.39 (53.03)	3.61 (3.43)	7.15 (7.07)
16	$[(Q_{Cl})_2SnCl_2]$	73	166–169	50.56 (50.23)	3.07 (2.98)	7.10 (6.89)
17	$[(Q_I)_2Sn(CH_3)_2]$	95	243–245	45.58 (45.27)	3.22 (3.17)	6.03 (5.87)
18	$[(Q_I)_2Sn(CH_3)Cl]$	68	240–242	43.37 (43.09)	2.88 (2.79)	5.94 (5.74)
19	$[(Q_I)_2SnCl_2]$	66	240–246	41.26 (41.00)	2.51 (2.43)	5.83 (5.63)
20	$[(Q_R)_2Sn(CH_3)_2]$	60	267–269	66.33 (66.75)	6.56 (6.72)	5.97 (6.23)
21	$[(Q_R)_2Sn(CH_3)Cl]$	94	130–160(dec.)	63.54 (63.96)	6.13 (6.24)	5.90 (6.09)
22	$[(Q_{Br}H)SnCl_4 \cdot [CH_2Cl_2]]$	55	264–268	30.48 (30.77)	2.01 (2.15)	3.63 (3.99)
23	$[(Q_{Br}H)Sn(CH_3)Cl_3 \cdot [Et_2O]_{0.5}]$	65	130–133	38.15 (37.87)	3.48 (3.34)	4.16 (4.42)
24	$[(Q_{Br}H)Sn(C_6H_5)Cl_3 \cdot [H_2O]]$	75	135–140(dec.)	40.53 (40.78)	3.01 (2.98)	4.03 (4.14)
25	$[(Q_FH)SnCl_4]$	73	290–296	36.54 (36.67)	2.31 (2.35)	4.80 (5.03)
26	$[(Q_FH)Sn(CH_3)Cl_3]$	86	137–140	39.90 (40.31)	2.98 (3.01)	5.11 (5.22)
27	$[(Q_FH)Sn(C_6H_5)Cl_3]$	90	120–122	45.80 (46.16)	4.80 (4.68)	5.05 (5.35)
28	$[(Q_RH)SnCl_4]$	80	219–221	44.90 (45.25)	4.30 (4.43)	4.10 (4.40)

Table 2
Selected IR data (m^{-1}) of complexes **1–28** [a]

Compound	1600–1500			ν(Sn–Cl)		ν(Sn–O)		Other data				
$Q_{Br}H$	1619s	1584s	1566sh					596s	542m	502m	468m	439m
	1557s	1518s	1501s					336m	224w	190w		
Q_FH	1630s	1591	1537s					589s	552m	504m	475w	375w
	1503s							352w	333m	269w		
$Q_{Cl}H$	1619s	1587s	1557s					593s	537m	504m	483m	442m
	1514s							343m	230m	186w		
Q_IH	1618s	1593s	1580s					593s	537m	500s	461m	435m
	1554s	1516s						329m	283m	242m		
Q_RH	1610s	1585sh	1550s					530m	509m	414w	374w	326w
								273w				
1	1596s	1587s	1580sh			455m	442m	592m	509m	455m	385m	332w
	1559m	1529s				407m	399m	280w	266w	205w	172m	
2	1587s	1567s	1546s			452m	440m	573w	552m	513m	296s	269m
	1528sh	1500s				390m	380m	243s				
3	1591s	1574s	1560sh			430s	399w	507m	510m	325m	279m	260m
	1533s					379m		164s				
4	1592s	1576s	1553s			451m	430m	554m	511m	329w	302w	281m
	1533s					385m		265m	203w	172m		
5	1606s	1576s	1558sh			451s	378s	574m	507m	333w	315m	300m
	1533s							288m	278m	216m	206w	176m
6	1588s	1574s	1558sh			436s	386s	511m	328w	303w	268m	209w
	1530s							169s				
7	1593s	1574s	1559s	321m	315sh	469s	447m	547m	509m	340w	303w	236m
	1542s	1520m				393s	380m	220m	200m			
8	1601s	1586s	1571s	338m	313s	474s	449m	505m	276m	263m	233m	200w
	1552s	1538s				389s		181w				
9	1603s	1585s	1566m	345s	315m	474s	457m	576m	546m	511s	288m	263m
	1547s	1532s				430m	411m	228m	210s	178m		
						396s	385m					
10	1588s	1567s	1555s	355vs	335m	479sbr	463w	510m	296w	280w	229m	
	1514m					395m						
11	1599s	1567s	1544s			452m	410m	527m	513m	344w	319m	275m
	1524sh					400sh		231m	205m	172s		
12	1601s	1575s	1552s	318sbr		465m	452m	543m	528m	517m	505m	492m
	1530s					413m		357m	230m			
13	1599s	1567s	1544s	348sbr		461m	414m	530m	504m	480m	371m	255m
	1524sh							238m	195m	182m		
14	1592s	1581s	1561s			473w	418sbr	592m	509m	473m	433w	335m
	1528s							322m	292m	272m	212m	174s
15	1597s	1591s	1574s	321sbr		452m	427m	547m	518m	481m	390m	264w
	1557s	1527s						206m	184m			
16	1593s	1568s	1555s	344s	338s	475m	434m	521m	487m	400m	365m	211s
	1540s	1500s										
17	1593s	1584s	1554s			448m	435m	591m	508m	373m	330m	270m
	1528s					407m	398m	257m	187m	170s		
18	1601s	1584s	1568s	325vs		463s	448sh	550m	544s	508m	375m	278w
	1549s	1533s	1511sh			396w		216m	196m	184m		
19	1594s	1584s	1563s	350vs	335sh	476m	458m	548m	508m	377m	278w	216m
	1549s	1510s				395w		193m				
20	1601s	1575s	1555s			447sbr		584s	551s	510s	292m	169m
	1532s							134s				
21	1595s	1576s	1557s	338mbr		487sbr		542m	511m	302m	282m	216m
	1524s							167br	147w			
22	1620s	1590s	1527s	354vs	329vs	458m		504m	393m	226m	166m	183m
								ν(N–H):	3164sbr,	3100s		
22 [b]	1612s	1590s	1579s	301sbr				ν(O–H):	3570sbr,	3531sbr		
	1561s	1524s						501w	378m			
23	1625s	1586s	1550s	310vs		458mbr		569m	534m	507m	498w	391m
	1530s							291s	214m	178m	160m	144m
								ν(O–H):	3418br,	ν(N–H):	3140br	
24	1622s	1585s	1570sh	326s	310s	456s		500w	391w	290s	279s	192m
	1526s							ν(O–H):	3580sbr,	ν(N–H):	3161sbr	
24 [c]	1620s	1603s	1584s					ν(O–H):	3500sbr			
	1555s	1528s										

Table 2 (continued)

Compound	1600–1500			ν(Sn–Cl)		ν(Sn–O)		Other data				
24 [b]	1619s	1602s	1587s	310sbr		454s		ν(O–H):	3500sbr		529m	515m
	1528s							501m	378m			
25	1609s	1597s	1577s	333vsbr		480m	446m	527m	513m	497m	418m	236m
								ν(N–H):	3126sbr			
25 [c]	1617s	1603s	1578s					ν(O–H):	3400sbr			
	1530s											
25 [b]	1618s	1602s	1582s					ν(O–H):	3540sbr		378m	
	1524s	1507s										
26	1632s	1593s	1528s	334vs	294vs	470m	415m	529m	517m	504m	256m	236m
	1508s							171m	153m			
								ν(O–H):	3580sbr,	ν(N–H):	3180sbr	
27	1615s	1595s	1585s	317s	296vs	463m	453m	528m	513m	502m	357m	257m
	1573s	1520s				423m		235m	192m	157m		
								ν(O–H):	3418sbr,	ν(N–H):	3140sbr	
27 [b]	1619s	1602s	1587s	301sbr		454m		ν(O–H):	3500sbr			
	1528s											
28	1607s	1580s	1557s	339vs		491m	448m	274m	235w	163s	145m	
	1524s							ν(O–H):	3574sbr;	ν(N–H):	3149sbr	

[a] Nujol mull. [b] Acetonitrile solution. [c] Acetone solution.

results for bis(pyrazol-1-yl)alkanes [5a], tetrakis(pyrazolyl)borates [5b] and other 4-acyl-5-pyrazolones [4,8]. When the reaction between Q_RH and anhydrous $SnCl_4$ was attempted in presence of base, the expected product $[(Q_R)_2SnCl_2]$ was not obtained even under extreme conditions (large excesses of proligand and refluxing solvent) but if the reaction solution was evaporated and $CHCl_3$ was added, the adduct $[(Q_rH)SnCl_4]$ (**28**) was obtained.

