DALTON
FULL PAPER

The interaction of organotin(IV) acceptors with 1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)butane-1,4-dione †

Claudio Pettinari,*[a] Fabio Marchetti,[a] Riccardo Pettinari,[a] Augusto Cingolani,[a] Andrei Drozdov *[b] and Sergei Troyanov [b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, 62032 Camerino, Italy. E-mail: claudio.pettinari@unicam.it*
[b] *Moscow State University, Chemistry Department, Vorobjevy Gory, 119899 Moscow, Russia. E-mail: drozdov@inorg.chem.msu.ru*

Received 24th July 2001, Accepted 23rd October 2001
First published as an Advance Article on the web 13th December 2001

From the interaction of organotin(IV) halides SnR_2Cl_2 with 1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dione ($Q2QH_2$) in methanol in the presence of base the complexes $[SnR_2(Q2Q)]$ (**1**: R = isobutyl (Bu^i); **2**: R = n-octyl (Ot); **3**: R = n-dodecyl (Do)) have been synthesised. The reaction between equimolar quantities of R_2SnO and $Q2QH_2$ in toluene yields the dinuclear derivatives $[SnR_2(Q2Q)]_2$ **4** (R = Me) and **5** (R = Bu^n) which have a *cis*-R_2Sn configuration in solution whereas from the reaction of $Q2QH_2$ with $SnMe_2Cl_2$ in CH_3OH in the presence of KOH, an insoluble probably polynuclear isomeric form of **4** formed. The reaction between $Q2QH_2$ and $(R_3Sn)_2O$ produces the derivative $[(SnR_3)_2(Q2Q)]$ (**6**: R = Bu^n; **7**: R = Ph). **6** reacts with water yielding the aquo complex $[(SnBu^n_3)_2(Q2Q)(H_2O)]$ **8**. The X-ray crystal structures of $[SnBu^n_2(Q2Q)]_2$ **5**, $[(SnBu^n_3)_2(Q2Q)]$ **6** and $[(SnPh_3)_2(Q2Q)]$ **7** have been determined. Compound **5** is a binuclear species with the tin atoms in a distorted octahedral Sn-*cis*-C_2O_4 environment (skewed trapezoidal bipyramidal) with the C–Sn–C angles ranging from 107.28(14) to 112.4(2)°. The two different carbonyl groups coordinate the metal with different donor abilities (the Sn–O bond lengths range from 2.132(2) to 2.209(2) Å). Compounds **6** and **7** contain a dianionic ligand $(Q2Q)^{2-}$ bridged to two triorganotin(IV) fragments with the tin atoms in a strongly distorted trigonal bipyramidal environment. ^1H, ^{13}C and ^{119}Sn NMR (rt and −55 °C) data indicate that the diorganotin(IV) derivatives **1**–**5** are not fluxional in solution whereas **6**–**8** slowly undergo disproportionation reaction, affording SnR_4 and $[SnR_2(Q2Q)]_2$.

Introduction

β-Diketonate donors represent one of the most important classes of chelating ligands in the field of coordination chemistry, because of their technological applications[1–3] and for theoretical structural studies performed on their metal derivatives.[4] Several investigations are reported in the literature regarding structural and spectroscopic features of tin(IV) β-diketonates,[5–13] including their application in catalysis and material science.[14,15]

Diorganotin(IV) derivatives containing two symmetric β-diketonate ligands adopt *trans* regular octahedral geometry[5] whereas dissymmetric β-diketonates form strongly deformed octahedral structures with both ligands generally pointing their equivalent arms in a *syn* configuration.[16–20] However an appropriate choice of peripheral substituents on the β-diketonate allows the synthesis of isomers with centrosymmetrical (*anti*) configuration.[21] It seems that the features determining the *cis* and *trans* configurations are subtle and more factors than those to date hypothesized are responsible. For example, in the octahedral bis(4-acyl-5-pyrazolonato)-diphenyltin complexes, the *cis* arrangement has been observed using Mössbauer spectroscopy.[17] However to our knowledge no crystal structure for *cis*-diorganotin(IV) bis(β-diketonates) is reported.

We have previously demonstrated that a better control of the tin(IV) coordination environment can be achieved through the use of highly predisposed ligands and that the tin coordination geometry and the orientation of the interaction sites in a given ligand provide the instructions, or blueprint, for the construction of the desired complex. For example 2-[(5-hydroxy-1-phenyl-3-methylpyrazol-4-yl)(5-oxo-1,5-dihydro-4-phenyl-2-methylpyrazol-4-ylidene)methyl]benzoic acid was able to form mononuclear, dinuclear and heterobimetallic complexes, the nuclearity and stoichiometry being a function of the nature of the starting organotin(IV) acceptor.[22]

Bidentate 4-acyl-3-methyl-1-phenyl-pyrazol-5-ones are β-diketonate chelators which were first synthesized at the turn of the nineteenth century.[23,24] Their complexing abilities, especially towards transition metals, lanthanide and actinide ions,[25–27] have also been long recognized and they are widely used for the separation of trace metals.[28] However it was not until 1983 that the tetradentate bis(4-acyl-2-pyrazolin-5-one) ligands were synthesized[29] and their coordination chemistry towards metal ions studied.[30,31] Based on the structure of the tetraketone, bis(acyl)pyrazolone should be efficient in forming multinuclear complexes and in design of supramolecular assemblies and defined configurations, as for example *cis*-R_2Sn octahedral geometries. We have previously reported that the interaction between 1,*n*-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)alkane-1,*n*-dione (Q*n*QH_2) (*n* = 0, 2–8, 10) with tin(IV) acceptors[32,33] can yield complexes with different nuclearity depending on the length of the polymethylene chain. For example the donor 1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)butane-1,4-dione ($Q2QH_2$) (Fig. 1) reacts with SnR_2Cl_2 (R = Me, Et or Cl) in MeOH yielding insoluble polymeric species, whereas no reaction occurs between $Q2QH_2$ and SnR_3Cl. Here we show that $Q2QH_2$ reacts with R_2SnO (R = Me or Bu^n) and $(R_3Sn)_2O$ (R = Bu^n or Ph) yielding the

---

† Coordination chemistry of bis(pyrazolones): a rational design of nuclearity tailored polynuclear complexes. Part 2.[22]

DOI: 10.1039/b106665j

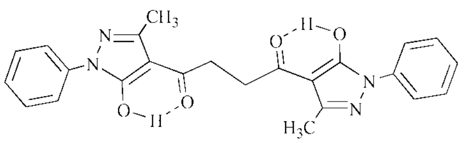


Fig. 1 The $Q2QH_2$ proligand used in this work.

soluble dinuclear octahedral species [Sn-*cis*-R_2(Q2Q)]$_2$ and the bimetallic trigonal bipyramid [$(SnR_3)_2$(Q2Q)] respectively. The reaction of $Q2QH_2$ with SnR_2Cl_2 (R = Bu^i, Ot, Do) is also described.

