Triorganotin(IV) derivatives of several 4-acyl-5-pyrazolonato ligands: synthesis, spectroscopic characterization and behavior in solution Crystal structure of aquotrimethyl(4-p-methoxybenzoyl-1-phenyl-3-methyl-pyrazolon-5-ato)tin(IV)

Fabio Marchetti [a,*], Claudio Pettinari [a], Augusto Cingolani [a], Giancarlo Gioia Lobbia [a], Alberto Cassetta [b], Luisa Barba [b]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, 62032 Camerino, Macerata, Italy*
[b] *Istituto di Strutturistica Chimica "G. Giacomello", Consiglio Nazionale dele Ricerche, Padriciano 99, 30412 Trieste, Italy*

Abstract

New triorganotin(IV) derivatives [(Q)SnR$_3$ · x(H$_2$O)] ($x = 0$, R = Ph; $x = 1$, R = Me and ^{n}Bu) (in general QH = 1-R'-3-methyl-4-R″ (C=O)-pyrazol-5-one; in detail Q'H: R' = C$_6$H$_5$, R″ = C$_6$H$_5$; Q$_A$H: R' = C$_6$H$_5$, R″ = p-CH$_3$O-C$_6$H$_4$; Q$_N$H: R' = C$_6$H$_5$, R″ = p-NO$_2$–C$_6$H$_4$; Q$_{Br}$H: R' = C$_6$H$_5$, R″ = p-Br-C$_6$H$_4$; Q″H: R' = C$_6$H$_5$, R″ = CH$_3$; Q$_{Cl}$H: R' = C$_6$H$_5$, R″ = CCl$_3$; Q$_F$H: R' = C$_6$H$_5$, R″ = CF$_3$; Q$_M$H: R' = CH$_3$, R″ = C$_6$H$_5$; Q$_D$H: R' = CH$_3$, R″ = CH$_3$) have been synthesized and characterized by analysis and spectral (IR and ^{1}H, ^{13}C and ^{119}Sn NMR) data. The (Q)SnPh$_3$ derivatives are five-coordinated in the solid state, with a likely skewed cis-trigonal bipyramidal (cis-TBP) geometry around the tin center and the ligand (Q)$^-$ acting in the bidentate form. In [(Q)SnR$_3$ · (H$_2$O)] derivatives (R = ^{n}Bu or Me) a coordination site is occupied by water, with the ligand (Q)$^-$ coordinating in a monodentate fashion. The crystal structure of [(Q$_A$)SnMe$_3$ · (H$_2$O)] has been determined: the tin atom is found in a distorted TBP environment, with the methyls in the equatorial positions. Two of the Sn–C bond lengths are normal (2.11(1) and 2.08(2) Å) whereas the third is longer (2.18(2) Å); the ligand binds the metal atom through one carbonyl oxygen in the apical position (Sn–O = 2.10(1) Å). The bond length between H$_2$O and Sn is longer (2.41(2) Å), and the O–Sn–O angle is 174.9(5)°. H atoms of water are involved in an intermolecular H-bond network with uncoordinated carbonyl and the pyridinic N atom of the ligand. In chloroform solution the [(Q)SnR$_3$ · (H$_2$O)] derivatives (R = Me or ^{n}Bu) lost the molecule of water and adopt a tetrahedral arrangement. They also give rise to a slow disproportionation, yielding SnR$_4$ and [(Q)$_2$SnR$_2$] derivatives.

Keywords: Tin; X-ray structure; Pyrazolonato complexes; Synthesis; NMR

1. Introduction

Many organotin(IV) derivatives are known as potential biocides [1]. The fungicidal and antibacterial properties in vitro of this class of compound have the following order of increased activity [2]:

$$RSnX_3 < R_2SnX_2 < R_4Sn \ll R_3SnX$$
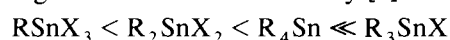
It has been previously suggested [3] that the X group can exert some effect on the biological properties of organotin compounds; Bluden et al. [4] observed a variation in activity on changing the coordination number about the tin atom. This encouraged us to investigate the linking between triorganotin(IV) center and 4-acyl-5-pyrazolones, a family of flexible β-diketonate ligands, widely used as extractants [5], and well known for their applications as analgesics, antipyretics, anti-inflammatories and insecticides [6].

In recent years we have studied the coordination behavior of these bidentate oxygen-donors and reported the synthesis and characterization of tin(II)bis(4-acyl-5-pyrazolonate) and of tin(IV)-, mono- or diorgano-

---

* Corresponding author.

tin(IV)-derivatives [7]. In this paper we extend our investigation to interaction between the 4-acyl-5-pyrazolones in Fig. 1, and triphenyl-, trimethyl- and tributyltin(IV) moieties, together with a close examination of the physicochemical and structural features of the derivatives obtained. This study is also directed to clarify the real behavior of 4-acyl-5-pyrazolones with respect to trioganotin(IV) moieties, because a recent paper [8] on the synthesis and characterization of some triphenyl- and tributyltin(IV)(4-acylpyrazolon-5-ato)

Table 1
Analytical data of compounds 1–27

Compound	No.	Yield (%)	M.p. (°C)	Elemental analyses: found(calcd.) (%)		
				C	H	N
(Q')SnPh$_3$	1	85	136–138	66.86	4.84	4.39
C$_{35}$H$_{28}$N$_2$O$_2$Sn				(67.01)	(4.49)	(4.46)
(Q$_A$)SnPh$_3$	2	52	127–129	65.71	4.84	4.14
C$_{36}$H$_{30}$N$_2$O$_3$Sn				(65.78)	(4.60)	(4.14)
(Q$_N$)SnPh$_3$	3	67	153–155	61.93	4.23	6.23
C$_{35}$H$_{27}$N$_3$O$_4$Sn				(62.53)	(4.05)	(6.25)
(Q$_{Br}$)SnPh$_3$	4	78	149–151	59.42	3.98	3.71
C$_{35}$H$_{27}$N$_2$O$_2$BrSn				(59.53)	(3.85)	(3.97)
(Q'')SnPh$_3$	5	80	137–138	63.55	4.85	4.58
C$_{30}$H$_{26}$N$_2$O$_2$Sn				(63.75)	(4.64)	(4.96)
(Q$_{Cl}$)SnPh$_3$	6	58	154–156	53.70	3.60	3.88
C$_{30}$H$_{23}$N$_2$O$_2$Cl$_3$Sn				(53.90)	(3.47)	(4.19)
(Q$_F$)SnPh$_3$	7	64	108–110	58.27	3.92	4.13
C$_{30}$H$_{23}$N$_2$O$_2$F$_3$Sn				(58.19)	(3.74)	(4.52)
(Q$_M$)SnPh$_3$	8	50	96–99	63.45	4.50	4.68
C$_{30}$H$_{26}$N$_2$O$_2$Sn				(63.75)	(4.64)	(4.96)
(Q$_D$)SnPh$_3$	9	52	94–97	59.46	4.96	5.41
C$_{25}$H$_{26}$N$_2$O$_2$Sn				(59.68)	(4.81)	(5.57)
[(Q')SnBu$_3$·(H$_2$O)]	10	77	110–113	59.78	7.38	4.75
C$_{29}$H$_{42}$N$_2$O$_3$Sn				(59.51)	(7.23)	(4.79)
[(Q$_A$)SnBu$_3$·(H$_2$O)]	11	86	102–107	58.23	7.52	4.33
C$_{30}$H$_{44}$N$_2$O$_4$Sn				(58.55)	(7.21)	(4.55)
[(Q$_N$)SnBu$_3$·(H$_2$O)]	12	90	108–115	55.06	6.71	6.45
C$_{29}$H$_{41}$N$_3$O$_5$Sn				(55.26)	(6.56)	(6.67)
[(Q$_{Br}$)SnBu$_3$·(H$_2$O)]	13	85	103–106	52.21	6.37	4.38
C$_{29}$H$_{41}$N$_2$O$_3$BrSn				(52.44)	(6.22)	(4.22)
[(Q'')SnBu$_3$·(H$_2$O)]	14	76	oil	54.89	7.65	5.17
C$_{24}$H$_{40}$N$_2$O$_3$Sn				(55.09)	(7.70)	(5.35)
[(Q$_{Cl}$)SnBu$_3$·(H$_2$O)]	15	60	oil	45.81	6.06	4.30
C$_{24}$H$_{37}$N$_2$O$_3$Cl$_3$Sn				(46.00)	(5.95)	(4.47)
[(Q$_F$)SnBu$_3$·(H$_2$O)]	16	75	oil	49.78	6.60	4.59
C$_{24}$H$_{37}$N$_2$O$_3$F$_3$Sn				(49.94)	(6.46)	(4.85)
[(Q$_M$)SnBu$_3$·(H$_2$O)]	17	64	103–107	54.69	7.84	5.18
C$_{24}$H$_{40}$N$_2$O$_3$Sn				(55.09)	(7.70)	(5.35)
[(Q$_D$)SnBu$_3$·(H$_2$O)]	18	56	oil	49.19	8.47	6.15
C$_{19}$H$_{38}$N$_2$O$_3$Sn				(49.48)	(8.30)	(6.07)
[(Q')SnMe$_3$·(H$_2$O)]	19	64	192–195	52.29	5.45	5.86
C$_{20}$H$_{24}$N$_2$O$_3$Sn				(52.32)	(5.27)	(6.10)
[(Q$_A$)SnMe$_3$·(H$_2$O)]	20	58	125–129	51.04	5.45	5.53
C$_{21}$H$_{26}$N$_2$O$_4$Sn				(51.57)	(5.36)	(5.73)
[(Q$_N$)SnMe$_3$·(H$_2$O)]	21	73	150–155	47.57	4.33	8.17
C$_{20}$H$_{23}$N$_3$O$_5$Sn				(47.65)	(4.60)	(8.34)
[(Q$_{Br}$)SnMe$_3$·(H$_2$O)]	22	68	228–230	44.96	4.21	5.36
C$_{20}$H$_{23}$N$_2$O$_3$BrSn				(44.65)	(4.31)	(5.21)
[(Q'')SnMe$_3$·(H$_2$O)]	23	70	227–229	45.67	5.36	7.25
C$_{15}$H$_{22}$N$_2$O$_3$Sn				(45.38)	(5.59)	(7.06)
[(Q$_{Cl}$)SnMe$_3$·(H$_2$O)]	24	55	110–114	35.76	3.76	5.43
C$_{15}$H$_{19}$N$_2$O$_3$Cl$_3$Sn				(36.01)	(3.83)	(5.60)
[(Q$_F$)SnMe$_3$·(H$_2$O)]	25	40	oil	40.16	4.51	6.32
C$_{15}$H$_{19}$N$_2$O$_3$F$_3$Sn				(39.95)	(4.25)	(6.21)
[(Q$_M$)SnMe$_3$·(H$_2$O)]	26	64	oil	45.22	5.83	6.89
C$_{15}$H$_{22}$N$_2$O$_3$Sn				(45.38)	(5.59)	(7.06)
[(Q$_D$)SnMe$_3$·(H$_2$O)]	27	62	120–124	35.48	6.26	8.07
C$_{10}$H$_{20}$N$_2$O$_3$Sn				(35.86)	(6.02)	(8.36)

