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Tin(IV) and organotin(IV) complexes containing the anion of some substituted-3-methyl-4-acyl-5-pyrazolones. Crystal structure of dimethylbis(1-phenyl-3-methyl-4-benzoyl pyrazolon-5-ato)tin(IV)

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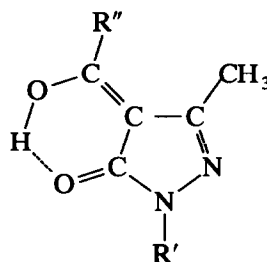
Abstract

Six-coordinate $[(Q)_2SnRX]$ compounds, where QH is 1- R' -3-methyl-4- R'' C(O)-5-pyrazolone (Q_P H: $R' = p\text{-NO}_2\text{-C}_6\text{H}_4$, $R'' = \text{C}_6\text{H}_5$; Q_M H: $R' = \text{CH}_3$, $R'' = \text{C}_6\text{H}_5$; Q_F H: $R' = \text{C}_6\text{H}_5$, $R'' = \text{CF}_3$), X = Cl or R, R = Cl or CH_3 , have been prepared and characterized by analyses, spectral (IR, ^1H -, ^{13}C - and ^{119}Sn -NMR data) and conductivity measurements. The crystal structure of $[(Q')_2Sn(\text{CH}_3)_2]$ (Q' H is 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone) was also determined: the sterically demanding ligand gives rise to severe distortion of the six-coordinate $[(Q')_2Sn(\text{CH}_3)_2]$ compound, similar to that noted in $[(Q')_2Sn(t\text{-C}_4\text{H}_9)_2]$ and $[(Q')_2Sn(n\text{-C}_4\text{H}_9)_2]$. The C–Sn–C axis is bent ($153.3(3)^\circ$) and two of the four Sn–O bonds are exceptionally long (2.337(4) and 2.412(4) Å) whereas the other two Sn–O bonds are normal (2.104(3) and 2.103(4) Å).

1. Introduction

4-acyl-5-pyrazolones are enolizable β -diketones [1] which afford stable chelates with several metals [2], a property used for metal extraction.

In a preceding paper, the results of interactions between tin(IV) and organotin(IV) compounds with the most representative members of the family of 4-acyl-5-pyrazolones (1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, namely Q' H, and 1-phenyl-3-methyl-4-acetyl-5-pyrazolone, namely Q'' H) have been reported [3]. Continuing our interest in tin(IV) chemistry we investigated organotin(IV) derivatives of other 1- R' -3-methyl-4- R'' (CO)-5-pyrazolones (Fig. 1), abbreviated Q_P H ($R' = p\text{-NO}_2\text{-C}_6\text{H}_4$, $R'' = \text{C}_6\text{H}_5$), Q_F H ($R' = \text{C}_6\text{H}_5$ and $R'' = \text{CF}_3$), and Q_M H ($R' = \text{CH}_3$ and $R'' = \text{C}_6\text{H}_5$), in order to compare chemical-physical and structural features with those of complexes previously synthesized [3,4]. An X-ray diffraction study of the



Q_P H: $R' = p\text{-NO}_2\text{Ph}$, $R'' = \text{Ph}$;
 Q_M H: $R' = \text{Me}$, $R'' = \text{Ph}$;
 Q_F H: $R' = \text{Ph}$, $R'' = \text{CF}_3$.

Fig. 1. Structure of 1- R' -3-methyl-4- R'' C(O)-5-pyrazolones.

structure of $[(Q')_2Sn(\text{CH}_3)_2]$ compared with those of related compounds $[(Q')_2Sn(t\text{Bu})_2]$ and $[(Q')_2Sn(n\text{Bu})_2]$, has been also reported. It is shown that the stable but sterically demanding Q' causes the tin cation to distort from octahedral symmetry, while maintaining six-coordination.

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2. Results and discussion

The reaction between $Q_P H$, $Q_M H$ or $Q_F H$ and $[(CH_3)_n SnCl_{4-n}]$ ($n = 0, 1$ or 2 ; $QH = Q_P H$, $Q_M H$, or $Q_F H$) in methanol containing potassium hydroxide yielded the compounds $[(Q)_2 Sn(CH_3)_n Cl_{4-n-2}]$ ($n = 0, 1$, or 2) (1–9) as colourless or brown solids characterized by analytical data, melting points, and yields (Table 1).

The complexes 1–6 ($(Q_P)^-$ and $(Q_M)^-$ derivatives) are moisture-stable, whereas the $(Q_F)^-$ derivatives, 7–9, gradually absorb water and decompose, regenerating $Q_F H$, as confirmed by elemental analyses, IR and 1H NMR spectra. The compounds decompose more quickly at ca. 80–90°C. However, the complexes 7–9 are sufficiently stable to be well characterized. The reactions between $Tl(Q')$ and $Tl(Q'')$, prepared according to the literature [2e], and $Me_3 SnCl$ in $CH_2 Cl_2$ (0°C) were also attempted: the expected $[(Q')_2 SnMe_3]$ and $[(Q'')_2 SnMe_3]$ were not isolated, but the 2:1 complexes $[(Q')_2 SnMe_2]$ and $[(Q'')_2 SnMe_2]$ always precipitated from the reaction solutions. $Me_3 SnCl$ probably disproportionates in presence of Q''^- and Q'^- to $Me_2 SnCl_2$ and $Me_4 Sn$. The presence of $Me_4 Sn$ in the reaction solutions was confirmed by 1H NMR spectroscopy.