Experimental

Materials and methods

1-Phenyl-3-methyl-pyrazolin-5-one, succinyl chloride and potassium hydroxide were purchased from Aldrich (Milwaukee) and used as received; organotin(IV) halides were obtained from Aldrich. Solvent evaporations were always carried out under vacuum using a rotary evaporator. The samples for microanalysis were dried *in vacuo* to constant weight (20 °C, *ca.* 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium; dichloromethane was distilled from calcium hydride. All solvents were degassed with dry nitrogen prior to use. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR spectra were recorded on a VXR-300 Varian instrument and on a Bruker AC 200 spectrometer operating at room temperature (respectively at 300 and 200 MHz for ^{1}H, 75 and 50 MHz for ^{13}C and 111.8 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^{1}H and ^{13}C calibration by internal deuterium solvent lock) and $SnMe_4$. Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_m, reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane solutions of complexes **1**–**8** were taken with a Crison CDTM 522 conductimeter at room temperature. The donor $Q2QH_2$ was synthesised by the procedure reported by Jensen[34] and re-crystallized from hot methanol. Molecular weight (MW) determinations, carried out on selected compounds, were performed at 40 °C with a Knauer KNA0280 vapour pressure osmometer calibrated with benzil. The solvent was Baker Analysed Spectrophotometric grade methanol. The results were reproducible to ±2%.

Syntheses

Bis[(1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)diisobutyltin(IV)] [$SnBu^i_2$(Q2Q)]$_2$ (1). To a methanol solution (30 ml) of $Q2QH_2$ (0.430 g, 1 mmol) potassium hydroxide (0.112 g, 1.0 mmol) and dichlorodiisobutyltin(IV) (0.303 g, 1 mmol) were added. The mixture was stirred overnight. A colourless precipitate formed which was filtered off and washed with methanol (10 ml), then re-crystallized from chloroform–methanol. Yield 86%. Mp: 256–259 °C. Anal. Calc. for $C_{32}H_{38}N_4O_4Sn$: C, 58.11; H, 5.79; N, 8.47. Found: C, 58.45; H, 5.85; N, 8.75%. Λ_m (CH_2Cl_2, 1 × 10^{-3} M): 0.1. MW ($CHCl_3$, $c = 1.5 \times 10^{-3}$ mol l^{-1}): 1310. IR (cm^{-1}): 1597vs ν(C=O), 442vs, 399m ν(Sn–O), 613s ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 0.86 (t, 6H, CH_3), 1.08 (t, 4H, CH_2), 1.35 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 2.05 (s, 6H, C_3-CH_3), 2.93 (dd, 4H, CH_2, $J_{AA'}$ = 15 Hz, J_{AX} = 240 Hz), 7.25 (t, 2H, CH_{arom}), 7.45 (t, 4H, CH_{arom}), 8.03 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 13.8 (s, Sn-Bu^i), 17.3 (s, C_3-CH_3), 25.6 (s, Sn-Bu^i, ^1J(^{13}C–^{119}Sn): 610 Hz, ^1J(^{13}C–^{117}Sn): 591 Hz), 26.7 (s, Sn-Bu^i, ^3J(^{13}C–$^{119/117}$Sn): 102 Hz), 27.9 (s, Sn-Bu^i, ^2J(^{13}C–$^{119/117}$Sn): 25 Hz), 31.5 (s, CH_2), 103.1, (s, C_4), 120.7, 125.4, 128.5, 138.4 (s, C_{arom}), 148.5 (s, C_3), 163.2 (s, C_5), 191.9 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −342.7.

Bis[(1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)dioctyltin(IV)] [$SnOt_2$(Q2Q)]$_2$ (2). Compound **2** was obtained as for **1** by using 1.0 mmol of dichlorodioctyltin(IV) ($SnOt_2Cl_2$). Yield 75%. Mp: 220–222 °C. Anal. Calc. for $C_{40}H_{54}N_4O_4Sn$: C, 62.11; H, 7.04; N, 7.24. Found: C, 61.78; H, 7.16; N, 7.25%. Λ_m (CH_2Cl_2, 1 × 10^{-3}M): 0.2. IR (cm^{-1}): 1597vs ν(C=O), 443vs, 390m ν(Sn–O), 570m, 497s ν(Sn–C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ, 0.84 (t, 6H, CH_3), 1.06 (t, 4H, CH_2), 1.25 (m br, 20H, CH_2), 1.55 (m, 4H, CH_2) 2.04 (s, 6H, C_3-CH_3), 2.92 (dd, 4H, CH_2, $J_{AA'}$ = 15.7 Hz, J_{AX} = 240 Hz), 7.22 (t, 2H, CH_{arom}), 7.47 (t, 4H, CH_{arom}), 8.02 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz) δ, 14.6 (s, CH_3), 17.8 (s, C_3-CH_3), 23.1(s, CH_2), 26.2 (s, CH_2), 26.5 (s, CH_2), 29.7 (s, CH_2), 29.9 (s, CH_2), 32.0 (s, CH_2), 32.4 (s, CH_2), 34.3 (s, CH_2), 103.15 (s, C_4), 121.2 (s, C_{arom}), 125.8 (s, C_{arom}), 129.0 (s, C_{arom}), 138.9 (s, C_{arom}), 148.9 (s, C_3), 163.6 (s, C_5), 192.3 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −342.6.

Bis[(1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)didodecyltin(IV)] [$SnDo_2$(Q2Q)]$_2$ (3). Compound **3** was obtained as for **1** by using 1.0 mmol dichlorodidodecyltin(IV). Yield 89%. Mp: 160–163 °C. Anal. Calc. for $C_{48}H_{70}N_4O_4Sn$: C, 65.09; H, 7.97; N, 6.33. Found: C, 65.12; H, 7.46; N, 6.20%. Λ_m (CH_2Cl_2, 1 × 10^{-3}M): 0.1. IR (cm^{-1}): 1595vs ν(C=O), 445vs, 393m ν(Sn–O), 556m, 497s ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 0.86 (t, 6H, CH_3), 1.06 (m), 1.18 (m), 1.52 (m), 1.65 (m) (46H, $CH_2(CH_2)_{10}CH_3$), 2.02 (s, 6H, C_3-CH_3), 2.89 (dd, 4H, CH_2, $J_{AA'}$ = 15 Hz, J_{AX} = 363 Hz), 7.23 (t, 2H, CH_{arom}), 7.43 (t, 4H, CH_{arom}), 8.00 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 14.1 (s, CH_3), 17.3 (s, C_3-CH_3), 22.7 (s, CH_2), 25.7 (s, CH_2), 26.0 (s, CH_2), 29.4 (s, CH_2), 29.5 (s, CH_2), 29.6 (s, CH_2), 29.7 (s, CH_2), 29.8 (s, CH_2), 31.5 (s, CH_2), 33.8 (s, CH_2), 103.0 (s, C_4), 120.7, 125.3, 128.5, 138.4 (s, C_{arom}), 148.4 (s, C_3), 163.2, (s, C_5), 191.8 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −342.6.

