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# Tin(IV) and organotin(IV) complexes with heterocyclic β-diketonates I. Bis-[4(1-phenyl-3-methylpyrazol-5-one)]-dioxoalkane derivatives †

Claudio Pettinari, Fabio Marchetti, Augusto Cingolani, Dante Leonesi, Giancarlo Gioia Lobbia and Adriana Lorenzotti

*Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, I-62032 Camerino (Italy)*

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**Abstract**

Stable [(Q0Q)SnRX], [(Q2Q)SnRX], [(Q3Q)SnRX] and [(Q4Q)SnRX] compounds, (where $H_2Q0Q$ = 1,2-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one]-1,2-dioxoethane, $H_2Q2Q$ = 1,4-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one]-1,4-dioxobutane, $H_2Q3Q$ = 1,5-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one]-1,5-dioxopentane and $H_2Q4Q$ = 1,6-bis-[(1-phenyl-3-methyl-pyrazol-5-one]-1,6-dioxohexane; X = Cl or R; R = Cl, Me, Et, $^n$Bu, $^t$Bu, vinyl, benzyl, phenyl, or cyclohexyl) have been obtained and characterized by analysis, spectral (IR and electronic spectra, $^1$H, $^{13}$C and $^{119}$Sn NMR data) and conductivity measurements. Some of the $(Q2Q)^{2-}$ derivatives have been shown to be dimeric in solution, whereas the $(Q0Q)^{2-}$ derivatives are tetramers. Tin (IV) chloride pentahydrate also reacts in chloroform with $H_2Q2Q$ and $H_2Q0Q$ to yield $(H_2Q2Q)(SnCl_4)_2 \cdot 4H_2O$ and $(H_2Q0Q)(SnCl_4) \cdot H_2O$, respectively.

## 1. Introduction

1-Phenyl-3-methyl-4-acyl-pyrazol-5-ones are potentially bidentate ligands originally investigated by Jensen [1], as reagents for radiochemical separations, and later by many others [2]. They show keto–enol tautomerism (Fig. 1): the enolic hydrogen may be replaced by a metal ion and a considerable number of their metal derivatives have been isolated and characterized [3].

Previously the interaction between tin(IV) and organotin(IV) derivatives with 1-phenyl-3-methyl-4-acyl-pyrazol-5-ones coordinating in the anionic [5] and in the neutral form [6], were reported.

More recently a new kind of 4-acyl-5-pyrazolones derivative, bis[4-(1-phenyl-3-methyl-pyrazol-5-one)dioxoalkane, $H_2QNQ$ (Fig. 2) and their complexes with $Cu^{II}$ [7], $Fe^{III}$, $Ca^{II}$, and $U^{VI}$ [8] were obtained. These potentially tetradentate ligands have two β-diketone subunits linked by a polymethylene chain of variable length.

No attempt has been made so far to synthesize organometal chelates of these ligands, so that in view of our interest in β-diketonates and tin(IV) chemistry, it was decided to investigate their interaction with tin(IV) and organotin(IV) salts.

## 2. Results and discussion

Interaction of bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]dioxoalkane ($H_2QNQ$ in general; in detail $H_2Q0Q$: 1,2-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,2-dioxoethane, $H_2Q2Q$: 1,4-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,4-dioxobutane, $H_2Q3Q$: 1,5-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,5-dioxopentane, $H_2Q4Q$: 1,6-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,6-dioxohexane) with tin(IV) and organotin(IV) halides, $R_nSnX_{4-n}$ (R = methyl, ethyl, n-butyl, t-butyl, cyclohexyl, vinyl, benzyl, or phenyl; X = Cl or Br) in methanol and alkali, gives the compounds **1–26**, reported in Tables 1 and 2, with empirical composition $[(QNQ)R_nSnX_{2-n}]$, as colourless or pale-yellow or pale-rose solids. The air-stable products were characterised by their analytical data together with the melting points, yields, and selected infrared data (C=O and Sn–Cl stretching frequencies) (Tables 1 and 2).

Correspondence to: Dr. C. Pettinari.

† In memory of Prof. Flavio Bonati who died on August 22, 1991.

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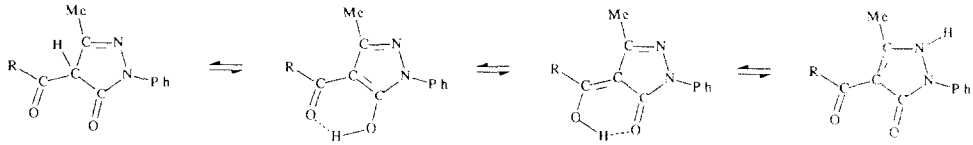
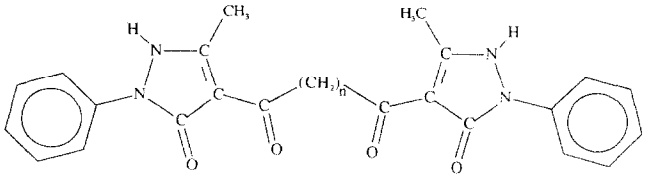


Fig. 1. Tautomeric structures possible for 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone; the last is found in the crystal [4].



$Q0QH_2$ : n = 0; $Q2QH_2$ : n = 2; $Q3QH_2$ : n = 3; $Q4QH_2$ : n = 4.