All the compounds 1–9 are insoluble in water but soluble in chlorinated solvents and some are soluble in acetone and DMSO. Conductivity measurements in acetone for compounds which are sufficiently soluble,

TABLE 2. Selected IR data ^a (cm^{-1}) of the complexes 1–9

Compound	$\nu(C=O)$	$\nu(Sn-O)$	$\nu(Sn-Cl)$
$Q_P H$	1635s		
$[(Q_P)_2 Sn(CH_3)_2]$	1608s	410m	
$[(Q_P)_2 SnCH_3 Cl]$	1612s	438w	310w
$[(Q_P)_2 SnCl_2]$	1614s	463s	352s
$Q_M H$	1630s		
$[(Q_M)_2 Sn(CH_3)_2]$	1600s	395m	
$[(Q_M)_2 SnCH_3 Cl]$	1600s	420w	320m
$[(Q_M)_2 SnCl_2]$	1580s	460m	340s
$Q_F H$	1675s		
$[(Q_F)_2 Sn(CH_3)_2]$	1605s	380m	
$[(Q_F)_2 SnCH_3 Cl]$	1620s	365w	340w
$[(Q_F)_2 SnCl_2]$	1600s	363s	350s

^a Nujol mull.

show that these complexes like $[(Q')_2 SnRX]$ [3] and $[(Q'')_2 SnRX]$ [3] are non-electrolytes.

The important infrared spectral bands and their tentative assignments are in Table 2. The shift of the $\nu(C=O)$ absorption band from 1630–1675 cm^{-1} in the free bases to 1580–1620 cm^{-1} in the chelates, and the non-appearance in the spectra of complexes of the broad absorption band due to $\nu(OH \cdots O)$ suggests that both the carbonyl groups are involved in bonding to the tin through oxygen atoms [5]. By analogy with assignments for bis(acetylacetonato)- and bis(benzoylacetonato)-tin(IV) chelates [6] we have assigned the

TABLE 1. Analytical and other data for $(Q_P)^-$, $(Q_M)^-$ and $(Q_F)^-$ derivatives

Compound ^a	Yields %	M.p. °C	Elem. Anal. (Found (calc.) (%))		
			C	H	N
1 $[(Q_P)_2 Sn(CH_3)_2]$	80	282–283	54.14 (54.50)	3.78 (3.81)	10.35 (10.59)
2 $[(Q_P)_2 SnCH_3 Cl]$	68	240–242	51.88 (51.66)	3.41 (3.34)	10.40 (10.33)
3 $[(Q_P)_2 SnCl_2]$	50	320–322	49.17 (48.95)	3.00 (2.90)	9.84 (10.07)
4 $[(Q_M)_2 Sn(CH_3)_2]$	72	201–202	54.20 (53.91)	4.88 (4.87)	9.55 (9.67)
5 $[(Q_M)_2 SnCH_3 Cl]$	65	120–122	50.24 (50.08)	4.35 (4.20)	8.91 (9.34)
6 $[(Q_M)_2 SnCl_2]$	58	175–177	46.15 (46.49)	3.59 (3.58)	8.86 (9.04)
7 $[(Q_F)_2 Sn(CH_3)_2]$	36	158–159	45.90 (45.45)	3.35 (3.23)	7.72 (8.15)
8 $[(Q_F)_2 SnCH_3 Cl] \cdot 2S \cdot 1/2H_2O$ ^b	45	106 dec	41.85 (41.54)	3.67 (3.62)	7.29 (7.18)
9 $[(Q_F)_2 SnCl_2]$	62	133–135	39.20 (39.60)	2.40 (2.22)	7.47 (7.70)

^a $Q_P H$ is 1-*p*-nitrophenyl-3-methyl-4-benzoyl-5-pyrazolone; $Q_M H$ is 1,3-dimethyl-4-benzoyl-5-pyrazolone; $Q_F H$ is 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone.

^b S = $CH_3 OH$.

bands around 450 cm^{-1} to predominant (Sn–O) stretching modes. Moreover, for the compounds **2**, **3**, **5**, **6**, **8** and **9**, bands assignable to $\nu(\text{Sn–Cl})$ are observed, consistent with their empirical formulae. In the spectrum of **8** there is also a strong peak centred at 3300 cm^{-1} with a shoulder at 3600 cm^{-1} , indicating coordinated or lattice water.

The ^1H NMR data of 4-acyl-5-pyrazolones and their complexes are listed in Table 3. The upfield shift of the methyl signals suggests a shielding of these protons upon coordination [7]. Moreover, the presence of several broad signals, (except in the spectra of $[(\text{Q})_2\text{SnMe}_2]$ **1**, **4** and **7**) for each magnetically equivalent proton group, indicates the presence of isomers in solution.

Investigation of ^{13}C NMR spectra (Table 4) of the chelates shows a downfield shift of methyl carbon resonances upon coordination indicating reduced shielding in the chelates. Furthermore, the isomers in solution inferred from the ^1H spectra is also evident in

the ^{13}C and ^{119}Sn NMR spectra (Table 5) (compounds **2**, **3**, **5**, **6**, **8** and **9**) in which several absorptions have been found for each carbon atom and for the tin nucleus. Only in the case of dimethyltin(IV) complexes were isomers not detectable, but this is likely to be due to fluxionality around the coordination centre rather than to the absence of isomers.

All the ^{119}Sn chemical shifts fall in the typical range of hexacoordinated tin(IV) derivatives [7] and are affected by the electronegativity of the groups bonded to tin and by geometric distortions which modify bond angles at tin. For all $[\text{Q}_2\text{Sn}(\text{CH}_3)_n\text{Cl}_{4-n-2}]$ ($n = 0, 1$, or 2) the ^{119}Sn chemical shift is a function of n (Fig. 2) as previously found for the $(\text{Q}')^-$ and $(\text{Q}'')^-$ complexes with tin(IV) [3].

In the Tables 3 and 4 spin–spin coupling constants of the 3- CH_3 protons and of $\text{CF}_3\text{–C(O)–}$ and 5- C(O) carbon atoms with fluorine (compounds **7**, **8** and **9**) are also reported. No significant difference with respect to the free neutral Q_FH is observed [8].