Bis[(1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)dimethyltin(IV)] [$SnMe_2$(Q2Q)]$_2$ (4). To a toluene solution (50 ml) of $Q2QH_2$ (0.430 g, 1 mmol) Me_2SnO (0.164 g, 1 mmol) was added. The clear solution was stirred for 24 h. The solvent was removed under reduced pressure and diethyl ether was then added to obtain a colourless precipitate. Re-crystallisation from chloroform–diethyl ether gave the pale-yellow derivative **4**. Yield 80%. Mp: 314–315 °C. Anal. Calc. for $C_{26}H_{26}N_4O_4Sn$: C, 54.10; H, 4.54; N, 9.71. Found: C, 54.43; H, 4.84; N, 9.52%. Λ_m (CH_2Cl_2, 1 × 10^{-3}M): 0.1. MW ($CHCl_3$, $c = 1.5 \times 10^{-3}$ mol l^{-1}): 1100. IR (cm^{-1}): 1614s, 1591vs ν(C=O), 443vs, 420m ν(Sn–O), 583m ν(Sn–C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ, 0.41 (s, 6H, Sn–CH_3, ^2J(Sn–^{1}H): 71.8 Hz), 2.08 (s, 6H, C_3-CH_3), 2.96 (dd, 4H, CH_2, $J_{AA'}$ = 16 Hz, J_{AX} = 240 Hz), 7.26 (t, 2H, CH_{arom}), 7.47 (t, 4H, CH_{arom}), 8.02 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 6.9 (s, Sn-CH_3 ^1J(^{119}Sn–^{1}H: 623 Hz), 14.1 (s, CH_3), 17.3 (s, C_3-CH_3), 31.7 (s, CH_2), 103.0 (s, C_4), 120.7, 125.4, 128.6, 138.4 (s, C_{arom}), 148.6 (s, C_3), 163.2, (s, C_5), 191.9 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −309.6.

Bis[(1,4-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)di-n-butyltin(IV)] [$SnBu^n_2$(Q2Q)]$_2$ (5). Compound **5** was obtained as for **4**. Yield 80%. Mp: 224–226 °C. Anal. Calc. for $C_{32}H_{38}N_4O_4Sn$: C, 58.11; H, 5.79; N, 8.47. Found: C, 58.35; H, 5.86; N, 8.34%. Λ_m (CH_2Cl_2, 1 × 10^{-3}M): 0.05. MW ($CHCl_3$, $c = 1.5 \times 10^{-3}$ mol l^{-1}): 1320. IR (cm^{-1}): 1603vs ν(C=O), 442vs, 395m ν(Sn–O), 619s, 611s, 570m ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 0.86 (t, 6H, CH_3), 1.08 (m, 4H, CH_2), 1.35 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 2.05 (s, 6H, C_3-CH_3), 2.93 (dd, 4H, CH_2, $J_{AA'} = 16$ Hz, $J_{AX} = 360$ Hz), 7.25 (t, 2H, CH_{arom}), 7.45 (t, 4H, CH_{arom}), 8.03 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 13.8 (s, CH_3), 17.3 (s, C_3-CH_3), 25.6 (s, CH_2, $^1J(^{13}C–^{119}Sn)$: 577 Hz), 26.7 (s, CH_2), 27.9 (s, CH_2), 31.5 (s, CH_2), 103.1 (s, C_4), 120.7, 125.4, 128.5, 138.4 (s, C_{arom}), 148.5 (s, C_3), 163.2, (s, C_5), 191.9 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −342.7.

(1,4-Bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)bis[tri-n-butyltin(IV)] [$(SnBu^n_3)_2(Q2Q)$] (6). To a toluene solution (30 ml) of $Q2QH_2$ (0.430 g, 1 mmol) bis(tri-n-butyltin)oxide (0.596 g, 1 mmol) was added. The clear mixture reaction was stirred at reflux for 1 h, the solvent was then removed and n-hexane added to the crude product. On cooling the solution the yellow crystalline **6** slowly precipitated. Yield 72%. Mp: 98–100 °C. Anal. Calc. for $C_{48}H_{74}N_4O_4Sn_2$: C, 57.17; H, 7.40; N, 5.56. Found: C, 56.95; H, 7.60; N, 5.36%. Λ_m (CH_2Cl_2, 1×10^{-3}M): 0.01. IR (cm^{-1}): 1604vs ν(C=O), 441s br, 395m ν(Sn–O), 520s, 612s ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 0.79 (m, 18H, CH_3), 1.11 (m, 12 H, CH_2), 1.23 (m, 12H, CH_2), 1.49 (m, 12 H, CH_2), 2.52 (s, 6H, C_3-CH_3), 3.04 (s, 4H, CH_2), 7.18 (t, 2H, CH_{arom}), 7.36 (t, 4H, CH_{arom}), 7.75 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 13.6 (s, CH_3), 17.3 (s, C_3-CH_3), 20.1 (s, CH_2, $^1J(^{13}C–Sn)$: 401 Hz), 27.1 (s, CH_2), 27.8 (s, CH_2), 34.2 (s, CH_2), 104.1 (s, C_4), 121.8, 125.7, 128.5, 138.4 (s, C_{arom}), 148.0 (s, C_3), 161.5, (s, C_5), 194.0 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, +88.7.

(1,4-Bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)bis[triphenyltin(IV)] [$(SnPh_3)_2(Q2Q)$] (7). Compound **7** was obtained in the same way as **6**. Yield 89%. Mp: 238–240 °C. Anal. Calc. for $C_{60}H_{50}N_4O_4Sn_2$: C, 63.86; H, 4.47; N, 4.96. Found: C, 63.73; H, 4.58; N, 4.93%. Λ_m (CH_2Cl_2, 1×10^{-3}M): 0.3. IR (cm^{-1}): 1607vs ν(C=O), 445vs, 429m, 390m ν(Sn–O), 454vs, 260m, 239vs ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 2.45 (s, 6H, C_3-CH_3), 3.05 (s, 4H, CH_2), 7.24–7.40 (m, 28H, CH_{arom}), 7.58 (m, 8H, CH_{arom}, $^2J(^1H–^{119}Sn)$: 60.0 Hz), 7.81 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 50 MHz) δ, 17.5 (s, C_3-CH_3), 33.9 (s, CH_2), 104.1 (s, C_4), 122.8, 123.6, 126.9, 128.1, 128.2, 128.8, 129.2, 129.4, 129.8, 136.6, 137.1, 137.6, 138.2 (s, C_{arom} and Sn–Ph), 148.3 (s, C_3), 161.5 (s, C_5), 194.8 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, −180.6.