Fig. 2. Structure of bis-[4-(1-phenyl-3-methyl-5-pyrazolone)]-dioxo-alkanes.

As previously found for 4-acyl-5-pyrazolones [5,6], no derivative could be isolated under our conditions when trimethyl- or triphenyl-chlorotin(IV) was employed, consistent with the low acidity of these organotin(IV) species. There is no reaction of $H_2Q0Q$ in methanol and alkali with $SnCl_4$ or $Ph_2SnCl_2$: this donor, with the pyrazolone moieties directly linked without a polymethylene chain, shows a lower tendency to form chelates than the other tetradentate ligands. When the reactions of $H_2Q2Q$ and $H_2Q0Q$ with $SnCl_4$ was carried out in $CHCl_3$ in absence of base, adducts $(H_2Q2Q)(SnCl_4)_2 \cdot 4H_2O$ (**27**) and $(H_2Q0Q)SnCl_4 \cdot H_2O$ (**28**) were obtained. The polymethylene chain influences the coordination mode and the stoichiometry of the two products: $H_2Q0Q$ cannot form a 1:2 adduct like $H_2Q2Q$ and yields a 1:1 adduct, for which the poor solubility and the presence in the IR spec-

TABLE 1. Analytical and other data for $(Q2Q)^{2-}$ derivatives

| Compound [a] | Yield (%) | M.p. (°C) | Elemental analyses (Found (calc.) (%)) | | | IR ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | $\nu$(C=O) [b] | $\nu$(Sn–Cl) |
| [(Q2Q)Sn($CH_3$)$_2$] (**1**) | 39 | 289–291 | 54.03 (54.01) | 4.54 (4.54) | 9.48 (9.71) | 1596s | |
| [(Q2Q)Sn($C_2H_5$)$_2$] (**2**) | 64 | 297–299 | 54.80 (55.56) | 5.08 (5.00) | 9.05 (9.26) | 1598s | |
| [(Q2Q)Sn(n-$C_4H_9$)$_2$] (**3**) | 49 | 224–226 | 57.52 (58.11) | 5.73 (5.79) | 8.55 (8.47) | 1602s | |
| [(Q2Q)Sn(t-$C_4H_9$)$_2$] (**4**) | 46 | 234–236 | 57.49 (58.11) | 5.83 (5.79) | 8.17 (8.47) | 1600s | |
| [(Q2Q)Sn($C_6H_{11}$)$_2$] (**5**) | 63 | 270–271 | 60.62 (60.61) | 5.95 (5.93) | 7.61 (7.85) | 1604s | |
| [(Q2Q)Sn($C_6H_5$)$_2$] (**6**) | 53 | 288–291 | 61.25 (61.65) | 4.44 (4.31) | 7.88 (7.66) | 1605s | |
| [(Q2Q)Sn($CH_2C_6H_5$)$_2$] (**7**) | 67 | 229–230 | 62.48 (62.57) | 4.53 (4.70) | 7.33 (7.68) | 1600s | |
| [(Q2Q)Sn($C_2H_3$)$_2$] (**8**) | 91 | 282–284 | 55.83 (55.94) | 4.40 (4.36) | 9.20 (9.32) | 1600s | |
| [(Q2Q)Sn$CH_3$Cl] (**9**) | 92 | 276–282 | 49.94 (50.24) | 3.90 (3.88) | 9.12 (9.37) | 1600s | 320m |
| [(Q2Q)Sn(n-$C_4H_9$)Cl] (**10**) | 71 | 225–230 | 52.39 (52.57) | 4.57 (4.57) | 8.42 (8.76) | 1600s | 320m 305w |
| [(Q2Q)Sn$C_6H_5$Cl] (**11**) | 92 | 263–268 (dec.) | 54.80 (54.62) | 3.87 (3.82) | 8.25 (8.49) | 1600s | 325m |
| [(Q2Q)Sn$Cl_2$] (**12**) | 96 | 285–287 | 46.86 (46.64) | 3.38 (3.26) | 8.96 (9.07) | 1593s | 365m 350s,br |

[a] $H_2Q2Q$ is 1,4-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,4-dioxobutane. [b] $\nu$(C=O) of $H_2Q2Q$: 1625 $cm^{-1}$.

TABLE 2. Analytical and other data for $(Q0Q)^{2-}$, $(Q3Q)^{2-}$ and $(Q4Q)^{2-}$ derivatives and for compounds **27** and **28**