TABLE 3. ^1H NMR data ^a for the derivatives 1–9 (in CDCl_3)

Compound	3- CH_3	N-R'	C(O)-R''	Sn-R	Other data ^b
Q_FH	2.12s	8.21d 8.35d	7.50–7.58m 7.62–7.70m		
1	1.85s	8.13d 8.27d	7.50–7.58m 7.60–7.67m	1.10s	$^2J(\text{H-Sn}) = 100$
2	1.65s br 1.75s br	7.95–8.10m	7.40–7.70m	1.25s br 1.30s br	
3	1.85s 1.88s 1.90s 1.93s 2.00s	7.95–8.40m	7.38–7.70m		
Q_MH	2.00s	3.63s	7.42–7.60m		8.10 (N-H) 10.80s (O-H) br
4	1.75s	3.58s	7.40–7.55m	0.90s	$^2J(\text{H-Sn}) = 101.2$
5	1.70s br 1.80s br	3.28d br 3.58d br	7.15–7.25d br 7.35–7.55m br	1.10s br 1.20s br	$^2J(\text{H-Sn}) = 130.4$ $^2J(\text{H-Sn}) = 121.7$
6	1.78s 1.82s 1.86s	3.45s 3.48s 3.62s 3.68s	7.40–7.70m		
Q_FH	2.47q	7.35t 7.48t 7.78d			$^6J(\text{H-F}) = 2.0$
7	2.43q	7.15t 7.20t		1.05s	$^2J(\text{H-Sn}) = 98.9$ $^6J(\text{H-F}) = 2.0$
8	2.20–2.45m broad	7.20–7.45m 7.55–7.75m broad		1.50s broad	3.48s(MeOH) broad
9	2.35s br 2.40s br 2.55q 2.58q	7.30–7.55m 7.65d 7.80d 7.88t			$^6J(\text{H-F}) = 1.6$ $^6J(\text{H-F}) = 1.9$

^a δ in ppm from internal TMS.

^b J in Hz.

The ^{19}F NMR data (Table 5) show the multiplicity found in the ^{119}Sn spectra. All the signals are shifted downfield (for example, for compound 7: $\delta = -71.2$ ppm) with respect to the free neutral $\text{Q}_\text{F}\text{H}$ ($\delta = -75.2$ ppm), as with $[(\text{hfac})_2\text{SnMe}_2]$ ($\delta = -77.1$ ppm) compared to hfacH ($\delta = -77.6$ ppm) $\text{hfacH} = 1,1,1,5,5,5$ -hexafluoro-2,4-pentanedione [9].

In Table 6 are some spectral data (IR, ^1H -, ^{13}C - and ^{119}Sn NMR) of our $[\text{Q}_2\text{SnMe}_2]$ compounds, compared with those of the analogous β -diketonates. The $^1J(^{119}\text{Sn}-^{13}\text{C})$ and the $^2J(^{119}\text{Sn}-^1\text{H})$ values observed

for our compounds are comparable with those reported in literature for $[(\text{acac})_2\text{SnMe}_2]$ [10] ($\text{acacH} = 2,4$ -pentanedione), $[(\text{hfac})_2\text{SnMe}_2]$ [10], $[(\text{bzac})_2\text{SnMe}_2]$ [10] ($\text{bzacH} = 1$ -phenyl-1,3-butanedione), and $[(\text{dbzm})_2\text{SnMe}_2]$ [10] ($\text{dbzmH} = 1,3$ -diphenyl-1,3-propanedione), to which *trans* structures in solution have been assigned on the basis of NMR, Raman and Mössbauer studies.

It has been noted that the ^{119}Sn chemical shift varies with the bonding geometry and the electronic density for hexacoordinated dimethyltin(IV) complexes [11]. In

TABLE 4. ^{13}C NMR data in CDCl_3

Compound	CH_3	$\text{N-R}'$	$\text{C(O)-R}''$	CO C(5)	C(3) C(4)	R-Sn	others ^a
$\text{Q}_\text{P}\text{H}$	16.2	132.5; 135.3 142.5; 144.8	119.3; 124.9 128.2; 128.6	188.0 165.1	149.1 104.6		
1	16.5	131.8; 138.9 143.2; 144.4	120.1; 124.6 127.8; 128.6	^b ^b	150.9 ^b	9.8	
2	16.0 16.3	132.6; ^b ^b	119.8; 120.1	^b	^b	^b	
3	16.4 16.5 16.6	132.5; 133.0 133.3; 133.5 133.8	119.4; 120.5 120.7; 120.8 121.0; 121.2 124.6; 124.7 124.9; 125.0 128.2; 128.3 128.5; 128.6 128.7; 128.9 129.2	^b ^b	^b ^b		
$\text{Q}_\text{M}\text{H}$	15.5	32.5	127.7; 128.3 130.0; 131.6 133.2; 138.5	193.0 169.6 102.4 160.4	147.0		
4	16.2	31.8	127.5; 128.2 130.9;	^b ^b	148.2 ^b	8.4	
5	16.1	32.0	127.9; 128.3 131.9	^b ^b	148.7 ^b	^b	
6	16.2 16.3 16.4	32.2 32.4 32.5	128.2; 128.4 128.5; 128.6 128.8; 128.9 132.2; 132.3 132.5; 132.7 136.3; 136.6	190.5 163.4	149.7 104.4		
$\text{Q}_\text{F}\text{H}$	14.8q	121.4; 128.0 129.3; 136.3	116.2q	177.3q 161.0	147.9 99.6		$^2J(\text{C-F}) = 284.3$ $^3J(\text{C-F}) = 38.8$ $^5J(\text{C-F}) = 3.9$
7	15.8q	121.4; 126.5 129.1; 137.3	117.2q	173.2q 164.2	148.4 101.2	9.1	$^2J(\text{C-F}) = 284.0$ $^3J(\text{C-F}) = 39.3$ $^5J(\text{C-F}) = 5.2$
8	15.3q	121.2; 127.1 129.0; 136.5	116.7q	^b ^b	148.4 ^b	8.5	$^2J(\text{C-F}) = 283.5$ $^5J(\text{C-F}) = 3.6$
9	14.7q 15.7q	121.2; 121.3 121.5; 121.8 123.3; 127.8 128.0; 128.2 129.0; 129.2 129.3; 129.4 135.8; 136.1	^b	^b ^b	148.0 97.8		$^2J(\text{C-F}) = 4.9$ $^2J(\text{C-F}) = 3.9$

^a J in Hz.