(1,4-Bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)-butane-1,4-dionate)bis(aquo){bis(tri-n-butyltin(IV)} [$(SnBu^n_3)_2$-$(Q2Q)(H_2O)_2$] (8). Compound **8** was afforded by prolonged standing of compound **6** in air. Mp: 97–100 °C. Anal. Calc. for $C_{48}H_{78}N_4O_6Sn_2$: C, 55.19; H, 7.53; N, 5.36. Found: C, 54.95; H, 7.60; N, 5.16%. Λ_m (CH_2Cl_2, 1×10^{-3}M): 0.3. IR (cm^{-1}): 2400–3300br ν(H_2O), 1619vs ν(C=O), 445vs, 431vs, 397s ν(Sn–O), 627s, 615s, 596s, 502m ν(Sn–C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ, 0.79 (m, 18H, CH_3), 1.11 (m, 12 H, CH_2), 1.23 (m, 12H, CH_2), 1.49 (m, 12 H, CH_2), 2.15 (br, 4H, H_2O), 2.52 (s, 6H, C_3-CH_3), 3.04 (s, 4H, CH_2), 7.18 (t, 2H, CH_{arom}), 7.36 (t, 4H, CH_{arom}), 7.75 (d, 4H, CH_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 13.6 (s, CH_3), 17.3 (s, C_3-CH_3), 20.1 (s, CH_2, $^1J(^{13}C–Sn)$: 401 Hz), 27.1 (s, CH_2), 27.8 (s, CH_2), 34.2 (s, CH_2), 104.1 (s, C_4), 121.8, 125.7, 128.5, 138.4 (s, C_{arom}), 148.0 (s, C_3), 161.5, (s, C_5), 194.0 (s, CO). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ, +91.9.

X-Ray crystallography

Crystals of **5** for X-ray crystallographic studies were isolated by re-crystallization from chloroform–methanol. In the case of derivatives **6** and **7** crystals suitable for X-ray diffraction studies were obtained by slow evaporation of mother liquids after the main portion of the complex had been removed by filtration.

The data for complexes **5**, **6** and **7** were collected on an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo-Kα radiation. Absorption correction was not applied. The structures were solved by direct methods (SHELXS-86)[35] and refined anisotropically for all non-hydrogen atoms using the crystallographic program package SHELXL-93.[36] All H atoms were included in the calculated positions and refined in a riding mode. Crystallographic data and some details of data collection and structure refinement are given in Table 1. In the structure of **5**, the butyl group bonded to Sn(2) was found to be slightly disordered. The most relevant bond distances and angles in the structures of **5**, **6** and **7** are listed in Table 2.

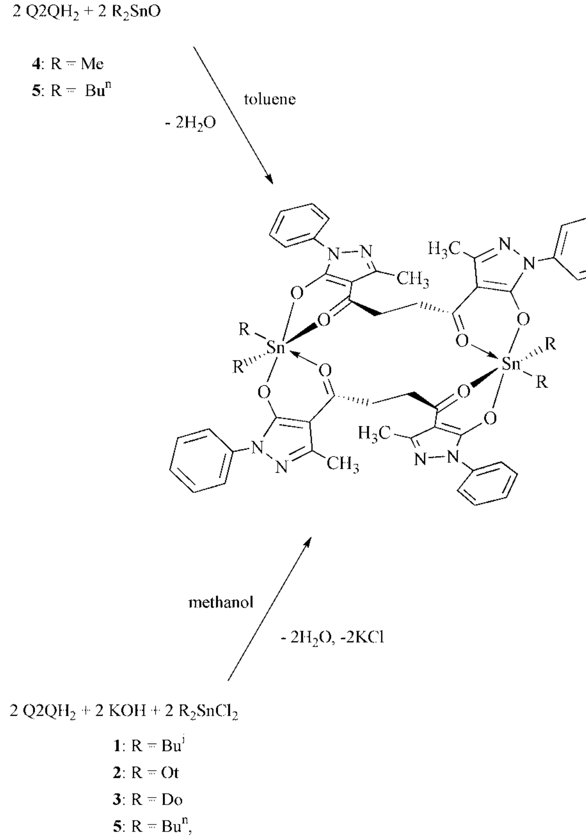
CCDC reference numbers 168761–168763.

See http://www.rsc.org/suppdata/dt/b1/b106665j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of metal derivatives 1–8

From interaction between R_2SnCl_2 (R = Bu^i, Ot, or Do) and the proligand $Q2QH_2$, in methanol in the presence of base (KOH or MeONa), derivatives $[SnR_2(Q2Q)]_2$ **1**–**3** have been obtained (Scheme 1). They show quite sharp melting points and are stable in air as solids and in solution, they are non-electrolytic in acetone and dichloromethane.



Scheme 1

The interaction of an equimolar amount of dimethyl- or di-n-butyl-tin(IV) oxide with the proligand $Q2QH_2$ in toluene yields the soluble derivatives $[(SnMe_2)(Q2Q)]_2$ **4** and $[(SnBu^n_2)$-$(Q2Q)]_2$ **5** having the same stoichiometry (Scheme 1), whereas from the reaction of R_2SnCl_2 (R = Me or Et) with $Q2QH_2$ in MeOH in the presence of KOH the insoluble likely polymeric species $[(SnMe_2)(Q2Q)]_n$ has been obtained, as previously reported by us.[32] Molecular weight determinations show that derivatives **1**, **4** and **5** are dimeric in solution and a structure like that proposed in Scheme 1 is possible.