| Compound [a] | Yield (%) | M.p. (°C) | Elemental analyses (Found (calc.) (%)) | | | IR ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | $\nu$(C=O) | $\nu$(Sn–Cl) |
| $[(Q0Q)Sn(CH_3)_2]$ (**13**) | 95 | 301–303 | 52.88 (52.49) | 4.16 (4.04) | 9.98 (10.20) | 1600s [b] | |
| $[(Q0Q)Sn(C_2H_5)_2]$ (**14**) | 90 | 262–265 | 54.00 (54.10) | 4.53 (4.54) | 9.85 (9.71) | 1600s | |
| $[(Q0Q)Sn(n\text{-}C_4H_9)_2]$ (**15**) | 81 | 272–274 | 57.12 (56.90) | 5.43 (5.41) | 8.51 (8.85) | 1600s | |
| $[(Q0Q)SnCH_3Cl]$ (**16**) | 88 | 301–303 | 47.68 (48.50) | 3.30 (3.36) | 9.72 (9.84) | 1600s | 320m |
| $[(Q3Q)Sn(CH_3)_2]$ (**17**) | 88 | 291–292 | 54.39 (54.85) | 4.83 (4.77) | 9.25 (9.48) | 1600s [c] | |
| $[(Q3Q)Sn(C_2H_5)_2]$ (**18**) | 91 | 280–282 | 55.90 (56.25) | 5.34 (5.21) | 9.07 (9.05) | 1600s | |
| $[(Q3Q)Sn(C_6H_5)_2]$ (**19**) | 70 | 274–277 | 61.48 (62.12) | 4.52 (4.31) | 7.64 (7.83) | 1605s | |
| $[(Q3Q)Sn(CH_2C_6H_5)_2]$ (**20**) | 80 | 132–145 (dec.) | 63.44 (63.01) | 4.81 (4.88) | 7.66 (7.54) | 1604s | |
| $[(Q3Q)Sn(C_2H_3)_2]$ (**21**) | 83 | 260–264 (dec.) | 56.70 (56.61) | 4.63 (4.59) | 9.01 (9.11) | 1600s | |
| $[(Q3Q)SnCH_3Cl]$ (**22**) | 89 | 303–306 (dec.) | 50.93 (51.06) | 4.11 (4.12) | 9.00 (9.16) | 1605s | 308s |
| $[(Q3Q)SnCl_2]$ (**23**) | 83 | 314–316 | 47.08 (47.51) | 3.65 (3.51) | 8.31 (8.86) | 1600s | 365s 340s,br |
| $[(Q4Q)Sn(CH_3)_2]$ (**24**) | 90 | 243 (dec.) | 55.33 (55.56) | 4.93 (5.00) | 9.03 (9.26) | 1601s [d] | |
| $[(Q4Q)SnCH_3Cl]$ (**25**) | 96 | 232–240 (dec.) | 51.70 (51.83) | 4.38 (4.35) | 8.80 (8.95) | 1605s | 320s |
| $[(Q4Q)SnCl_2]$ (**26**) | 97 | 230–231 | 48.88 (48.33) | 3.87 (3.74) | 8.23 (8.67) | 1605s | 345vs |
| $[(H_2Q2Q)(SnCl_4)_2 \cdot 4H_2O]$ (**27**) | 38 | 316–317 | 28.13 (28.16) | 2.75 (2.95) | 5.34 (5.47) | 1620s | 340s,br |
| $[(H_2Q0Q)(SnCl_4) \cdot H_2O]$ (**28**) | 76 | 338–340 | 39.19 (38.81) | 3.02 (2.96) | 7.77 (8.23) | 1610s | 345s,br |

[a] $H_2Q0Q$ is 1,2-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,2-dioxoethane; $H_2Q3Q$ is 1,5-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,5-dioxopentane; $H_2Q4Q$ is 1,6-bis-[4-(1-phenyl-3-methyl-pyrazol-5-one)]-1,6-dioxohexane. [b] $\nu$(C=O) of $H_2Q0Q$: 1602 $cm^{-1}$. [c] $\nu$(C=O) of $H_2Q3Q$: 1598 $cm^{-1}$. [d] $\nu$(C=O) of $H_2Q4Q$: 1632 $cm^{-1}$.

trum of a broad absorption in the 2700–2200 $cm^{-1}$ region, assignable to intramolecular hydrogen-bonded OH stretching, suggests the formation of a coordination polymer with the pyrazolone coordinating to tin(IV) in a bridging bidentate manner, as proposed in Fig. 3.

TABLE 3. Molecular weight and conductivities of compounds **6**, **8**, **9** and **12–14**

| Conductivities [a] | | | | Molecular weight [b] | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Solvent | $\Lambda$ | $c$ | FW | MW | $r$ | Solvent | $c$ |
| **6** | Acetone | 2.4 | 0.5 | 701.35 | 1371 | 1.95 | $CHCl_3$ | 1.5 |
| **8** | $CH_2Cl_2$ | 1.3 | 0.5 | 601.23 | 1169 | 1.94 | $CHCl_3$ | 1.3 |
| | Acetone | 4.4 | 0.5 | | | | | |
| **9** | $CH_2Cl_2$ | 1.1 | 0.6 | 597.63 | 1217 | 2.04 | $CHCl_3$ | 1.2 |
| | Acetone | 6.6 | 0.4 | | | | | |
| | DMSO | 8.9 | 0.5 | | | | | |
| **12** | Acetone | 6.3 | 0.5 | 618.05 | 1320 | 2.14 | $CHCl_3$ | 1.3 |
| **13** | $CH_2Cl_2$ | 2.5 | 0.2 | 549.16 | 2204 | 4.01 | $CHCl_3$ | 0.9 |
| **14** | $CH_2Cl_2$ | 2.9 | 0.3 | 577.21 | 2399 | 4.15 | $CHCl_3$ | 1.2 |

[a] In $ohm^{-1}$ $cm^2$ $mol^{-1}$ at room temperature; $c$ is molar concentration ($\times 10^3$). [b] FW means formula weight, MW the experimental formula weight, $r$ = MW/FW, and $c$, in this case, is the concentration (% w/w).