Table 2
IR data [a] of ligands and derivatives 1–27

Compound	> 2500	1700–1500	Sn–O	Sn–C
Q'H	2700s br	1599s, 1570sh, 1560s, 1554s, 1536sh, 1498s		
(Q')SnPh$_3$ **1**	3070w, 3052w	1600s, 1593m, 1587m, 1570m, 1561s, 1540w 1518s, 1508sh	450vs, 404m	450vs, 277s 233s
	[b] 3070w, 3050w	1604vs, 1597m, 1587m, 1574m, 1525m 1518m, 1514w, 1510w	451 vs	451 vs, 277 vs 235s
[(Q')SnBu$_3$·(H$_2$O)] **10**	3150s br, 3070w 3045w	1665m, 1599s, 1592s, 1568s, 1538vs, 1516m 1505m	441m, 376w	607m, 507s
	[b] 3691s, 3450s br 3070w	1660m, 1620sh, 1610s, 1597sh, 1577m 1530m, 1522m, 1512m, 1501s	454m	614m, 507m
[(Q')SnMe$_3$·(H$_2$O)] **19**	3140s br, 3070w 3035w	1662m, 1599s, 1591s, 1568s, 1540s, 1515s 1504m	433m, 369w	558s, 546s
	[b] 3682s, 3440m br 3071w, 3035w	1618sh, 1610s, 1599s, 1578m, 1536m, 1524m 1517m, 1502m	466m, 366w	552s, 541s
Q$_A$H	2800s br	1608s, 1560s, 1515s, 1500m		
(Q$_A$)SnPh$_3$ **2**	3073w, 3048w	1599vs, 1583s, 1574m, 1567m, 1563m, 1558s 1539m, 1531s, 1520m, 1515m, 1505vs	451vs, 421m	451vs, 277s 238s
	[b] 3053w	1602s, 1596s, 1584s, 1564s, 1537m, 1524m 1513m	450vs, 419w	450vs, 270vs 235m
[(Q$_A$)SnBu$_3$·(H$_2$O)] **11**	3120s br, 3042w	1660m, 1609s, 1599m, 1589s, 1567m, 1555m 1537s, 1504m	457m, 419m 410m	605s, 510s
	[b] 3692s, 3378m br	1612sh, 1603vs, 1572m, 1566sh, 1532m 1512sh, 1505m	452m, 443m 421m	610vs, 509s
[(Q$_A$)SnMe$_3$·(H$_2$O)] **20**	3140s br, 3068w 3037w	1657m, 1604s, 1594s, 1568m, 1556m, 1537s 1504s	464m, 422m	557m, 545s
	[b] 3676s, 3412m br	1645m, 1604vs, 1571m, 1566sh, 1532m 1508s, 1504m	442m, 422m	549vs, 536sh 513m
Q$_N$H	2600s br	1633s, 1621s, 1615s, 1600m, 1574m, 1557s 1537m, 1519s, 1504s		
(Q$_N$)SnPh$_3$ **3**	3075w, 3050w	1608s, 1593vs, 1584s, 1574s, 1565m, 1557s 1538m, 1530m, 1520s, 1506m	452vs, 392m	439s, 278vs 234vs
	[b] 3069w, 3050w	1609s1601s, 1596s, 1586s, 1578m, 1570sh 1532m, 1528m, 1524w, 1518m, 1514w, 1498s	451vs, 383m	451vs, 279s 233s
[(Q$_N$)SnBu$_3$·(H$_2$O)] **12**	3130s br, 3044w	1655m, 1612m, 1593sh, 1583vs, 1572m 1562sh, 1537vs, 1529s, 1515sh, 1502m	452s, 391m	614s, 510s
	[b] 3684s, 3450s br 3063w, 3050w	1710m, 1620s, 1599s, 1583sh, 1529m 1518m, 1514m, 1502s	451s, 381m	612m, 509s
[(Q$_N$)SnMe$_3$·(H$_2$O)] **21**	3140s br, 3031w	1663m, 1610s, 1595sh, 1590s, 1568m 1540s, 1525s, 1510s	470s, 419w	558s, 550s
	[b] 3676s, 3400s br 3063w, 3044w	1620s, 1599s, 1536s, 1520m, 1509s 1502m	452s, 418m	552vs, 538m
Q$_{Br}$H	2750s br	1637sh, 1617s, 1591s, 1583s, 1565s, 1555s 1515s, 1498s		
(Q$_{Br}$)SnPh$_3$ **4**	3068w, 3046w	1596s, 1584s, 1572m, 1560m, 1555sh, 1524s 1518sh, 1510m	457vs, 394s	445vs, 278vs 239vs
	[b] 3064w, 3020w	1605s, 1587s, 1578sh, 1569m, 1560m, 1508m	449vs, 399m	449vs, 279vs 235s
[(Q$_{Br}$)SnBu$_3$·(H$_2$O)] **13**	3160s br, 3045w	1666m, 1593s, 1584sh, 1565m, 1556m, 1536s 1514s, 1503s	468m, 403m	609s, 508s
	[b] 3688s, 3438m br	1649sh, 1612vs, 1598s, 1588s, 1561m, 1530m 1506m	441s, 404m	613s, 508vs
[(Q$_{Br}$)SnMe$_3$·(H$_2$O)] **22**	3160s br, 3070w 3034w	1654sh, 1622s, 1617sh, 1588s, 1557m, 1538s 1503m	440m, 383m	554s, 507m
	[b] 3682s, 3378m br	1655sh, 1620s, 1612vs, 1589s, 1558m, 1537m 1503s	450sh, 443vs 388m	553s, 538m 509s
Q"H	2600s br	1622s, 1614s, 1609s, 1592s, 1580s, 1574s 1567s, 1557s, 1538m, 1495s		
(Q")SnPh$_3$ **5**	3070w, 3050w	1613s, 1597m, 1588m, 1577m, 1568m 1561w, 1544w, 1524s, 1519sh, 1508m	448vs, 403m	448vs, 277vs 237vs
[(Q")SnBu$_3$·(H$_2$O)] **14**	3150s br, 3045w	1667m, 1618sh, 1596s, 1581s, 1567sh, 1528s 1501m	445s, 396s	606s, 511m
[(Q")SnMe$_3$·(H$_2$O)] **23**	3150s br, 3075w	1595s, 1571s, 1540s, 1523s, 1505s	437m, 397w	551vs, 511s

Table 2 (continued)

Compound	> 2500	1700–1500	Sn–O	Sn–C
$Q_{Cl}H$	2700s br	1671s, 1654s, 1636s, 1628sh, 1592s, 1578sh 1560s, 1533m, 1519m, 1504s		
$(Q_{Cl})SnPh_3$ 6	3065w, 3045w	1633s, 1622vs, 1616s, 1595s, 1569m, 1577m 1538w, 1531w, 1515s, 1505s	451vs, 396s	443vs, 280s 237s
$[(Q_{Cl})SnBu_3 \cdot (H_2O)]$ 15	3120s br	1665m, 1641s, 1598m, 1560w, 1517s, 1500s	457m, 397w	614m, 522m
$[(Q_{Cl})SnMe_3 \cdot (H_2O)]$ 24	3120s br	1665sh, 1658s, 1598s, 1554w, 1526s, 1500s	465m, 390w	552vs, 545s
$Q_F H$	2500s br	1681, 1651s, 1634m, 1622s, 1594m, 1585sh 1557s, 1538m, 1515m, 1505m		
$(Q_F)SnPh_3$ 7	3064w, 3044w	1634vs, 1620sh, 1594s, 1581m, 1570m 1561sh, 1532s, 1507m	455s, 370m	444vs, 280s 229s
$[(Q_F)SnBu_3 \cdot (H_2O)]$ 16	3130s br	1662m, 1649vs, 1599m, 1529s, 1502s	453w, 363m	615m, 508m
$[(Q_F)SnMe_3 \cdot (H_2O)]$ 25	3120s br	1666m, 1654s, 1598s, 1545s, 1523s, 1502s	424m, 377w	570s, 512m
$Q_M H$	2500s br	1632s, 1620sh, 1614s, 1599s, 1584s, 1574s 1568m, 1557m, 1538m, 1510m, 1505s		
$(Q_M)SnPh_3$ 8	3052w	1603s, 1595sh, 1574s, 1558m, 1537m, 1525m 1520m, 1510sh, 1503s	461s, 391m	456s, 273s 240s
$[(Q_M)SnBu_3 \cdot (H_2O)]$ 17	3150s br, 3035w	1656m, 1605s, 1575s, 1522s, 1505m	455m, 387m	608vs, 526s
$[(Q_M)SnMe_3 \cdot (H_2O)]$ 26	3170s br, 3040w	1599s, 1592s, 1588m, 1573s, 1557m, 1538m 1520s, 1504s	465m, 396s	552s, 528m
$Q_D H$	2600s br	1631s, 1591s, 1584sh, 1520s, 1506s		
$(Q_D)SnPh_3$ 9	3067w, 3045w	1602vs, 1584s, 1573s, 1558m, 1536sh, 1531s 1514s, 1502sh	455vs	440s, 280vs 228s
$[(Q_D)SnBu_3 \cdot (H_2O)]$ 18	3130s br	1660m, 1613s, 1594s, 1673s, 1556s, 1537s 1522s, 1508s	452s, 396m	608vs, 510m
$[(Q_D)SnMe_3 \cdot (H_2O)]$ 27	3150s br	1667m, 1605s, 1585s, 1574m, 1557m, 1537m	455m, 407s	552s, 543s

^{a} Nujol mull. ^{b} Chloroform solution.

derivatives, showed some spectroscopic results with questionable attributions, not supplied by indubitable structural data. We also report the crystal structure of the derivative $[(Q_A)SnMe_3 \cdot (H_2O)]$, and a comparison with related triorganotin(IV) compounds.