By reaction of $Q2QH_2$ with $(R_3Sn)_2O$ (R = Bu^n or Ph) in refluxing toluene, derivatives $[(SnBu^n_3)_2(Q2Q)]$ **6** and $[(SnPh_3)_2$-

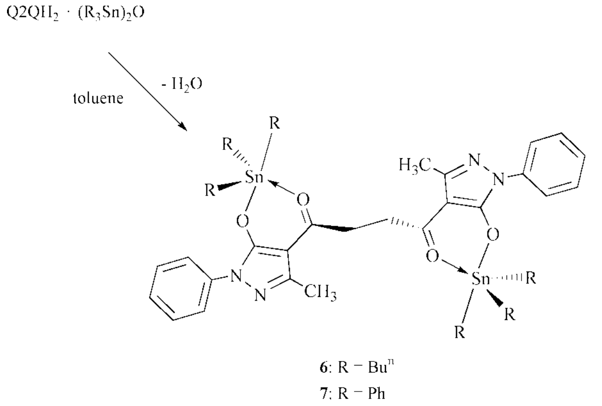
Table 1 Crystallographic data, details of data collection and refinement for **5**, **6** and **7**

	$[\mathrm{SnBu^n_2(Q2Q)}]_2$ **(5)**	$(\mathrm{SnBu^n_3})_2(\mathrm{Q2Q})$ **(6)**	$(\mathrm{SnPh_3})_2(\mathrm{Q2Q})$ **(7)**
Molecular formula	$C_{64}H_{76}N_8O_8Sn_2$	$C_{48}H_{74}N_4O_4Sn_2$	$C_{60}H_{50}N_4O_4Sn_2$
M	1322.71	1008.49	1128.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
a/Å	23.419(5)	16.300(3)	15.084(4)
b/Å	18.696(3)	10.425(2)	16.320(3)
c/Å	16.978(4)	16.598(3)	10.821(3)
α/°	90	90	90
β/°	127.39(2)	117.14(3)	109.78(3)
γ/°	90	90	90
Volume/Å^3	5906.2(21)	2509.9(8)	2506.6(11)
Z	4	2	2
D_c/Mg m^{-3}	1.488	1.334	1.495
Absorption coefficient/mm^{-1}	0.909	1.038	1.049
Crystal size/mm	0.7 × 0.5 × 0.4	0.6 × 0.2 × 0.15	0.6 × 0.2 × 0.07
Temperature/K	180(2)	200(2)	180(2)
Data collection, θ_{max}/°	27.1	28.0	26.9
Reflections collected	25489	15815	15726
Independent refls (R_{int})	6424 (0.0392)	5897 (0.0422)	5291 (0.1118)
Data/parameters	5452/385	4947/266	3392/317
Goodness of fit on F^2	1.031	0.936	1.078
wR_2	0.0624	0.0723	0.1309
R_1	0.0250	0.0283	0.0527
Largest diff. peak and hole/e Å^{-3}	0.507, −0.573	0.697/−0.668	0.830/−0.750

Table 2 The most relevant bond distances (Å) and angles (°) in the structures of **5**, **6** and **7**[a]

	5	**6**	**7**
Sn(1)–O(1)	2.132(2)	2.505(2)	2.313(5)
Sn(1)–O(2)	2.209(2)	2.096(2)	2.102(5)
Sn(2)–O(3)	2.205(2)		
Sn(2)–O(4)	2.127(2)		
Sn–C	2.143(2); 2.132(3)	2.147(3); 2.161(3); 2.179(3)	2.146(7); 2.153(8); 2.134(8)
C(1)–O(1)	1.275(3)		
C(2)–O(1)		1.255(3)	1.256(8)
C(11)–O(2)	1.257(3)	1.299(3)	1.293(8)
C(14)–O(3)	1.266(3)		
C(15)–O(4)	1.284(3)		
O(1)–Sn–O(2)	82.52(6)/82.87(6)[b]	76.97(7)	78.2(2)
C–Sn–C	107.3(1); 112.4(2)	126.7(1); 107.4(1); 105.8(1)	103.3(3); 105.1(3); 111.4(3)

[a] Atom numbers for structure **5**. [b] The angle O(3)–Sn(2)–O(4).



Scheme 2

(Q2Q)] **7** are afforded (Scheme 2). They are not electrolytes in acetone and dichloromethane solution, but have lower melting points with respect to **1**–**5**. The derivative $[(\mathrm{SnBu^n_3})_2(\mathrm{Q2Q})]$ **6** rapidly absorbs water from the atmosphere when exposed to air for more than 1 h, giving compound $[(\mathrm{SnBu^n_3})_2(\mathrm{Q2Q})(\mathrm{H_2O})_2]$ **8**, which contains two water molecules bonded to tin, whereas **7**, being also anhydrous, is more stable to moisture, a difference already observed in analogous triorganotin(IV) derivatives of acylpyrazolones.[37–39] This further supports the tendency of trialkyltin(β-diketonate) derivatives to absorb water and to hydrolyse. In chlorinated solvents compound **6** slowly undergoes a disproportionation like the following:

$$\underset{\mathbf{6}}{2[(\mathrm{SnBu^n_3})_2(\mathrm{Q2Q})]} \xrightarrow{\mathrm{CHCl_3}} \underset{\mathbf{5}}{[\mathrm{SnBu^n_2(Q2Q)}]_2} + 2\mathrm{SnBu^n_4} \qquad (1)$$

which affords the derivative $[\mathrm{SnBu^n_2(Q2Q)}]_2$ **5** previously reported, together with $\mathrm{SnBu^n_4}$, as also confirmed from $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR chemical shifts, two peaks at *ca.* −324 and −7 ppm due to **5** and $\mathrm{SnBu^n_4}$ respectively being immediately detected.

Spectroscopic characterization

IR data. In the IR spectra of the anhydrous derivatives **1**–**7** the *ν*(C=O) stretching band of the $\mathrm{Q2Q^{2-}}$ ligand is shifted to lower frequencies upon coordination, whereas in the hydrate compound **8** it remains essentially unchanged and a broad absorption between 2500 and 3400 cm^{-1} is observed, probably due to H-interactions involving water H-atoms with N- and/or O-atoms of the ligand $\mathrm{Q2Q^{2-}}$ as H-acceptor.[40] Two or more bands in the range 350–450 cm^{-1}, due to symmetric and asymmetric *ν*(Sn–O),[41,42] have been detected for **1**–**8**, together with additional bands assignable to *ν*(Sn–C) in the range 500–650 cm^{-1},[43–46] apart from the phenyltin(IV) derivative **7** which exhibits two absorptions at 260 and 239 cm^{-1}.[47] The presence of two or more ν(Sn–C) in derivatives **1**–**5** indicates a *cis*-arrangement of organic groups on tin (see also crystallographic studies below). This has been confirmed by comparison of the IR spectra of **1**–**5** with those of *trans*-diorganotin(IV)-bis(acylpyrazolonate) species which show only one absorption due to Sn–C stretching vibrations.[16–21] In the case of derivatives **6**–**8**, the presence of a symmetric Sn–C vibration mode (only Raman-active in trigonal planar SnC_3 structures with local D_{3h} symmetry) is in accordance with a deviation from planarity (local C_{3v} symmetry).