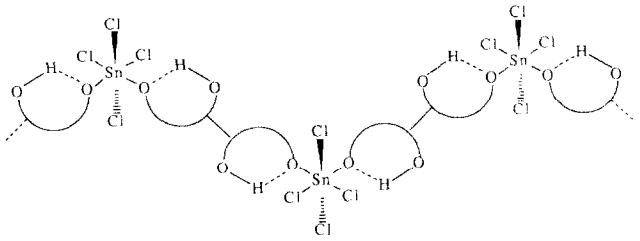


Fig. 3. Structure proposed for 1:1 adduct of $H_2Q0Q$.

The infrared spectra of complexes **1–26** show all the expected ligand and acceptor bands. Upon chelation $\nu$(C=O) shifts from 1625, to *ca.* 1600 $cm^{-1}$ and the broad O–H---O absorption band in the region 2700–2500 $cm^{-1}$ disappears, suggesting that the coordination of the tin atom takes place through all the oxygen atoms of the carbonyl groups. The $\nu$(Sn–Cl) stretching frequencies, observed for the compounds **9–12**, **16**, **22–26**, confirm that in the case of $SnCl_4$ and $RSnCl_3$ only two chloride groups were replaced.

All the $(Q2Q)^{2-}$ derivatives (with exception of **1** and **2**, totally insoluble in the common organic solvents) are soluble in chloroform, dichloromethane and acetone, in which **6**, **8**, **9** and **12** are non-electrolytes, as reported in Table 3, thus ruling out ionic structures in this solvent. Molecular weight determinations, also reported in Table 3, carried out in chloroform show that **6**, **8**, **9**, **12** are dimeric in solution and a structure like that in Fig. 4 is possible.

In the case of compounds **1** and **2**, their insolubility is probably due to the formation of polymers.

All the $(Q0Q)^{2-}$ complexes are soluble in acetone, chloroform, and dichloromethane (in the last solvent **13** and **14** are non-electrolytes) whereas $(Q3Q)^{2-}$ and $(Q4Q)^{2-}$ derivatives are less soluble. The molecular weight determinations on **13** and **14** indicate that these derivatives are tetramers in solution, constant with the structure proposed in Fig. 5. It has been previously noted [7] that the $(Q0Q)^{2-}$ is not able to form cyclic

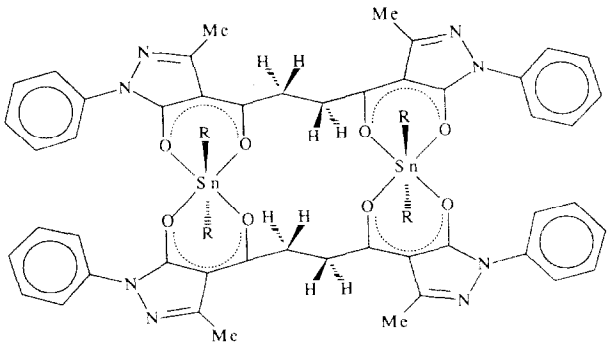
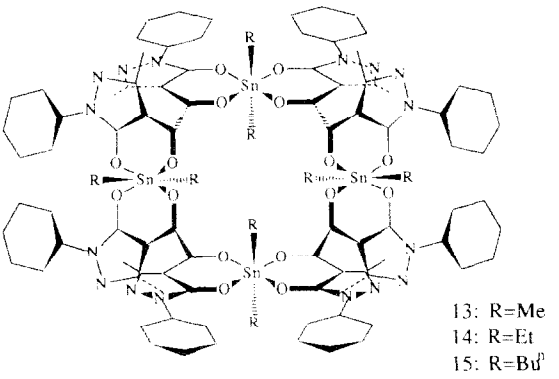


Fig. 4. Octahedral hexacoordinated structure proposed for the compounds **3–12**.



13: R=Me
14: R=Et
15: R=Bu$^n$

Fig. 5. Tetrameric structure proposed for $[(Q0Q)SnR_2]_4$.

dimeric or trimeric chelates because of the limitations imposed by its structure. It was not possible to perform molecular weight determinations for $(Q3Q)^{2-}$ and $(Q4Q)^{2-}$ derivatives due to their poor solubility: a polymeric structure is also suggested.

The electronic spectra in chloroform are unchanged after a few days, reflecting the stability of the samples. The absorption spectra of the complexes are similar to those of the free donors. All the compounds exhibit two absorption bands, characteristic of $\pi-\pi^*$ transitions assigned to conjugated ring systems [7,9]. Upon chelation, the absorptions maxima at 242 and 272 nm observed for $H_2Q2Q$ shift to 246 and 294 nm in $[(Q2Q)SnPh_2]$ (**6**) and to 242 and 296 in $[(Q2Q)SnCl_2]$ (**12**), whereas the $\lambda_2$ for $H_2Q0Q$ (348 nm) shifts to lower wavelengths (for example 304 nm in $[(Q0Q)]$-$SnMe_2$].