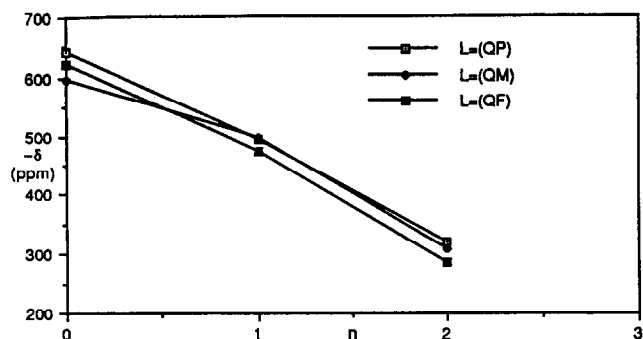
^b Not observed due to low solubility.

TABLE 5. ^{119}Sn and ^{19}F NMR data in CDCl_3

No.	Compound	$-\delta(\text{ppm})^a$ ^{119}Sn	$-\delta(\text{ppm})^b$ ^{19}F
1	$[(\text{Q}_P)_2\text{Sn}(\text{CH}_3)_2]$	321.0	
2	$[(\text{Q}_P)_2\text{SnCH}_3\text{Cl}]$	491.6 496.2	
3	$[(\text{Q}_P)_2\text{SnCl}_2]$	632.2 634.6 638.1 665.2	
4	$[(\text{Q}_M)_2\text{Sn}(\text{CH}_3)_2]$	308.7	
5	$[(\text{Q}_M)_2\text{SnCH}_3\text{Cl}]$	492.0 495.5 499.3	
6	$[(\text{Q}_M)_2\text{SnCl}_2]$	564.4 564.9 629.2 632.4	
7	$[(\text{Q}_F)_2\text{Sn}(\text{CH}_3)_2]^c$	286.4	71.2
8	$[(\text{Q}_F)_2\text{SnCH}_3\text{Cl}]$	471.1 474.5	71.2 72.2 75.9
9	$[(\text{Q}_F)_2\text{SnCl}_2]$	620.8 622.8 626.0	70.2 70.6 70.7 76.3

^a $\text{Sn}(\text{CH}_3)_4$ external std.^b CFCl_3 internal std.^c $-\delta(\text{Q}_F\text{H}) = 75.2$ ppm.

fact, the ^{119}Sn resonances of the $(\text{Q}')^-$, $(\text{Q}'')^-$, $(\text{Q}_P)^-$, $(\text{Q}_M)^-$ and $(\text{Q}_F)^-$ derivatives are shifted downfield with respect to $[(\text{acac})_2\text{SnMe}_2]$, $[(\text{bzac})_2\text{SnMe}_2]$, and

Fig. 2. Effect of the substitution on the ^{119}Sn chemical shift of $[(\text{Q})_2\text{SnR}_n\text{Cl}_{2-n}]$ (average values for $n = 0$ and $n = 1$).

$[(\text{dbzm})_2\text{SnMe}_2]$, in keeping with a lower donating ability of the pyrazolonates, and also with a marked distortion from octahedral geometry in our compounds. Furthermore, the introduction of an electron withdrawing group (Q_P^-) or of a less sterically hindered group (Q_M^-) into the pyrazolone moiety does not produce any electronic modification around the metal atom, whereas an electron withdrawing group in the 4-acyl moiety (Q_F^-) reduces the donor capacity, as indicated by the downfield ^{119}Sn chemical shift and by the lower $\nu(\text{Sn}-\text{O})$ stretching frequency compared to all the other β -diketonate complexes.

2.1. X-Ray crystal structure $[(\text{Q}')_2\text{Sn}(\text{CH}_3)_2]$

The crystal structure involves discrete molecules, with no $\text{Sn} \cdots \text{Sn}$ interactions. An ORTEP [12] represen-

TABLE 6. Comparison with several bis(β -diketonate)dimethyltin(IV) compounds

Compounds ^a	$\nu(\text{C}=\text{O})$	$\nu(\text{Sn}-\text{O})$	$(-\delta)^{119}\text{Sn}$	$^1\text{H}(\text{Sn}-\text{CH}_3)$	$^2\text{J}(\text{Sn}-\text{H})$	$^1\text{J}(\text{Sn}-\text{C})$
$[(\text{Q}_P)_2\text{Sn}(\text{CH}_3)_2]$	1608	410	320.98	1.10	100.0	^b
$[(\text{Q}_M)_2\text{Sn}(\text{CH}_3)_2]$	1600	395	308.67	0.90	101.2	893
$[(\text{Q}_F)_2\text{Sn}(\text{CH}_3)_2]$	1605	380	286.44	1.05	100.0	888
$[(\text{Q}')_2\text{Sn}(\text{CH}_3)_2]^c$	1598	400	318.50	1.02	99.0	933
$[(\text{Q}'')_2\text{Sn}(\text{CH}_3)_2]^c$	1602	395	320.60	0.83	105.0	919
$[(\text{acac})_2\text{Sn}(\text{CH}_3)_2]$	1565 ^d	430 ^d	365.00 ^e	0.50 ^d	99.3 ^f	977 ^f
$[(\text{hfac})_2\text{Sn}(\text{CH}_3)_2]$	1560 ^g	375 ^g	309.30 ^g	1.09 ^g	99.6 ^g	838 ^e
$[(\text{bzac})_2\text{Sn}(\text{CH}_3)_2]$	< 1600 ^d	450 ^d	353.50 ^e	^h	98.4 ^f	931 ^f
$[(\text{dbzm})_2\text{Sn}(\text{CH}_3)_2]$	< 1600 ^d	425 ^d	348.00 ^e	0.93 ^d	97.0 ^f	913 ^f

^a acacH = 2,4-pentanedione; hfacH = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; bzacH = 1-phenyl-1,3-butanedione; dbzmH = 1,3-diphenyl-1,3-propanedione.^b Not observed.^c Ref. [3]^d Ref. [6]^e Ref. [11]^f Ref. [10]^g Unpublished results.^h Not reported in literature.

tation of the molecule and the numbering scheme are shown in Fig. 3.