NMR data. The ^1H NMR spectra of **1**–**8** always show the expected resonances for both organotin fragments and $Q2Q^{2-}$ ligands. Only one set of signals has been observed for the $Q2Q^{2-}$ moiety in **1**–**8**. The methylene chain protons in the unbound $Q2QH_2$ ligand give rise to only one signal, whereas the diorganotin compounds **1**–**5** give rise to an AA′XX′ system probably due to non-equivalence of the methylene protons in the rigid dinuclear species which inhibit free rotation around the C–C methylene chain bond. On the other hand only one resonance for the methylene chain protons, higher-field shifted, is found in the proton spectra of triorganotin compounds **6**–**8**, thus indicating free rotation around the C–C bond in these symmetric species. The resonances of the organic groups bonded to tin in **1**–**3** and **5** are complex multiplets, so that it was not possible to find the ^2J(H–Sn), which are useful in showing the existence in solution of *cis* or *trans* isomers. In **4** the $^2J(^1H–Sn)$ value of 71.8 Hz clearly indicates the existence of the *cis*-Me_2 species also in solution.[48] In **7** the $^2J(^1H–Sn)$, having a value of 60 Hz, is typical of a trigonal bipyramidal SnO_2C_3 environment.[49,50]

^{13}C NMR data are also listed in the experimental section. No significant shift has been observed for aromatic and pyrazole ring carbon atoms in the complexes with respect to the unbound proligand $Q2QH_2$. In **1**–**5** the carbon atom of the chain carbonyl is shielded to the extent of 4–5 ppm whereas that of the ring carbonyl is deshielded to about 3–4 ppm, in accordance with chelation of the ligand through both the oxygen atoms. In **6**–**8** both carbonyl groups undergo only very limited shifts to about 1–2 ppm, thus indicating the electron density donation from $Q2Q^{2-}$ to tin is less in **6**–**8** than in **1**–**5**. The $^1J(^{13}C–^{119}Sn)$ coupling constant values found for compounds **1**, **4** and **5** are 610, 623 and 577 Hz respectively. On the basis of Howard[51] (eqn. 2)

$$\angle \text{C–Sn–C} = 0.178 \times {}^1J({}^{119}\text{Sn–}{}^{13}\text{C}) + 14.74 \qquad (2)$$

the C–Sn–C angle in **5** is estimated to *ca.* 117°. This value compares well with the C–Sn–C angle found in the solid state.

The ^{119}Sn NMR data of compounds **1**–**5** are in the range typical of six-coordinate tin centres with a SnC_2O_4 central core.[49,50] The ^{119}Sn resonances of **6** and **8** fall in the range typical of four-coordinate $SnOC_3$ tin centres,[49,50] which could be formed upon dissolution of the samples in $CDCl_3$ solution. The ^{119}Sn resonance for **5** falls at −181 ppm, in accordance with the existence of a SnO_2C_3 tin core in solution.[49,50] No change has been observed when the ^1H, ^{13}C and ^{119}Sn NMR spectra of **4** and **5** have been recorded at +50 °C or at −55 °C, suggesting that our diorganotin(IV) species are not fluxional in solution.

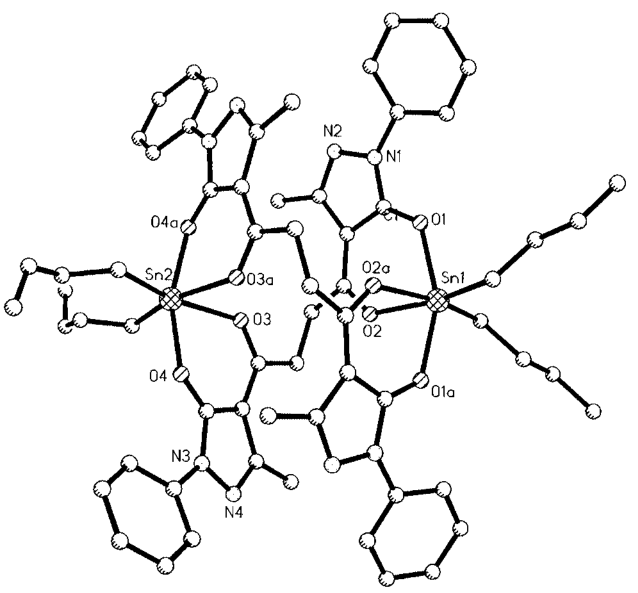


Fig. 2 Molecular structure of the dinuclear complex $[SnBu^n_2(Q2Q)]_2$ **5**. The letter “a” refers to the symmetrically equivalent atoms due to the rotation around the two-fold axis at 0.5, 0, 0.25.

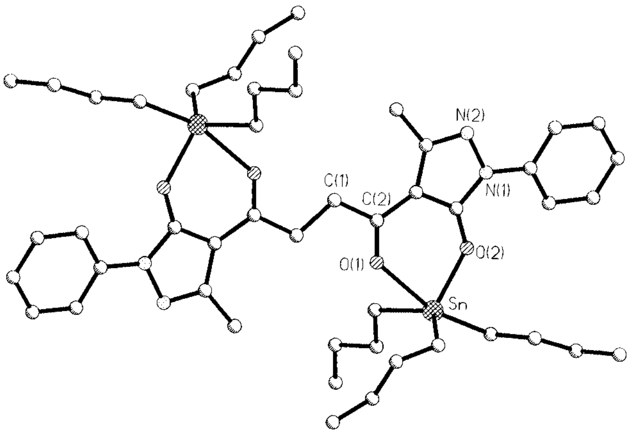


Fig. 3 Molecular structure of the complex $[(SnBu^n_3)_2(Q2Q)]$ **6**.

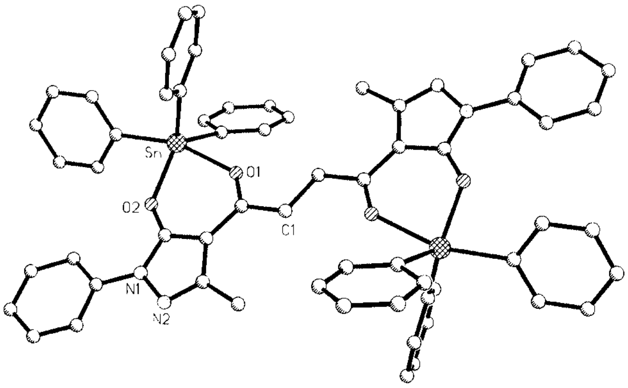


Fig. 4 Crystal structure of the complex $[(SnPh_3)_2(Q2Q)]$ **7**.