$^1H$, (Tables 4 and 5) $^{13}C$ (Tables 6 and 7), as well as $^{119}Sn$ NMR data (Table 8) support the formulae proposed. For $(Q2Q)^{2-}$ derivatives the pattern of chemical shifts on going from the free neutral donor to the dianionic ligand in the same solvent is the same as that already observed with various 4-acyl-5-pyrazolonate derivatives [10]: in chloroform the chemical shifts of the aromatic protons of the ligand is moved downfield, while the chemical shifts of the methyl protons are displaced to a higher field. In the NMR spectrum of the unbound donor, one signal is observed for the methylene protons, whereas the $\beta$-diketonate complexes show two (compounds **3–8**, **12**) and six multiplets (**9**, **10**, **11**). This can be explained by non-equivalence of the methylene protons in these rigid dimeric compounds, free rotation around the C–C methylene chain bonds is not possible, and carbonyl nearer the chain deshields one of the two geminal protons, give rise to an AA'XX' system.

The $^{13}C$ NMR chemical shifts of the carbon of the methylene bridge and of the methyl of the $(Q2Q)^{2-}$ derivatives move upfield and downfield, respectively, upon complexation; no significant shift is observed for

the C(3), C(4) and aromatic carbon, whereas the carbon atoms of chain carbonyl are shielded to the extent of 4–5 ppm, and those of ring carbonyl are deshielded to about 3–4 ppm [11]. This further supports the chelation of the ligand through both the carbonyl groups.

If the tin atom in these complexes is hexacoordinate, in an approximately octahedral, or a skewed trapezoidal bipyramidal environment, three isomers are possible in the case of $[\{(Q2Q)SnR_2\}_2]$ (Fig. 6), but in the $^1H$ NMR spectra of compounds **1–8** only one singlet for the methyl of the ligand and two multiplets for the methylene chain protons were detected, indicating fluxionality or the absence of isomers. For the compounds $[\{(Q2Q)SnRX\}_2]$ (**9–11**) for which eight isomers are possible, four singlets and six multiplets were always assignable to the ligand methyl and to methylene chain protons in the $^1H$ NMR spectra and two or four signals in the $^{119}Sn$ NMR spectra consistent with the absence of fluxionality.

The NMR data of the $(Q0Q)^{2-}$ derivatives allow some other conclusions to be reached: in the $^1H$ and

TABLE 4. $^1H$ NMR data [a] for derivatives of $(Q2Q)^{2-}$ (in $CDCl_3$)

| Compound | 3-Me | Chain [b] | R-Sn |
|---|---|---|---|
| $H_2Q2Q$ | 2.58s | 3.24s | |
| **3** | 2.07s | 2.35m (16.0) | 0.86t; 1.10m |
| | | 3.53m | 1.30–1.40m |
| | | | 1.50–1.62m |
| **4** | 2.04s | 2.29m (15.5) | 1.27s [c] |
| | | 3.59m | |
| **5** | 2.05s | 2.32m (15.3) | 1.25d |
| | | 3.55m | 1.45–1.75m |
| | | | 1.98t |
| **6** | 2.06s | 2.30m (14.6) | 7.30–7.35m |
| | | 3.60m | 7.60m |
| **7** | 1.80s | 1.76m (14.2) | 2.44s |
| | | 2.92m | 6.8–7.0m |
| **8** | 2.04s | 2.38m (14.5) | 5.78dd [d] |
| | | 3.54m | 6.07dd |
| | | | 6.43dd |
| **9** | 1.83s | 2.44m; 2.58m (13.7) | 0.96s [e] |
| | 2.00s | 2.63m; 3.34m (13.6) | 1.00s [f] |
| | 2.10s | 3.58m; 3.78m (17.1) | |
| | 2.12s | | |
| **10** | 1.84s | 2.48m; 2.58m (14.1) | 0.90m |
| | 1.98s | 2.64m; 3.32m (13.5) | 1.35–1.50m |
| | 2.09s | 3.58m; 3.78m (16.2) | 1.55–1.70m |
| | 2.10s | | |
| **11** | 1.90s | 2.42m; 2.62m (14.7) | 7.5–7.7m |
| | 1.98s | 2.75m; 3.42m (15.5) | |
| | 2.08s | 3.61m; 3.78m (17.9) | |
| | 2.10s | | |
| **12** | 2.00s | 2.70m (14.7) | |
| | | 3.60m | |

[a] $\delta$ in ppm internal TMS. [b] Main $J_{gem}$ in parentheses (in Hz). [c] $^3J$(Sn–H) 114.1 Hz. [d] $J_{gem}$ 2.4 Hz; $J_{cis}$ 12.9; $J_{trans}$ 20.1 Hz. [e] $^2J$(Sn–H) 120.0 Hz. [f] $^2J$(Sn–H) 121.8 Hz.

TABLE 5. $^1H$ NMR data [a] for $(Q0Q)^{2-}$, $(Q3Q)^{2-}$, $(Q4Q)^{2-}$ derivatives (in $CDCl_3$)

