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PREPARATION AND SPECTROSCOPIC STUDIES OF TRI(*p*-TOLYL)-TIN(IV) COMPOUNDS. X-RAY CRYSTAL STRUCTURE OF THE QUINOLINE-*N*-OXIDE ADDUCT OF TRI(*p*-TOLYL)TIN(IV) BROMIDE

V.G. KUMAR DAS*, YAP CHEE KEONG, NG SEIK WENG, CHEN WEI
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)

and THOMAS C.W. MAK*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)

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Summary

Syntheses and spectroscopic data are presented for R_3Sn^{IV} compounds, where R is predominantly *p*-tolyl, of the following types: $R_3SnX \cdot L$ (X = Cl, Br or NCS; L = neutral, monodentate oxygen donor), R_3SnY (YH = 1,2,4-triazole, *N*-phenyl-*N*-benzoylhydroxamic, succinanilic, levulinic and hippuric acids) and $[R_3SnL_2]^+[Ph_4B]^-$ (L = neutral, monodentate or 1/2 bidentate oxygen donor). The spectroscopic data (IR and Mössbauer) are interpreted in terms of discrete or weakly polymeric trigonal bipyramidal structures, with the R_3Sn skeleton forming the equatorial plane for most of the compounds. A *cis*-geometry is inferred for the case where the anionic residue is the chelating *N*-phenyl-*N*-benzoylhydroxamate ligand, while a *meridional* geometry is predicted for the cationic complexes involving the chelating ligands, 2,2′-bipyridine *N,N′*-dioxide and ethylenebis(diphenylphosphine oxide). Both the ^{13}C NMR and the IR data suggest that the Lewis acceptor strength falls in the order $(p\text{-}ClC_6H_4)_3Sn > (C_6H_5)_3Sn \geq (p\text{-}MeC_6H_4)_3Sn$. Crystals of (*p*-tolyl)$_3$SnBr · quinoline-*N*-oxide are triclinic, space group $P\bar{1}$, with *a* 10.245(4), *b* 10.862(2), *c* 13.153(5) Å, α 84.10(2), β 68.39(3), and γ 80.88(3)°. The structure was refined to $R = 0.070$ for 4548 observed Mo-K_α reflections and comprises independent, non-interacting molecules which are pentacoordinate at tin. The quinoline-*N*-oxide ligand is coordinated apically to tin in the trigonal-bipyramidal unit; the three tolyl rings occupy the trigonal plane but the tin atom is displaced by 0.17(1) Å towards the other apical bromide ligand.

Introduction

Our recent investigations on the structural chemistry of phenyltin(IV) compounds have focused on the effects of substituents on the phenyl ring and on

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heteroaryl ligand groups additionally linked to the metal via carbon or the heteroatom. Thus, $(p\text{-tolyl})_2SnCl_2 \cdot$ bipy was shown to adopt a *cis*-$[SnR_2]$ octahedral configuration [1] as opposed to the *trans*-structure generally observed for the chelate adducts of diphenyl- and dialkyltin dihalides [2,3], and the much sought-after pair of *cis/trans* isomers in octahedral diorganotin(IV) dihalide complexes was isolated [4] and crystallographically characterized [5] for the first time in the case of $(p\text{-}ClC_6H_4)_2SnCl_2 \cdot$ 4,4′-dimethyl-2,2′-bipyridine. More recently, we added to this list, with crystallographic substantiation, the first example of a six-coordinate tetraorganotin compound in bis{*C*,*N*-[3-(2-pyridyl)-2-thienyl]}diphenyltin(IV) [6].

In an extension of this work into pentacoordination at tin, we now report the synthesis and spectroscopic properties of several tri(*p*-tolyl)tin compounds and, for comparison, those of a limited range of other analogous triorganotin derivatives. The tri(*p*-tolyl)tin compounds, in common with their triphenyltin analogues [7], possess high biological activity and relatively low mammalian toxicity, and their potency as larvicides against the mosquito, *Aedes aegypti* (L), has been described [8]. Accumulated results from our laboratories [9] and elsewhere [10] indicate that although contributions to the overall toxicity of R_3SnX compounds by the anionic residue, X, on tin are generally negligible in comparison with those of the organic R groups [7], they may be appreciable in certain species-dependent cases. Our continuing interest in structure-activity studies has also prompted the work described herein on the combination of the tri(*p*-tolyl)tin moiety with various anionic and neutral ligand groups. Spectral techniques, especially Mössbauer spectroscopy (for a discussion of the Mössbauer spectral parameters in triorganotin systems, see references 11 and 12), have been used to establish the structures of the resulting compounds. In one particular case, viz. the adduct of $(p\text{-tolyl})_3SnBr$ with quinoline-*N*-oxide (QuinO), the structure was confirmed by a single crystal X-ray study.

Experimental section

Tri(*p*-tolyl)tin(IV) chloride was prepared by comproportionation of tetra-*p*-tolyltin and tin tetrachloride in 70% yield, m.p. 98–99°C (Lit: 98°C [13]). Tri(*p*-chlorophenyl)tin(IV) chloride was similarly prepared in 75% yield, m.p. 109–110°C (Lit: 109–110°C [14]). Tri(*p*-tolyl)tin(IV) isothiocyanate was prepared from the corresponding chloride by metathetical reaction with KSCN in acetone. The product, obtained in 70% yield, was recrystallised from toluene, m.p. 133–134°C (Lit: 128°C [15]).

Tri(*p*-tolyl)tin hydroxide, m.p. 108–109°C, was prepared by vigorously stirring an ethereal solution of tri(*p*-tolyl)tin chloride with 5 *M* aqueous NaOH. Upon work-up, the ether layer yielded the crude hydroxide, which was recrystallized from ethanol (65% yield). The hydroxide was readily converted into the bis-oxide, $[(p\text{-tolyl})_3Sn]_2O$, m.p. 106–107°C (Lit: m.p. 106–107.5°C [16]), when placed under vacuum. Bis[tri(*p*-chlorophenyl)tin] oxide, m.p. 121–123°C, was prepared as previously described [16]. Tri(*p*-tolyl)tin(IV) bromide was obtained by treating an ethereal solution of the corresponding hydroxide with 20% aqueous HBr in ether. Recrystallization from petroleum ether (60–80°C) gave a 60% yield of the product, m.p. 96–98°C. Dimethyl(*p*-tolyl)tin bromide was obtained in low yield (35%) as an oil by controlled bromination of a DMF solution of $Me_2Sn(p\text{-tolyl})_2$ at 0°C. Purification was achieved by column chromatography on silica gel with

hexane/acetone (10/1 v/v) mixture as eluant. Other organotin compounds used were commercial products. Quinoline-*N*-oxide and pyridine-*N*-oxide were prepared from the corresponding amines by literature methods [17]. DiphosO_2 ($Ph_2P(O)$-$CH_2CH_2P(O)Ph_2$) was prepared from 1,2-bis(diphenylphosphino)ethane as previously described [18]. Succinanilic acid, $PhNHC(O)(CH_2)_2CO_2H$, was synthesized from succinic anhydride and aniline, duplicating the method of Vogel [19]. All other ligands were commercial samples which were used without further purification.

Preparation of complexes

These were prepared by similar methods; the following syntheses are representative.

(p-Tolyl)$_3$SnBr · quinoline-N-oxide. To a solution of (p-tolyl)$_3$SnBr (2.00 g) in $CHCl_3$ was added a solution of quinoline-*N*-oxide (0.77 g) in $CHCl_3$. Concentration of the resulting solution to a small volume followed by addition of petroleum ether (60–80°C) to turbidity yielded a white solid, 2.10 g (80% yield), m.p. 133–134°C. Needle-like crystals of the adduct, suitable for X-ray analysis, were obtained by slow evaporation of a solution of the compound in chloroform/hexane.

(p-Tolyl)$_3$SnCl · (Me$_2$N)$_3$PO. The organotin halide was heated in the presence of a slight excess of HMPA and the solution subsequently chilled. Addition of a few drops of petroleum ether (60–80°C) resulted in a slow precipitation of the product, which was filtered off and washed with further amounts of petroleum ether; yield 70%.

[(p-Tolyl)$_3$Sn(diphosO$_2$)]$^+$[Ph$_4$B]$^-$. 0.30 g (p-Tolyl)$_3$SnCl in ethanol was added to a warm ethanol solution containing 0.30 g diphosO_2 and 0.24 g $Na[BPh_4]$. Dropwise addition of water with stirring caused precipitation of the cationic complex in 60% yield.

[(p-Tolyl)$_3$SnBrCl]$^-$[Ph$_3$PMe]$^+$. Separate solutions of 0.50 g of (p-tolyl)$_3$SnCl and 0.42 g of $[Ph_3PMe]Br$ in i-propanol were warmed then mixed. Immediate precipitation of the anionic complex (0.63 g) occurred. A further crop was obtained by concentration of the mother liquor.

Preparation of ester and other derivatives

(p-Tolyl)$_3$Sn succinanilate. An equimolar mixture of tri(p-tolyl)tin hydroxide (2.00 g) and succinalinic acid (0.97 g) was refluxed in toluene with a Dean and Stark trap to remove the water liberated. Work-up of the solution yielded 2.40 g (80% yield) of the product, which was recrystallized from $CHCl_3$.