All the compounds **1–28** have been characterized by analytical data (Table 1), and IR (4000–100 cm^{-1}) (Table 2), ^{1}H NMR (Table 3), ^{13}C NMR (Table 4), and ^{119}Sn NMR spectra (Table 5).

Complexes **1–21** are stable in air, insoluble in water, and soluble in chlorinated solvents, DMSO, and acetone. The adducts **22–28** are soluble in acetone, DMSO, methanol, ethanol, and acetonitrile, but insoluble in water and in chlorinated solvents; they are not stable to moisture and exposure to atmosphere effects slow decomposition. The compounds **22**, **23** and **25** gradually lose hydrogen chloride when heated at 80–90°C under reduced pressure and, as inferred from IR and NMR spectra, decompose to the enolate complexes **13**, **12** and **16**, respectively, according to Eq. (4).

$$2[QHR_nSnX_{4-n}]\cdot xS \longrightarrow \\ \times\,[(Q)_2SnR_nX_{2-n}] \\ + 2HX + R_nSnX_{4-n} + xS \qquad (4)$$

Complexes **1–28** are not electrolytes in acetone, thus ruling out ionic structures such as $[Q_3Sn]_2[SnX_6]$ for **10**, **13**, **16**, and **19**, or $[Sn(QH)_3][SnCl_6]_2$ for **22**, **25**, and **28**.

Molecular weight determinations in acetone for **1** (859), **9** (893) and **10** (880) (concentrations ca. 1.0% w/w) are very close to the values expected for monomeric complexes (861.2, 923.7 and 902.0, respectively).

2.1. IR spectra

The IR spectra of β-diketonate and β-diketone-metal derivatives have been studied extensively [9]. However, assignment of all the bands in the IR spectra of **1–28** (Table 2) is not straightforward due to overlapping bands.

The main changes in the spectra of **1–21** found upon coordination of the 4-aroyl-5-pyrazolones are the disappearance of the strong broad band (O–H ··· O stretch) centred at 2600 cm^{-1} and the shift of the highest frequency carbonyl band at ca. 1620 cm^{-1} to ca. 1590 cm^{-1} in the complexes [10]. The absence of bands between 3100 and 3500 cm^{-1} indicates the absence of N–H groups and this excludes the donor coordinating in the amino-diketo tautomeric form.

In the region 600–100 cm^{-1} the spectra of **1–21** correspond closely to those of bis(acetylacetonate)tin(IV) derivatives [11]. On this basis we tentatively assigned the two strong bands (absent in the spectra of the proligands) near 450 cm^{-1} to Sn–O stretching modes and the broad strong absorptions at *ca.* 320 cm^{-1} to the Sn–Cl stretching mode.

Finally, no band attributable to ν(Sn–C) has been identified with any certainty, presumably because it is obscured by the ring out-of-plane vibrations of the ligand.

The increase in the frequency of the Sn–O bands, on going from $[Q_2SnR_2]$ (R = alkyl or aryl) to $[Q_2SnRCl]$ and $[Q_2SnCl_2]$ may well be associated with the greater electron-withdrawing power of Cl com-

Table 3
[a]H NMR (δ) data of complexes **1–28**

Compound	3–CH$_3$	Aromatics	R–Sn	Other data
$Q_{Br}H$ [a]	2.12s	7.30t; 7.45d; 7.52d 7.67d; 7.86d		11.5s br (O–H ··· O)
$Q_{Br}H$ [b]	2.10s	7.36t; 7.50–7.90m		
1 [a]	1.85s	7.25m; 7.41d 7.63d; 7.92d	0.98s	$^{2}J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 93$ $^{2}J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 87$
2 [a]	1.70s br 1.60s sh	7.20m br; 7.35 m br 7.57d; 7.75m br 7.86d br		
3 [a]	1.88s	7.23m; 7.42d; 7.64d 7.96d	0.74m 1.28m 1.60m	
4 [a]	1.67s	7.30m; 7.62d; 7.95d	3.01s 6.90m	$^{2}J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 121.9$ $^{2}J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 117.2$
5 [a]	1.80s	7.22m; 7.33m 7.59d; 7.89d	5.87dd 6.10dd 6.53dd	$J_{gem} = 2.14$ $J_{cis} = 12.82$ $J_{trans} = 19.85$
6 [a]	1.87s	7.20m; 7.45d 7.66d; 7.98m	1.27s	$^{3}J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 135.3$ $^{3}J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 127.3$
7 [a]	1.50s br 1.65s br 1.90s br 2.00s br	725m br; 7.48m br 7.70m br, 7.90m br	1.25s br 1.21s sh	$^{2}J_{(\mathrm{Sn}-\mathrm{H})} = 128.6$
8 [a]	1.50s 1.58s 1.62s 1.67s 1.82s 1.96s 2.03s	7.20m; 7.50m; 7.65m 7.85m; 8.03m		
9 [a]	1.73s br	7.18m br; 7.55d br	0.88t br 1.30m br	
10 [a]	1.72s 1.81s 1.92s 2.00s 2.12s	7.30m; 7.70m 7.95m		
Q_FH [a]	2.15s	7.22t; 7.35d 7.50d; 7.70dd 7.88dd		9.00s br (O–H ··· O)
Q_FH [b]	2.10s	7.20–7.40m 7.50m; 7.70–7.90m		9.05s br (O–H ··· O)
11 [a]	1.88s	7.25m; 7.58dd 7.95dd	1.00s	$^{2}J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 102$ $^{2}J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 97.9$
12 [a]	1.65s br 1.75s br 1.82s br 1.95s br	7.30m br; 7.65m br 7.95m br	1.28s br 0.90s 0.86s 0.82s	
13 [a]	1.72s 1.82s 1.94s 2.02s	7.18m; 7.25m 7.52m; 7.68m 7.95d		
$Q_{Cl}H$ [a]	2.13s	7.32t; 7.50m 7.62d; 7.88d		8.70s br (O–H ··· O)
14 [a]	1.87s	7.25m; 7.48d 7.97d	1.00s	$^{2}J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 101.9$ $^{2}J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 98.8$
15 [a]	1.75s br 1.65s br	7.22m br; 7.45m br 7.90m br	1.28s br	
16 [a]	1.72s 1.82s 1.92s 2.02s	7.30m; 7.55m 7.67m; 7.95d		

Table 3 (continued)