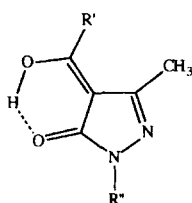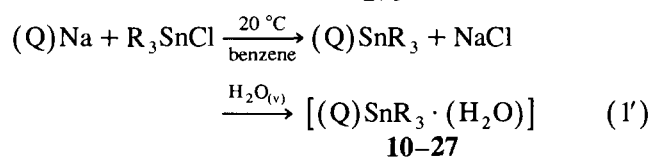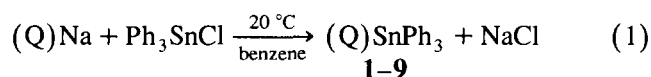| QH	R'	R"
Q'H	C_6H_5	C_6H_5
$Q_A H$	C_6H_5	p-CH_3O-C_6H_4
$Q_N H$	C_6H_5	p-NO_2-C_6H_4
$Q_{Br}H$	C_6H_5	p-Br-C_6H_4
Q"H	C_6H_5	CH_3
$Q_{Cl}H$	C_6H_5	CCl_3
$Q_F H$	C_6H_5	CF_3
$Q_M H$	CH_3	C_6H_5
$Q_D H$	CH_3	CH_3

Fig. 1. QH ligands used in this work.

2. Results and discussion

2.1. Synthesis of the derivatives

The $[(Q)SnR_3 \cdot x(H_2O)]$ (R = Ph, $x = 0$; R = ^{n}Bu or Me, $x = 1$) derivatives 1–27 (see Table 1) were synthesized from interaction between the sodium salts of 4-acyl-5-pyrazolones and R_3SnCl (R = Me, ^{n}Bu or Ph) in benzene or toluene solution at room temperature (Eqs. (1) and (1')):

$$(Q)Na + Ph_3SnCl \xrightarrow[\text{benzene}]{20\ ^\circ C} (Q)SnPh_3 + NaCl \qquad (1)$$
$$\mathbf{1-9}$$

$$(Q)Na + R_3SnCl \xrightarrow[\text{benzene}]{20\ ^\circ C} (Q)SnR_3 + NaCl$$

$$\xrightarrow{H_2O_{(v)}} [(Q)SnR_3 \cdot (H_2O)] \qquad (1')$$
$$\mathbf{10-27}$$

(R = ^{n}Bu or Me)

The tributyl- and trimethyltin(IV) compounds 10–27 absorb water when exposed to atmosphere, whereas the triphenyltin(IV) derivatives 1–9 are air and moisture stable.

Table 3
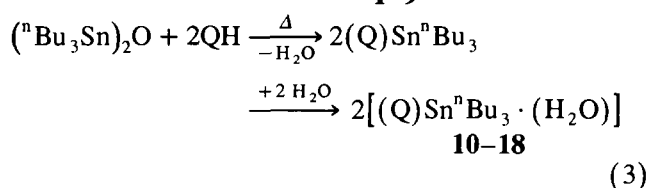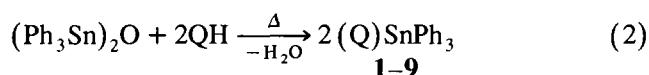^{1}H NMR data in CDCl$_3$ of free ligands and of derivatives **1–27**

Compound	3-CH$_3$	Aromatics	Sn–R	Other data [a]
Q'H	2.11s	7.30m; 7.55m; 7.90m		10.5s br (O–H)
(Q')SnPh$_3$ **1**	1.85s	7.40m; 7.50m; 7.80m 7.90d	— [b]	
[(Q')SnBu$_3$ · (H$_2$O)] **10**	1.96s	7.25t; 7.45m; 7.60m 7.83d	0.86t; 1.30m 1.55m	1.80s br (H$_2$O)
[(Q')SnMe$_3$ · (H$_2$O)] **19**	1.86	7.25t; 7.47m; 7.54m 7.85d	0.53s	1.75s br (H$_2$O) $^2J = 56.66$; 55.35
Q$_A$H	2.20s	7.03d; 7.31t; 7.47t 7.68d; 7.90d		3.90s (OCH$_3$)
(Q$_A$)SnPh$_3$ **2**	2.00s	6.98d; 7.36m; 7.52d 7.77m; 7.84d	— [b]	3.90s (OCH$_3$)
[(Q$_A$)SnBu$_3$ · (H$_2$O)] **11**	2.07s	6.96d; 7.25t; 7.45t 7.68d; 7.70d	0.85t; 1.20m 1.50m	3.87s (OCH$_3$) 1.85s br (H$_2$O)
[(Q$_A$)SnMe$_3$ · (H$_2$O)] **20**	1.98s	6.90d; 7.20t; 7.37t 7.50d; 7.76d	0.47s	1.82s (OCH$_3$) 2.30s br (H$_2$O) $^2J = 57.87$; 55.55
Q$_N$H	2.05s	7.35t; 7.50t; 7.78d 7.85d; 8.37d		
(Q$_N$)SnPh$_3$ **3**	1.80s	7.35m; 7.45d; 7.73m 7.77d; 8.30d	— [b]	
[(Q$_N$)SnBu$_3$ · (H$_2$O)] **12**	1.98s	7.22t; 7.30d; 7.40t 7.76t; 8.28d	0.85t; 1.25m 1.52m	1.90s br (H$_2$O)
[(Q$_N$)SnMe$_3$ · (H$_2$O)] **21**	1.92s	7.30t; 7.45t; 7.72d 7.78d; 8.35d	0.50s	1.83s br (H$_2$O) $^2J = 57.07$; 54.63
Q$_{Br}$H	2.10s	7.30t; 7.45t; 7.52d 7.66d; 7.85d		11.60s br (O–H)
(Q$_{Br}$)SnPh$_3$ **4**	1.90s	7.33m; 7.45m; 7.62d 7.75m; 7.82d	— [b]	
[(Q$_{Br}$)SnBu$_3$ · (H$_2$O)] **13**	2.02s	7.35t; 7.44t; 7.48d 7.60d; 7.78d	0.85t; 1.23m 1.48m	1.95s br (H$_2$O)
[(Q$_{Br}$)SnMe$_3$ · (H$_2$O)] **22**	1.95s	7.25m; 7.35m; 7.55d 7.73m	0.53s	1.90s br (H$_2$O) $^2J = 56.02$
Q''H	2.46s	7.29m; 7.44m; 7.83d		2.48 (CH$_3$C=O) 12.00s Br (O–H)
(Q'')SnPh$_3$ **5**	2.42s	7.30m; 7.40m; 7.70m 7.80d	— [b]	2.42s (CH$_3$C=O)
[(Q'')SnBu$_3$ · (H$_2$O)] **14**	2.45s	7.22t; 7.38t; 7.77d	0.90t; 1.34m 1.60m	2.35s (CH$_3$C=O) 2.00s br (H$_2$O)
[(Q'')SnMe$_3$ · (H$_2$O)] **23**	2.45s	7.22t; 7.42t; 7.68d	0.52s	2.40s (CH$_3$C=O) 1.95s br (H$_2$O) $^2J = 60.12$; 57.54
Q$_{Cl}$H	2.68s	7.30t; 7.45t; 7.75d		11.50s br (O–H)
(Q$_{Cl}$)SnPh$_3$ **6**	2.56s	7.40m; 7.70m	— [b]	
[(Q$_{Cl}$)SnBu$_3$ · (H$_2$O)] **15**	2.62s	7.28t; 7.42t; 7.75d	0.93t; 1.30m 1.58m	1.90s br (H$_2$O)
[(Q$_{Cl}$)SnMe$_3$ · (H$_2$O)] **24**	2.58s	7.30t; 7.42t; 7.62d	0.48s	1.95s br (H$_2$O) $^2J = 66.72$; 63.41
Q$_F$H	2.47q	7.35t; 7.48t; 7.78d		
(Q$_F$)SnPh$_3$ **7**	2.28q	7.18t; 7.38m; 7.58d 7.68d	— [b]	
[(Q$_F$)SnBu$_3$ · (H$_2$O)] **16**	2.40q	7.28t; 7.40t; 7.67d	0.85t; 1.25m 1.55m	1.72s br (H$_2$O)
[(Q$_F$)SnMe$_3$ · (H$_2$O)] **25**	2.40q	7.30t; 7.40t; 7.78d	0.48s	2.10s br (H$_2$O) $^2J = 62.02$; 59.08
Q$_M$H	2.00s	7.45t; 7.55t; 7.67d		10.80s br (O–H) 3.63s (N–CH$_3$)
(Q$_M$)SnPh$_3$ **8**	1.82s	7.30m; 7.45m; 7.55t 7.80d	— [b]	3.50s (N–CH$_3$)

Table 3 (continued)

| Compound	3-CH$_3$	Aromatics	Sn–R	Other data [a]
[(Q$_M$)SnBu$_3$ · (H$_2$O)] 17	1.80s	7.45m; 7.55m	0.92t; 1.30m 1.65m	3.51s (N–CH$_3$) 1.75s br (H$_2$O)
[(Q$_M$)SnMe$_3$ · (H$_2$O)] 26	1.97s	7.45m; 7.55t; 8.02d	0.53s	3.52s (N–CH$_3$) 1.80s (H$_2$O) $^2J = 61.53$
Q$_D$H	2.40s			2.41s (CH$_3$C=O) 3.58s (N–CH$_3$)
(Q$_D$)SnPh$_3$ 9	2.37s		7.38m; 7.65d 7.45m; 7.70m	2.32s (CH$_3$C=O) 3.56s (N–CH$_3$)
[(Q$_D$)SnBu$_3$ · (H$_2$O)] 18	2.37s		0.93t; 1.35m 1.65m	2.31s (CH$_3$C=O) 3.48s (N–CH$_3$) 1.95s br (H$_2$O)
[(Q$_D$)SnMe$_3$ · (H$_2$O)] 27	2.32s		0.61s	2.32s (CH$_3$C=O) 3.45s (N–CH$_3$) 2.10s br (H$_2$O) $^2J = 64.80$; 62.02

[a] J in Hz. [b] Sn–Ph protons are indistinguishable from aromatic protons of ligands.