The hippurate and levulinate esters were similarly prepared. In the case of tri(n-butyl)tin levulinate, TBTO (6.00 g, 10 mmol) was added to 2 ml (20 mmol) of levulinic acid, $CH_3C(O)(CH_2)_2CO_2H$, to give the solid ester in 80% yield.

The compound, bis[tri(p-tolyl)tin] sulphide, was prepared by the method previously described for the corresponding trialkyltin derivatives [20], while tri(p-tolyl)tin *N*-phenyl-*N*-benzoylhydroxamate and 1-[tri(p-tolyl)tin]-1,2,4-triazole were synthesized by methods similar to those used for analogous triphenyltin compounds [21,22].

The compounds prepared, their microanalytical data (Australian Microanalytical Service, Melbourne, and Microanalytical Service, University College, London (UK)) and decomposition points (uncorrected) are listed in Table 1.

TABLE 1

ANALYTICAL DATA[a] FOR TRI(*p*-TOLYL)TIN COMPOUNDS AND SOME RELATED ARYL AND ALKYLTIN DERIVATIVES

Compound[b]	M.p.[c] (°C)	%C	%H	%N
$(p\text{-tolyl})_3SnCl\cdot Ph_3PO$	126–128	65.42(66.38)	4.75 (5.11)	
$(p\text{-tolyl})_3Sn(NCS)\cdot Ph_3PO$	136–137	66.05(65.97)	4.95 (4.95)	1.78 (1.92)
$(p\text{-tolyl})SnMe_2Br\cdot Ph_3PO$	125–127	54.70(54.23)	5.08 (4.69)	
$(p\text{-}ClC_6H_4)_3SnCl\cdot Ph_3PO$	153–154	55.09(56.36)	3.44 (3.52)	
$(p\text{-tolyl})_3SnBr\cdot QuinO$	133–134	58.89(58.39)	4.48 (4.54)	2.23 (2.27)
$(p\text{-}ClC_6H_4)_3SnCl\cdot QuinO$	159–161	51.10(51.14)	2.88 (2.99)	2.06 (2.21)
$Ph_2SnBuBr\cdot QuinO$	103–104	54.35(54.10)	4.61 (4.69)	2.63 (2.53)
$Ph_3SnCl\cdot QuinO$	160–162	60.99(61.11)	4.13 (4.15)	2.64 (2.64)
$(p\text{-tolyl})_3SnCl\cdot DMSO$	86– 88	55.05(54.64)	5.30 (5.34)	
$(p\text{-tolyl})_3Sn(NCS)\cdot DMSO$	138–140	54.35(54.59)	5.29 (5.12)	2.79 (2.65)
$(p\text{-}ClC_6H_4)_3SnCl\cdot DMSO$	120–122	42.54(42.36)	3.11 (3.18)	
$(p\text{-tolyl})_3SnCl\cdot HMPA$	133–134	51.02(53.46)	6.02 (6.43)	6.67 (6.93)
$(p\text{-tolyl})_3Sn(NCS)\cdot HMPA$	168–170	53.10(53.45)	6.27 (6.20)	9.08 (8.91)
$(p\text{-}ClC_6H_4)_3SnCl\cdot HMPA$	174–176	43.96(43.14)	4.65 (4.49)	6.40 (6.29)
$(p\text{-tolyl})_3SnBr\cdot PyO$	124–125	55.87(55.08)	4.74 (4.59)	2.08 (2.47)
$(p\text{-tolyl})_3SnCl\cdot Ph_3AsO$	185–187	62.15(62.46)	4.81 (4.81)	
$[(p\text{-tolyl})_3SnBrCl]^-[Ph_3PMe]^+$	186–188	61.46(61.22)	5.00 (4.97)	
$[(p\text{-tolyl})_3Sn(diphosO_2)]^+[Ph_4B]^-$	228–230	74.35(74.71)	5.82 (5.70)	
$[(p\text{-tolyl})_3Sn(Ph_3PO)_2]^+[Ph_4B]^-$	153–155	76.25 (76.75)	5.54 (5.61)	
$[(p\text{-tolyl})_3Sn(Ph_3AsO)_2]^+[Ph_4B]^-$	192–194	71.66(71.78)	5.45 (5.24)	
$[(p\text{-tolyl})_3Sn(DMSO)_2]^+[Ph_4B]^-$	151–153	67.71(67.85)	6.22 (6.12)	
$[(p\text{-tolyl})_3Sn(bipyO_2)]^+[Ph_4B]^-$	130–132	71.58(73.45)	5.59 (5.45)	2.50 (3.11)
$(p\text{-tolyl})_3SnON(Ph)COPh$	55– 57	67.24(67.59)	5.43 (5.14)	2.09 (2.32)
$(p\text{-tolyl})_3Sn(1,2,4\text{-triazole})$	304–306	60.24(60.05)	5.24 (5.00)	8.96 (9.1)
$[(p\text{-tolyl})_3Sn]_2S$	143–144	59.76(61.87)	5.05 (5.15)	
$Ph_3SnOC(O)CH_2N(H)C(O)Ph$	163–164	59.12(59.39)	4.74 (4.73)	
$(p\text{-tolyl})_3SnOC(O)CH_2$ N(H)C(O)Ph	> 280[d]	60.91(63.20)	4.99 (5.09)	2.76 (2.46)
$(p\text{-}ClC_6H_4)_3SnOC(O)CH_2$ N(H)C(O)Ph	108–111	51.23(51.34)	3.33 (3.17)	2.11 (2.22)
$Bu_3SnOC(O)CH_2N(H)C(O)Ph$	semi-solid[e]	52.59(53.08)	7.32 (7.48)	3.12 (3.01)
$Ph_3SnOC(O)CH_2CH_2C(O)N(H)Ph$	138–140	60.06(61.40)	4.46 (4.36)	2.63 (2.66)
$Cyh_3SnOC(O)CH_2CH_2C(O)N(H)Ph$	155–157	59.90(60.03)	7.76(7.68)	2.40 (2.50)
$(p\text{-tolyl})_3SnOC(O)CH_2CH_2$ C(O)N(H)Ph	132–134	62.49(63.74)	5.29 (5.31)	2.58 (2.40)
$(p\text{-}ClC_6H_4)_3SnOC(O)CH_2$ $CH_2C(O)N(H)Ph$	> 300	53.16(52.09)	3.61 (3.14)	2.24 (2.17)
$Bu_3SnOC(O)CH_2CH_2$ C(O)N(H)Ph	oil	54.39(54.81)	7.62 (7.68)	2.95 (2.91)
$Ph_3SnOC(O)CH_2C(O)CH_3$	133–134	58.42(58.49)	4.10 (4.06)	
$Cyh_3SnOC(O)CH_2CH_2C(O)CH_3$	semi-solid	56.91(57.18)	8.14 (8.27)	
$(p\text{-}ClC_6H_4)_3SnOC(O)CH_2$ $CH_2C(O)CH_3$	118–120	48.90(48.58)	3.54 (3.34)	
$Bu_3SnOC(O)CH_2CH_2C(O)CH_3$	72– 73	50.42(50.41)	8.44 (8.40)	

[a] Calculated values in parentheses. [b] Bu = n-Butyl; Cyh = cyclohexyl. [c] With decomposition. [d] Decomposes above 280°C. [e] Lit. m.p. 52°C Ref.: M. Frankel, D. Gertner, D. Wagner and A. Zilkha, J. Org. Chem., 30 (1965) 1596.

TABLE 2

ELEMENT–OXYGEN [a] STRETCHING FREQUENCIES FOR TRIORGANOTIN COMPLEXES OF OXYGEN-DONOR LIGANDS

Compound [b]	ν(E–O) [c] (cm^{-1})
(p-tolyl)$_3$SnCl·Ph$_3$PO	1150
(p-tolyl)$_3$Sn(NCS)·Ph$_3$PO	1140
(p-ClC$_6$H$_4$)$_3$SnCl·Ph$_3$PO	1146
(p-tolyl)SnMe$_2$Br·Ph$_3$PO	1160
(p-tolyl)$_3$SnCl·DMSO	1000
(p-tolyl)$_3$Sn(NCS)·DMSO	990
(p-ClC$_6$H$_4$)$_3$SnCl·DMSO	995
(p-tolyl)$_3$SnCl·HMPA	1140
(p-tolyl)$_3$Sn(NCS)·HMPA	1132
(p-ClC$_6$H$_4$)$_3$SnCl·HMPA	1135
(p-tolyl)$_3$SnBr·QuinO	1225
Ph$_3$SnCl·QuinO	1225
Ph$_2$BuSnBr·QuinO	1224
(p-ClC$_6$H$_4$)$_3$SnCl·QuinO	1215
(p-tolyl)$_3$SnCl·PyO	1215
(p-tolyl)$_3$SnCl·Ph$_3$AsO	878
[(p-tolyl)$_3$Sn(DMSO)$_2$]$^+$ [Ph$_4$B]$^-$	980
[(p-tolyl)$_3$Sn(Ph$_3$PO)$_2$]$^+$ [Ph$_4$B]$^-$	1154
[(p-tolyl)$_3$Sn(Ph$_3$AsO)$_2$]$^+$ [Ph$_4$B]$^-$	860
[(p-tolyl)$_3$Sn(diphosO$_2$)]$^+$ [Ph$_4$B]$^-$	1181, 1135, 1120, 1080
[(p-tolyl)$_3$Sn(bipyO$_2$)]$^+$ [Ph$_4$B]$^-$	1260, 1222, 1204

[a] IR data refer to Nujol mulls. [b] DMSO = dimethylsulphoxide; HMPA = hexamethylphosphoramide; PyO = pyridine *N*-oxide; Ph$_3$PO = triphenylphosphine oxide; QuinO = Quinoline-*N*-oxide; Ph$_3$AsO = triphenylarsine oxide. [c] ν(E–O)values for the uncomplexed bases are as follows: 1190 (Ph$_3$PO), 1047 (DMSO), 1244 (PyO), 1218 (HMPA), 1240 (QuinO), 880 (Ph$_3$AsO) cm^{-1}.