Compound	3-CH$_3$	Aromatics	R–Sn	Other data
Q$_I$H [a]	2.12s	7.40m; 7.90m		9.50s br (O–H $\cdots$ O)
17 [a]	1.90s	7.28m; 7.86d 7.95d	1.02s	$^2J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 102.2$ $^2J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 97.8$
18 [a]	1.65s br 1.90s br	7.30m br; 7.80m br	1.25s br	$^2J_{(\mathrm{Sn}-\mathrm{H})} = 128.6$
19 [a]	1.73s 1.83s 1.94s 2.02s	7.30m; 7.50m 7.70m; 7.90m		
Q$_R$H [a]	2.15s	7.30m; 7.48t 7.60d; 7.96d		2.70t; 1.66m 1.32m; 0.90t
Q$_R$H [c]	2.11s	7.30m; 7.70d 7.96d		2.76t; 1.70m; 1.42m; 0.90m
20 [a]	1.85s	7.28m; 7.45d 7.96d	0.98s	2.70t; 1.66m 1.30; 0.90t $^2J_{(\mathrm{Sn}-\mathrm{H})} = 129.1$
21 [a]	1.90sbr	7.0–8.0mbr	1.20sbr	2.65mbr; 1.70mbr 1.30mbr; 0.90t
22 [c]	2.00s 2.33s 2.00s	7.5–8.0mbr		
23 [b]	2.22s	7.6–8.0mbr	1.50s	3.54q, 1.25t [Et$_2$O] $^2J_{(\mathrm{Sn}^{119}-\mathrm{H})} = 126.0$ $^2J_{(\mathrm{Sn}^{117}-\mathrm{H})} = 121.7$
24 [b]	2.22s	7.6–8.0mbr		
25 [b]	2.20s	7.30–7.90mbr		
26 [b]	2.30s	7.5–7.90mbr	1.50s	
27 [b]	2.30s	7.40–7.90mbr		
28 [c]	2.0s	7.30–7.70m 8.0d		0.90t; 1.30m 1.70mbr; 2.70t

[a] In CDCl$_3$ solution. [b] In acetonitrile-d_3 solution. [c] In acetone-d_6 solution.

pared to R and a corresponding increase in the strength of the Sn–O [11a].

The IR spectra of the adducts **22**–**28** differ significantly from the spectra of the β-diketonate complexes **1**–**21**. There are bands assignable to (N–H) around 3200–3100 cm^{-1} and a broad absorption at 3500 cm^{-1} for the adduct **24** which contains a hydrogen bonded water molecule, the ν(C–O) in the adducts is 15–20 cm^{-1} to higher frequency compared with the corresponding β-diketonate complexes, which indicates coordination of the ligands in their ketonic neutral form. The IR spectra of **22**, **24**, **25** and **27** are also obtained from solutions in acetonitrile and acetone. The bands around 3200–3100 cm^{-1} disappear and the ν(Sn–Cl) generally show a different pattern. In addition, the ν(C–O) shows a small shift to lower frequencies which is possibly due to dissociation of these compounds in solution. However, different coordination modes of the ligands and decomposition to enolate complexes cannot be excluded. The IR spectra of the complexes **1**, **2**, **8**, **10** in acetone solution are similar to those recorded in Nujol mull.

2.2. ^{1}H and ^{13}C NMR spectra

In the ^{1}H spectrum of **1**–**21** (Table 3) it is clear that the enolic protons of the β-diketones are lost upon complexation. The presence of more than one isomer when at least one halide group is bonded to tin, is revealed by the presence of three or more methyl groups in the ^{1}H- and ^{13}C-NMR spectra of several derivatives. Cooling the samples to −60°C or heating to 50°C caused no significant changes in the spectra (CDCl$_3$ solution).

The ^{13}C NMR spectra indicate that the carbon atom of the aroyl carbonyl is shielded by ca. 4–5 ppm, whereas C(3), C(4) and C(5) are deshielded by ca. 4–5 ppm upon complexation.

The $^2J(^{119}\mathrm{Sn}-^1\mathrm{H})$ values (Table 3) for **1**, **11**, **14** and **17** are comparable with those reported for [(acac)$_2$SnMe$_2$] (acac = acetylacetonate) [11b] and [(dbzm)$_2$SnMe$_2$] (dbzm = dibenzoylmethane) [11b] to which *trans* structures in solution have been assigned, on the basis of NMR and Raman studies. However, the $^2J(^{119}\mathrm{Sn}-^1\mathrm{H})$ value observed for compound **20** differs significantly, being 128.0 Hz. The θ value (C–Sn–C angle) of this compound, calculated from the equation of Lockhart and Manders [12] is 131.8°, suggesting a cis structure.

$$\theta(\mathrm{C-Sn-C}) = 0.0161\left[^2J(^{119}\mathrm{Sn}-^1\mathrm{H})\right]^2 - 1.32\left[^2J(^{119}\mathrm{Sn}-^1\mathrm{H})\right] + 133.4$$

In recording NMR spectra non-coordinating solvents are generally chosen rather than coordinating

Table 4
Selected ^{13}C NMR Data (δ) of Complexes 1–28

Compound	CH_3	C(=O) and C(5)		C(3) and C(4)		Sn–C and other data
$Q_{Br}H$ [a]	15.9	191.2	161.1	147.7	103.5	
$Q_{Br}H$ [b]	16.1	n.o	161.3	145.8	104.6	
1	16.7	189.3	162.5	149.1	104.7	9.3
2	16.4	n.o.	n.o.	n.o.	n.o.	
3	17.2	190.6	163.3	149.5	105.3	14.1; 26.4; 27.5; 29.9
4	16.4	189.8	163.2	148.9	105.0	36.9; 124.6; 127.6; 128.9; 137.7
5	16.5	189.6	162.5	149.1	105.1	133.4; 143.5
6	17.3	191.2	164.0	149.2	106.5	29.9; 51.8
7	16.3	n.o.	n.o.	149br	105br	12.0 br
8	16.2	n.o.	n.o.	149.7		
	16.3			149.8		
	16.5					
	16.6					
9	16.3	190.2	161.6	150.3	106.0	14.2; 26.3; 27.5; 31.4
10	16.4	189.4	162.9	150.0	105.5	
	16.5	189.8	163.0	150.1	105.6	
	16.6	190.2	163.2	150.2	105.7	
	16.7	190.3		150.3	105.8	
Q_FH	15.9	190.9	162.1	147.6	103.4	$^1J_{C-F} = 249.5$; $^2J_{C-F} = 21.9$
						$^3J_{C-F} = 9.2$; $^4J_{C-F} = 3.0$
Q_FH	15.9	190.6	162.8	147.9	103.8	
11	16.6	n.o.	n.o.	149.1	n.o.	9.2
						$^2J_{C-F} = 21.9$; $^3J_{C-F} = 8.5$
12	16.8 b	190.3br	163.3br	149.9br	106.0br	12.5
						$^1J_{C-F} = 250.2$ $^2J_{C-F} = 21.7$
13	16.3	189.4	163.0	149.9	105.4	$^1J_{C-F} = 253$; 255; 255
	16.4	189.8	163.2	150.0	105.6	$^2J_{C-F} = 21.8$; 21.9; 22.5; 22.8
	16.5	190.1	163.3	150.1	105.8	$^3J_{C-F} = 9.1$
	16.6			150.2		$^4J_{C-F} = 3.0$; 3.1
$Q_{Cl}H$	16.4	191.6	161.5	148.1	104.0	
14	17.1	190.2	163.2	149.6	105.1	9.8
15	16.3	n.o.	n.o.	149.9	n.o.	12.4
	16.8					12.5
16	16.3	189.4	n.o.	150.0	n.o.	
	16.4	189.7		150.1		
	16.5					
	16.6					
Q_IH	16.4	191.8	161.5	148.1	103.9	
17	17.2	190.4	163.1	149.6	105.1	9.8
18	16.3 b	n.o.	n.o.	149.4br		n.o.
19	16.9	n.o.		150.1	101.0	
	17.0	n.o.		150.2	101.8	
	17.1					
Q_RH	16.4	n.o.	163.0	148.9	n.o.	14.7; 23.6; 32.7; 32.9; 36.8
20	17.0	191.8	163.2	149.8	105.2	9.8
						14.6; 23.1; 29.6; 31.7; 32.3; 36.5
21	16.8br	n.o.	n.o.	148.6	n.o.	12.0br
				150.2		14.6; 23.1; 29.5; 31.6; 32.2; 36.5
22	16.6	191.0br	164.0br	151.2	106.0br	
	17.0			151.4		
23	15.6	191.8	164.0	151.0	n.o.	12.0br
24	14.9	n.o.	164.2	151.6	n.o.	133.4; 124.5
	15.6					134.4
25	14.8	194.7	162.4	152.3	105.1	
26						
27	14.6	n.o.	n.o.	151.6	n.o.	134.3; 130.6; 124.8
	15.6					$^1J_{C-F} = 250.0$; $^3J_{C-F} = 9.2$
28	17.0	192.6	164.6	151.4	106.0	14.7; 23.6, 29.4; 32.3; 32.9; 36.9

[a] In $CDCl_3$ solution. [b] In acetonitrile-d_3 solution. [c] In acetone-d_6 solution.

ones because the latter produce changes in coordination. In the case of the adducts **22–28**, however, the spectra were measured in acetonitrile d_3, or in acetone for reasons of solubility. The spectra in acetonitrile of the adducts show all the expected signals, in accordance with the structures proposed, whereas those in acetone (for example in the ^{1}H and ^{13}C spectra of **22**) reveal three methyl resonances of different intensity, presumably due to dissociation, and the spectra change over several days.