The triphenyl- and tributyltin(IV) complexes were also obtained by reaction of $(R_3Sn)_2O$ with the neutral ligand QH in refluxing benzene or toluene (Eqs. (2) and (3)):

$$(Ph_3Sn)_2O + 2QH \xrightarrow[-H_2O]{\Delta} 2(Q)SnPh_3 \qquad (2)$$
$$\mathbf{1-9}$$

$$(^nBu_3Sn)_2O + 2QH \xrightarrow[-H_2O]{\Delta} 2(Q)Sn^nBu_3$$

$$\xrightarrow{+2H_2O} 2[(Q)Sn^nBu_3 \cdot (H_2O)]$$
$$\mathbf{10-18}$$
$$(3)$$

The compounds are low melting solids or thick oils, very soluble in the common organic solvents such as alcohols, acetone, DMSO, CH_2Cl_2, $CHCl_3$ and benzene, but insoluble in hydrocarbons and water. Conductivity measurements carried out in acetone, acetonitrile and dichloromethane attested to their covalent nature.

In chloroform solutions, the tributyl and the trimethyltin(IV) complexes are unstable and slowly give rise to the disproportionation equilibrium (4):

$$2[(Q)SnR_3 \cdot (H_2O)]$$
$$\mathbf{10-27}$$
$$\xrightleftharpoons{CHCl_3} (Q)_2SnR_2 + SnR_4 + 2H_2O \qquad (4)$$
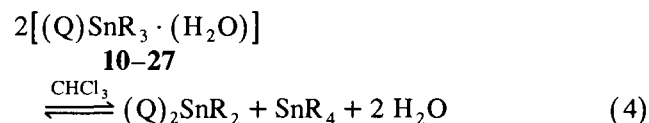
The existence of equilibrium (4) was confirmed by the presence in the ^1H and ^{119}Sn NMR spectra of resonances due to diorganotin(IV)bis(4-acyl-5-pyrazolonato) [7] and tetraorganotin(IV) species [9]. A similar dissociation was previously found also for $Me_3Sn(acac)$ [10], $Cl_3Sn(acac)$ [11] and $Me_3Sn(oxin)$ [12] (where acac = 2,4-pentanedionato and oxin = 8-hydroxyquinolinato). The reaction (4) also occurred when compounds 19–27 were maintained under reduced pressure at ca. 25°C for some weeks. In contrast, triphenyltin(IV) derivatives 1–9 are stable in solution for several days.

2.2. IR spectra

Selected IR data for the ligands and their complexes 1–27 are reported in Table 2. A complete assignment of all the bands was not possible because of the presence of overlapped absorptions; however, several indications were obtained from a close comparison between the spectra of the free ligands and those of related complexes.

The strong broad band centered in the donors at ca. 2600 cm^{-1}, due to the intramolecular hydrogen bond (O–H $\cdots$ O), disappeared in the triphenyltin(IV) derivatives 1–9 and the carbonyl absorption at ca. 1620–1640 cm^{-1} shifted to lower frequencies at ca. 1610–1595 cm^{-1}, in accordance with deprotonation of the ligand and involvement of carbonyls in bonding to tin.

In the spectra of tributyl- and trimethyltin(IV) derivatives 10–27, a broad absorption at ca. 3200–3100 cm^{-1} and a medium band at ca. 1660 cm^{-1}, assignable to $\nu(H_2O)$ and to $\delta(H_2O)$ respectively, were observed, this suggesting presence of water intermolecularly H-bonded.

In the spectra of our complexes we assigned the strong or medium absorptions in the range 470–380 cm^{-1} to symmetric and asymmetric $\nu(Sn–O)$ modes, also on the basis of the wide literature available on β-diketonato derivatives [13]. Moreover, in the spectra of triphenyltin derivatives 1–9, the symmetric and asymmetric stretching vibrations of the SnPh$_3$ moiety, described as 'y' and 't' modes in Whiffen's notation [14], appear at ca. 450, 270 and 230 cm^{-1}. The band at 1070 cm^{-1} is probably due to a C–H in-plane deformation vibration of the phenyls bonded to tin [15]. In some cases we observed the band at 450 cm^{-1} hidden under some $\nu(Sn–O)$ absorptions. Finally, in the spectra of trimethyltin derivatives 19–27, we assigned the strong

or medium bands in the region 570–500 cm^{-1} to ν_{sym} and ν_{asym}(Sn–C) modes [16], whereas in the spectra of tributyltin derivatives **10–18** the same vibrations [17] were observed at ca. 610 and 510 cm^{-1}. The presence of the ν_{sym}(Sn–C) mode (only Raman-active in trigonal planar SnC$_3$ structures having local D$_{3h}$ symmetry) indicated a deviation from planarity (local C$_{3\nu}$ symmetry).

The IR spectra of triphenyltin(IV) derivatives in chloroform solution are similar to those recorded in the solid state. In chloroform solution, tributyl and trimethyltin(IV) compounds show a broad absorption at ca. 3400 cm^{-1}, highfield shifted with respect to that at ca. 3100 cm^{-1} observed in nujol. Moreover, a strong sharp band appeared at ca. 3650–3680 cm^{-1}. We have hypothesized that these differences are probably due to the breaking of the Sn–OH$_2$ bond. The ^{119}Sn NMR spectroscopy (see below), confirmed our hypothesis: in fact the $\delta(^{119}$Sn) observed for these compounds are in accordance with the formation of tetracoordinate species.

Table 4
^{13}C NMR data in CDCl$_3$ of the ligands Q'H, Q$_A$H, Q"H and Q$_D$H and of some of their derivatives [a]

Compound	CH$_3$	Aromatics	CO,C(5)	C(3),C(4)	Sn–R [b]	Other data
Q'H	15.8	120.8, 126.7, 127.9 128.3, 129.1, 131.9 137.3, 137.6	192.0 162.5	148.0 103.6		
(Q')SnPh$_3$ 1	15.9	122.4, 126.4, 127.4 128.2, 128.7, 130.8 135.4, 139.7	192.0 162.8	148.4 104.0	142.8, 137.0 128.4, 129.4	$^2J = 50.4$ Hz $^3J = 63.0$ Hz $^4J = 14.7$ Hz
[(Q')Sn^{n}Bu$_3$ · (H$_2$O)] 10	16.5	122.7, 126.5, 128.3 128.7, 129.1, 131.2 138.9, 141.6	191.9 162.2	149.3 104.5	19.8br, 28.2 27.6, 14.1	$^1J = 365.8$ Hz $^2J = 19.5$ Hz $^3J = 73.2$ Hz $^4J < 10$ Hz
[(Q')SnMe$_3$ · (H$_2$O)] 19	16.2	121.8, 126.0, 127.6 128.2, 128.7, 130.8 138.1, 140.5	191.5 160.3	148.8 104.5	0.8	$^1J = 301.6$ Hz
Q$_A$H	16.1 55.5	113.7, 120.7, 126.5 129.1, 129.7, 130.4 137.4, 161.9	190.5 162.9	147.7 103.7		
(Q$_A$)SnPh$_3$ 2	16.8 55.9	113.9, 122.8, 126.8 129.2, 130.7, 138.3 162.9	191.9 162.8	148.8 104.5	143.7, 137.5 128.8, 129.9	$^2J = 49.4$ Hz $^3J = 64.8$ Hz $^4J = 13.2$ Hz
[(Q$_A$)Sn^{n}Bu$_3$ · (H$_2$O)] 11	16.5 55.9	113.8, 122.7, 126.5 129.1, 131.1, 138.8 162.8	191.1 162.7	149.4 104.8	19.4br, 28.1 27.5, 14.1	$^1J = 355.9$ Hz $^2J = 18.3$ Hz $^3J = 69.1$ Hz $^4J < 10$ Hz
[(Q$_A$)SnMe$_3$ · (H$_2$O)] 20	16.5 55.9	113.9, 122.3, 126.6 129.2, 130.8, 131.0 138.6, 161.8	191.2 167.1	149.2 104.9	0.4	$^1J = 323.4$ Hz
Q"H	15.6 26.6	120.6, 126.5, 129.1 137.2	194.3 160.4	147.7 104.2		
(Q")SnPh$_3$ 5	17.2 28.6	122.8, 126.8, 129.2 138.2	194.7 162.2	148.7 104.8	144.0, 137.5 128.8, 129.8	$^2J = 49.0$ Hz $^3J = 64.6$ Hz $^4J = 13.0$ Hz
[(Q")Sn^{n}Bu$_3$ · (H$_2$O)] 14	17.4 29.4	122.5, 126.3, 129.0 138.8	193.3 161.2	148.6 105.2	20.0br, 28.3 27.6, 14.1	$^1J = 350.3$ Hz $^2J = 18.4$ Hz $^3J = 65.9$ Hz $^4J < 10$ Hz
Q$_D$H	15.3 27.3 32.3		195.0 159.4	146.6 103.0		
(Q$_D$)SnPh$_3$ 9	16.4 27.8 32.1		193.9 n.o.	146.8 103.8	135.1, 136.7 128.4, 129.4	$^2J = 42.3$ Hz $^3J = 61.9$ Hz
[(Q$_D$)Sn^{n}Bu$_3$ · (H$_2$O)] 18	17.2 29.2 32.3		192.9 160.9	147.1 104.3	19.7br, 28.3 27.5, 14.2	$^1J = 371.7$ Hz $^2J = 18.7$ Hz $^3J = 66.7$ Hz $^4J < 10$ Hz

[a] It was not possible to obtain the ^{13}C spectra of derivatives [(Q")SnMe$_3$ · (H$_2$O)] (**23**) and [(Q$_D$)SnMe$_3$ · (H$_2$O)] (**27**), because during the time necessary to acquire a sufficient number of transients, they disproportionated and the absorptions observed were those of (Q)$_2$SnR$_2$ derivatives.
[b] When R = ^{n}Bu, C(α), C(β), C(γ), C(δ); when R = Ph: C(i), C(o), C(m), C(p).
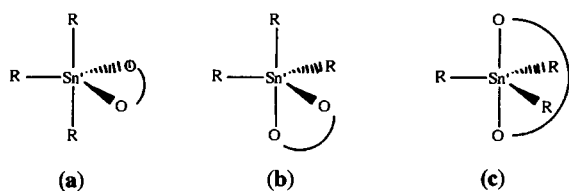
Fig. 2. Possible isomers for (Q)SnPh$_3$.