The interatomic distances and bond angles are listed in Table 7. The molecule exhibits no crystallographic

symmetry and all atoms occupy general positions, though it is possible to imagine C_{2v} symmetry with a mirror plane passing through Sn, C(22), C(22a) and the midpoints of the segments O(14)–O(14a) and O(15)–

TABLE 7. Interatomic distances (Å) and bond angles (deg) with e.s.d.'s in parentheses

<i>In the coordination sphere</i>			
Sn–O(14)	2.337(4)	Sn–O(14a)	2.412(4)
Sn–O(15)	2.104(3)	Sn–O(15a)	2.103(4)
Sn–C(22)	2.095(8)	Sn–C(22a)	2.090(8)
O(14)–Sn–O(15)	80.9(1)	O(14a)–Sn–O(15a)	80.7(1)
O(14)–Sn–C(22)	82.3(2)	O(14a)–Sn–C(22)	84.4(3)
O(14)–Sn–C(22a)	85.2(2)	O(14a)–Sn–C(22a)	82.2(3)
O(14)–Sn–O(15a)	157.3(1)	O(14a)–Sn–O(15)	157.4(2)
O(15)–Sn–C(22)	102.5(3)	O(15a)–Sn–C(22)	96.6(2)
O(15)–Sn–C(22a)	98.6(3)	O(15a)–Sn–C(22a)	103.9(2)
O(14)–Sn–O(14a)	121.6(1)	C(22)–Sn–C(22a)	153.3(3)
O(15)–Sn–O(15a)	77.2(1)		
<i>In the bidentate-5-pyrazolonate ligands</i>			
N(1)–N(2)	1.398(7)	N(1a)–N(2a)	1.406(5)
N(2)–C(3)	1.320(8)	N(2a)–C(3a)	1.318(6)
C(3)–C(4)	1.423(7)	C(3a)–C(4a)	1.427(6)
C(4)–C(5)	1.410(7)	C(4a)–C(5a)	1.422(5)
C(5)–N(1)	1.357(6)	C(5a)–N(1a)	1.343(6)
N(1)–C(6)	1.420(8)	N(1a)–C(6a)	1.420(6)
C(3)–C(12)	1.516(9)	C(3a)–C(12a)	1.503(6)
C(4)–C(13)	1.401(6)	C(4a)–C(13a)	1.406(6)
C(5)–O(15)	1.306(5)	C(5a)–O(15a)	1.284(6)
C(13)–O(14)	1.266(6)	C(13a)–O(14a)	1.259(7)
C(13)–C(16)	1.494(7)	C(13a)–C(16a)	1.477(6)
N(2)–N(1)–C(5)	110.0(4)	N(2a)–N(1a)–C(5a)	111.9(3)
N(2)–N(1)–C(6)	118.0(5)	N(2a)–N(1a)–C(6a)	119.2(4)
C(5)–N(1)–C(6)	130.7(4)	C(5a)–N(1a)–C(6a)	128.8(4)
N(1)–N(2)–C(3)	106.0(4)	N(1a)–N(2a)–C(3a)	105.2(4)
N(2)–C(3)–C(4)	112.1(5)	N(2a)–C(3a)–C(4a)	111.8(4)
N(2)–C(3)–C(12)	116.9(5)	N(2a)–C(3a)–C(12a)	118.3(4)
C(4)–C(3)–C(12)	130.8(5)	C(4a)–C(3a)–C(12a)	129.8(4)
C(3)–C(4)–C(5)	103.7(4)	C(3a)–C(4a)–C(5a)	104.5(3)
C(3)–C(4)–C(13)	132.4(5)	C(3a)–C(4a)–C(13a)	131.1(4)
C(5)–C(4)–C(13)	123.2(4)	C(5a)–C(4a)–C(13a)	123.9(4)
C(4)–C(5)–N(1)	108.2(4)	C(4a)–C(5a)–N(1a)	106.5(4)
C(4)–C(5)–O(15)	132.2(4)	C(4a)–C(5a)–O(15a)	132.3(4)
N(1)–C(5)–O(15)	119.6(4)	N(1a)–C(5a)–O(15a)	121.0(4)
N(1)–C(6)–C(7)	122.0(6)	N(1a)–C(6a)–C(7a)	119.2(6)
N(1)–C(6)–C(11)	119.1(6)	N(1a)–C(6a)–C(11a)	119.6(5)
C(4)–C(13)–O(14)	122.1(4)	C(4a)–C(13a)–O(14a)	122.0(4)
C(4)–C(13)–C(16)	123.4(4)	C(4a)–C(13a)–C(16a)	121.6(5)
O(14)–C(13)–C(16)	114.5(4)	O(14a)–C(13a)–C(16a)	116.3(4)
Sn–O(14)–C(13)	130.8(3)	Sn–O(14a)–C(13a)	128.5(3)
Sn–O(15)–C(5)	124.5(3)	Sn–O(15a)–C(5a)	128.9(3)
C(13)–C(16)–C(17)	122.5(4)	C(13a)–C(16a)–C(17a)	120.0(6)
C(13)–C(16)–C(21)	117.3(4)	C(13a)–C(16a)–C(21a)	122.0(6)
<i>In the phenyl rings (weighted average of bond distances and endocyclic angles)^a</i>			
C(joint)–C(ortho)	1.385(5)	C(ipsa)	119.6(7)
C(ortho)–C(meta)	1.388(4)	C(ortho)	119.9(4)
C(meta)–C(para)	1.378(5)	C(meta)	120.7(3)
		C(para)	118.9(7)

^a These values were calculated according to ref. [20].

O(15a), the other mirror plane coinciding with the four oxygen atoms. The shortest intermolecular approaches are normal van der Waals contacts.