2.3. ^{119}Sn NMR spectra

The ^{119}Sn chemical shifts for the complexes **1–28** are reported in Table 5.

In our case all the signals fall in the range typical for hexacoordinated tin(IV) derivatives [13] and the same pattern previously observed for bis(4-acetyl- and bis(4-benzoyl-5-pyrazolonato)-tin(IV) [4] complexes was found. The introduction of alkyl or aryl groups bound to the tin atom reduces the Lewis acidity of the tin(IV) and produces a downfield shift of the tin resonances.

The presence of isomers is also confirmed, even in ^{119}Sn NMR spectra, when electronegative (at least one halide) and bulky substituents are present.

The presence in solution of both cis and trans isomers is suggested in the spectra of **12** and **15** by the presence of signals at −570.1 and at −569.8 in addition to those usually detected at ca. −490 ppm for derivatives $[Q_2SnMeCl]$.

The ^{119}Sn NMR spectra of the adducts **22, 24, 25, 27** in acetonitrile, and of **22** and **28** in acetone, are also reported. In acetonitrile these adducts show a single absorption which falls in the range typical of hexacoordinate compounds and very different from the shifts recorded for organotin acceptors in acetonitrile (for example δ for $PhSnCl_3$: ca. 244 ppm). This excludes complete dissociation of the complexes. The spectra recorded in acetone for **22** and **28** (for which no isomers are possible) show three absorptions, probably due to the presence of enolate complexes.

2.4. Diffraction study of $[(Q_{Br})_2SnMe_2]$

The crystal structure of the title compound, $[(Q_{Br})_2SnMe_2]$, is built up from well separated discrete molecules. Atomic coordinates for non-H atoms are given in Table 6 and those for H atoms are available from the Cambridge Crystallographic Data Base [14]. Figure 2 shows a computer generated drawing of the

Table 5
^{119}Sn NMR Data of Compounds **1–28** in $(CDCl_3)$

No.	Compound	δ/(-ppm)	No.	Compound	δ/(-ppm)
1	$[(Q_{Br})_2Sn(CH_3)_2]$	315.5	**15**	$[(Q_{Cl})_2Sn(CH_3)Cl]$	491.8
2	$[(Q_{Br})_2Sn(C_6H_5)_2]$	480.7			492.3
		483.8			495.8
		485.5			569.8
3	$[(Q_{Br})_2Sn(n\text{-}C_4H_9)_2]$	353.5	**16**	$[(Q_{Cl})_2SnCl_2]$	631.0
4	$[(Q_{Br})_2Sn(CH_2C_6H_5)_2$	451.2			634.2
5	$[(Q_{Br})_2Sn(C_2H_3)_2]$	494.6			637.2
6	$[(Q_{Br})_2Sn(t\text{-}C_4H_9)_2]$	453.4	**17**	$[(Q_I)_2Sn(CH_3)_2]$	317.0
7	$[(Q_{Br})_2Sn(CH_3)Cl]$	491.3	**18**	$[(Q_I)_2Sn(CH_3)Cl]$	491.4
		494.6			494.5
		495.4			495.5
8	$[(Q_{Br})_2Sn(C_6H_5)Cl]$	564.4	**19**	$[(Q_I)_2SnCl_2]$	631.2
		564.9			634.2
9	$[(Q_{Br})_2Sn(n\text{-}C_4H_9)Cl]$	466.7			637.2
		598.2	**20**	$[(Q_R)_2Sn(CH_3)_2]$	321.7
10	$[(Q_{Br})_2SnCl_2]$	629.4	**21**	$[(Q_R)_2Sn(CH_3)Cl]$	494.7
		632.5			496.1
		635.5			498.5
11	$[(Q_F)_2Sn(CH_3)_2]$	318.2			500.0
12	$[(Q_F)_2Sn(CH_3)Cl]$	492.5	**22** [a]	$[(Q_{Br}H)SnCl_4]$	620.2
		493.4			635.0
		495.0			640.0
		497.1	**23** [b]	$[(Q_{Br}H)MeSnCl_3]$	not obs.
		570.1	**24** [b]	$[(Q_{Br}H)PhSnCl_3]$	502.7
13	$[(Q_F)_2SnCl_2]$	631.6	**25** [b]	$[(Q_FH)SnCl_4]$	634.7
		635.0	**2b** [b]	$[(Q_FH)MeSnCl_3]$	not obs.
		638.0	**27** [b]	$[(Q_FH)PhSnCl_3]$	498.0
14	$[(Q_{Cl})_2Sn(CH_3)_2]$	317.2	**28** [a]	$[(Q_RH)SnCl_4]$	621.0
		318.1			635.0
					639.4

[a] In acetone-d_6 solution. [b] In acetonitrile-d_3 solution.

molecule with H atoms omitted. Bond distances and angles are given in Tables 7 and 8 respectively. The tin atom is six coordinate with two Q_{Br} ligands and two methyl groups. Each ligand chelates the metal through two oxygen atoms. The four oxygens and the metal may be considered as forming the equatorial plane of an octahedron while the methyl groups are *trans* to each other. However, a strong distortion is seen, as the *trans* methyl axis angle is much smaller than 180° and the C(20)–SN(1)–C(21) angle is 154.5(3)°. The pyrazolonate shows a marked asymmetry as one oxygen, O(1), is 2.104(4) Å from the metal and the other, O(2), is 2.385(5) Å. The bond lengths for the other Q_{Br} ligand, Sn(1)–O(1A) and Sn(1)–O(2A), are 2.099(4) and 2.436(5) Å, respectively. The organometallic bonds Sn–C(20) and Sn–C(21) are equal, 2.097(8) and 2.099(8) Å, as normally found in organotin compounds.