| Compound | 3-Me | Chain | R-Sn |
|---|---|---|---|
| $H_2Q0Q$ | 2.55s | | |
| **13** | 2.22s | | 0.85s [b] |
| | | | 1.28s |
| **14** | 2.25s | | 1.22t; 1.58q |
| | | | 1.36t; 1.90q |
| **15** | 2.22s | | 0.72t; 0.88t |
| | | | 1.22–1.30m |
| | | | 1.42 [c] |
| | | | 1.75–1.95m |
| **16** | 1.50–1.70m | | 0.90–1.30m |
| | 2.00–2.25m | | |
| $H_2Q3Q$ | 2.48s | 2.23 [d] | |
| | | 2.92t | |
| **18** | 2.40–2.60m | 2.10–2.30m | 1.23m |
| | | 2.82–2.96n | 1.50–1.62m |
| **20** | 2.15br | 1.60br | 2.25br |
| | | 2.30–2.70br | 6.80–7.10br |
| **21** | 2.20br | 1.70–2.00br | 5.95dd,br |
| | | 2.30–2.70br | 6.20dd,br |
| | | | 6.60dd,br |
| **22** | 2.50–2.70m | 2.10–2.40m | 1.05–1.35m |
| | | 2.90–3.05m | |
| **23** | 2.30–2.65m | 2.10–2.20m | |
| | | 2.80–3.05m | |
| $H_2Q4Q$ | 2.50s | 1.88–1.94m | |
| | | 2.85t,br | |
| **25** | 2.10–2.60m | 1.60–1.80m | 0.90–1.30m |
| | | 2.70–3.00m | |
| **26** | 2.25–2.60m | 1.50–1.70m | |
| | | 2.80–3.00m | |

[a] $\delta$ in ppm from internal TMS. [b] $^2J$(Sn–H) 101.5 Hz. [c] Pseudoquintet. [d] Quintet.

$^{13}C$ spectra of **13**, two signals are observed for the methyl groups bonded to tin but only one resonance for the methyl of the ligand. This non-equivalence was also found in the spectra of **14** and **15**, probably due to lack of fluxionality around the coordination site (Fig. 5). Other differences are observed: the chemical shift of aromatic *meta* protons, unlike what was previously observed for $(Q2Q)^{2-}$ derivatives, is displaced upfield and the methyl carbon atoms of the pyrazolone are deshielded by about 2–3 ppm. Probably steric hindrance and electronic effects of close groups is the reason.

$^1H$ NMR data for soluble $(Q3Q)^{2-}$ and $(Q4Q)^{2-}$ derivatives in Table 5 show the pattern of chemical shifts observed for the $(Q2Q)^{2-}$ complexes, but a complete assignment of the methyl and methylene signals was not possible owing to overlapping broad lines.

It has been noted [12] that the tin–proton spin–spin coupling constants in dimethyltin(IV) derivatives are very sensitive to the structure and to the nature of the

ligands. The coupling constants are related [13] via the Fermi contact term to the s-electron density in the bond. The magnitude of $^2J(^1H-^{119}Sn)$ has been related to the C–Sn–C interbond angles in dimethyltin(IV) compounds for which recently Lockhart and Manders [13] observed a quadratic relationship.

$$\theta(C\text{–}Sn\text{–}C) = 0.0161[^2J(Sn\text{–}H)]^2 - 1.32[^2J(Sn\text{–}H)] + 133.4$$

The value of $\theta$ of compound **13**, calculated from this equation, is 164.3°, very similar to those found in other *trans*-dimethyltin-$\beta$-diketonates [5,14,15] and suggests a *trans* configuration for the four tin atoms in the proposed structure.

The $^{119}Sn$ chemical shifts are affected by the electronegativity of the groups attached to tin and by distortions which modify bond angles on tin: in fact, in the $[(Q2Q)R_nSnCl_{2-n}]$ ($n = 0$, 1 or 2) compounds the $^{119}Sn$ chemical shift is a function of $n$ (Fig. 7) for R = methyl, butyl, or phenyl.

Howard *et al.* [14] observed that the $^{119}Sn$ chemical shift moves upfield with increasing ligand bite: the

TABLE 6. $^{13}C$ NMR for $(Q2Q)^{2-}$ derivatives (in $CDCl_3$)

| Compound | $CH_3$ | $CH_2$ | CO, C(5) | C(3), C(4) | R-Sn |
|---|---|---|---|---|---|
| $H_2Q2Q$ | 15.8 | 32.9 | 196.0 | 147.5 | – |
| | | | 159.5 | 103.5 | |
| **3** | 17.3 | 31.5 | 191.2 | 148.5 | 13.8; 25.6 |
| | | | 163.2 | 103.1 | 26.7; 27.9 |
| **4** | 17.3 | 30.9 | 191.6 | 148.3 | 31.2; 43.8 |
| | | | 163.3 | 103.3 | |
| **5** | 17.3 | 31.0 | 192.0 | 148.4 | 27.0; 29.1 |
| | | 31.1 | 163.3 | 103.2 | 29.2; 42.3 |
| **6** | 17.4 | 31.8 | 192.8 | 148.1 | 128.3; 134.8 |
| | | | 163.2 | 103.6 | 148.7 |
| **7** | 17.0 | 31.1 | 192.3 | 148.3 | 33.6; 123.4 |
| | | | 162.9 | 103.3 | 127.7; 127.9 |
| | | | | | 140.9 |
| **8** | 17.3 | 31.8 | 192.4 | 148.7 | 132.9; 145.6 |
| | | | 163.1 | 103.4 | |
| **9** | 16.9 | 31.6 | 192.4 | 148.7 | 10.3; 10.5 |
| | 17.2 | 31.7 | 192.5 | 148.9 | |
| | 17.3 | 31.9 | 192.7 | 149.0 | |
| | | 32.0 | 192.8 | 149.2 | |
| | | | 162.2 | 103.7 | |
| | | | 162.4 | 103.9 | |
| | | | 162.5 | 104.2 | |
| | | | 162.6 | 104.7 | |
| **10** | 16.9 | 31.9 | 192.3 | 148.7 | 13.7; 25.8 |
| | 17.3 | 32.1 | 192.6 | 148.9 | 27.4; 30.5 |
| | 17.4 | | 192.7 | 149.0 | 30.6 |
| | | | 192.9 | 149.2 | |
| | | | 162.4 | 104.1 | |
| | | | 162.5 | 104.2 | |
| | | | | 104.3 | |
| **11** | 16.9 | 31.7 | 193.2 | 148.9 | 129.7; 129.9 |
| | 17.2 | 31.9 | 193.1 | 149.0 | 133.8; 133.9 |
| | 17.4 | 32.1 | 192.8 | 149.1 | 145.8; 146.0 |
| | | 32.2 | 162.6 | 104.0 | |
| | | | 162.7 | 104.3 | |
| | | | 162.8 | 105.0 | |
| **12** | 16.9 | 31.9 | 193.3 | 149.4 | |
| | 17.0 | 32.0 | 161.7 | 104.3 | |
| | | 32.2 | | | |