The tin atom is six-coordinate, but the environment is hardly octahedral. Such a distortion has already been found in $[(Q')_2Sn(t-C_4H_9)_2]$ [3]. In the present compound the *cis*-angles range from 77.2(1) to 121.6(1)° and the *trans*-angles from 153.3(3) to 157.4(2)°, compared with 74.1(2)–127.4(2)° and 150.0(5)–153.1(2)°, respectively, in $[(Q')_2Sn(t-C_4H_9)_2]$ [3]. The distortion is inherent in the sterically demanding ligand, regardless of the bulkiness of the two alkyl groups, but the less bulky methyl groups give rise to a slightly smaller distortion.

There are two sets of Sn–O bonds; Sn–O(15) and Sn–O(15a) (2.104(3) and 2.103(4) Å) are normal, whereas Sn–O(14) and Sn–O(14a) are exceptionally long (2.337(4) and 2.412(4) Å), a peculiarity observed elsewhere [3] and attributed to the asymmetry of β -diketonato ring in the $(Q)^-$ ligand. The shorter Sn–O bonds are connected with the longer C–O bonds and *vice versa*, as in $[(Q')_2Sn(t-C_4H_9)_2]$ [3].

Other effects of the small volume of the methyl groups can be seen in the shorter Sn–C and Sn–O distances in $[(Q')_2Sn(CH_3)_2]$ (see Table 8). The separations between O(14) and C(22) or C(22a), and between O(14a) and C(22) or C(22a), are 2.923(9)–3.037(9) Å, compared to 3.04(1)–3.25(1) Å in $[(Q')_2Sn(t-C_4H_9)_2]$ [3]. The C–Sn–C axis is bent 153.3(3)° in such a way to arrange the alkyls in the space between O(14) and O(14a), which are 4.145(6) Å apart. The bite of the two $(Q)^-$ ligands, 80.9(1)° for

TABLE 8. Comparison of structural features (Å and deg) in $[(Q')_2Sn(CH_3)_2]^a$, $[(Q')_2Sn(^nBu)_2]^b$ and $[(Q')_2Sn(^iBu)_2]^c$

	a	b	c,d
Sn–O(14)	2.337(4)	2.381(7)	2.35(2)
Sn–O(14a)	2.412(4)	2.461(6)	2.38(2)
Sn–O(15)	2.104(3)	2.145(5)	2.12(2)
Sn–O(15a)	2.103(4)	2.135(6)	2.11(1)
Sn–C(22)	2.095(8)	2.204(11)	2.07(2)
Sn–C(22a)	2.090(8)	2.196(17)	2.12(2)
O(14)–Sn–O(14a)	121.6(1)	127.4(2)	118.7(4)
O(15)–Sn–O(15a)	77.2(1)	74.1(2)	79.2(5)
O(14)–Sn–O(15)	80.9(1)	79.8(2)	82.0(4)
O(14a)–Sn–O(15a)	80.7(1)	79.3(2)	80.3(4)
O(14)–Sn–C(22)	82.3(2)	82.9(4)	87.0(6)
O(14)–Sn–C(22a)	85.2(2)	83.6(6)	83.9(6)
O(14a)–Sn–C(22)	84.4(3)	84.9(3)	80.5(7)
O(14a)–Sn–C(22a)	82.2(3)	82.3(5)	83.4(7)
O(15)–Sn–C(22)	102.5(3)	106.9(3)	100.1(7)
O(15)–Sn–C(22a)	98.6(3)	96.8(4)	101.8(6)
O(15a)–Sn–C(22)	96.6(2)	98.4(4)	98.5(6)
O(15a)–Sn–C(22a)	103.9(2)	105.6(6)	97.9(6)
O(14)–Sn–O(15a)	157.3(1)	153.1(2)	160.9(4)
O(14a)–Sn–O(15)	157.4(2)	152.1(2)	159.3(4)
C(22)–Sn–C(22a)	153.3(3)	150.0(5)	154.7(8)

^a This work.

^b *trans*-di(*t*-butyl)bis(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)tin(IV) [3].

^c *trans*-di(*n*-butyl)bis(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)tin(IV) [13].

^d The numbering of atoms is the same as used for our compound.

O(14)–Sn–O(15) and 80.7(1)° for O(14a)–Sn–O(15a), is nearly the same as in $[(Q')_2Sn(t-C_4H_9)_2]$ and $[(Q')_2Sn(n-C_4H_9)_2]$ [13] (Table 8).

The six-membered chelate rings show different conformations. The Sn, O(15), C(5), C(4), C(13), O(14) ring adopts the half-chair form. The puckering parameters calculated according to Cremer and Pople [14] are $Q = 0.282$ Å, $\theta = 55.6^\circ$, $\phi = 29.9^\circ$, compared with $\theta = 45.2^\circ$ and $\phi = 30^\circ$ for the ideal half-chair.

The other ring, O(14a), C(13a), C(4a), C(5a), O(15a), Sn, adopts the boat form. The O(14a) and C(5a) atoms are the bow and the stern, with displacements from the plane Sn, O(15a), C(13a), C(4a) of $-0.229(5)$ and $-0.093(5)$ Å, respectively. The puckering parameters are $Q = 0.194$ Å, $\theta = 108.2^\circ$, $\phi = 176.1^\circ$, compared with $\theta = 90^\circ$ and $\phi = 180^\circ$ for the inverted boat conformation. The rules concerning the bond angles [15] apply inside both pyrazole rings.