Table 6
Atomic coordinates and isotropic displacement parameters with their e.s.d.'s in parentheses
$B_{eq} = (4/3) * \mathrm{SUM(ij)[a(i)a(j)b(ij)]}$

	x	y	z	B_{eq}
Sn(1)	0.3127(1)	0.26058(3)	0.20421(2)	2.73(1)
Br(1)	−0.5521(2)	−0.1681(1)	0.4163(1)	7.34(4)
Br(1a)	0.9170(1)	−0.0115(1)	−0.15471(4)	5.22(2)
O(1)	0.2948(8)	0.3513(4)	0.2828(2)	4.0(1)
O(2)	0.0863(8)	0.1624(4)	0.2694(2)	4.1(1)
O(1a)	0.4823(8)	0.3944(4)	0.1805(2)	3.8(1)
O(2a)	0.4452(9)	0.2119(4)	0.1026(2)	5.0(1)
N(1)	0.3429(9)	0.3552(5)	0.3824(2)	3.6(1)
N(2)	0.273(1)	0.3066(6)	0.4373(2)	4.6(2)
N(1a)	0.6180(8)	0.5302(4)	0.1188(2)	3.0(1)
N(2a)	0.7105(8)	0.5439(5)	0.0608(2)	3.4(1)
C(3)	0.151(1)	0.2359(7)	0.4251(3)	4.0(2)
C(4)	0.1329(9)	0.2354(5)	0.3615(3)	3.2(1)
C(5)	0.261(1)	0.3153(5)	0.3377(3)	3.3(1)
C(6)	0.507(1)	0.4208(6)	0.3809(3)	4.1(2)
C(7)	0.590(2)	0.4687(8)	0.3291(4)	6.2(3)
C(8)	0.757(2)	0.5235(9)	0.3297(5)	6.8(3)
C(9)	0.845(2)	0.5364(8)	0.3804(5)	6.7(3)
C(10)	0.766(2)	0.4884(9)	0.4336(5)	7.1(3)
C(11)	0.596(1)	0.4300(9)	0.4343(4)	5.9(3)
C(12)	0.057(1)	0.171(1)	0.4761(3)	6.3(3)
C(13)	0.048(1)	0.1643(6)	0.3250(3)	3.4(1)
C(14)	−0.094(1)	0.0837(5)	0.3505(3)	3.5(2)
C(15)	−0.061(1)	−0.0283(6)	0.3328(3)	4.0(2)
C(16)	−0.193(1)	−0.1048(7)	0.3528(3)	4.7(2)
C(17)	−0.364(1)	−0.0659(7)	0.3900(3)	4.4(2)
C(18)	−0.403(1)	0.0445(7)	0.4099(3)	4.8(2)
C(19)	−0.265(1)	0.1195(6)	0.3893(3)	3.9(2)
C(20)	0.041(1)	0.3339(7)	0.1671(4)	4.8(2)
C(21)	0.540(1)	0.1252(6)	0.2263(4)	4.9(2)
C(3a)	0.7100(9)	0.4479(5)	0.0357(3)	3.1(1)
C(4a)	0.6177(8)	0.3668(5)	0.0757(2)	2.8(1)
C(5a)	0.5625(8)	0.4259(5)	0.1287(2)	2.8(1)
C(6a)	0.591(1)	0.6206(5)	0.1585(3)	3.5(2)
C(7a)	0.412(1)	0.6437(6)	0.1950(4)	4.7(2)
C(8a)	0.387(2)	0.7329(7)	0.2330(4)	6.4(3)
C(9a)	0.537(2)	0.7994(7)	0.2344(4)	7.1(3)
C(10a)	0.714(2)	0.7776(8)	0.1985(5)	7.4(4)
C(11a)	0.744(1)	0.6881(7)	0.1595(4)	5.3(2)
C(12a)	0.795(1)	0.4386(6)	−0.0281(3)	3.6(2)
C(13a)	0.567(1)	0.2582(5)	0.0664(3)	3.2(1)
C(14a)	0.656(1)	0.1940(5)	0.0122(2)	3.1(1)
C(15a)	0.525(1)	0.1514(7)	−0.0227(3)	4.8(2)
C(16a)	0.602(1)	0.0910(8)	−0.0726(4)	5.3(2)
C(17a)	0.810(1)	0.0715(5)	−0.0865(3)	3.8(2)
C(18a)	0.945(1)	0.1106(7)	−0.0511(3)	4.8(2)
C(19a)	0.864(1)	0.1725(6)	−0.0018(3)	4.3(2)

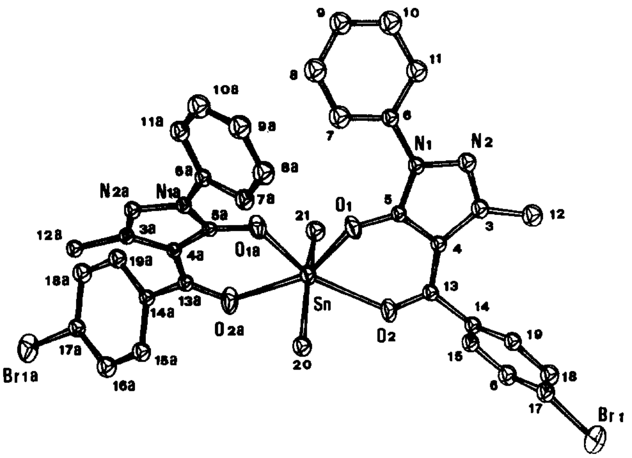


Fig. 2. Computer generated drawing of the molecule; H atoms omitted.

The shorter Sn–O (primary) bonds form an interbond angle that is much smaller than that made by the longer (secondary) bonds, as O(1)–Sn(1)–O(1A) is 75.5(2)° and O(2)–Sn(1)–O(2A) is 126.7(2)°. The methyl groups are accommodated on the side of the secondary bonds. This distortion of the octahedron has been described by Kepert as a skewed trapezoidal bipyramidal configuration (STB) [15]. The least-squares plane of the four oxygens is such that all of the O atoms are within a standard deviation (0.08 Å) from it. The tin atom is 0.007 Å from the plane. Both pyrazolonate ligands are planar since deviation of their atoms from the least-squares plane is less than 0.004 in one case and 0.002 Å in the other. One chelate ring has a half-chair conformation described by a plane containing the O(2)–C(13)–C(4)–C(5) moiety and Sn(1) and O(1) outside this plane by 0.20 and −0.26 Å, respectively. The other chelate ring has a twist-boat conformation with the best four-atom plane defined by O(2A)–C(13A)–C(4A)–C(5A). The relative deviations from this plane are −0.02 Å, O(2A); 0.03 Å, (C13A), −0.03 Å, C(4A) and 0.02 Å, C(5A); Sn(1) and O(1A) deviate from the plane by 0.20 and 0.28 Å, respectively.

The title compound can be compared with three similar tin complexes recently described, namely, dialkylbis(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)-tin(IV), $[(Q')_2SnR_2]$ (alkyl = n-butyl [16], t-butyl [4a], or methyl [4b]. The ligand Q_{Br} differs from Q' because it has a 4-bromobenzoyl group instead of the benzoyl in position 4 of the pyrazolone ring. The three com-

Table 7
Bond lengths with e.s.d.'s in parentheses

Sn(1)–O(1)	2.104(4)
Sn(1)–O(2)	2.385(5)
Sn(1)–O(1a)	2.099(4)
Sn(1)–O(2a)	2.436(5)
Sn(1)–C(20)	2.097(8)
Sn(1)–C(21)	2.099(8)
O(1)–C(5)	1.292(7)
O(2)–C(13)	1.251(7)
O(1a)–C(5a)	1.293(7)
O(2a)–C(13a)	1.255(8)
Br(1)–C(17)	1.900(7)
Br(1a)–C(17a)	1.893(7)
N(1)–N(2)	1.402(8)
N(1)–C(5)	1.325(7)
N(1)–C(6)	1.427(9)
N(2)–C(3)	1.309(9)
N(1a)–N(2a)	1.399(7)
N(1a)–C(5a)	1.347(7)
N(1a)–C(6a)	1.414(8)
N(2a)–C(3a)	1.301(8)
C(3)–C(4)	1.442(8)
C(3)–C(12)	1.49(1)
C(4)–C(5)	1.418(9)
C(4)–C(13)	1.417(8)
C(6)–C(7)	1.37(1)
C(6)–C(11)	1.40(1)
C(7)–C(8)	1.36(1)
C(8)–C(9)	1.35(1)
C(9)–C(10)	1.39(2)
C(10)–C(11)	1.40(1)
C(13)–C(14)	1.495(9)
C(14)–C(15)	1.389(9)
C(14)–C(19)	1.39(1)
C(15)–C(16)	1.38(1)
C(16)–C(17)	1.38(1)
C(17)–C(18)	1.39(1)
C(18)–C(19)	1.40(1)
C(3a)–C(4a)	1.445(8)
C(3a)–C(12a)	1.494(9)
C(4a)–C(5a)	1.407(8)
C(4a)–C(13a)	1.413(8)
C(6a)–C(7a)	1.37(1)
C(6a)–C(11a)	1.39(1)
C(7a)–C(8a)	1.38(1)
C(8a)–C(9a)	1.36(1)
C(9a)–C(10a)	1.36(2)
C(10a)–C(11a)	1.39(1)
C(13a)–C(14a)	1.499(8)
C(14a)–C(15a)	1.385(9)
C(14a)–C(19a)	1.37(1)
C(15a)–C(16a)	1.38(1)
C(16a)–C(17a)	1.37(1)
C(17a)–C(18a)	1.391(9)
C(18a)–C(19a)	1.38(1)

plexes mentioned above also have STB geometry. Table 9 shows selected geometrical features of these complexes along with those of the complex [$(acac)_2SnMe_2$] [17]. This complex has the same chelate frame as the other complexes although unlike them, it is a perfect octahedron.