Fig. 3. Interconversion process proposed for (Q)SnPh$_3$ derivatives.
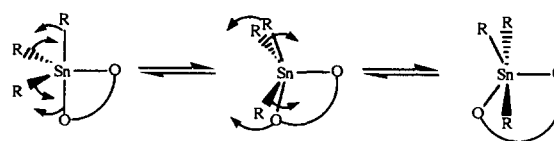
2.3. ^{1}H and ^{13}C NMR spectra

The ^{1}H NMR data of derivatives 1–27 are given in Table 3. Previous papers [7] on 4-acyl-5-pyrazolonato-tin(IV) derivatives provided the basis for the assignments. The broad signal due to enolic hydrogen, always observed in the spectra of the ligands, disappeared in the spectra of complexes, thus suggesting that the donors coordinate the tin atom in the deprotonated form.

The 3-CH$_3$ resonances in the ligands shifted upfield upon coordination, the shift being generally higher in triphenyl- and trimethyltin derivatives than in tributyltin ones. Assignments of the aromatic proton signals of ligands and, for 1–9 compounds, of Ph$_3$Sn resonances were not possible due to the presence of several overlapped bands; however, integration took their presence into account.

The protons of butyl groups were observed as a complex pattern in the region 0.85–1.65 ppm. The Sn–CH$_3$ protons absorbed as a singlet in the range 0.47–0.61 ppm. In the spectra of 10–27 the signal of water was generally detected at ca. 1.90–2.00 ppm.

In the ^{13}C spectra, carried out only for some derivatives (Table 4), the methyl and aromatic ligand signals were shifted downfield. This is due to deshielding upon

coordination. The chain and ring carbonyls undergo only a slight displacement. The organic groups linked to tin showed one set of resonances in the range typical of R$_3$Sn derivatives [18]. In the spectra of 10, 11, 14, 18, 19 and 20 the tin–carbon coupling constants were always observed. It was impossible to record the ^{1}J(Sn–C) of compounds 1, 2, 6 and 9 owing to the very low intensity of ipso-carbon absorption.

In the NMR spectra of our complexes we observed only one set of resonances for each magnetically equivalent proton or carbon of the ligand Q and of the R$_3$Sn moiety. In the likely pentacoordinated triphenyltin(IV) derivatives 1–9 (see below), at least two cis-trigonal bipyramidal (cis-TBP) isomers should be possible (Figs. 2(a) and 2(b)), whereas the trans-TBP isomer (Fig. 2(c)) is not feasible, because of steric requirements of the bidentate ligand. In this case, the equivalence of the phenyl groups bonded to tin found in the ^{13}C NMR spectra could be explained with a fast intramolecular interconversion process in solution [10,12,18] (Fig. 3).

In tributyl and trimethyltin(IV) derivatives 10–27 the ^{1}J(Sn–C) and ^{2}J(Sn–H) are of the same order of magnitude to those observed for tetracoordinated species [18]. By applying the empiric relationships proposed by Lockhart and Mandes [19] and Holecek and Lycka [20], values of θ(C–Sn–C) angles of ca 110° are obtained (Table 5), which are typical of tetrahedral configura-

Table 5
^{1}J(Sn–C) and ^{2}J(Sn–H) of derivatives 10, 11, 14, 18–27 (in CDCl$_3$ solution), and related (C–Sn–C) angles calculated on the basis of Lockhart's and Holecek's relationships [19,20]

Compound	No.	[^{2}J(Sn–H)] (H$_z$)	[^{1}J(Sn–C)] (H$_z$)	(1) [a] (deg)	(2) [b] (deg)	(3) [c] (deg)
[(Q')Sn^{n}Sn$_3$ · (H$_2$O)]	10		365.8			111
[(Q$_A$)Sn^{n}Bu$_3$ · (H$_2$O)]	11		355.9			110
[(Q'')Sn^{n}Bu$_3$ · (H$_2$O)]	14		350.3			110
[(Q$_D$)Sn^{n}Bu$_3$ · (H$_2$O)]	18		371.7			112
[(Q')SnMe$_3$ · (H$_2$O)]	19	56.66	301.6	103	110	
[(Q$_A$)SnMe$_3$ · (H$_2$O)]	20	57.87	323.4	105	111	
[(Q$_N$)SnMe$_3$ · (H$_2$O)]	21	57.07			110	
[(Q$_{Br}$)SnMe$_3$ · (H$_2$O)]	22	56.02			110	
[(Q'')SnMe$_3$ · (H$_2$O)]	23	60.12			112	
[(Q$_{Cl}$)SnMe$_3$ · (H$_2$O)]	24	66.72			117	
[(Q$_F$)SnMe$_3$ · (H$_2$O)]	25	62.02			113	
[(Q$_M$)SnMe$_3$ · (H$_2$O)]	26	61.53			113	
[(Q$_D$)SnMe$_3$ · (H$_2$O)]	27	64.80			115	

[a] (1) [^{1}J(Sn–C)] = 11.4 θ(C–Sn–C) − 875 [19].
[b] (2) θ(C–Sn–C) = 0.0161 [^{2}J(Sn–H)]^2 − 1.32 [^{2}J(Sn–H)] + 133.4 [19].
[c] (3) [^{1}J(Sn–C)] = 9.99 θ(C–Sn–C) − 746 [20].

Table 6
^{119}Sn NMR data [a] of compounds 1–27 in $CDCl_3$

Compound	No.	δ(ppm)	Compound	No.	δ(ppm)
(Q')SnPh$_3$	1	−173	[(Q$_{Cl}$)Sn^{n}Bu$_3$·(H$_2$O)]	15	+136
(Q$_A$)SnPh$_3$	2	−178	[(Q$_F$)Sn^{n}Bu$_3$·(H$_2$O)]	16	+143
(Q$_N$)SnPh$_3$	3	−166	[(Q$_M$)Sn^{n}Bu$_3$·(H$_2$O)]	17	+103
(Q$_{Br}$)SnPh$_3$	4	−153	[(Q$_D$)Sn^{n}Bu$_3$·(H$_2$O)]	18	+93
(Q")SnPh$_3$	5	−185	[(Q')SnMe$_3$·(H$_2$O)]	19	+145
(Q$_{Cl}$)SnPh$_3$	6	−134	[(Q$_A$)SnMe$_3$·(H$_2$O)]	20	+71
(Q$_F$)SnPh$_3$	7	−132	[(Q$_N$)SnMe$_3$·(H$_2$O)]	21	+148
(Q$_M$)SnPh$_3$	8	−182	[(Q$_{Br}$)SnMe$_3$·(H$_2$O)]	22	+152
(Q$_D$)SnPh$_3$	9	−191	[(Q")SnMe$_3$·(H$_2$O)]	23	+57
[(Q')Sn^{n}Bu$_3$·(H$_2$O)]	10	+126	[Q$_{Cl}$]SnMe$_3$·(H$_2$O)	24	+106
[(Q$_A$)Sn^{n}Bu$_3$·(H$_2$O)]	11	+130	[(Q$_F$)SnMe$_3$·(H$_2$O)]	25	+113
[(Q$_N$)Sn^{n}Bu$_3$·(H$_2$O)]	12	+139	[(Q$_M$)SnMe$_3$·(H$_2$O)]	23	+88
[(Q$_{Br}$)Sn^{n}Bu$_3$·(H$_2$O)]	13	+135	[(Q$_D$)SnMe$_3$·(H$_2$O)]	24	+89
[(Q")Sn^{n}Bu$_3$·(H$_2$O)]	14	+100			

[a] From external standard $SnMe_4$.

tions. We suggest that in solution these complexes dissociate in accordance with Eq. (5):

$$[(Q)SnR_3·(H_2O)] \xrightarrow{CHCl_3} (Q)SnR_3 + H_2O \qquad (5)$$
$$10\text{–}27$$

$(R = {}^nBu \text{ or } Me)$
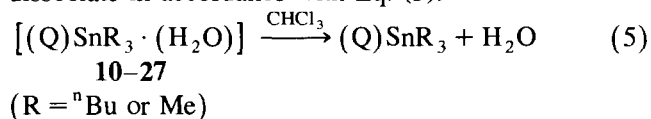
2.4. ^{119}Sn NMR spectra

The ^{119}Sn NMR data of derivatives 1–27 are reported in Table 6. All the compounds show only one resonance.