As for the regions expected to be planar, the four oxygens and the tin atom do not lie in a plane and the following out-of-plane displacements (Å) are observed: Sn, 0.0004(3); O(14), $-0.089(4)$; O(15), 0.073(4); O(14a), 0.060(5); O(15a), $-0.108(4)$. The two pyrazole rings are different: the ring N(1)–C(5) is non-planar

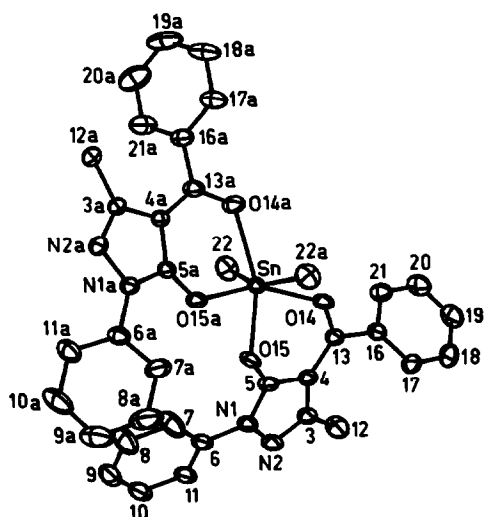


Fig. 3. ORTEP plot and numbering scheme of atoms. Thermal ellipsoids enclose 25% of the electron density. Hydrogen atoms are omitted for clarity.

(maximum displacement N(2) = 0.006(5) Å) whereas the other ring N(1a)–C(5a) is planar (maximum displacement N(2a) = –0.003(4) and C(3a) = 0.003(5) Å). The dihedral angles are 18.3(6)° between the pyrazole N(1)–C(5) and its adjacent chelate ring, and 7.7(9)° between the pyrazole N(1a)–C(5a) and its adjacent chelate ring.

The phenyl rings C(16)–C(21) and C(16a)–C(21a) are rotated by 40.0(2)° and 68.0(2)° with respect to the corresponding chelate rings, whereas the phenyl rings C(6)–C(11) and C(6a)–C(11a) are rotated by 14.2(9) and 36.0(4)° with respect to the corresponding pyrazole rings.

3. Experimental section

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 1106 instrument. Infrared spectra were recorded from 4000 to 600 cm⁻¹ with a Perkin Elmer 1600 Series FTIR. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (300 MHz for ¹H, 75 MHz for ¹³C and 111.9 MHz for ¹¹⁹Sn). Melting points were taken on an Electrothermal IA 8100 instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature. All the reagents were of analytical grade and used without further purification. Q_PH and Q_FH were synthesized by the procedure reported by Jensen [1], while Q_MH, prepared for the first time was obtained as follows.

3.1. 1,3-dimethyl-4-benzoyl-5-pyrazolone, Q_MH

1,3-Dimethyl-5-pyrazolone (synthesized by the procedure reported in the literature [16]) (6.0 g, 53.5 mmol) was placed in a flask equipped with a stirrer, separating funnel and a reflux condenser and dissolved in dioxane (60 ml) by warming. Calcium hydroxide (10.0 g, 135 mmol) and benzoyl chloride (11 ml, 13.3 g, 94.7 mol) were added, the latter dropwise during 10 min. The mixture was heated to reflux overnight and then poured into HCl 2 N (200 ml) to decompose the calcium complex. Two phases formed. The organic phase, separated from the aqueous phase, was evaporated and the oily mass obtained treated with water (100 ml), to give a red solid (4.0 g, 18.5 mmol). This was recrystallized from methanol-water, and dried to constant weight. Analysis for C₁₂H₁₂N₂O₂ found: C 67.17, H 5.73, N 12.41; calc.: C 66.65, H 5.59, N 12.95% M.p. = 137–139°C.

3.1.1. [(Q_P)₂Sn(CH₃)₂] (1)

To a methanol solution (50 ml) of Q_PH (0.65 g, 2 mmol) were added potassium hydroxide (0.11 g, 2 mmol) and dichlorodimethyltin(IV) (0.22 g, 1 mmol): a precipitate was formed. The mixture was set aside overnight and the precipitate of **1** was filtered off and washed with methanol (*ca.* 10 ml), and recrystallized from chloroform/methanol. Compounds **2**, **3** and **9** were obtained similarly.

3.1.2. [(Q_M)₂Sn(CH₃)₂] (4)

To a methanol solution (50 ml) of Q_MH (0.43 g, 2 mmol) were added potassium hydroxide (0.11 g, 2 mmol) and dichlorodimethyltin(IV) (0.22 g, 1 mmol). After water addition (10 ml) the clear solution yielded a precipitate of **4**, which was filtered off and washed with H₂O (10 ml). Compounds **5–8** were obtained similarly.

3.2. X-Ray data collection and structure determination.

A pale yellow single crystal with dimensions of 0.07 × 0.14 × 0.69 mm was selected for the X-ray analysis and mounted on the Enraf Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation of the Centro Grandi Strumenti, Università di Pavia.

TABLE 9. Crystal data: collection of data and Refinement of the structure

Formula	C ₃₆ H ₃₂ N ₄ O ₄ Sn
Formula weight	704.7
space group	P $\bar{1}$
colour	pale-yellow
a, Å	15.327(1)
b, Å	16.753(1)
c, Å	6.606(1)
α, deg	97.50(1)
β, deg	94.44(1)
γ, deg	80.33(1)
Vc, Å ³	1655.2(2)
Z	2
D calcd, gcm ⁻³	1.41
cryst. size, mm	0.07 × 0.14 × 0.69
μ(Cu Kα), cm ⁻¹	67.4
data colln instrument	Enraf-Nonius CAD4
radiation (monochromated)	Cu Kα (λ = 1.5418 Å)
T of data collection, K	293
scan mode	ω/2θ
data colln range	4 < 2θ < 70
stds (measd every 100 min)	4 6 2, 2 4 1, 4 5 2
no. of unique reflcns measd	6513 (± h, ± k, l)
no. of data with F ₀ ² ≥ 3σ(F ₀ ²)	5655
No. of param refined	406
R ^a and R _w ^b	0.050, 0.053

$$^a R = (\sum \|F_0 - k|F_c|\|) / \sum |F_0|$$

$$^b R_w = [\sum w(|F_0 - k|F_c|)^2 / \sum w|F_0|^2]^{1/2}$$

The SEARCH program was used to obtain 25 reflections, from which approximate cell dimensions were derived by the INDEX program. Accurate lattice parameters, given in Table 9, were obtained by least-squares refinement of these reflections. The triclinic cell quoted was confirmed by use of the TRACER program [17]. The $\omega/2\theta$ scan technique was used to collect the intensities of 6513 independent reflections within the angular range $4 \leq 2\theta \leq 70^\circ$. Three standard reflections were