The asymmetric chelation of ligands Q has been observed in other metal complexes. For example, in [$Eu(Q')_3(OP^tBu_3)_3$] [18] the Eu–O bond distances to Q′ differ by 0.06, 0.12 and 0.13 Å and for [$UO_2(Q')_2(Me_2SO)$] [19] U–O bond lengths are 2.325(7) and 2.403(6) Å in one Q′ ligand.

The dihedral angle between the pyrazolonate ring, N(1)–N(2)–C(3)–C(4)–C(5), and the phenyl ring C(6)–C(7)–C(8)–C(9)–C(10)–C(11), is 13.7°. The dihedral angle between the rings C(6A)–C(7A)–C(8A)–C(9A)–C(10A)–C(11A) and N(1A)–N(2A)–C(3A)–C(4A)–C(5A) in the other ligand is 39.8°. These values compare well with those of the complex [$(Q')_2SnMe_2$] [4b], which are 14.2° and 36.0°, respectively. The differences may be ascribed to packing forces.

The atom N(1) appears in a planar environment as the bond angles C(5)–N(1)–C(6), C(5)–N(1)–N(2) and C(6)–N(1)–N(2) total 360° (they are 129.7(6), 110.5(5) and 118.8(5)°, respectively). The smallest bond angle, 110.5(5)°, is determined by constraints of the pyrazolonate ring but the dramatic difference between the other two angles arises from a specific feature related to the planarity between the phenyl and the pyrazolonate rings. In fact, the opening of C(5)–N(1)–C(6) may be explained in terms of the related length H (of C(7))–O(1), 2.21(1) Å which is shorter than the corresponding sum of the van der Waals radii of H and O (1.2 and 1.40 Å, respectively [20]).

In the other Q_{Br} ligand the bond angle C(5A)–N(1A)–C(6A) is 128.1(5)° and the distance O(1A)–H (of C(7A)) is 2.508(9) Å. This contact is longer than that for the former Q_{Br} because of the greater twist (39.8°) of the rings described above.

The angles corresponding to C(5)–N(1)–C(6) in our complex are 131(1)° and 134(4)° for [$(Q')_2Sn^nBu_2$], 129.4(7) and 130.8(4)° for [$(Q')_2Sn^tBu_2$] and 130.7(4) and 128.8(4) for [$(Q')_2SnMe_2$]. We have calculated H-coordinates at the *ortho* positions, of phenyls for organotin complexes of Q′, C(7) and C(7A) in our complex, and have checked the distances between them and the corresponding O atoms. Thus, for [$(Q')_2Sn^nBu_2$] these parameters are 2.14 Å in one case and 2.52 Å in the other; 2.26 and 2.33 Å for [$(Q')_2Sn^tBu_2$], and 2.20 and 2.47 Å for [$(Q')_2SnMe_2$]. The short O–H contact is a common feature for Q′ and Q_{Br} in these complexes. Since oxygen is not expected to form hydrogen bonds with an aromatic H atom this interaction should be repulsive. The rotation of the phenyl ring around the N(1)–C(6) bond in our complex could displace the interacting H atom to avoid the repulsive O–H interaction. However, this rotation is apparently not allowed. We conclude that planarity between the above mentioned rings is required by these complexes to increase the number of conjugated double bonds that can participate in a stabilizing mesomeric effect. The resultant stabilization stemming

Table 8
Bond angles with e.s.d.'s in parentheses

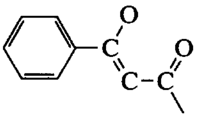
C(20)–Sn(1)–C(21)	154.5(3)
O(2a)–Sn(1)–O(1)	154.5(2)
O(1a)–Sn(1)–O(2)	153.7(2)
O(1)–Sn(1)–O(2)	78.5(2)
O(1a)–Sn(1)–O(2a)	79.5(2)
O(1)–Sn(1)–O(1a)	75.5(2)
O(2)–Sn(1)–O(2a)	126.7(2)
C(20)–Sn(1)–O(1)	101.4(3)
C(20)–Sn(1)–O(2)	83.4(3)
C(20)–Sn(1)–O(1a)	97.5(3)
C(20)–Sn(1)–O(2a)	86.5(3)
C(21)–Sn(1)–O(1)	98.5(3)
C(21)–Sn(1)–O(2)	85.2(3)
C(21)–Sn(1)–O(1a)	102.8(2)
C(21)–Sn(1)–O(2a)	82.2(3)
C(5)–O(1)–Sn(1)	128.5(4)
C(13)–O(2)–Sn(1)	130.6(4)
C(5a)–O(1a)–Sn(1)	129.9(3)
C(13a)–O(2a)–Sn(1)	130.1(4)
C(5)–N(1)–N(2)	110.5(5)
C(6)–N(1)–N(2)	118.8(5)
C(6)–N(1)–C(5)	129.7(6)
C(3)–N(2)–N(1)	106.5(5)
C(5a)–N(1a)–N(2a)	111.5(5)
C(6a)–N(1a)–N(2a)	120.4(5)
C(6a)–N(1a)–C(5a)	128.1(5)
C(3a)–N(2a)–N(1a)	105.6(5)
C(4)–C(3)–N(2)	111.2(6)
C(12)–C(3)–N(2)	117.6(6)
C(12)–C(3)–C(4)	131.2(6)
C(5)–C(4)–C(3)	103.1(5)
C(13)–C(4)–C(3)	133.4(6)
C(13)–C(4)–C(5)	122.7(5)
N(1)–C(5)–O(1)	122.1(5)
C(4)–C(5)–O(1)	129.3(5)
C(4)–C(5)–N(1)	108.6(5)
C(7)–C(6)–N(1)	123.1(7)
C(11)–C(6)–N(1)	118.1(7)
C(11)–C(6)–C(7)	118.7(7)
C(8)–C(7)–C(6)	120.5(8)
C(9)–C(8)–C(7)	123(1)
C(10)–C(9)–C(8)	118.3(9)
C(11)–C(10)–C(9)	120.4(9)
C(10)–C(11)–C(6)	119.4(8)
C(4)–C(13)–O(2)	123.2(6)
C(14)–C(13)–O(2)	114.6(5)
C(14)–C(13)–C(4)	122.2(5)
C(15)–C(14)–C(13)	119.5(6)
C(19)–C(14)–C(13)	121.6(6)
C(19)–C(14)–C(15)	118.9(6)
C(16)–C(15)–C(14)	121.7(7)
C(17)–C(16)–C(15)	118.1(7)
C(18)–C(17)–C(16)	122.5(7)
Br(1)–C(17)–C(16)	118.9(6)
Br(1)–C(17)–C(18)	118.6(6)
C(19)–C(18)–C(17)	118.0(7)
C(18)–C(19)–C(14)	120.8(7)
C(4a)–C(3a)–N(2a)	112.0(5)
C(12a)–C(3a)–N(2a)	117.6(5)
C(12a)–C(3a)–C(4a)	130.3(5)
C(5a)–C(4a)–C(3a)	103.6(5)
C(13a)–C(4a)–C(3a)	131.8(5)
C(13a)–C(4a)–C(5a)	124.2(5)
N(1a)–C(5a)–O(1a)	121.2(5)
C(4a)–C(5a)–O(1a)	131.4(5)
C(4a)–C(5a)–N(1a)	107.3(5)
C(7a)–C(6a)–N(1a)	120.7(6)
C(11a)–C(6a)–N(1a)	119.4(7)
C(11a)–C(6a)–C(7a)	119.9(6)
C(8a)–C(7a)–C(6a)	120.0(7)
C(9a)–C(8a)–C(7a)	121(1)
C(10a)–C(9a)–C(8a)	120.1(9)
C(11a)–C(10a)–C(9a)	121(1)
C(10a)–C(11a)–C(6a)	118.6(9)
C(4a)–C(13a)–O(2a)	121.8(6)
C(14a)–C(13a)–O(2a)	117.4(5)
C(14a)–C(13a)–C(4a)	120.7(5)
C(15a)–C(14a)–C(13a)	118.9(6)
C(19a)–C(14a)–C(13a)	121.5(5)
C(19a)–C(14a)–C(15a)	119.6(6)
C(16a)–C(15a)–C(14a)	120.6(7)
C(17a)–C(16a)–C(15a)	119.0(7)
C(18a)–C(17a)–C(16a)	121.4(7)
Br(1a)–C(17a)–C(16a)	119.5(5)
Br(1a)–C(17a)–C(18a)	119.1(6)
C(19a)–C(18a)–C(17a)	118.5(7)
C(18a)–C(19a)–C(14a)	120.8(6)