TABLE 7. $^{13}C$ NMR for $(Q0Q)^{2-}$ and $(Q4Q)^{2-}$ derivatives (in $CDCl_3$)

| Compound | $CH_3$ | Chain | CO, C(5) | C(3), C(4) | R-Sn |
|---|---|---|---|---|---|
| $H_2Q0Q$ | 17.1 | – | 184.4 | 154.3 | – |
| | | | 158.2 | 105.0 | |
| **13** | 14.8 | – | 184.1 | 149.0 | 7.3; 11.4 |
| | | | 163.0 | 102.0 | |
| **14** | 14.8 | – | 185.2 | 148.8 | 9.2; 9.7 |
| | | | 163.2 | 102.3 | 21.6; 23.8 |
| **15** | 14.8 | – | 185.2 | 148.7 | 13.4; 13.6 |
| | | | 163.0 | 102.4 | 25.3; 26.1 |
| | | | | | 26.6; 27.1 |
| | | | | | 27.8; 31.0 |
| **16** | 14.5 | – | n.o. | n.o. | 11.6; 12.5 |
| | 16.1 | | | | |
| $H_2Q4Q$ | 15.8 | 23.9; 38.9 | 197.0 | 147.3 | – |
| | | | 160.8 | 103.7 | |
| **25** | 17.2 | 38.2; 38.3 | n.o. | n.o. | n.o. |
| | 17.4 | 38.6; 38.9 | | | |
| **26** | 17.0 | 23.8; 24.0 | 196.6 | 149.5 | – |
| | 17.1 | 24.7; 25.1 | 196.2 | 149.3 | |
| | 17.3 | 25.2; 25.3 | n.o. | 105.2 | |
| | 17.4 | 25.4; 37.8 | | 105.7 | |
| | | 38.2; 38.8 | | | |

TABLE 8. $^{119}Sn$ NMR data (in $CDCl_3$)

| Compound | $-\delta$ (ppm) | Compound | $-\delta$ (ppm) |
|---|---|---|---|
| **3** | 341.22 | **13** | 309.08 |
| **4** | 439.68 | **14** | 345.91 |
| **5** | 409.94 | **15** | 337.91 |
| **6** | 487.57 | **16** | 487.43 |
| | | | 481.67 |
| **7** | 432.83 | | 483.71 |
| **8** | 480.93 | | 484.91 |
| | | | 485.91 |
| **9** | 488.38 | | 486.66 |
| | 488.00 | | |
| | | **26** | 625.13 |
| **10** | 504.99 | | 626.84 |
| | 505.14 | | 628.01 |
| | | | 630.79 |
| **11** | 560.14 | | |
| | 562.48 | | |
| | 573.40 | | |
| | 574.10 | | |
| **12** | 625.99 | | |
| | 626.64 | | |
| | 628.66 | | |
| | 659.43 | | |

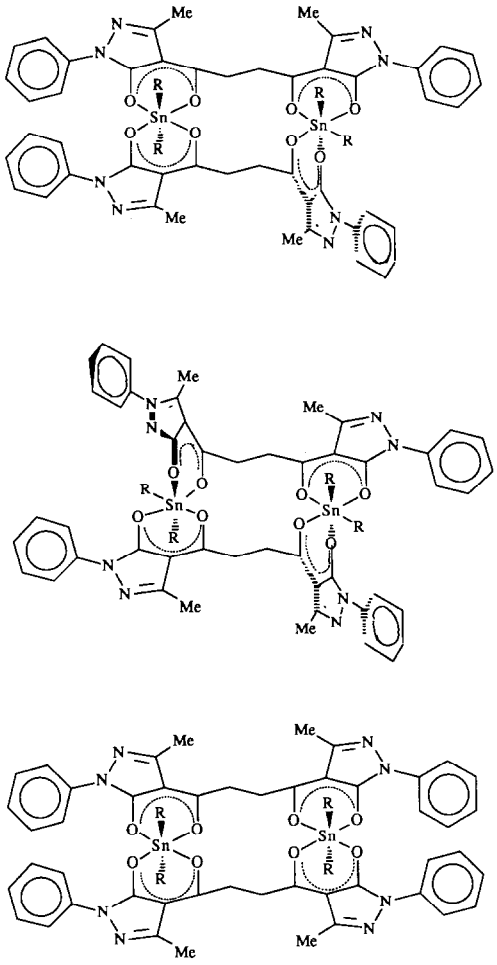


Fig. 6. The three possible isomers for $[(Q2Q)SnR_2]_2$.