X-Ray crystallography. Compounds **5**, **6** and **7** have a molecular structure. The compound **5** $[SnBu^n_2(Q2Q)]_2$ (Fig. 2), which is the first crystallographically characterized *cis*-$(alkyl)_2Sn(\beta\text{-diketonate})_2$ complex, is binuclear, with two $(Q2Q)^{2-}$ ligands acting as bridging tetradentate donors. Both tin atoms lie on a two-fold axis and have a distorted *cis*-octahedral SnC_2O_4 coordination with Sn–O distances (2.127–2.209 Å, average 2.168 Å) which are a little shorter than in the triorganotin(IV) derivatives **6** (Fig. 3) (2.102 and 2.313 Å, average 2.208 Å) and **7** (Fig. 4) (2.096 and 2.505 Å, average 2.300 Å). This molecule with a crystallographically imposed two-fold symmetry can be compared with a similar binuclear manganese(II) complex containing the analogous ligand 1,5-bis(5-hydroxy-1-phenyl-3-methyl-1*H*-pyrazol-4-yl)pentane-1,5-dionate, recently described.[52] The difference in arrangement and geometries of the dibutyltin(IV) cation with respect to the manganese(II) one can be explained taking into consideration the different number of CH_2 groups in the methylene chain linking two pyrazolonate fragments. The Sn–C bonds in **7** (2.132 and 2.143 Å) are similar to those in Bu_2SnCl_2 (average

2.124 Å)[53] and its adduct with 3,9,13,19-tetraoxo-4,8,14,18-tetraoxa-1,11-di(1,3)benzenecycloicosaphane (average 2.101 Å),[54] but the C–Sn–C bond angle in the compound in question is appreciable smaller (107.3 and 112.4°, for two different Sn atoms) if compared with 132.06° in Bu_2SnCl_2[53] and 123.75° in its adduct.[54] This fact arises from the different coordination environment and mainly from the different coordination numbers of tin: it is six-coordinated in **7** and at least five-coordinated in Bu_2SnCl_2 and its adduct (taking into consideration a weak Sn ··· Cl interaction of 3.514 Å in Bu_2SnCl_2[53]). The O–Sn–O bite angle compares well with that previously reported for *trans*-diorganotin(IV)bis(acylpyrazolonate) complexes,[16–21] whereas the Sn–O bond lengths in **5** are very close to each other, in contrast to *trans*-diorganotin(IV)bis(acylpyrazolonate) derivatives[16–21] which show two different sets of Sn–O distances.

The compounds $[(SnBu^n_3)_2(Q2Q)]$ **6** and $[(SnPh_3)_2(Q2Q)]$ **7** are dinuclear with a tetradentate μ_2-bridging $(Q2Q)^{2-}$ ligand acting as bidentate toward each SnR_3 moiety, the inversion centre being situated at the middle of the C(1)–C(1′) bond. The values of Sn–O distances are very different in both structures (2.096(2), 2.505(2) Å in **6** and 2.102(5), 2.313(5) Å in **7**) falling in the region typical for Sn–O bonds in triorganotin(IV) β-diketonates.[37–39] The average Sn–C distance in **7** (2.144 Å) remains almost unchanged with respect to $SnPh_3Cl$ (2.123 Å)[55] or other triphenyltin derivatives such as triphenyltin(IV) 2-aminophenylsulfide (2.116 Å),[56] but the average C–Sn–C bond angle in the $SnPh_3$ fragment is slightly lower (106.6° in **7** compared to 112.25° in $SnPh_3Cl$[55] and 112.06° in triphenyltin(IV) 2-aminophenylsulfide[56]). The coordination environment of tin atoms in **6** and **7** can be described as heavily distorted trigonal bipyramidal with one carbon and one oxygen atom in apical positions. It is surprising that the structure of the tributyltin(IV) derivative **6** is very similar to that of triphenyltin(acylpyrazolonate),[39] but very different with respect to the structure of trimethyl(aquo)tin(acylpyrazolonate)[38] in which a molecule of water takes the place of one of the carbonyl arms of the diketones. In addition the triphenyl derivative **7** is different with respect to triphenyltin(acylpyrazolonate), one of the C–Sn–C angles being sensibly smaller than the two others and the difference between the Sn–O length bonds being 0.212 Å smaller than that reported for triphenyltin(acylpyrazolonate).[39] The bite angles O–Sn–O in **6** and **7** are similar to that in triphenyltin(acylpyrazolonate). It is also interesting to note that **6** is the first trialkyltin(IV) derivative containing a chelating β-diketonato ligand.

Conclusion

The results obtained show the interaction of di- and triorganotin(IV) derivatives with the polydentate bis(acylpyrazolonate) donor $Q2Q^{2-}$ to afford binuclear complexes. The use of a strong base in the case of dimethyltin(IV) species results in the formation of an insoluble polymeric compound that demonstrates the strong influence of the reaction media on the nature of the complex. The $Q2Q^{2-}$ ligand seems to be efficient in forming multinuclear complexes and in design of defined configurations as *cis*-R_2Sn octahedral geometries. The *cis*-$(alkyl)_2Sn(\beta\text{-diketonate})_2$ and $(alkyl)_3Sn(\beta\text{-diketonate})$ complexes have been crystallographically characterized for the first time.

Acknowledgements

Financial support from the Università degli Studi of Camerino and Fondazione CARIMA, Russian Fund of Basic Research (grant RFBR 00-03-32662) and an individual INTAS grant from Dr. Andrei Drozdov (YS 2000-220), Cooperazione Italia-Russia are gratefully acknowledged.