Infrared spectra

Infrared spectra were usually recorded on a Perkin–Elmer 1330 spectrometer as Nujol mulls between NaCl windows, and the spectra were calibrated with polystyrene. In a few cases, however, improved resolution of the bands was obtained using a Nicolet 5-MX Fourier Transform Spectrometer. The infrared data are listed in Tables 2 and 9.

Nuclear Magnetic Resonance spectra

^{1}H and ^{13}C NMR spectra were recorded on a Fourier-transform JEOL JNM-FX 100 spectrometer operating at 99.55 MHz for ^{1}H and 25.00 MHz for ^{13}C. Solutions for ^{13}C spectra were placed in 10 mm (o.d.) NMR tubes and $CDCl_3$ was used as solvent and internal lock; The solutions were either approximately of concentration 0.1 g ml^{-1} or, where possible, saturated. Complete proton decoupling irradiation was used to record the ^{13}C spectra (Table 4). The chemical shifts are accurate to $\pm$0.1 ppm and the coupling constants, $^nJ(^{119}Sn–^{13}C)$, which were usually obtained within a scan range of 4000 pulses, are accurate to within 0.5 Hz.

Mössbauer spectra

The ^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512 channel

TABLE 3. ^{119m}Sn MÖSSBAUER DATA [a] FOR TRIORGANOTIN COMPLEXES AND THEIR PARENT LEWIS ACIDS AT 80 K

Compound	*IS* [b]	*QS*	Γ_1	Γ_2
(*p*-tolyl)$_3$SnCl	1.24	2.69	1.01	1.09
(*p*-tolyl)$_3$SnBr	1.28	2.70	0.94	0.97
(*p*-tolyl)$_3$Sn(NCS)	1.38	3.67	1.87	1.65
(*p*-ClC$_6$H$_4$)$_3$SnCl	1.24	2.73	0.99	0.96
(*p*-tolyl)$_3$SnCl·Ph$_3$PO	1.26	3.30	1.13	1.10
(*p*-tolyl)$_3$Sn(NCS)·Ph$_3$PO	1.19	3.60	0.94	0.96
(*p*-tolyl)SnMe$_2$Br·Ph$_3$PO	1.33	3.57	0.91	0.93
(*p*-ClC$_6$H$_4$)$_3$SnCl·Ph$_3$PO	1.22	3.25	1.00	1.05
(*p*-tolyl)$_3$SnBr·QuinO	1.26	3.11	0.93	0.91
(*p*-ClC$_6$H$_4$)$_3$SnCl·QuinO	1.22	3.18	1.01	1.02
Ph$_3$SnCl·QuinO	1.24	3.14	1.00	1.09
Ph$_2$BuSnBr·QuinO	1.36	3.24	1.23	1.22
(*p*-tolyl)$_3$SnCl·DMSO	1.27	3.02	1.12	1.05
(*p*-tolyl)$_3$Sn(NCS)·DMSO	1.21	3.59	1.05	1.05
(*p*-ClC$_6$H$_4$)$_3$SnCl·DMSO	1.22	3.26	1.14	1.18
(*p*-tolyl)$_3$SnCl·HMPA	1.22	3.42	0.96	0.98
(*p*-tolyl)$_3$Sn(NCS)·HMPA	1.19	3.67	1.00	0.99
(*p*-ClC$_6$H$_4$)$_3$SnCl·HMPA	1.20	3.25	0.91	0.89
(*p*-tolyl)$_3$SnBr·PyO	1.28	3.23	1.15	1.04
(*p*-tolyl)$_3$SnCl·Ph$_3$AsO	1.17	3.31	0.95	0.91
[(*p*-tolyl)$_3$SnBrCl]$^-$[Ph$_3$PMe]$^+$	1.32	3.02	0.93	0.98
[(*p*-tolyl)$_3$Sn(diphosO$_2$)]$^+$[Ph$_4$B]$^-$	1.31	4.08	1.16	1.18
[(*p*-tolyl)$_3$Sn(Ph$_3$PO)$_2$]$^+$[Ph$_4$B]$^-$	1.18	3.91	1.00	0.91
[(*p*-tolyl)$_3$Sn(Ph$_3$AsO)$_2$]$^+$[Ph$_4$B]$^-$	1.15	3.43	0.97	0.92
[(*p*-tolyl)$_3$Sn(DMSO)$_2$]$^+$[Ph$_4$B]$^-$	1.28	3.70	0.88	0.95
[(*p*-tolyl)$_3$Sn(bipyO$_2$)]$^+$[Ph$_4$B]$^-$	1.28	3.48	0.99	0.97
(*p*-tolyl)$_3$SnON(Ph)COPh	0.86	1.82	1.00	1.30
(*p*-tolyl)$_3$Sn(1,2,4-triazole)	1.14	2.94	0.91	0.90
[(*p*-tolyl)$_3$Sn]$_2$S	1.22	1.41	1.04	1.03

[a] Error ±0.05 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$.

TABLE 4

^{13}C NMR DATA FOR THE ORGANOTIN MOIETY IN SOME TRIARYLTIN(IV) COMPOUNDS [a,b]

Compound	$\delta(C_i)$	$\delta(C_o)$	$\delta(C_m)$	$\delta(C_p)$	^1J	^2J	^3J	^4J
(*p*-tolyl)$_3$SnCl	133.9	136.0	129.9	140.4	625.0	50.8	66.4	13.8
(*p*-tolyl)$_3$SnCl·DMSO	134.6	136.0	129.8	140.2	644.5	50.8	65.4	13.7
(*p*-tolyl)$_3$SnCl·HMPA	134.6	136.1	129.7	140.1	639.7	51.3	65.9	13.4
(*p*-tolyl)$_3$SnCl·QuinO	135.2	136.0	129.5	139.8	664.1	50.8	68.4	13.7
(*p*-tolyl)$_3$SnCl·Ph$_3$AsO	140.3	136.5	129.3	138.9	788.0	51.3	73.3	14.7
[(*p*-tolyl)$_3$BrCl]$^-$[Ph$_3$PMe]$^+$	135.0	136.2	129.6	139.9	777.0 [c]	52.2	66.5	14.2
(*p*-tolyl)$_3$SnOC(O)(CH$_2$)$_2$C(O)NHPh	134.2	136.7	129.8	140.3	651.9	50.1	65.3	13.4
(*p*-ClC$_6$H$_4$)$_3$SnCl	135.0	137.6	130.1	137.9	634.8	55.7	69.3	16.7
(*p*-ClC$_6$H$_4$)$_3$SnCl·DMSO	136.9	137.2	129.3	136.7	– [d]	54.7	69.3	16.4
(*p*-ClC$_6$H$_4$)$_3$SnCl·HMPA	135.9	137.3	128.7	140.5	736.3 [c]	53.7	76.1	15.6
(*p*-ClC$_6$H$_4$)$_3$SnCl·QuinO	139.2	137.2	128.6	135.8	785.2	53.7	72.3	16.6
Ph$_3$SnCl [e]	137.1	136.0	129.0	130.4	614.3	50.0	64.5	13.4
Ph$_3$SnCl·QuinO	139.7	136.1	128.7	129.7	695.4	46.9	66.4	15.6
Ph$_3$SnCl·DMSO [e,f]	143.8	136.1	128.5	129.1	810.6	47.9	71.3	14.6
Ph$_3$SnCl·HMPA [e,g]	143.1	133.9	125.5	126.1	839.8	48.8	73.2	17.1

[a] In concentrated $CDCl_3$ solutions, unless otherwise indicated. [b] *i*, (*ipso*), *o* (*ortho*), *m* (*meta*), *p* (*para*); coupling constants reported are for $^nJ(^{119}Sn-^{13}C)$. [c] Tentative. [d] Coupling constant cannot be estimated from data. [e] Ref. 45. [f] In DMSO-d_6. [g] In $CDCl_3$/HMPA (1/1 v/v).