$^{119}Sn$ chemical shifts recorded for our compounds are about 45–55 ppm less shielded than in analogous 2,4-pentanedionate ($acac^-$) and 1-phenyl-1,3-butanedionate ($bzac^-$) derivatives [14,15]. For example: $\delta(^{119}Sn)$ of $[(Q0Q)SnMe_2]$: −309.1 $(bzac)_2SnMe_2$: −353.5; $(acac)_2SnMe_2$: −365 ppm). The comparable values for [(QNQ)RXSn], indicate a smaller bite of those observed till now in hexacoordinate tin(IV)-β-diketonate complexes, with a lower donor strength than the $(QNQ)^{2-}$, and in accordance with those previously recorded for other organotin(IV)-4-acyl-5-pyrazolonate derivatives [5].

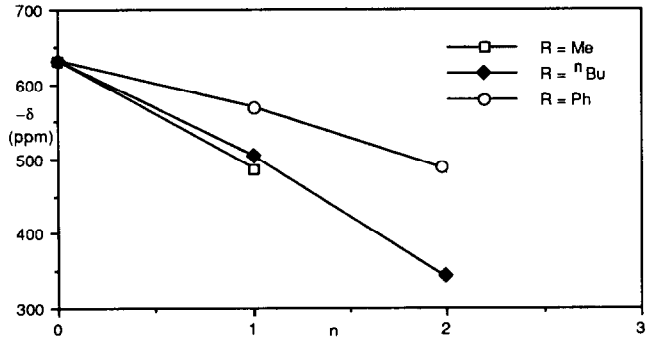



Fig. 7. Effect of the substitution on the $^{119}Sn$ chemical shift of $[(Q2Q)SnR_nX_{2-n}]$ complexes.

## 3. Experimental details

The samples were dried *in vacuo* to constant weight (20°C, *ca.* 0.1 torr). Elemental analyses were carried out in the house with a Carlo Erba Strumentazione 1106 instrument. The molecular weight determinations were performed at Pascher Mikroanalytisches Laboratorium, Remagen, Germany. Infrared spectra from 4000 to 600 and from 4000 to 250 $cm^{-1}$ were recorded with a Perkin–Elmer 1600 Series FTIR and with a Perkin–Elmer 457 instrument, respectively. $^1H$, $^{13}C$ and $^{119}Sn$ NMR spectra were recorded on an XR-300 Varian spectrometer operating at room temperature (300 for $^1H$, 75 for $^{13}C$ and 111.9 MHz for $^{119}Sn$). Electronic spectra in $CHCl_3$ were recorded on an HP 8452A diode array spectrophotometer. Melting points were taken on a IA 8100 Electrothermal instrument. The electrical conductances 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. The donors were synthesized by the procedure reported by Jensen [1] and purified by several recrystallizations from methanol.

### *3.1. [(Q2Q)Sn(CH$_3$)$_2$] (1)*

To a methanol solution (50 ml) of $H_2Q2Q$ (1 mmol) were added potassium hydroxide (2 mmol) and dichlorodimethyltin(IV) (1 mmol). A precipitate was formed. The mixture was set aside overnight and the precipitate then filtered off, washed with methanol (*ca.* 10 ml), and recrystallized from chloroform/methanol. Compounds **2**, **4–9**, **11–18**, **20–25** were obtained similarly. Compounds **3**, **19**, **26** were recrystallized from chloroform/diethyl ether.

### *3.2. [(Q2Q)Sn($^n$Bu)Cl] (10)*

To a methanol solution (50 ml) of $H_2Q2Q$ (1 mmol) were added potassium hydroxide and n-butyltrichlorotin(IV) (1 mmol). After 2 d the solution was evaporated to dryness, the residue was washed twice with diethyl ether (2 × 30 ml) and with methanol (2 × 20 ml), leaving the product.

### *3.3. H$_2$(Q2Q)(SnCl$_4$)$_2$·4H$_2$O (27)*

To a stirred chloroform solution (50 ml) of $H_2Q2Q$ (1 mmol) was added tetrachlorotin(IV) pentahydrate (2

mmol). After 1 d a precipitate was formed, which was filtered off, washed with chloroform (*ca.* 10 ml). $^1$H NMR ($CD_3CN$): $\delta$ 7.55–7.70 (m, 10H, Ph); 5.80 (br, 8H, $H_2O$); 3.58 (s, 4H, $CH_2$); 2.90 (s, 6H, $CH_3$); $^{13}$C NMR ($CD_3CN$) $\delta$ 201.0 (s, C=O chain); 162.0 (s, C(5)); 152.9 (s, C(3)); 132.6, 131.3, 130.9, 125.2 (s, Ph); 105.6 (s, C(4)); 35.3 (s, $CH_2$); 15.8 (s, $CH_3$). $^{119}$Sn NMR: $\delta = -629$ ($\delta$ in ppm).

Adduct **28** was prepared similarly.

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