from co-planarity allows the repulsive O–H forces to remain and a compromise is reached.

Kepert showed that in complexes of the type [M(bidentate)$_2$(unidentate)$_2$] for symmetrical chelating ligands (A ··· A′) one donor atom A is expected to bind more strongly (M–A bond short) than the other (M–A′ bond long) [15]. He found bond shortening of about 5%. Theoretical calculations of his model, which associates the complex geometry with the minimization of electron repulsion of the six atoms surrounding the metal, indicate a further increase of the difference between primary and secondary bonds, M–A and M–A′, for smaller unidentate ligands. This was confirmed experimentally for the complexes [Mo(bidentate)$_2$O$_2$] and [V(bidentate)$_2$O$_2$], as the small covalent radius of the O atom determined further differences of 10% and 7%, respectively. In the complexes shown in Table 9 all of the unidentate ligands are C moieties. One can speculate that by replacing these groups by ligands having larger atoms that bind to the metal, a non-skewed complex might be obtained for Q′ and Q_{Br}. We are exploring this possibility with complexes of the type [Q$_2$SnCl$_2$] because [(acac)$_2$SnCl$_2$] [21] is a *cis*-octahedral complex whereas [(acac)$_2$SnMe$_2$] [17] is *trans*-octahedral.

Kepert also showed that bidentate ligands that form 5- or 6-membered chelate rings and have large normalized bites normally give *trans*-octahedral complexes [M(bidentate)$_2$(unidentate)$_2$]. Calculations show that as the normalized bit is decreased, the equatorial rectangle formed by the two bidentate ligands becomes distorted and forms a planar trapezium, with the unidentate ligands skewed towards the long edge of the trapezium (the area of secondary bonds). In this stabilized STB geometry two mirror planes are retained ($C_{2\nu}$ symmetry). Calculations show that the chelating atoms that are bound more strongly to the metal (those forming primary bonds) exert a higher repulsion than those less strongly bound [15]. In Table 9 the bite of acac in [(acad)$_2$SnMe$_2$] is greater than those found in ligands giving STB geometry. This matches Kepert's expectations. Therefore, one reason for the differing behaviour in complexes in Table 9 may be the small bite of the chelating asymmetric ligands. The bite of Q_{Br} and Q′ may be related to the O–H repulsive force mentioned above. This force would push the primary O atom towards the secondary O atom, so that a small bite angle of the chelating ligand would be obtained.

In complexes of the type [M′(bzac)$_2$] where M′ is VO$_2$, Cu, Pd, or Zn · EtOH and bzac is the asymmetric ligand benzoylacetonate, a comparison of C–O bonds indicates more double-bound character for the C–O group closer to the methyl group [22]. This is associated with (a) the difference between the metal–O bond closer to the phenyl and that closer to the methyl (the former is shorter than the latter) and (b) the difference between the two C–C bonds within the chelate (generally that closer to the phenyl is shorter than that closer to the methyl which indicates more double-bond character for the former). This leads to the conclusion [22] that the ligand is acting as indicated thus



with the ligand geometrical asymmetry in the complex determined by the different electronic properties of the phenyl (electron-withdrawing) and the methyl (electron-releasing). Definitive conclusions could not be reached, however, since estimated standard deviations and in some cases high R_{final} factors are too large. An analogous analysis in our complex shows that the bond lengths C(13)–O(2), 1.251(7) Å, and C(5)–O(1), 1.292(7) Å, may be considered significantly different as they differ about by 6σ (see further discussion in Experimental section).

Consequently, the almost double bond character of the former can explain the weak Sn(1)–O(2) interaction of 2.385(5) Å. However, the asymmetry of our ligand is not reflected in the bonds C(4)–C(5) and C(4)–C(13), 1.418(9) and 1.417(8) Å, respectively (in the other ligand the corresponding values are 1.407(8) and 1.413(8) Å). Nevertheless, these two bonds appear equivalent, within less than 3σ. We note that in our complex the aromatic arm of the ligand, C(14)–C(15)–C(16)–C(17)–C(18)–C(19), is closer to the carbonyl moiety, C(13)–O(2), of the chelate while in the studies mentioned above the phenyl arm of benzoylacetonate was farther [22]. The complex [(Q′)$_2$SnMe$_2$] has significantly different C–O bond lengths for one ligand, 1.259(7) and 1.284(6) Å. In [Q′$_2$Sn^{t}Bu$_2$] both C–O bonds are of the same order whereas in the complex [Q′$_2$Sn^{n}Bu$_2$] higher standard deviations preclude comparison.

In the more planar ligand, the N–C pyrazolonate bonds (1.325(7) and 1.309(9) Å) appear more similar than in the other heterocycle (1.347(7) and 1.301(8) Å).

2.5. Conclusions

In complexes [Q$_2$SnR$_2$] the asymmetric ligands Q show some planarity between the pyrazolonate ring and its attached phenyl, probably due to increased conjugation of double bonds. This planar arrangement causes a short contact between the neighbouring pyrazolonate oxygen and one *ortho* H atom of the phenyl. The O atom is therefore pushed towards the other O

Table 9
Selected geometrical data in the coordination sphere for bis(β-diketonate)diorganotin compounds

	[(Q$_{Br}$)$_2$SnMe$_2$]	[Q′$_2$Sn^{n}Bu$_2$]	[Q′$_2$Sn^{t}Bu$_2$]	[Q′$_2$SnMe$_2$]	[(acac)$_2$SnMe$_2$]
Sn–O$_p$ (a)	2.104(4)	2.12(2)	2.145(5)	2.104(3)	2.18(1)
	2.099(4)	2.11(1)	2.135(6)	2.103(4)	2.20(2)
Sn–O$_s$ (b)	2.385(5)	2.35(2)	2.381(7)	2.337(4)	
	2.436(5)	2.38(2)	2.461(6)	2.412(4)	
Sn–C	2.097(8)	2.07(2)	2.20(1)	2.095(8)	2.14(2)
	2.099(8)	2.12(2)	2.20(2)	2.090(8)	
O$_p$–Sn–O$_p$	75.5(2)	79.2(5)	74.1(2)	77.2(1)	94(1)
O$_s$–Sn–O$_s$	126.7(2)	118.7(4)	127.4(2)	121.6(1)	
O$_p$–Sn–O$_s$ (bite)	78.5(2)	82.0(4)	79.3(2)	80.9(1)	86(1)
	79.5(2)	80.3(4)	79.8(2)	80.7(1)	
C–Sn–C	154.5(3)	154.7(8)	150.0(5)	153.3(3)	180(0)
Geometry (c)	STB	STB	STB	STB	octahedral
Ref.	this work	[16]	[4a]	[4b]	[17]

Note: (a), (b) Sn–O$_p$ and Sn–O$_s$ stands for primary and secundary bonds, respectively; (c) STB stands for skewed trapezoidal bipyramidal.

atom in the chelate ring causing a closing of the chelate bite O–Sn–O. The lowering of this bite angle increases repulsion among the atoms of the metal environment so that a skewed trapezoidal bipyramidal geometry is stabilized.