TABLE 5

X-RAY DATA COLLECTION AND PROCESSING PARAMETERS FOR (p-TOLYL)$_3$SnBr·QUINOLINE-N-OXIDE

Molecular formula	$C_{30}H_{28}BrNOSn$
Molecular weight	617.15
Cell constants	a 10.245(4) Å α 84.10(2)°
	b 10.862(2) Å β 68.39(3)°
	c 13.153(5) Å γ 80.88(3)°
	V 1342.0(8) Å^3 $Z = 2$
D_{exp}	1.50 (flotation in KI/H_2O) g cm^{-3}
$D_{calcd.}$	1.527 g cm^{-3}
Space group	$P\bar{1}$
Radiation	graphite-monochromatized Mo-K_α, λ 0.71069 Å
Absorption coefficient	24.50 cm^{-1}
Crystal size	0.20×0.20×0.24 mm
Mean μ_r	0.12 mm
Transmission factors	0.761 to 0.816
Scan type and speed	$\omega - 2\theta$; 2.02–8.37° min^{-1}
Scan range	1° below K_{α_1} to 1° above K_{α_2}
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	h, $\pm k$, $\pm l$; $2\theta_{max}$ 54°
Unique data measured	5161
Observed data with $\|F_o\| > 3\sigma\|F_o\|$, n	4548
Number of variables, p	316
$R_F = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.070
Weighting scheme	$w = [\sigma^2(F_o) + 0.0015\|F_o\|^2]^{-1}$
$R_{wF^2} = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.095
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	1.70
Residual extrema in final difference map	+0.86 to −2.23 e Å^{-3}

data store, and a 15 mCi $Ca^{119m}SnO_3$ source at room temperature. The spectra were recorded on a Hewlett-Packard 7225B plotter and fitted with Lorenztian functions by a least-squares fitting programme [23]. The Mössbauer data are listed in Tables 3 and 10. Temperature control for the variable-temperature studies was effected with a heating unit manufactured by Lake Shore Cryotronics, Inc. (U.S.A.), and the temperature was controlled to ±0.1 K.

X-Ray analysis

The X-ray crystal data of the quinoline-N-oxide adduct of tri(p-tolyl)tin bromide were obtained by established procedures described previously [1]. The data collection and processing parameters are listed in Table 5. A sharpened Patterson map revealed the positions of the Sn and Br atoms in the asymmetric unit which sufficiently phased the structure, and the remaining non-hydrogen atoms were located from subsequent difference-Fourier maps. All non-hydrogen atoms were refined anisotropically. The 19 ring H atoms were located geometrically (C–H 0.96

(Continued on p. 298)

TABLE 6

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ for Sn; $\times 10^4$ for other atoms)

Atom	x	y	z
Sn	39103(4)	21182(4)	26441(4)
Br	2843(1)	3933(1)	1610(1)
O	4875(5)	319(4)	3565(4)
N	4166(6)	−673(5)	3896(4)
C(1)	3236(8)	−735(7)	4941(6)
C(2)	2446(8)	−1718(8)	5296(7)
C(3)	2578(9)	−2636(8)	4602(7)
C(4)	3612(8)	−2603(6)	3524(7)
C(5)	3827(11)	−3503(7)	2785(8)
C(6)	4845(11)	−3434(9)	1764(9)
C(7)	5649(10)	−2444(8)	1431(7)
C(8)	5447(8)	−1537(7)	2134(6)
C(9)	4426(7)	−1596(5)	3176(5)
C(10)	6081(7)	2291(6)	1742(5)
C(11)	6479(8)	3260(7)	907(6)
C(12)	7861(8)	3489(7)	408(7)
C(13)	8906(8)	2799(7)	739(6)
C(14)	8550(8)	1819(9)	1528(6)
C(15)	7177(8)	1577(7)	2011(6)
C(16)	10419(9)	3097(10)	214(8)
C(17)	3084(8)	2998(6)	4178(6)
C(18)	1662(8)	3405(7)	4688(7)
C(19)	1155(9)	4037(8)	5661(6)
C(20)	2066(9)	4288(7)	6119(6)
C(21)	3463(10)	3904(8)	5619(7)
C(22)	3995(9)	3267(8)	4655(7)
C(23)	1531(13)	5015(9)	7159(7)
C(24)	2649(7)	868(6)	2431(5)
C(25)	1478(7)	524(6)	3295(6)
C(26)	683(8)	−295(7)	3171(6)
C(27)	986(9)	−818(7)	2187(7)
C(28)	2146(10)	−496(7)	1307(6)
C(29)	2961(8)	333(7)	1422(6)
C(30)	44(15)	−1752(12)	2087(10)

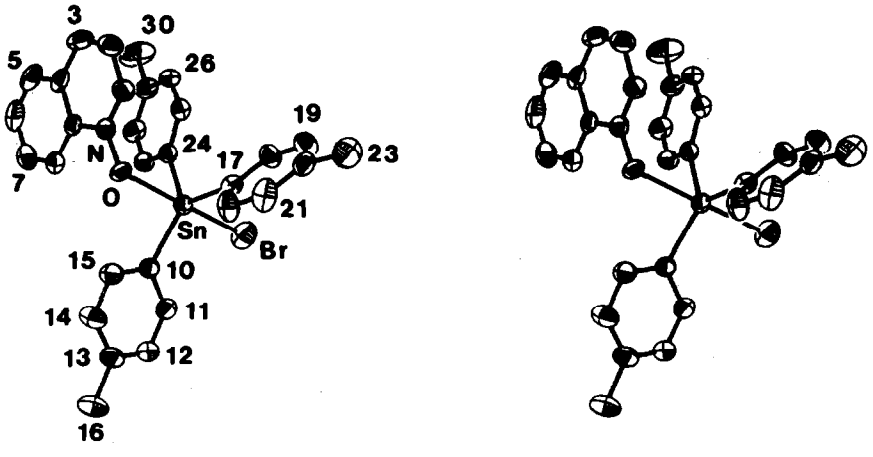


Fig. 1. The molecular structure of (p-tolyl)$_3$SnBr·quinoline-N-oxide, with the atom numbering scheme.

TABLE 7

MOLECULAR DIMENSIONS (BOND LENGTHS (Å), ANGLES (°)) OF (p-TOLYL)$_3$SnBr·QUINOLINE-N-OXIDE, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Sn–Br	2.606(1)	Sn–O	2.459(5)
Sn–C(10)	2.129(6)	Sn–C(17)	2.141(7)
Sn–C(24)	2.120(8)	O–N	1.341(7)
N–C(1)	1.355(8)	N–C(9)	1.377(9)
C(1)–C(2)	1.38(1)	C(2)–C(3)	1.38(1)
C(3)–C(4)	1.42(1)	C(4)–C(5)	1.39(1)
C(4)–C(9)	1.42(1)	C(5)–C(6)	1.37(1)
C(6)–C(7)	1.40(1)	C(7)–C(8)	1.36(1)
C(8)–C(9)	1.39(1)	C(10)–C(11)	1.43(1)
C(10)–C(15)	1.40(1)	C(11)–C(12)	1.38(1)
C(12)–C(13)	1.39(1)	C(13)–C(14)	1.40(1)
C(13)–C(16)	1.52(1)	C(14)–C(15)	1.37(1)
C(17)–C(18)	1.38(1)	C(17)–C(22)	1.38(1)
C(18)–C(19)	1.40(1)	C(19)–C(20)	1.36(1)
C(20)–C(21)	1.35(1)	C(20)–C(23)	1.53(1)
C(21)–C(22)	1.39(1)	C(24)–C(25)	1.39(1)
C(24)–C(29)	1.41(1)	C(25)–C(26)	1.36(1)
C(26)–C(27)	1.38(1)	C(27)–C(28)	1.38(1)
C(27)–C(30)	1.55(2)	C(28)–C(29)	1.37(1)
Br–Sn–O	176.6(1)	Br–Sn–C(10)	97.1(2)
O–Sn–C(10)	83.9(2)	Br–Sn–C(17)	94.9(2)
O–Sn–C(17)	87.6(2)	C(10)–Sn–C(17)	113.8(3)
Br–Sn–C(24)	91.7(2)	O–Sn–C(24)	85.2(2)
C(10)–Sn–C(24)	128.6(3)	C(17)–Sn–C(24)	115.7(3)
Sn–O–N	118.7(4)	O–N–C(1)	118.2(6)
O–N–C(9)	119.2(5)	C(1)–N–C(9)	122.7(6)
N–C(1)–C(2)	119.7(7)	C(1)–C(2)–C(3)	121.0(7)
C(2)–C(3)–C(4)	119.0(8)	C(3)–C(4)–C(5)	122.4(8)
C(3)–C(4)–C(9)	119.2(7)	C(5)–C(4)–C(9)	118.3(7)
C(4)–C(5)–C(6)	120.1(9)	C(5)–C(6)–C(7)	121.2(10)
C(6)–C(7)–C(8)	120.1(8)	C(7)–C(8)–C(9)	119.6(7)
N–C(9)–C(4)	118.2(5)	N–C(9)–C(8)	121.0(6)
C(4)–C(9)–C(8)	120.8(7)	Sn–C(10)–C(11)	120.9(5)
Sn–C(10)–C(15)	122.4(5)	C(11)–C(10)–C(15)	116.3(6)
C(10)–C(11)–C(12)	122.0(8)	C(11)–C(12)–C(13)	119.8(7)
C(12)–C(13)–C(14)	119.2(7)	C(12)–C(13)–C(16)	119.3(7)
C(14)–C(13)–C(16)	121.5(8)	C(13)–C(14)–C(15)	120.9(8)
C(10)–C(15)–C(14)	121.8(7)	Sn–C(17)–C(18)	122.7(7)
Sn–C(17)–C(22)	120.0(5)	C(18)–C(17)–C(22)	117.2(7)
C(17)–C(18)–C(19)	121.7(9)	C(18)–C(19)–C(20)	120.2(7)
C(19)–C(20)–C(21)	118.4(8)	C(19)–C(20)–C(23)	120.7(8)
C(21)–C(20)–C(23)	120.9(10)	C(20)–C(21)–C(22)	122.5(10)
C(17)–C(22)–C(21)	119.9(8)	Sn–C(24)–C(25)	120.9(6)
Sn–C(24)–C(29)	122.3(5)	C(25)–C(24)–C(29)	116.8(7)
C(24)–C(25)–C(26)	121.3(7)	C(25)–C(26)–C(27)	122.1(7)
C(26)–C(27)–C(28)	118.2(9)	C(26)–C(27)–C(30)	120.1(7)
C(28)–C(27)–C(30)	121.7(8)	C(27)–C(28)–C(29)	120.3(8)
C(24)–C(29)–C(28)	121.4(6)		