The ^{119}Sn NMR chemical shifts of complexes 1–9 are in the range −130 to −190 ppm, typical of cis-TBP triphenyltin derivatives [18a], while 10–27 are found to resonate in the range +90 to +150 ppm, typical of tetracoordinate tin complexes [18b,21,22]. This behavior could arise from the higher inductive electron-releasing character of methyl and butyl groups with respect to phenyl ones; the former probably weaken one Sn–O bond to a greater extent. This hypothesis is confirmed by instability and ease of disproportionation of compounds 10–27. Sometimes several absorptions are observed at −300 to −400 ppm: they have previously been attributed to triorganotin derivatives [8], whereas they are due to (Q)$_2$SnR$_2$ species [7], formed from (Q)SnR$_3$ by the disproportionation reaction (4).
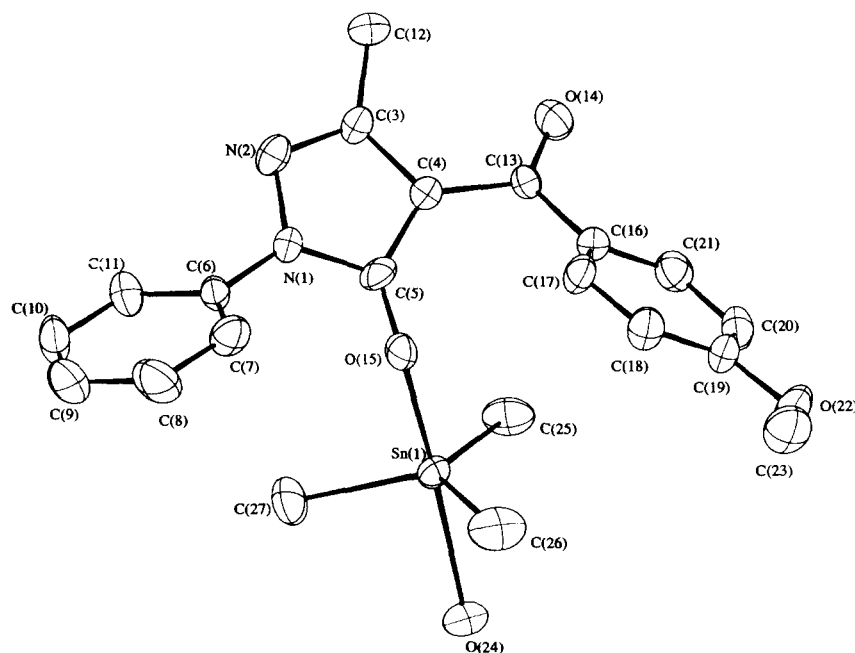

Fig. 4. Structure of [(Q$_A$)SnMe$_3$·(H$_2$O)] drawn with thermal ellipsoids at 50% probability.
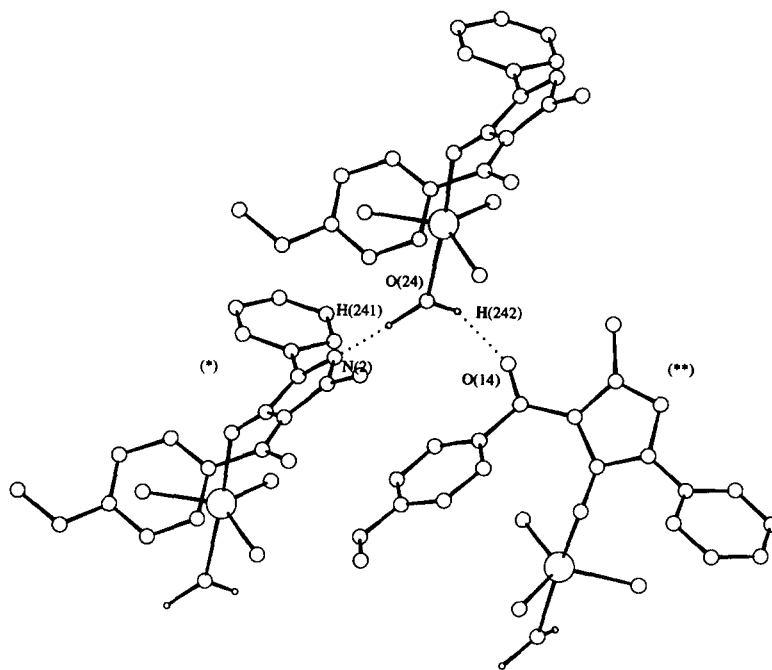
Fig. 5. View of the hydrogen bond network. Symmetry operator: (*) $-1 + x$, y, z; (**) $1/2 + x$, $1/2 - y$, z.

2.5. Crystal structure of $[(Q_A)SnMe_3 \cdot (H_2O)]$

The structure of the title compound is shown in Fig. 4 along with the atom labeling scheme used, while the intermolecular association through the hydrogen bond network is shown in Fig. 5. Interatomic distances and angles are reported in Tables 7 and 8 respectively. Atomic coordinates and isotropic thermal parameters are in Table 9 and crystal data are in Table 10. Least square planes and anisotropic thermal parameters are available as supplementary material. The tin atom is found in a distorted TBP environment, slightly deviated from the plane of the three equatorial methyl groups. The Sn(1)–C(27) is much longer (2.18(2) Å) with respect to the other two Sn–C bond distances (Sn(1)–C(26) is 2.11(1) Å and Sn(1)–C(25) is 2.08(2) Å). It is also the greatest Sn–C bond length between those reported in literature for trimethyltin(IV) derivatives [23]. The C(26)–Sn(1)–C(27) angle is 120.8(8)°, whereas the other two C–Sn–C angles are 123.8(10)° and 113.3(9)°.

The marked distortion from the ideal TBP geometry is probably due to steric hindrance of the 4-acyl-5-pyrazolonate ligand and to its different donor ability with respect to the water molecule: in fact the Sn(1)–O(15) is normal (2.10(1) Å), whereas the Sn(1)–O(24) is longer (2.41(2) Å); C–Sn–O(15) angles are higher than C–Sn–O(24) angles, because the O(15) atom exerts a higher repulsion on the methyls with respect to O(24).

The O(15)–Sn(1)–O(24) axis is bent to 174.8(5)° toward the edge C(26)–C(27) of the trigonal plane C(25)–C(26)–C(27).

The 4-acylpyrazolon-5-ato ligand acts in the monodentate form through the ring carbonyl oxygen atom. So far, this is the first example of crystal structure of triorganotin(IV) compounds containing a monodentate β-diketonate ligand. The different behavior of Q^- with respect to acetylacetonato ligands is due to its lower donor ability. This is in fact in accordance with crystallographic studies carried out on related $(Q)_2SnR_2$ complexes [7], where Sn–O bond distances are generally longer than those observed in analogous $(acac)_2SnR_2$ complexes [24].

Table 7
Interatomic distances (Å) with e.s.d.s in parentheses, for $[(Q_A)SnMe_3 \cdot (H_2O)]$

Sn–O(15)	2.10(1)	C(6)–C(7)	1.38(2)
Sn–O(24)	2.41(2)	C(6)–C(11)	1.40(2)
Sn–C(25)	2.11(1)	C(13)–C(16)	1.48(2)
Sn–C(26)	2.08(2)	C(16)–C(17)	1.36(2)
Sn–C(27)	2.18(2)	C(16)–C(21)	1.41(2)
O(14)–C(13)	1.22(2)	C(19)–C(18)	1.37(2)
O(15)–C(5)	1.23(2)	C(19)–C(20)	1.37(2)
O(22)–C(19)	1.38(2)	C(7)–C(8)	1.39(2)
O(22)–C(23)	1.47(2)	C(8)–C(9)	1.41(3)
N(1)–N(2)	1.37(2)	C(10)–C(11)	1.40(2)
N(1)–C(5)	1.36(2)	C(17)–C(18)	1.40(2)
N(1)–C(6)	1.41(2)	C(20)–C(21)	1.38(2)
N(2)–C(3)	1.34(2)	C(4)–C(13)	1.47(2)
C(3)–C(4)	1.42(2)	N(2)–H(241)(*)	1.76(2)
C(3)–C(12)	1.48(2)	O(14)–H(242)(**)	1.87(1)
C(4)–C(5)	1.45(2)		

(*) Equivalent position: $1 + x$, y, z. (**) Equivalent position: $1/2 + x$, $1/2 - y$, $-1 + z$.

Table 8

Bond angles (deg) with e.s.d.s in parentheses, for $[(Q_A)SnMe_3 \cdot (H_2O)]$

O(15)–Sn–O(24)	174.8(5)	O(15)–C(5)–C(4)	134.6(14)
O(15)–Sn–C(25)	100.8(8)	N(1)–C(5)–C(4)	102.7(12)
O(24)–Sn–C(25)	84.4(8)	N(1)–C(6)–C(7)	120.4(11)
O(15)–Sn–C(26)	90.9(7)	N(1)–C(6)–C(11)	119.1(13)
O(24)–Sn–C(26)	85.8(6)	C(7)–C(6)–C(11)	120.5(13)
C(25)–Sn–C(26)	123.8(10)	O(14)–C(13)–C(4)	119.7(14)
O(15)–Sn–C(27)	92.9(7)	O(14)–C(13)–C(16)	120.1(13)
O(24)–Sn–C(27)	85.4(7)	C(4)–C(13)–C(16)	120.2(12)
C(25)–Sn–C(27)	113.3(9)	C(13)–C(16)–C(17)	121.6(13)
C(26)–Sn–C(27)	120.8(8)	C(19)–C(18)–C(17)	117.9(14)
Sn–O(15)–C(5)	136.5(11)	C(19)–C(20)–C(21)	119.4(16)
C(19)–O(22)–C(23)	117.2(12)	C(16)–C(21)–C(20)	119.1(15)
N(2)–N(1)–C(5)	115.1(10)	C(17)–C(16)–C(21)	119.9(13)
N(2)–N(1)–C(6)	119.0(10)	C(13)–C(16)–C(21)	118.4(14)
C(5)–N(1)–C(6)	124.7(11)	C(18)–C(19)–C(20)	122.3(14)
N(1)–N(2)–C(3)	104.9(10)	O(22)–C(19)–C(18)	122.6(13)
N(2)–C(3)–C(4)	111.2(11)	O(22)–C(19)–C(20)	115.1(13)
N(2)–C(3)–C(12)	120.8(12)	C(6)–C(11)–C(10)	118.4(17)
C(4)–C(3)–C(12)	127.9(12)	C(6)–C(7)–C(8)	120.2(15)
C(3)–C(4)–C(5)	106.0(11)	C(7)–C(8)–C(9)	119.1(19)
C(3)–C(4)–C(13)	126.4(12)	C(8)–C(9)–C(10)	120.3(16)
C(5)–C(4)–C(13)	127.6(12)	C(9)–C(10)–C(11)	121.5(17)
O(15)–C(5)–N(1)	122.6(12)	C(16)–C(17)–C(18)	121.2(13)