It is noted that β-diketones such as thenoyltrifluoroacetone [23] are widely used as extracting agents. Therefore, the facility of formation of (4-aroyl-5-pyrazolone)tin chelates, along with their stability in air and in solution, suggest a possible use of 4-aroyl-5-pyrazolones for organotin trace analysis.

3. Experimental section

Solvents were dried by standard techniques. Reagents were purchased from Aldrich. The samples were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses were carried out in-house with a Carlo Erba Strumentazione 1106 instrument. The molecular weight determinations were performed at Pascher Mikroanalytisches Laboratorium, Remagen, Germany. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin-Elmer 2000 FT-IR instrument. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on an XR-300 Varian spectrometer operating at room temperature (300 for ^{1}H, 75 for ^{13}C and 111.9 MHz for ^{119}Sn). Proton, carbon and tin chemical shifts are reported in ppm vs. Me_4Si 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 centre of the window. Each tin spectrum was acquired in ca. 4h. Melting points were taken with an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The compounds $Q_{Cl}H$, $Q_{Br}H$, Q_{FH}, Q_RH, and Q_IH were prepared by published methods [1a].

3.1. *Dimethylbis[1-phenyl-3-methyl-4-(4-bromobenzoyl)-pyrazolon-5-ato]tin(IV), $[(Q_{Br})_2Sn(CH_3)_2]$, (1)*

(i) To a methanolic solution (50 ml) of $Q_{Br}H$ (0.70 g, 2 mmol) were added potassium hydroxide (0.11 g, 2 mmol) and dichlorodimethyltin(IV) (0.22 g, 1 mmol). A precipitate was immediately formed. The mixture was set aside overnight and the precipitate was filtered off and washed with methanol (ca. 10 ml), shown to be compound **1**, and recrystallized from chloroform/methanol. Compound **2–19**, **21** were obtained similarly.

(ii) TlQ_{Br} (1.12 g, 2.0 mmol) was added to a solution of dichlorodimethyltin(IV) (0.44 g, 2 mmol) in dichloromethane (30 ml). The TlCl formed was filtered off and complex **1** was precipitated by the addition of methanol (30 ml).

3.1.1. *Dimethylbis[1-phenyl-3-methyl-4(4-heptylbenzoyl)-pyrazolon-5-ato]tin(IV), $[(Q_R)_2Sn(CH_3)_2]$, (20)*

To a methanolic solution (50 ml) of Q_RH (0.75 g, 2 mmol) were added potassium hydroxide (0.11 g, 2 mmol) and dichlorodimethyltin(IV) (0.22 g, 1 mmol). The clear solution was set aside overnight and after evaporation of the solution to dryness under reduced pressure, the residue was stirred with chloroform (20 ml) and filtered. The filtrate was concentrated and slow addition of diethyl ether gave the compound **20**.

3.1.2. *Tetrachloro[1-phenyl-3-methyl-4(4-fluorobenzoyl)-pyrazol-5-one]tin(IV), $[Q_FHSnCl_4]$ (25)*

Anhydrous $SnCl_4$ (0.521, 2 mmol) was added to a stirred Et_2O solution (50 ml) of Q_FH (0.592 g, 2 mmol) under a stream of N_2. A colourless precipitate was obtained immediately: It was filtered off and washed with Et_2O under a stream of N_2. Compounds **22–24**, **26** and **27** were obtained similarly.

3.1.3. *Tetrachloro[1-phenyl-3-methyl-4(4-heptylbenzoyl)-pyrazol-5-one]tin(IV), $[Q_RHSnCl_4]$ (28)*

To a methanolic solution (50 ml) of Q_RH (0.75 g, 2 mmol) were added potassium hydroxide (0.11 g, 2 mmol) and tin tetrachloride (0.260 g, 1 mmol). The clear solution was set aside overnight and after evaporation to dryness under reduced pressure the residue was stirred with chloroform (20 ml) and filtered. The

Table 10
Summary of Crystal Data

Formula	$C_{36}H_{30}N_4O_4Br_2Sn$
Formula Weight	861.17
a (Å)	6.6135(5)
b (Å)	11.879(1)
c (Å)	22.445(2)
α (deg)	86.778(7)
β (deg)	84.820(7)
γ (deg)	81.261(6)
Volume (Å)	1734.1(2)
Space Group	P-1
Z	2
Crystal dimensions (mm)	0.25 × 0.25 × 0.10
Density calcd. (gcm^{-3})	1.650
Temperature	298 K
F(000)	852.000
μ (cm^{-1})	95.754
Diffractometer	Syntex $P2_1$
Radiation	Cu Kα
Data Collection Mode	$2\Theta-\Theta$
scan speed (deg/min)	2
Scan range (deg)	0.8, 0.8
background counts	1/4 of scan time at the end of scan range
2 theta range (deg)	3–140
Reflections collected	6580
Reflections used $I > 3\sigma(I)$	4861
Final no. variables	424
R_f, R_w	0.048, 0.068

colourless precipitate was washed with Et_2O (ca. 10 ml) and shown to be compound **28**.

3.2. Crystallographic study

Data were collected with a Syntex $P2_1$ diffractometer. Monitoring of the reflections [−1, 1, −2], [0, 1, 1], [0, −1, −1] and [1, 2, 0], taken every 100 reflections, indicated no decay during data collection. A ψ-scan of the reflections [−1, 0, 0] and [1, 0, 0], which have the χ angle close to 90° or 270°, showed absorption phenomena with minimum transmission of 27%. The corresponding correction was therefore applied along with those for Lorentz and polarization effects. Table 10 provides a summary of experimental crystallographic data. The positions of the non-H atoms were obtained using direct methods with the program SHELXTL-PLUS, a computer facility of the diffractometer [24] provided by Siemens. Subsequent refinement by least-squares were performed with the CAOS program [25] on a Vax 3300 computer. The function minimized was $\Sigma\omega(|F_o| - |F_c|)$ with weights [26] of the type $\omega = a + F_o + cF_o^2$, where a and c are of the order of $2F_o$(min) and $2/F_o$(max). In the final cycles of least squares the H atoms were included at fixed position, d(C–H) = 0.96 Å. Refinement for a molecule containing isotropic N and C atoms and anisotropic Sn, Br and O atoms converged to R_f 0.059 (R_w 0.083). Figure 2 reflects this stage of refinement. Since the high number of useful reflections allowed more parameters to be refined, all the non-H atoms were refined anisotropically and final convergence gave R_{final} 0.048 and R_w 0.068. A final Fourier difference map showed no additional peaks. At R_f 0.059, the bond lengths C(5)–O(1) and C(13)–O(2) (1.295(9) and 1.238(9) Å) are significantly different, whereas at R_{final} 0.048 (1.292(7) and 1.251(7) Å) they are no longer so, notwithstanding the smaller standard deviations. Atomic scattering factors and anomalous dispersion terms were taken from The International Tables for X-ray Crystallography [27].

4. Supplementary material available

Anisotropic displacement parameters for Sn, Br and O atoms are available from the authors or from the Cambridge Crystallographic Data Centre.

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