TABLE 8

LEAST-SQUARES PLANES [a]

Plane	Atoms fitted	l	m	n	d (Å)	rms (Å×10^4)
1	O, N, C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9)	0.6997	−0.4189	0.5787	6.6850	327
2	C(24), C(25), C(26), C(27), C(28), C(29), C(30)	0.5819	−0.6896	0.4310	2.4305	17
3	C(10), C(11), C(12), C(13), C(14), C(15), C(16)	−0.1623	0.6215	0.7664	4.7591	195
4	C(17), C(18), C(19), C(20), C(21), C(22), C(23)	0.1081	0.8878	−0.4473	0.4021	95
5	C(24), C(10), C(17)	0.3449	−0.7326	0.5868	2.4547	–

Angles between planes (standard deviations ~ 0.9°): 1–2, 19.0°; 1–3, 85.9°; 1–4, 123.7°; 1–5, 27.4°; 2–3, 101.0°; 2–4, 137.9°; 2–5, 16.5°; 3–4, 79.0°; 3–5, 93.5°; 4–5, 151.1°

[a] Plane equation is of the form $lx_0 + my_0 + nz_0 = d$, where x_0, y_0, z_0 are coordinates in A referred to orthogonal axes a_0, b_0, c_0 respectively, with a_0 parallel to a^*, b_0 to $c \times a^*$, and c_0 to c.

Å), assigned fixed isotropic temperature factors, and allowed to ride on their respective parent C atoms. Some methyl hydrogens were located by Fourier synthesis and the methyl groups were refined as rigid groups. All calculations were performed using a Data General Nova 3/12 minicomputer with the SHELXTL programme package. Analytical expressions of neutral atom scattering factors were

TABLE 9

INFRARED DATA (cm^{-1}) FOR ORGANOTIN ESTER DERIVATIVES

Compound	ν(NH)	ν(C=O)	ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$
Benzoylglycine (LH)	3324(3390) [a]	1600(1602) [a]	1740(1745) [a]	1180(1185) [a]	560(560) [a]
Ph_3SnL	3410(3441) [a]	1660(1659) [a]	1560(1557) [a]	1420(1411) [a]	140(146) [a]
$(p\text{-}ClC_6H_4)_3SnL$	3400	1648	1570	1450	120
$(p\text{-tolyl})_3SnL$	3350	1652	1575	1448	127
Bu_3SnL	3360	1648	1565	1440	125
Succinanilic acid (L'H)	3300	1598	1685	1185	500
Ph_3SnL'	3320	1676	1548	1438	110
$(p\text{-}ClC_6H_4)_3SnL'$	3300	1648	1558	1440	118
$(p\text{-tolyl})_3SnL'$	3290	1660	1556	1430	126
Bu_3SnL'	3310	1655	1560	1450	110
Cyh_3SnL'	3295	1658	1546	1445	105
Levulinic acid (L''H)	–	1700 [b]	1700 [b]	1160	540
Ph_3SnL''	–	1705	1532(1538) [c]	1424(1420) [c]	108
$(p\text{-}ClC_6H_4)_3SnL''$	–	1710	1560	1430	130
Bu_3SnL''	–	1720	1570	1420	150
Cyh_3SnL''	–	1708	1556	1435	121

[a] Values in parentheses obtained from ref. 59. [b] Overlap of ketonic and carboxyl bands. [c] Values in parentheses obtained from ref. 70.

TABLE 10

^{119m}Sn MÖSSBAUER DATA [a] FOR TRIORGANOTIN ESTER DERIVATIVES AT 80 K

Compound	*IS* [b]	*QS*	Γ_1	Γ_2
$Ph_3SnOC(O)CH_2N(H)C(O)Ph$	1.22	3.40	1.02	1.09
$(p\text{-tolyl})_3SnOC(O)CH_2N(H)C(O)Ph$	1.12	3.26	1.02	1.35
$(p\text{-ClC}_6H_4)_3SnOC(O)CH_2N(H)C(O)Ph$ [d] (1)	1.19	3.30	1.05	1.17
$Bu_3SnOC(O)CH_2N(H)C(O)Ph$	1.41	3.61	1.01	0.94
$Ph_3SnOC(O)CH_2CH_2C(O)NHPh$	1.22	2.69	1.06	1.12
$Cyh_3SnOC(O)CH_2CH_2C(O)NHPh$	1.54	3.59	1.07	1.12
$(p\text{-tolyl})_3SnOC(O)CH_2CH_2C(O)NHPh$	1.18	3.18	1.21	1.43
$(p\text{-ClC}_6H_4)_3SnOC(O)CH_2CH_2C(O)NHPh$ [d] (2)	1.19	3.33	1.04	1.07
$Bu_3SnOC(O)CH_2CH_2C(O)NHPh$	1.41	3.78	1.09	1.17
$Ph_3SnOC(O)CH_2CH_2C(O)CH_3$	1.20	3.44	1.02	1.02
	(1.28	3.43) [c]		
$Cyh_3SnOC(O)CH_2CH_2C(O)CH_3$	1.44	3.73	1.20	1.41
$(p\text{-ClC}_6H_4)_3SnOC(O)CH_2CH_2C(O)CH_3$	1.16	3.52	1.05	1.28
$Bu_3SnOC(O)CH_2CH_2C(O)CH_3$	1.37	3.67	0.97	0.99

[a] Error ± 0.05 mm s^{-1}. [b] Relative to $CaSnO_3$ or $BaSnO_3$. [c] Ref. 70. [d] Variable-temperature Mössbauer data for these compounds are as follows (-10^2 *a*; $-r$; temp. range; no. of points):
1: 1.65 K^{-1}; 0.999; 81.9–129.1 K; 6
2: 2.29 K^{-1}; 0.991; 79.3–129.2 K; 6.

employed, and anomalous dispersion corrections were incorporated (International Tables for X-ray Crystallography, Vol. IV). The final discrepancy factors and other parameters at the conclusion of refinement are given in Table 5. Fractional atomic coordinates of the non-hydrogen atoms are given in Table 6, bond distances and angles in Table 7, and dihedral angles and least-squares planes in Table 8; tables of hydrogen coordinates and their corresponding temperature factors, structure factors, and anisotropic thermal parameters are available (from TCWM) on request. A stereoview, with atom labelling, of the molecular structure of the adduct is shown in Fig. 1.

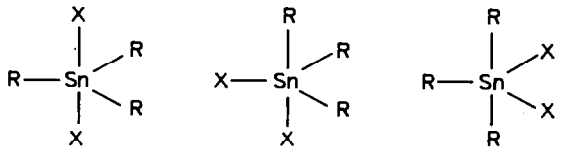
Results and discussion

Complexes

Triorganotin(IV) halides and pseudohalides are known to react with neutral and anionic ligands to form discrete pentacoordinate complexes of trigonal bipyramidal geometry [24]. With oxygen donor ligands containing the $\rangle$C=O, $\rangle$S=O, $\rangle$N → O, $\rangle$P=O or $\rangle$As=O groupings the shift to lower frequencies of the element–oxygen stretching bands, $\Delta\nu$(E–O), in the infrared is diagnostic of the donor interaction [25,26], and inspection of the data in Table 2 indicates this to be clearly the case for the stoichiometric adducts of $(p\text{-tolyl})_3SnX$ and $(p\text{-ClC}_6H_4)_3SnX$ with these ligands. This means that the tin atoms are five-coordinate.

^{119m}Sn Mössbauer spectral studies on the adducts and ionic complexes $[(p\text{-tolyl})_3SnL_2]^+[Ph_4B]^-$ (L = Ph_3PO, Ph_3AsO, DMSO) and $[(p\text{-tolyl})_3SnBrCl]^-[Ph_3PMe]^+$ reveal quadrupole splittings (*QS*) in the range 3.1–3.9 mm s^{-1} (Table 3), which are typical of trigonal-bipyramidal structures with equatorial locations of the organic R groups (structure I), and in consonance with the predictions of the point-charge model [11,12,27]. Indeed, the equatorial structure appears to be general

for pentavalent triorganotin(IV) compounds, as revealed by spectroscopic studies



(I) (II) (III)

and crystal structure determinations on several complexes similar to those described in the present study. The following examples from the literature with crystallographic documentation are illustrative: $Ph_3SnNO_3 \cdot PyO$ [28]; $Ph_3SnCl \cdot$ tetramethylurea [29]; $[n\text{-}Bu_3Sn(H_2O)_2]^+[C_5(CO_2Me)_5]^-$ [30]; $[Me_3Sn(HMPA)_2]^+$ $[Me_3SnBr_2]^-$ [31] and $[Ph_3SnCl_2]^-[Ph_3AsCH_2C(O)Ph]^+$ [32]. There appears to be little evidence, on the other hand, for the stereoisomeric *cis* (structure II) and *meridional* (structure III) geometries among $R_3SnX \cdot L$ adducts. However, we have previously suggested [18] that these alternative geometries might be accessible by use of chelating bidentate ligands (Ch), and among the earliest examples provided by us in this connection were the series of cationic complexes, $[R_3Sn(Ch)]^+[BPh_4]^-$, which were characterized as having *meridional* structures by Mössbauer spectroscopy [12]. The *cis*-geometry, with X-ray structural corroboration, has been encountered, for example, in $Ph_3Sn[ONPhC(O)Ph]$ [33], $Ph_3Sn[OCPhCHCPhO]$ [34] and $Ph_3Sn[O_2CC_6H_4(N_2R')\text{-}o]$ (R' = 2-hydroxy-5-methylphenyl) [35], and recently also in the pseudo-pentacoordinated triphenyltin ester derivatives, Ph_3Sn-$[O_2CC_6H_4Y]$ (Y = *o*-OH, *o*-OMe, *p*-SMe, *o*-NH_2, *p*-NH_2, *o*-NMe_2) [36,37]. In this connection we synthesised a few analogous chelate and ester derivatives (vide infra) containing the tri(*p*-tolyl)tin moiety.