Table 9

Atomic coordinates and isotropic equivalent thermal parameters (with e.s.d. in parentheses) for non-hydrogen atoms of $[(Q_A)SnMe_3 \cdot (H_2O)]$

Atom	x	y	z	U_{eq} [a] (Å^2)
Sn(1)	0.6665(3)	0.11460(3)	0.6642(2)	0.0398(2)
O(14)	0.981(1)	0.2875(6)	0.434(1)	0.063(4)
O(15)	0.844(1)	0.0983(6)	0.576(1)	0.053(4)
O(22)	0.423(1)	0.1693(6)	0.192(1)	0.072(4)
N(1)	1.077(1)	0.0971(5)	0.6335(9)	0.042(3)
N(2)	1.197(1)	0.1321(5)	0.6236(9)	0.045(3)
C(3)	1.156(1)	0.1859(6)	0.561(1)	0.043(4)
C(4)	1.012(1)	0.1834(7)	0.523(1)	0.045(4)
C(5)	0.960(2)	0.1238(7)	0.575(1)	0.045(6)
C(6)	1.086(1)	0.0325(6)	0.682(1)	0.046(4)
C(13)	0.933(1)	0.2317(7)	0.446(1)	0.045(4)
C(16)	0.799(1)	0.2122(8)	0.381(1)	0.044(5)
C(19)	0.551(1)	0.1811(7)	0.255(1)	0.051(4)
O(24)	0.459(2)	0.1224(5)	0.765(1)	0.049(4)
C(7)	1.024(1)	− 0.0206(7)	0.621(1)	0.056(5)
C(8)	1.037(2)	− 0.0847(9)	0.667(2)	0.082(7)
C(9)	1.115(2)	− 0.094(1)	0.776(2)	0.090(8)
C(10)	1.176(2)	− 0.043(1)	0.835(2)	0.082(7)
C(11)	1.163(2)	0.226(9)	0.790(1)	0.066(5)
C(12)	1.259(2)	0.237(1)	0.534(2)	0.065(6)
C(17)	0.778(1)	0.1503(7)	0.335(1)	0.053(4)
C(18)	0.654(2)	0.1335(8)	0.269(1)	0.060(5)
C(20)	0.566(2)	0.2430(9)	0.305(1)	0.055(5)
C(21)	0.691(2)	0.2601(7)	0.367(1)	0.055(5)
C(23)	0.407(2)	0.1065(8)	0.126(2)	0.077(7)
C(25)	0.661(3)	0.2200(6)	0.668(2)	0.064(5)
C(26)	0.546(2)	0.057(1)	0.542(2)	0.074(7)
C(27)	0.763(2)	0.071(1)	0.826(1)	0.072(7)

[a] U_{eq} is defined as the mean of the principal axes of the thermal ellipsoid.

Table 10

Data collection and refinement of the structure of $[(Q_A)SnMe_3 \cdot (H_2O)]$.

Formula	$C_{21}H_{26}N_2O_4Sn$
Formula weight	489.137
Space group	Cc
a (Å)	9.644(5)
b (Å)	29.058(7)
c (Å)	11.503(4)
β (deg)	95.77(5)
V_c (Å^3)	2213.84(1.56)
Z	4
D_c (g cm^{-3})	1.4675
μ(Mo K α) (cm^{-1})	96.156
$F(000)$	992.0
Radiation (monochromated)	Cu K α(λ = 1.5406 Å)
T of data collection (K)	293
Scan mode	$\omega - 2\theta$
Scan width (deg)	$\Delta\omega = A + B \tan(\theta)$, $A = 1260°$, $B = 0.30°$
Scan speed max. (deg min^{-1})	32
Background/scan ratio	0.5
Data collection range (deg)	$5 \leq 2\theta \leq 124$
Standards (measured every 97 reflections)	− 1, 1, − 1 − 1, 3, 0 − 2, 0, 2
No. of unique reflections measured	1799
No. of data with $I > 3\sigma(I)$	1690
Refinement	Full-matrix least squares on F
No. of parameters refined	254
R [a]	0.054
R_w [b]	0.061
S [c] (Godness of fit)	1.04

[a] $R = (\Sigma||F_o| - k|F_c||)/\Sigma|F_o|$.
[b] $R_w = [\Sigma_w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
[c] $S = [\Sigma_w(|F_o| - k|F_c|)^2/(N_{obs} - N_{par})]^{1/2}$.

In the title compound the planarity between the phenyl ring and the heterocyclic ring of pyrazolone, previously observed in $(Q)_2SnR_2$ [7], is absent.

Fig. 5 shows the H-bond network, involving the hydrogens of water, the chain carbonyl and the pyridinic N(2) atom of the Q^- ligands of two different asymmetric units. The H-bond contacts are O(14)–H(242) = 1.87(1) Å and N(2)–H(241) = 1.76(2) Å and the H(241)–O(24)–H(242) is 125.6(10)°.

3. Conclusions

On the basis of analytical and spectral (IR and NMR) data, we suggest that in $(Q)SnPh_3$ derivatives 1–9 the ligand (Q^-) coordinates through both the carbonyl groups, with the tin in a cis-TBP environment, similar to that found in $Ph_3Sn(bzac)$ [10]. The tributyl and trimethyltin(IV) derivatives rapidly absorb a molecule of water when exposed to atmosphere, adopting a distorted trans-TBP configuration. In these complexes the Q^- ligand acts in the monodentate anionic O-donor form and a molecule of water is coordinated to tin. In chloroform solution the derivatives 10–27 lose the water and adopt a tetracoordinated geometry. Subsequently they easily undergo the disproportionation reaction (4).

4. Experimental

The reactions were carried out under N_2 stream using Schlenk techniques. Solvents were dried by standard techniques. The samples were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in house with a Carlo-Erba Strumentazione 1106 instrument. IR spectra from 4000 to 100 cm^{-1} were recorded with a Perkin–Elmer 2000 FT-IR instrument. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Proton and carbon and tin chemical shifts are reported in ppm vs. Me_4Si and Me_4Sn respectively. The tin spectra were run with a spectral width of 1000 ppm, and the chemical shifts were checked for aliasing by varying the center of the window. Each tin spectrum was acquired in ca. 1/2 h (ca. 300 transients). Melting points were measured with an IA 8100 Electrothermal instrument. The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

4.1. Reagents

The ligands $Q'H$, Q_AH, $Q_{Br}H$, Q_NH, $Q''H$, $Q_{Cl}H$, Q_FH, Q_MH and Q_DH were prepared by the published methods [5]. All the other chemicals were analytical reagent grade.

4.2. Syntheses of the complexes

4.2.1. [Aquotrimethyl(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)tin(IV)], [(Q')SnMe₃ · (H₂O)], 19

Compound 19 was prepared with the following procedure. A benzene solution (30 cm³) of the ligand Q'H (1.0 mmol, 278 mg) was added to a methanolic solution (10 cm³) of sodium methoxide (1.0 mmol, 54 mg) and refluxed for 1 h. A benzene solution (20 cm³) of Me_3SnCl (1.0 mmol, 199 mg) was then added to the above solution drop by drop and the reaction mixture was stirred at room temperature for about 3 h. Sodium chloride was filtered off and the solvent removed under reduced pressure on a rotary evaporator until a thick oil was obtained. This was treated with diethyl ether and light petroleum, and a pale yellow solid afforded. This was recrystallized from toluene–petroleum ether mixture and shown to be compound 19. Compounds 1–18 and 20–27 were obtained similarly. An alternative synthesis can also be used.

4.2.2. [Triphenyl(1-phenyl-3-methyl-4-benzoyl-pyrazolon-5-ato)tin(IV)], [(Q')SnPh₃], 1

A benzene solution (30 cm³) of $(Ph_3Sn)_2O$ (1.0 mmol, 716 mg) was added to a benzene solution (30 cm³) of the ligand Q'H (2.0 mmol, 556 mg), and the reaction mixture was refluxed for about 3 h. After removing the solvent under reduced pressure on a rotary evaporator, a thick oil was obtained. This was treated with diethyl ether and petroleum ether, and a pale yellow solid afforded. This was recrystallized from benzene–petroleum ether mixture and shown to be compound 1.

4.3. Crystallographic study of [(Q₄)SnMe₃ · (H₂O)]

Crystals of the compound were grown from a chloroform solution by slow evaporation. A colorless crystal, of approximate dimensions $0.50 \times 0.30 \times 0.30$ mm³, was mounted on a Rigaku AFC5 automatic four circle diffractometer equipped with a Rigaku rotating anode (45 kV, 100 mA). The crystal system was found to be monoclinic, and accurate cell parameters were obtained by least squares refinement of 40 reflections with $35 \leq 2\theta \leq 80°$; the space group was found to be Cc.

1919 reflections were collected with $0 \leq h \leq 11$, $0 \leq k \leq 23$ and $-13 \leq l \leq 13$; no decay was observed during the data collection. The ψ-scan of three different reflections (021, 042, 063) gave a minimum and maximum transmission factor equal to 0.86 and 1.00; the data were then corrected for the absorption by using a semi-empirical method [25].

The structure was solved by direct methods using the SIR92 program [26], six of the 28 non-hydrogen atoms in the asymmetric unit were found at this level, that is the tin atom and its five first neighbours.