TABLE 10. Final coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses)

Atom	x	y	z	B (Å ²)
<i>Non-hydrogen atoms</i>				
Sn	0.37290(2)	0.22515(2)	0.12127(5)	3.296(7)
N(1)	0.1240(2)	0.1527(3)	-0.0674(8)	4.3(1)
N(2)	0.0916(3)	0.0825(3)	-0.0340(9)	5.1(1)
C(3)	0.1442(3)	0.0509(3)	0.1129(9)	4.7(1)
C(4)	0.2133(3)	0.0970(3)	0.1794(8)	3.8(1)
C(5)	0.1969(2)	0.1618(2)	0.0580(7)	3.8(1)
C(6)	0.0891(3)	0.1915(4)	-0.2416(10)	4.5(1)
C(7)	0.1188(6)	0.2594(5)	-0.2899(12)	7.7(2)
C(8)	0.0879(6)	0.2926(5)	-0.4684(14)	8.3(2)
C(9)	0.0257(5)	0.2591(5)	-0.5991(12)	6.8(2)
C(10)	-0.0036(5)	0.1911(5)	-0.5502(12)	6.2(2)
C(11)	0.0273(4)	0.1579(4)	-0.3721(11)	5.4(2)
C(12)	0.1270(4)	-0.0295(4)	0.1706(13)	7.3(2)
C(13)	0.2903(3)	0.0814(2)	0.3062(7)	3.7(1)
O(14)	0.3531(2)	0.1221(2)	0.3119(7)	5.14(9)
O(15)	0.2366(2)	0.2245(2)	0.0522(6)	4.38(9)
C(16)	0.3056(3)	0.0158(3)	0.4441(8)	3.8(1)
C(17)	0.2430(4)	0.0062(3)	0.5763(10)	4.7(1)
C(18)	0.2629(5)	-0.0541(4)	0.7064(11)	6.0(2)
C(19)	0.3459(6)	-0.1029(4)	0.7074(11)	6.5(2)
C(20)	0.4087(5)	-0.0922(4)	0.5795(13)	6.0(2)
C(21)	0.3892(4)	-0.0337(4)	0.4456(11)	4.8(1)
C(22)	0.3745(6)	0.2932(5)	0.4107(12)	6.1(2)
N(1a)	0.3493(2)	0.4372(2)	-0.1986(6)	3.60(9)
N(2a)	0.4144(2)	0.4757(2)	-0.2664(7)	3.9(1)
C(3a)	0.4907(2)	0.4315(2)	-0.2165(7)	3.5(1)
C(4a)	0.4786(2)	0.3643(2)	-0.1149(7)	3.3(1)
C(5a)	0.3851(2)	0.3711(2)	-0.1078(7)	3.4(1)
C(6a)	0.2584(3)	0.4694(3)	-0.2344(9)	4.2(1)
C(7a)	0.1999(4)	0.4673(5)	-0.0893(13)	6.6(2)
C(8a)	0.1107(5)	0.5005(6)	-0.1261(18)	8.8(3)
C(9a)	0.0808(5)	0.5353(5)	-0.3006(18)	8.2(3)
C(10a)	0.1419(6)	0.5364(5)	-0.4418(15)	7.6(2)
C(11a)	0.2312(5)	0.5039(4)	-0.4111(12)	5.4(2)
C(12a)	0.5747(3)	0.4578(3)	-0.2671(9)	4.4(1)
C(13a)	0.5401(3)	0.3074(3)	-0.0174(9)	3.9(1)
O(14a)	0.5167(3)	0.2630(3)	0.1016(8)	6.1(1)
O(15a)	0.3360(2)	0.3249(2)	-0.0473(7)	4.45(9)
C(16a)	0.6359(3)	0.2965(3)	-0.0496(11)	4.2(1)
C(17a)	0.6964(4)	0.3077(5)	0.1169(13)	5.8(2)
C(18a)	0.7863(4)	0.2946(6)	0.0906(16)	7.8(3)
C(19a)	0.8185(5)	0.2680(6)	-0.1018(19)	8.7(3)
C(20a)	0.7593(6)	0.2550(7)	-0.2677(17)	9.0(3)
C(21a)	0.6690(5)	0.2712(5)	-0.2393(14)	6.5(2)
C(22a)	0.4226(6)	0.1297(5)	-0.0964(12)	6.0(2)

measured every 100 min and showed small random deviations within the limits of statistical fluctuation. The intensities were corrected for Lorentz and polarization factors and for absorption according to North *et al.* [18] (minimum and maximum absorption factors 0.6770 and 0.9998). A total of 5655 reflections with $I \geq 3\sigma(I)$ was regarded as observed.

The structure was solved by Patterson and Fourier methods. The position of the Sn atom was obtained from the three-dimensional Patterson map. A difference electron density synthesis based upon the Sn signs revealed the position of all the non-hydrogen atoms. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters reduced R to 0.050 and R_w to 0.053. The hydrogen atoms located in calculated positions and checked on a difference Fourier map were included in the calculations in fixed positions with the same isotropic thermal parameters of their bonded atoms. The largest shift/esd ratio in the last cycle was 0.24. The largest residual peaks on the final difference Fourier map were 0.488 and $-0.540 \text{ e}\text{\AA}^{-3}$, both close to the Sn atom. No extinction correction was applied.

All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package [19] and with local programs. The final atomic coordinates for non-hydrogen atoms are given in Table 10.

4. Supplementary material available

Tables of anisotropic thermal parameters for non-hydrogen atoms, final coordinates and equivalent isotropic thermal parameters involving hydrogen atoms, planarity of molecular regions, and a list of structure factors can be obtained from one of the authors (B. Bovio).

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