For the series of adduct complexes, $(p\text{-}ZC_6H_4)_3SnX \cdot L$ (Z = H, Me, Cl), applying the generalization that, for a given ligand, the larger the magnitude of $\Delta\nu$(E–O) the stronger the donor interaction [38], we observe the following order of acceptor strengths: $(p\text{-tolyl})_3Sn < Ph_3Sn < (p\text{-}ClC_6H_4)_3Sn$. The trend is particularly noticeable with DMSO and Ph_3PO, though less so with quinoline *N*-oxide, where the possibility of the exertion of a 'levelling effect' by the stronger Lewis base cannot be discounted. A similar acid strength sequence was previously derived by Eng and Dillard [39] on the basis of the change in the chemical shift difference between the *meta*- and *ortho*-ring protons on going to donor solvents from CCl_4. On the other hand, a rather erratic trend in *QS* values is noted for the complexes of the three triaryltin halide (Table 3). Surprisingly, however, the triaryltin isothiocyanates, which appear to be stronger acceptors than the halides, show regular variations in both the IR and Mössbauer parameters which reinforce the acceptor order of the Lewis acids.

The order of donor strengths of ligands with respect to a given Lewis acid, although often derived in the literature from spectroscopic data, is seldom straightforward. Thus, while the order DMSO < Ph_3PO < PyO < Ph_3AsO has been observed [25] for $Me_3SnBr \cdot L$ complexes from ^1H NMR data, notably the variation of the coupling constant, $|^2J(^{119}Sn\text{–}Me)|$, with L, the relative thermodynamic stabilities of 1 : 1 adducts of Me_3SnCl with the heterocyclic nitrogen bases, 3,5-dimethylpyrazole (dmp, pK_a 4.1) and pyridine (py, pK_a 5.2), bear no relationship to the basicities of the ligands, $Me_3SnCl \cdot$ dmp being an order of magnitude more stable

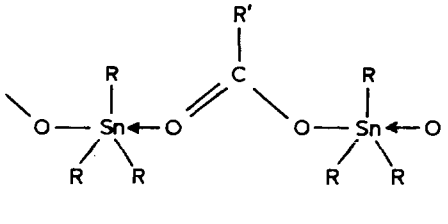
than $Me_3SnCl \cdot py$ in CCl_4 [40]. However, confining our comparison to structurally similar ligands, we see from both IR and Mössbauer data that HMPA is a stronger donor than Ph_3PO towards $(p\text{-tolyl})_3SnCl$, and PyO than QuinO. Wedd and Sams [41] have previously similarly compared the donor strengths of a series of phosphine oxides and sulphoxides with respect to Ph_3SnCl, and derived the orders n-Pr_2SO < n-Bu_2SO < DMSO and $(PhO)_3PO < Ph_3PO < (MeO)_3PO$, respectively. The isomer shift (*IS*) values remained essentially unaltered in the above complexes relative to Ph_3SnCl [41], and this is also the case for our data on the tolyl complexes (Table 3). In contrast with this is the recent report of pronounced differences in the *IS* value of Me_3SnCl when engaged in complexation with a series of sulphoxides [n-Pr_2SO < n-Bu_2SO < DMSO < Bz_2SO] [42], a feature which may be due, in part, to stronger donor–acceptor interactions involving Me_3SnCl.

^{13}C NMR spectroscopy [43,44] has recently been used to examine the coordination geometry of the tin atom in some triphenyltin compounds [45]. It was shown that the *ipso*-carbon of the phenyl ring exhibits small downfield shifts upon the increase in coordination number of the tin atom from four to five, and that $^1J(^{119}Sn-^{13}C)$ values of 750–850 Hz are typical for equatorial R_3Sn geometries (structure I) [45]. We have thus obtained ^{13}C spectra for the substituted phenyltin complexes, where possible in $CDCl_3$, and the data are reported in Table 4. It is seen that the *ipso*-carbon atoms of the aryl rings in the complexes resonate downfield relative to the uncomplexed Lewis acids. Only for the cases of $(p\text{-tolyl})_3SnCl \cdot Ph_3AsO$, $[(p\text{-tolyl})_3SnBrCl]^-[Ph_3PMe]^+$ and $(p\text{-}ClC_6H_4)_3SnCl \cdot$ QuinO, are the ^1J values > 750 Hz. This indicates that the complexes are largely dissociated in solution, although the progressive trends in $\delta(^{13}C)$ values suggest that a certain degree of coordinative interaction is retained. It is instructive that the ^1J values for the QuinO complexes confirm the acceptor strength sequence, $(p\text{-tolyl})_3Sn < Ph_3Sn < (p\text{-}ClC_6H_4)_3Sn$, previously deduced from the IR measurements. An attempted ^{13}C spectral investigation of the cationic complexes involving the chelate ligands, $diphosO_2$ and $bipyO_2$, was thwarted by their extremely poor solubility in $CDCl_3$. However, these complexes are assigned a *meridional* geometry by analogy to the previously reported trialkyltin and triphenyltin cationic complexes of the relevant ligands which show similar quadrupole splittings [12]: the point charge treatment predicts [12,46] a *QS* of ca. 3.28 mm s^{-1} for *mer*-Ph_3SnL_2 systems. The tri(*p*-tolyl)tin derivative of *N*-phenyl-*N*-benzoylhydroxylamine, on the other hand, yields a *QS* of 1.82 mm s^{-1} which is close to that of the analogous triphenyltin derivative (1.94 mm s^{-1}), which has a crystallographically authenticated *cis*-SnR_3 geometry (structure II) [34]. An alternative tetrahedral structure for the tolyl complex is considered unlikely in view of the value of the *QS*/*IS* ratio. This ratio, ρ, suggested earlier [47] to be an index of coordination number for di- and tri-organotin(IV) structures with values > ca. 2.1 characteristic of coordination numbers greater than four, has a value of 2.12 for the complex; by comparison, bis[tri(*p*-tolyl)tin] sulphide, has a ρ value of 1.15. The tri(*p*-tolyl)tin derivative of 1,2,4-triazole shows a *QS* of 2.94, which is close to the values reported in the literature for the trimethyltin (2.96) [47] and the triphenyltin (2.89) [48] analogues, although somewhat less than that for the tricyclohexyltin derivative (3.26 mm s^{-1}) [49]. The latter has been shown crystallographically [50] to have a polymeric intermolecularly-associated structure, with the R_3Sn skeletal unit having essentially geometry I. A similar polymeric structure may be envisaged also for the tolyl case.

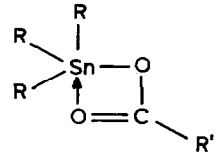
In order to substantiate the equatorial geometry inferred thus far from spectroscopic studies for the series of adduct complexes, a single crystal X-ray analysis was undertaken for (p-tolyl)$_3$SnBr · QuinO. The molecular structure of the complex is shown in Fig. 1 together with the atomic numbering scheme. An examination of the packing diagram reveals no unusual intermolecular contacts. Thus, there is a discrete pentacoordinated molecule of trigonal-bipyramidal geometry in which the three tolyl groups are located in equatorial positions but the rings are mutually twisted in the trigonal plane (defined by C(10), C(17) and C(24)) to avoid steric congestion. The dihedral angles (Table 8) between the rings defined by C(24)–C(30), C(17)–C(23) and C(10)–C(16) and the trigonal plane are 16, 151, and 93°, respectively. In the adduct Ph_3SnNO_3 · PyO [28] the pyridine ring is positioned between two of the phenyl groups when viewed along the apical O–Sn–O axis, whereas in Ph_2SnCl_2 · 2,6-$Me_2C_5H_3NO$ [51], the pyridine ring avoids steric encumbrance by positioning itself directly below the chlorine atom which, with the phenyl groups, occupies the trigonal plane. In the present study, the quinoline ring lies over one of the tolyl rings (dihedral angles 19(1)°, Table 8), and the torsional angle defined by N, O, Sn and C(*ipso*) of the tolyl ring in question is −16.5(7)°. The Sn atom does not lie exactly in the trigonal plane, but is displaced towards the Br atom by 0.17(1) Å. This seems odd, since the sterically demanding quinoline *N*-oxide ligand might be expected to repel the tolyl rings towards the other apical occupant, i.e., the Sn atom should be displaced away from the Br atom. The Br–Sn–O angle is 176.6(1)°, and the sum of the equatorial angles in the trigonal girdle subtended at tin by the 3 *ipso*-carbons is 358.1(9)° (Table 7). The Sn–O–N angle is 118.7(4)°, but consideration of the near orthogonality of the Sn–O–N plane with the mean plane of the quinoline ring [87(1)°] suggests that there is distorted sp^3 rather than sp^2 hybridization at the coordinated oxygen atom [51]. The Sn–O, Sn–Br and Sn–C bond distances (Table 7) are within the range of values commonly encountered for five-coordinate organotin complexes [2,3].