The other non-hydrogen atoms were located by means of a Fourier difference map, performed by using the CRYSTALS package [27] and an isotropic refinement of these atoms gave an R equal to 0.086. Along with the refinement, a test was performed in order to choose the correct absolute structure for the molecule, refining the Flack parameter [28] along with all the other parameters, starting from values of 0 and 1 and converging in both cases to the values of 0.1 (0.03), without applying the Friedels law and including the anomalous scattering correction. At this stage the hydrogens were imposed by model with $d = 1.06$ Å. The structure was then anisotropically refined with the hydrogens refined as riding (U_{iso} were fixed at 20% greater than the bonded atoms) giving an R equal to 0.061. A final refinement was performed after an optimization of the weighting scheme [29–31], where a third order optimized truncated Cheybishev polynomial with coefficients $a_1 = 4.40$, $a_2 = -0.205$, $a_3 = 2.68$, was employed [31], refining the extinction parameter as well.

The R factor was equal to 0.054 at the end of the last refinement cycle, with a maximum r.m.s. shift equal to 0.175.

All the refinements were done taking account of the anomalous scattering contributions; the scattering factors and the anomalous contributions were taken from the *International Tables for Crystallography* [32]. All the calculations were carried out on a personal computer; the program PARST [33] has been used for some geometrical calculations.

Acknowledgements

References

[1] A.G. Davies and P.J. Smith, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 2, Pergamon Press, Oxford, 1982, pp. 519–627.

[2] (a) G.J.M. van der Kerk and J.G.A. Luijten, *J. Appl. Chem.*, 4 (1954) 314; (b) G.J.M. van der Kerk and J.G.A. Luijten, *J. Appl. Chem.*, 6 (1956) 56.

[3] (a) G. Domazetis, R.J. Magee and B.D. James, *J. Organomet. Chem.*, 141 (1977) 57; (b) G. Domazetis, R.J. Magee and B.D. James, *Inorg. Chim. Acta*, 32 (1979) L48; (c) K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckermann and I. Haiduc, *Inorg. Chem.*, 18 (1979) 3507; (d) A.J. Pieters, *Proc. British Insecticides and Fungicides Conf., Brighton, November, 1961*.

[4] S.J. Bluden, P.J. Smith and B. Sugavanam, *Pestic. Sci.*, 15 (1984) 253.

[5] (a) B.S. Jensen, *Acta Chem. Scand.*, 13 (1959) 1347, 1668, 1890; (b) S. Miyazaki, H. Mukai, S. Umetani, S. Kihara and M. Matsui, *Inorg. Chem.*, 28 (1989) 3014 and references cited therein; (c) R. Morales, H. Nekimken, C.S. Bartholdi and P.T. Cunningham, *Spectrochim. Acta A*, 44 (1988) 165 and references cited therein; (d) M.Y. Mirza and R.T. Bailey, *J. Inorg. Nucl. Chem.*, 42 (1979) 772; (e) M.Y. Mirza and F.J. Nwabue, *Talanta*, 28 (1981) 53; (f) F. Bonati, L.A. Oro and M.T. Pinillos, *Polyhedron*, 4 (1985) 357 and references cited therein; (g) M.S. Nagar, P.B. Ruikar and M.S. Subramanian, *Polyhedron*, 6 (1987) 1913; (h) E.C. Okafor and B.A. Uzoukwu, *Synth. React. Inorg. Met. Org. Chem.*, 23 (1993) 97 and references cited therein; (i) E.C. Okafor, B.A. Uzoukwu, *Synth. React. Inorg. Met. Org. Chem.*, 23 (1993) 85.

[6] J. Elguero, Pyrazoles and their benzoderivatives, in A.R. Katritzky (ed.), *Comprehensive Heterocyclic Chemistry*, Pergamon Press, UK, 1984, Chapter 4, para. 4.04.4.

[7] (a) C. Pettinari, G. Rafaiani, G. Gioia Lobbia, A. Lorenzotti, F. Bonati and B. Bovio, *J. Organomet. Chem.*, 405 (1991) 75; (b) C. Pettinari, F. Bonati, A. Cingolani, G. Gioia Lobbia and F. Marchetti, *Gazz. Chim. Ital.*, 122 (1992) 261; (c) B. Bovio, A. Cingolani, F. Marchetti and C. Pettinari, *J. Organomet. Chem.*, 458 (1993) 39; (d) F. Marchetti, C. Pettinari, A. Cingolani and D. Leonesi, *Synth. React. Inorg. Met. Org. Chem.*, 23 (1993) 1485; (e) C. Pettinari, F. Marchetti, A. Cingolani, C. Marciante, R. Spagna and M. Colapietro, *Polyhedron*, 13 (1994) 939; (f) C. Pettinari, F. Marchetti, D. Leonesi, M. Rossi and F. Caruso, *J. Organomet. Chem.*, 483 (1994) 123.

[8] A. Jain, S. Saxena and A.K. Rai, *Ind. J. Chem. A*, 30 (1991) 881.

[9] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, 16 (1985) 73.

[10] G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham, *J. Chem. Soc. Dalton Trans.*, (1975) 973.

[11] P.W. Thompson and J.F. Lefelhocz, *J. Organomet. Chem.*, 47 (1973) 103.

[12] K. Kawakami and R. Okawara, *J. Organomet. Chem.*, 6 (1966) 249.

[13] (a) R.C. Mehrotra, R. Bohra and D.P. Gaur, *Metal β-Diketonates and Allied Derivatives*, Academic Press, London, 1978, Chapter 2, and references cited therein; (b) K. Nakamoto, C. Udovich and J. Takemoto, *J. Am. Chem. Soc.*, 92 (1970) 3973, and references cited therein.

[14] (a) J.R. May, W.R. McWhinnie and R.C. Poller, *Spectrochim. Acta A*, 27 (1971) 969; (b) A.L. Smith, *Spectrochim. Acta A*, 24 (1967) 695; (c) M.S. Dance, W.R. McWhinnie and R.C. Poller, *J. Chem. Soc. Dalton Trans.*, (1976) 2349; (d) D.H. Whiffen, *J. Chem. Soc.*, (1956) 1350.

[15] (a) R.C. Poller, *J. Inorg. Nucl. Chem.*, 24 (1962) 593; (b) V.S. Griffith and G.A.W. Derwish, *J. Mol. Spectrosc.*, 2 (1960) 148.

[16] (a) B.Y.K. Ho and J.J. Zuckermann, *Inorg. Chem.*, 12 (1973) 1552; (b) R. Okawara, D.E. Webster and E.G. Rochow, *J. Am. Chem. Soc.*, 82 (1960) 3287.

[17] G.K. Sandhu, G. Kaur, J. Holecek and A. Lycka, *J. Organomet. Chem.*, 345 (1988) 51.

[18] (a) J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem.*, 241 (1983) 177; (b) M. Nadvornik, J. Holecek, K. Handlir and A. Lycka, *J. Organomet. Chem.*, 275 (1984) 43; (c) S. Weng Ng and V.G. Kumar Das, *J. Organomet. Chem.*, 409 (1991) 143; (d) B.D. James, S. Gioskos, S. Chandra, R.J. Magee and J.D. Cashion, *J. Organomet. Chem.*, 436 (1992) 155.

[19] T.P. Lockhart and W.F. Manders, *Inorg. Chem.*, 25 (1986) 892.

[20] J. Holecek and A. Lycka, *Inorg. Chim. Acta*, 118 (1986) L15.

[21] (a) J. Klein, F. Thunecke and R. Borsdorf, *Fresenius J. Anal. Chem.*, 346 (1993) 789; (b) C.H. Yoder, R.A. Morreall, C.I.

Butoi, W.J. Kowalski and J.N. Spencer, J. Organomet. Chem., 448 (1993) 59.

[22] (a) D. Daktemieks, H. Zhu, D. Masi and C. Mealli, Inorg. Chem., 31 (1992) 3601 and references cited therein; (b) R. Kappor, V. Sood and P. Kapoor, Polyhedron, 14 (1995) 489 and references cited therein; (c) F. Huber, M. Vornefeld, G. Ruisi and R. Barbieri, Appl. Organomet. Chem., 7 (1993) 243 and references cited therein..

[23] (a) R. Hulme, J. Chem. Soc., (1963) 1524; (b) J. Buckle, P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc. Chem. Commun., (1972) 1104; (c) B.Y.K. Ho and J.J. Zuckermann, J. Organomet. Chem., 49 (1973) 1; (d) N.W. Alcock and R.E. Timms, J. Chem. Soc. A, (1968) 1873; (e) P.G. Harrison, R.C. Phillips and J.R. Richards, J. Organomet. Chem., 114 (1976) 47; (f) T.J. King and P.G. Harrison, J. Chem. Soc. Chem. Commun., (1972) 815; (g) I.E. Khoo, J.-P. Charland, E.J. Gabe and F.E. Smith, Inorg. Chim. Acta, 128 (1987) 139; (h) K.C. Molloy, M.F. Mahon, I. Haiduc and C. Silvestru, Polyhedron, 14 (1995) 1169; (i) S.-G. Teoh, G.-Y. Yeap, S.-B. Teo and H.-K. Fun, Polyhedron, 14 (1995) 1051.

[24] (a) G.A. Miller and E.O. Schlemper, Inorg. Chem., 12 (1973) 677; (b) G. Poli, C.J. Cheer and W.H. Nelson, J. Organomet. Chem., 305 (1986) 347.

[25] A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Crystallogr. Sect. A:, 24 (1968) 351.

[26] A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 26 (1993) 343.

[27] D.J. Watkin, J.R. Carruthers and P.W. Bettridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985.

[28] H.D. Flack, Acta Crystallogr. Sect. A:, 39 (1983) 876.

[29] J.R. Carruthers and D.J. Watkin, Acta Crystallogr. Sect. A:, 35 (1979) 698.

[30] D.J. Watkin, Acta Crystallogr. Sect. A:, 50 (1994) 411.

[31] E. Prince and P.T. Boggs, in A.J.C. Wilson (ed.), International Tables for Crystallography, Vol. C, Kluwer, Dodrecht, 1992.

[32] A.C. Larson, in F.R. Ahmed, S.R. Hall and C.P. Huber (eds.), Crystallographic Computing, Munksgaard, Copenaghen, 1970, p. 291.

[33] M. Nardelli, Comput. Chem., 7 (1983) 95.