References

1 P. Dobrzynski, J. Kasperczyk and M. Bero, *Macromolecules*, 1999, **32**, 4735.
2 A. Maverick and G. L. Griffin, in *The Chemistry of Metal CVD*, T. T. Kodas and M. J. Hampden-Smith eds., VCH, Weinheim, 1994, ch. 4 and references therein.
3 M. Bero, J. Kasperczyk and P. Dobrzynski, *Polym. Bull.*, 1999, **42**, 131.
4 S. Di Bella, G. Lanza, A. Gulino and I. Fragalà, *Inorg. Chem.*, 1996, **35**, 3885.
5 G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.
6 D. W. Thompson, J. F. Lefelhocz and K. S. Wong, *Inorg. Chem.*, 1972, **11**, 1139.
7 N. Serpone and K. A. Hersh, *Inorg. Chem.*, 1974, **13**, 2901.
8 G. A. Miller and E. O. Schlemper, *Inorg. Chim. Acta*, 1978, **30**, 131.
9 G. Poli, C. J. Cheer and W. H. Nelson, *J. Organomet. Chem.*, 1986, **306**, 347.
10 C. D. Chandler, G. D. Fallon and A. J. Koplick, *Aust. J. Chem.*, 1987, **40**, 1247.
11 J. Otera, *J. Organomet. Chem.*, 1981, **221**, 57.
12 R. Willem, M. Gielen, H. Pepermans, J. Brocas, D. Fastenakel and P. Finocchiaro, *J. Am. Chem. Soc.*, 1985, **107**, 1146.
13 R. Willem, M. Gielen, H. Pepermans, K. Hallenga, A. Recca and P. Finocchiaro, *J. Am. Chem. Soc.*, 1985, **107**, 1153.
14 R. Merten and G. Loew, *US Pat.* 3055845, 1962.
15 M. Vrnata, V. Myslik, F. Vyslouzil and M. Jelinek, *J. Electr. Eng.*, 1998, **49**, 200.
16 C. Pettinari, G. Rafaiani, G. Gioia Lobbia, A. Lorenzotti, F. Bonati and B. Bovio, *J. Organomet. Chem.*, 1991, **405**, 75.
17 F. Caruso, D. Leonesi, F. Marchetti, E. Rivarola, M. Rossi, V. Tomov and C. Pettinari, *J. Organomet. Chem.*, 1996, **519**, 29.
18 C. Pettinari, F. Marchetti, A. Cingolani, A. Lorenzotti, E. Mundorff, M. Rossi and F. Caruso, *Inorg. Chim. Acta*, 1997, **262**, 33.
19 C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, E. Mundorff, M. Rossi and F. Caruso, *J. Organomet. Chem.*, 1998, **557**, 187.
20 F. Marchetti, C. Pettinari, M. Rossi and F. Caruso, *Main Group Met. Chem.*, 1998, **21**, 255.
21 F. Caruso, M. Rossi, F. Marchetti and C. Pettinari, *Organometallics*, 1999, **18**, 2398.
22 Part 1: C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov and S. Troyanov, *J. Chem. Soc., Dalton Trans.*, 2001, 1790.
23 F. Stoltz, *J. Prakt. Chem.*, 1897, **55**, 145.
24 A. Michaelis and F. Engelhardt, *Chem. Ber.*, 1908, **41**, 2668.
25 L. Ying, A. Yu, X. Zhao, Q. Li, D. Zhou, C. Huang, S. Umetani and M. Matsui, *J. Phys. Chem.*, 1996, **100**, 18387.
26 C. Pettinari, F. Accorroni, A. Cingolani, F. Marchetti, A. Cassetta and L. Barba, *J. Organomet. Chem.*, 1998, **566**, 187 and references therein.
27 F. Caruso, M. Rossi, J. Tanski, R. Sartori, R. Variego, S. Moya, S. Diez, E. Navarrete, A. Cingolani, F. Marchetti and C. Pettinari, *J. Med. Chem.*, 2000, **43**, 3665 and references therein.
28 B. A. Dianotouba, I. Guiguemde, A. Tayeb, G. J. Goetz-Grandmont and J. P. Brunette, *Solvent Extr. Ion Exch.*, 1994, **12**, 325.
29 X. C. Dong, F. C. Liu and Y. L. Zhao, *Acta Chim. Sin.*, 1983, **41**, 848.
30 S. Miyazaki, H. Mukai, S. Umetani, S. Kihara and M. Matsui, *Inorg. Chem.*, 1989, **28**, 3014.
31 D. Zhou, Q. Li, C. Huang, G. Yao, S. Umetani, M. Matsui, L. Ying, A. Yu and X. Zhao, *Polyhedron*, 1997, **16**, 1381.
32 C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, G. Gioia Lobbia and A. Lorenzotti, *J. Organomet. Chem.*, 1993, **454**, 59.
33 C. Pettinari, F. Marchetti, G. Gioia Lobbia and A. Cingolani, *Gazz. Chim. Ital.*, 1994, **124**, 285.
34 B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1347; B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1668; B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1890.
35 G. M. Sheldrick, SHELXS-86, University of Göttingen, 1986.
36 G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.
37 M. F. Mahon, K. C. Molloy, B. A. Omotowa and M. A. Mesubi, *J. Organomet. Chem.*, 1996, **511**, 227.
38 F. Marchetti, C. Pettinari, A. Cingolani, G. Gioia Lobbia, A. Cassetta and L. Barba, *J. Organomet. Chem.*, 1996, **517**, 141.
39 F. Marchetti, C. Pettinari, A. Cingolani, L. Brocanelli, M. Rossi and F. Caruso, *J. Organomet. Chem.*, 1999, **580**, 344.
40 F. Marchetti, C. Pettinari, A. Cingolani, D. Leonesi, A. Drozdov and S. I. Troyanov, *J. Chem. Soc., Dalton Trans.*, 1998, 3325.
41 R. C. Mehrotra, R. Bohra and D. P. Gaur, *Metal β-Diketonates and Allied Derivatives*, Academic Press, London, 1978, ch. 2 and references therein.

42 K. Nakamoto, C. Udovich and J. Takemoto, *J. Am. Chem. Soc.*, 1970, **92**, 3973 and references therein.
43 J. R. May, W. R. McWhinnie and R. C. Poller, *Spectrochim. Acta, Part A*, 1971, **27**, 969.
44 A. L. Smith, *Spectrochim. Acta, Part A*, 1967, **24**, 695.
45 M. S. Dance, W. R. McWhinnie and R. C. Poller, *J. Chem. Soc., Dalton Trans.*, 1976, 2349.
46 D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.
47 G. K. Sandhu, G. Kaur, J. Holecek and A. Lycka, *J. Organomet. Chem.*, 1988, **345**, 51.
48 T. P. Lockhart and W. P. Manders, *Inorg. Chem.*, 1986, **25**, 892.
49 B. Wreckmeyer, *Annu. Rep. NMR Spectrosc.*, 1985, **16**, 73.
50 C. Pettinari, Heteronuclear NMR Applications (Ge, Sn, Pb), Encyclopedia of Spectroscopy and Spectrometry, ed. J. C. Lindon, Academic Press, London, 1999, p. 704.
51 W. F. Howard, R. W. Crecely and W. H. Nelson, *Inorg. Chem.*, 1985, **24**, 2204.
52 L. Yang, W. Jin and J. Lin, *Polyhedron*, 2000, **19**, 93.
53 J. F. Sawyer, *Acta Crystallogr., Sect. C*, 1988, **44**, 633.
54 P. Dapporto, S. Roelans and P. Rossi, *Croat. Chem. Acta*, 1999, **72**, 327.
55 N. G. Bokii, G. N. Zakharova and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1970, **11**, 895.
56 S. W. Ng, V. G. K. Das, F. L. Lee, E. J. Gabe and F. E. Smith, *Acta Crystallogr., Sect. C*, 1989, **45**, 1294.