Ester derivatives

Triorganotin carboxylates are known to form pentacoordinate structures in the solid state, either through intermolecular association involving bridging carboxylate groups (structure IV) or through intramolecular (anisobidentate) chelation (structure V) yielding discrete structures. The chain structure IV has been substantiated



(IV)



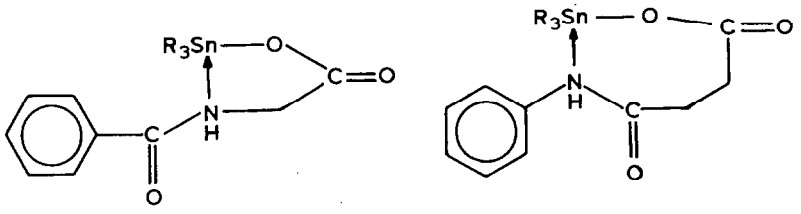
(V)

by X-ray analysis for both trimethyltin acetate [52] and tribenzyltin acetate [53]. Triphenyltin acetate, on the other hand, appears upon careful X-ray analysis to be six-coordinate [54]. The chain structure has also been confirmed for trimethyltin glycinate, but the axial positions here are occupied by only one of the carboxylate

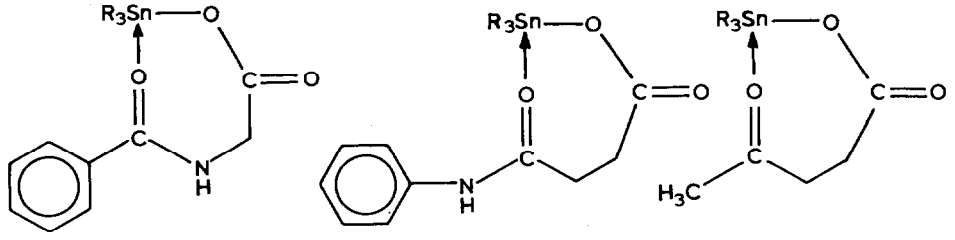
oxygen atoms and the less electronegative nitrogen atom [55]. The enhanced donor character of the nitrogen at the expense of oxygen in the above amino acid derivative has been attributed to hydrogen-bonding interactions of the amino group with the carboxyl oxygens [37].

The *cis*-geometry represented in structure V has been observed for triphenyltin arylazobenzoates [56], triphenyltin esters of anthranilic acid analogues [36] and the triphenyltin esters of salicyclic acid, *o*-anisic acid, and *p*-methylthiobenzoic acid [37]. Examples of this geometry among trialkyltin esters, however, are extremely rare [57], and this has been rationalised on the basis of the lower electronegativity of the alkyl than of the phenyl group, which disfavours axial occupancy of the alkyl group in the trigonal-bipyramidal structure [37].

For triorganotin derivatives of carboxylic acids which are potentially polydentate, several interesting possibilities arise since triorganotin compounds adopt higher coordination whenever favourable conditions exist [58]. The carboxylic acids chosen for the present study are hippuric acid (benzoylglycine), succinanilic acid, and levulinic acid. Benzoylglycine and succinanilic acid possess four potential coordination sites, namely the carboxylate oxygen atoms (structure IV or V), the amido nitrogen atom (structure VI), or the weakly basic ketonic oxygen atom (structure VII). For levulinic acid, coordination could occur through the carboxylic oxygens



(VI)



(VII) (VIII)

(structure IV or V) or the ketonic oxygen (structure VIII). The above structural possibilities are considered in the following sections on the basis of infrared and Mössbauer spectral measurements.

(a) Infrared spectra

Coordination via the amide nitrogen in the organotin derivatives of benzoylglycine and succinanilic acid, if present, can be readily detected in the infrared from positions of the N–H stretching frequency in the 3200–3500 cm^{-1} region. Thus,

relative to the uncomplexed ligands, the N–H stretching frequencies in the complexes (Table 9) show only zero or positive shifts, attesting to the non-participation of the nitrogens in coordination to the metal centre. A similar conclusion was drawn for the case of trimethyl- and triphenyltin benzoylglycinates [59].

The ketonic CO group stretching frequency in the series of ester derivatives generally shifts to higher values with respect to the free carboxylic acid ligands (Table 9). A lowering of ν(C=O) would be expected if the ketonic oxygen is involved in coordination. Indeed, the value of ν(C=O) of the organotin benzoylglycinate is comparable with those noted for ethyl (1642 [60]) and trimethylsilyl (1661 cm^{-1} [61]) esters of this amino acid. We thus conclude that in organotin derivatives of benzoylglycine, succinanilic acid, and levulinic acid, the ketonic oxygen shows no tendency to coordinate to tin. This leaves for consideration only the carboxylate moieties, and hence the structural possibilities IV and V.

The asymmetric carboxyl stretch, ν_{asym}(OCO), is most sensitive to structural changes in the carboxylate group coordination. Chain structures such as that of trimethyl- and tribenzyltin acetates show absorptions (1576 [62] and 1565 [53], respectively) in the same region as sodium acetate (1578 [63]), whereas for normal ester linkages, such as that in trimethylsilyl acetate, the absorption is located at 1725 cm^{-1} [62]. In the case of benzoylglycine, the alkali metal (Na, K) salts absorb at 1604 [64] and ethyl and trimethylsilyl esters at 1754 and 1740 cm^{-1} [61], respectively. Inspection of the data in Table 9 reveals that ν_{asym}(OCO) for the series of organotin ester derivatives studied lies in the range 1555 ± 25 cm^{-1}. For the simpler tri(*p*-tolyl)tin acetate, ν_{asym}(OCO) appears at 1540 cm^{-1} [65]. Also listed in Table 10 are the symmetric stretching frequencies, ν_{sym}(OCO), which for the complexes lie in the range 1435 ± 15 cm^{-1}. The magnitude of the separation between ν_{asym} and ν_{sym} is $\lesssim 150$ cm^{-1}, which suggests that the carboxylate moiety acts as either a bridging or a chelating ligand [66,67]. For monodentate behaviour, this difference is expected to exceed 200 cm^{-1} [64,68], as has been found for Cu^{II} bis(benzoylglycinate)$\cdot 4H_2O$, a dimeric molecule in which, as revealed by X-ray analysis, coordination occurs only through the terminal carboxyl oxygen in a monodentate arrangement [69].

(b) Mössbauer spectra

The Mössbauer spectra for all the ester derivatives show well-resolved doublets and the parameters are listed in Table 10. In all cases the ratio of quadrupole splitting (QS) to isomer shift (IS) is > 2.1, implying a coordination of more than four at tin [47]. The magnitudes of the QS values support the equatorial trigonal-bipyramidal R_3Sn configuration depicted in structure IV. This necessarily involves intermolecular association. However, the compounds do not give room-temperature spectra, including triphenyltin levulinate for which a helical chain structure has been previously proposed based on IR [70] and variable temperature Mössbauer [71] measurements. The temperature coefficient of the Mössbauer recoil-free fraction, a, as derived from variable-temperature studies (see refs. 48, 72 and refs. therein for a discussion of variable-temperature Mössbauer spectroscopy), provides a measure of the tightness with which the tin atom is bound into the lattice, and hence the degree of molecular association. A survey of a/structure relationships for methyl, phenyl and cyclohexyltin derivatives reveals that, by and large, rigid polymeric lattices have $-a$ values less than 1.1×10^{-2} K^{-1}, while polymers possessing more flexible

tertiary structures that permit greater vibrational freedom to the tin have $-a$ values approaching those of non-associated lattices, i.e. in the range $(1.3–2.8) \times 10^{-2}$ K^{-1} [48]. Variable-temperature Mössbauer studies in the temperature range 79.3 to 129.2 K were performed with two selected ester compunds, $(p\text{-}ClC_6H_4)_3Sn$ succinanilate and $(p\text{-}ClC_6H_4)_3Sn$ benzoylglycinate. These showed $-a$ values of 1.65×10^{-2} and 2.29×10^{-2}, respectively, which are indicative of a weakly polymeric lattice structure. The other ester derivatives described herein probably have similar structures. The intermolecular association may be expected to be drastically weakened in solution, as is observed in the case of $(p\text{-tolyl})_3Sn$ succinanilate (Table 4), for which the $^1J(^{119}Sn–^{13}C)$ value indicates a tetrahedral configuration. A similar conclusion was reached for Me_3SnOAc, whose $^1J(^{117,119}Sn–^{13}C)$ value of 530 Hz in the solid state (as determined from its high resolution cross polarization magic angle spinning proton-decoupled ^{13}C NMR spectrum) falls to 401 Hz in solution ($CDCl_3$) [73].

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References

1 V.G. Kumar Das, W. Chen, C.K. Yap and T.C.W. Mak, J. Organomet. Chem., 299 (1986) 41.
2 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
3 P.J. Smith, J. Organomet. Chem. Library, 12 (1981) 97.
4 V.G. Kumar Das, C.K. Yap and P.J. Smith, J. Organomet. Chem., 291 (1985) C17.
5 V.G. Kumar Das, W. Chen, C.K. Yap, P.J. Smith and T.C.W. Mak, J. Chem. Soc., Dalton Trans., in press.
6 V.G. Kumar Das, W. Chen, K.M. Lo and T.C.W. Mak, Organometallics, submitted.
7 R. Bock, in F.A. Gunther and J.D. Gunther (Eds.), Residue Reviews, Springer-Verlag, Vol. 79, 1981, pp. 2–270; C.J. Evans and S. Karpel, J. Organomet. Chem. Libr, 16 (1985) pp. 1–279.
8 V.G. Kumar Das, Y.K. Liew, K.I. Sudderuddin, C.K. Chang, V. Thomas, C.K. Yap, M.K. Lo, G.C. Ong, W.K. Ng and H.S. Yong, Toxicology, 32 (1984) 57.
9 V.G. Kumar Das, Intl. Symp. Techn. Cult. Develop., Dec. 1983, Kuala Lumpur; see Institute of Advanced Studies Seminar Proceedings No. 1, pp. 576–613 (Eds. Ungku A. Aziz, Y.H. Yip and C.P. Ling), University of Malaya Press, 1984.
10 S.J. Blunden, P.J. Smith and B. Sugavanam, Pestic. Sci., 15 (1984) 253.
11 G.M. Bancroft and R.H. Platt, Adv. Inorg. Chem. Radiochem., 15 (1972) 59.
12 G.M. Bancroft, V.G. Kumar Das, T.K. Sham and M.G. Clark, J. Chem. Soc., Dalton Trans., (1976) 643.
13 K.A. Kocheshkov, M.M. Nadi and A.P. Aleksandrov, Chem. Ber., 67B (1934) 1348; CA 28 (1934) 7253.
14 A. Stern and E.T. Becker, J. Org. Chem., 29 (1964) 3221.
15 T.N. Srivastava and S.N. Bhattacharya, J. Inorg. Nucl. Chem., 28 (1966) 2445.
16 E.J. Kupchik and E.F. McInerney, J. Organomet. Chem., 11 (1968) 294.
17 E. Ochiai, J. Org. Chem., 18 (1953) 1661.
18 V.G. Kumar Das, J. Inorg. Nucl. Chem., 38 (1976) 1241.
19 A.I. Vogel, A Text-book of Practical Organic Chemistry, 3rd Edition, Longman, 1962.
20 T. Harada, Bull. Chem. Soc. Jap., 17 (1942) 281; CA 41 (1947) 4444.
21 J.G.A. Luijten and G.J.M. van der Kerk, Rec. Trav. Chim. Pays-Bas, 82 (1963) 1181.
22 P.G. Harrison, Inorg. Chem., 12 (1973) 1545.
23 F.W.D. Woodhams, Software Microsyst., 1 (1982) 108.

24 A.G. Davies and P.J. Smith, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 2, pp. 519–627.
25 V.G. Kumar Das and W. Kitching, J. Organomet. Chem., 13 (1968) 523; Aust. J. Chem., 21 (1968) 2401.
26 R.S. Drago and D.W. Meek, J. Phys. Chem., 65 (1961) 1446, and references therein.
27 M.G. Clark, A.G. Maddock and R.H. Platt, J. Chem. Soc., Dalton Trans., (1972) 281.
28 C. Pelizzi, G. Pelizzi and P. Tarasconi, J. Organomet. Chem., 124 (1977) 151; G. Pelizzi, Inorg. Chim. Acta, 24 (1977) L31.
29 S. Calogero, G. Valle and U. Russo, Organometallics, 3 (1984) 1205.
30 A.G. Davies, J.P. Goddard, M.B. Hursthouse and N.P.C. Walker, J. Chem. Soc., Chem. Commun., (1983) 597.
31 L.A. Aslanov, V.M. Attiya, V.M Ionov, A.B. Permin and V.S. Petrosyan, J. Struct. Chem. (Engl. Transl.), 18 (1977) 884.
32 P.G. Harrison, K.C. Molloy, R.C. Phillips, P.J. Smith and A.J. Crowe, J. Organomet. Chem., 160 (1978) 421.
33 P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., (1974) 2298.
34 G.M. Bancroft, B.W. Davies, N.C. Payne and T.K. Sham, J. Chem. Soc., Dalton Trans., (1975) 973.
35 P.G. Harrison, K. Lambert and T.J. King, J. Chem. Soc., Dalton Trans., (1983) 363.
36 R.G. Swisher, J.F. Vollano, V. Chandrasekhar, R.O. Day, R.R. Holmes, Inorg. Chem., 23 (1984) 3147.
37 J.F. Vollano, R.O. Day, D.N. Rau, V. Chandrasekhar, R.R. Holmes, Inorg. Chem., 23 (1984) 3153.
38 F.A. Cotton, R. Francis and W.D. Horrocks, J. Phys. Chem., 64 (1960) 1534.
39 G. Eng and C.R. Dillard, Inorg. Chim. Acta, 31 (1978) 227.
40 R. Ettorre and G. Plazzogna, Inorg. Chim. Acta, 15 (1975) 21.
41 R.W.J. Wedd and J.R. Sams, Can. J. Chem., 48 (1970) 71.
42 A. Abras, C.A.L. Filgueiras and J.M.K. Baba, J. Inorg. Nucl. Chem., 43 (1981) 2249.
43 T.N. Mitchell, Org. Magn. Reson., 1 (1975) 610.
44 V.S. Petrosyan, Prog. NMR Spectros., 11 (1977) 115.
45 J. Holeček, M. Nádvorník, K. Handlíř, A. Lyčka, J. Organomet. Chem., 24 (1983) 177; 280 (1985) 323.
46 B.Y.K. Ho and J.J. Zuckerman, Inorg. Chem., 12 (1973) 1552.
47 R.H. Herber, H.A. Stöckler and W.T. Reichle, J. Chem. Phys., 42 (1965) 2447.
48 K.C. Molloy and K. Quill, J. Chem. Soc., Dalton Trans., (1985) 1417.
49 S.J. Blunden and R. Hill, Inorg. Chim. Acta, 98 (1985) L7.
50 I. Hammann, K.H. Büchel, K. Bungarz and L. Born, Pflanzenschutz-Nachr. Bayer, 31 (1978) 61.
51 A.L. Rheingold, S.W. Ng and J.J. Zuckerman, Organometallics, 3 (1984) 233.
52 H. Chih and B.R. Penfold, J. Cryst. Mol. Struct., 3 (1973) 285.
53 N.W. Alcock and R.E. Timms, J. Chem. Soc., A, (1968) 1873.
54 K.C. Molloy, T.G. Purcell, K. Quill and I.W. Nowell, J. Organomet. Chem., 267 (1984) 237.
55 B.Y.K. Ho, J.A. Zubieta and J.J. Zuckerman, J. Chem. Soc., Chem. Commun., (1975) 88.
56 P.G. Harrison, K. Lambert, T.J. King and B. Magee, J. Chem. Soc., Dalton Trans., (1983) 363.
57 P.G. Harrison, T.J. King and K.C. Molloy, J. Organomet. Chem., 185 (1980) 199.
58 B.Y.K. Ho and J.J. Zuckerman, J. Organomet. Chem., 49 (1973) 1.
59 G. Roge, F. Huber, A. Silvestri and R. Barbieri, Z. Naturforsch. B, 37 (1982) 1456.
60 H.M. Randall, R.G. Fowler, N. Fuson and J.R. Dangl, Infrared Determination of Organic Structures, Van Nostrand, New York, 1949.
61 M. Meyer zur Heide and S. Wunder, Z. Anal. Chem., 247 (1969) 42.
62 R. Okawara, D.E. Webster and E.G. Rochow, J. Amer. Chem. Soc., 82 (1960) 3287.
63 K. Itoch and H.J. Bernstein, Can. J. Chem., 34 (1956) 170.
64 G. Marcotrigiano and G.C. Pellacani, Z. Anorg. Allg. Chem., 413 (1975) 171; 415 (1975) 268.
65 C.P. Sharma, N. Kumar, S. Chandra and V.G. Bhide, J. Inorg. Nucl. Chem., 43 (1981) 2659.
66 N.F. Curtis, J. Chem. Soc., A, (1968) 1579.
67 G. Micera, L.S. Erre, A. Panzanelli, P. Piu and F. Cariati, J. Coord. Chem., 13 (1984) 231.
68 G.B. Deacon, F. Huber and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.
69 J.N. Brown and L.M. Trefonas, Inorg. Chem., 12 (1973) 1730.
70 B.F.E. Ford, B.V. Liengme and J.R. Sams, J. Chem. Soc., Chem. Commun., (1968) 1333.
71 H. Sano and R. Kuroda, Chem. Phys. Lett., 11 (1971) 512.
72 K.C. Molloy, M.P. Bigwood, R.H. Herber and J.J. Zuckerman, Inorg. Chem., 21 (1982) 3709.
73 W.F. Manders and T.P. Lockhart, J. Organomet. Chem., 297 (1985) 143.