APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 779–790 (1996)

Di- and Tri-organotin(IV) Complexes of *N*-Acetyltriglycine and *N*-Benzoyltriglycine: Synthesis and Spectroscopic Characterization

Giuseppe Ruisi,* Maria Teresa Lo Giudice,* Friedo Huber† and Michael Vornefeld†

* Università di Palermo, Dipartimento di Chimica Inorganica, 26 Via Archirafi, I-90123 Palermo, Italy, and † Fachbereich Chemie, Universität Dortmund, Otto-Hahn Straße 6, D-44221 Dortmund, Germany

Di- and tri-organotin(IV) derivatives of *N*-acetyltriglycine and *N*-benzoyltriglycine (HA) were obtained by refluxing equimolar mixtures of the ligand and the organotin(IV) oxide or hydroxide in methanol or acetone. According to the spectroscopic data, triorganotin(IV) derivatives adopt a trigonal-bipyramidal structure in which the planar R_3Sn^{IV} unit is bonded by a monodentate carboxylate group and a donor group, presumably the amide C=O. The reaction of HA with the appropriate diorganotin(IV) compounds gave both dicarboxylates R_2SnA_2, with six-coordinated tin, and dimeric tetraorganodistannoxanes $\{[R_2SnA]_2O\}_2$, in which the tin atoms are essentially five-coordinated.

Keywords: organotin; *N*-acetyltriglycine; *N*-benzoyltriglycine; Mössbauer

INTRODUCTION

Organotin(IV) carboxylates are widely employed in many fields, e.g. as homogeneous catalysts, or as biocides in agriculture. It is therefore not surprising that they have been studied extensively, particularly from the structural viewpoint.[1] It is interesting to observe that these compounds can adopt a variety of structural types, depending on the nature of the organic substituent R at tin and on the organic group R′ of the carboxylate ligand R′COO. The additional *O*- and *N*-functional groups in amino-acids and peptides make these carboxylate ligands special, and it is of particular interest to study how the organotin moiety ties to protein constituents, and whether the additional coordination sites in the carboxylate ligand can effect structural variations.

Diorganotin(IV) derivatives of *N*-benzoylglycylglycine have been investigated previously.[2] They were believed to be dimeric tetraorganodistannoxanes in which the carboxylate groups alternatively act as monodentate and bridging bidentate ligands, the tin atoms being essentially five-coordinated. Any involvement of peptide/amide groups in bonding to the metal centre was ruled out. On the other hand, in triorganotin(IV) derivatives of *N*-benzoylglycylglycine[2] and *N*-benzoylglycine,[3] planar R_3Sn units are bridged by carboxylate groups. A different coordination type is observed in triorganotin(IV) derivatives of amino-acids and *N*-acetylated dipeptides: X-ray diffraction studies on trimethyltin(IV) glycinate[4] and vibrational and Mössbauer data for the other derivatives[5,6] showed that the carboxylate group acts essentially as a monodentate ligand, and that the amino[4] or amide C=O group[5,6] coordinates to another R_3Sn^{IV} unit. In this way pentacoordination of tin and a polymeric structure result. The amide C=O group seems not to be able to coordinate to the tin atom in the *N*-benzoyl derivatives, presumably as a consequence of the reduced donor power of the oxygen atom, due to the inductive effect($-I$) of the phenyl group.

In this work we studied the products of the reaction of Me_2SnO, n-Bu_2SnO, n-Oct_2SnO, $(n\text{-}Bu_3Sn)_2O$ and Ph_3SnOH with *N*-benzoyltriglycine and *N*-acetyltriglycine in order to examine how a longer peptide chain and the nature of the substituent of the amino nitrogen affect the coordination mode.

CCC 0268–2605/96/100779–12

Received 15 November 1995
Accepted 5 February 1996

EXPERIMENTAL

Materials

The organometallic compounds used for the syntheses were obtained from Sigma–Aldrich (Steinheim, Germany) and Schering AG (Bergkamen, Germany). The other reagents were products from C. Erba (Milan, Italy) and Sigma–Aldrich. Except for methanol, which was refluxed over metallic magnesium and distilled to remove the excess water, all of the reagents were used as received. The ligands *N*-benzoyltriglycine [$C_6H_5(CONHCH_2)_3COOH$, HBzTG] and *N*-acetyltriglycine [$CH_3(CONHCH_2)_3$ COOH, HAcTG] were synthesized by reacting glycylglycylglycine with benzoyl chloride and with acetic anhydride, respectively, according to the literature.[7,8] Me_2SnO was synthesized by treating a methanol Me_2SnCl_2 solution with aqueous ammonia.

Physical measurements

IR spectra were recorded with a Perkin–Elmer 580B spectrophotometer using KBr pellets or nujol and hexachlorobutadiene mulls on CsI discs.

NMR spectra were recorded with a Bruker AC 250E spectrophotometer, operating at 250.1 MHz for ^1H and at 62.89 MHz for ^{13}C.

The Mössbauer spectra were recorded with conventional spectrometers operating in the transmission mode. The source was $Ca^{119}SnO_3$ (Radiochemical Centre, Amersham; 10 mCi), moving at room temperature with constant acceleration in a triangular waveform. The driving system was from Halder (Seehausen, Germany), and the NaI(Tl) detector from Harshaw (De Meern, The Netherlands). Multichannel analysers and the related electronics were obtained from Laben (Milan, Italy; model 4000) and Takes (Bergamo, Italy; model 269). The solid absorber samples, containing *ca* 0.5 mg $^{119}Sn\ cm^{-2}$, were held at 77.3 K in an MNC 200 liquid-nitrogen cryostat, from AERE (Harwell, UK); the solution samples, in 0.5 cm path sample holders, were frozen by immersion in liquid nitrogen. Data reduction was effected by fitting the experimental spectra with Lorentzian lineshapes, using computer programs based upon iterative non-linear least-squares analysis.[9] Calibration was effected with spectra from $Ca^{119}SnO_3$ and ^{57}Fe.

Synthesis of the complexes

The synthesis of the complexes was complicated by the circumstance that the reaction of the diorganotin(IV) oxides with HBzTG and HAcTG in methanol and in ethanol generally gave a mixture of products including the methyl and ethyl esters of the ligand, respectively. On the other hand, the use of another solvent (acetone) was possible only for the synthesis of $Me_2Sn(AcTG)_2$, $[n\text{-}Bu_2Sn(AcTG)]_2O$ and the triorganotin(IV) derivatives of *N*-benzoyltriglycine. The analytical data are reported in Table 1.

n-Bu_3Sn(BzTG)

A mixture of 0.5 mmol $(n\text{-}Bu_3Sn)_2O$ and 1 mmol HBzTG in *ca* 30 cm^3 of acetone was refluxed for 2 h and subsequently filtered. The solution was concentrated under reduced pressure; on cooling, colourless needle crystals were obtained.

Ph_3Sn(BzTG)

A mixture of 1 mmol Ph_3SnOH and 1 mmol HBzTG in *ca* 30 cm^3 of acetone was refluxed for

Table 1 Analytical data for *N*-benzoyltriglycine, *N*-acetyltriglycine and organotin(IV) derivatives

Compound	Elemental analysis (%): found (calcd) C	H	N	M.p.[a] (°C)
HBzTG	52.91	5.23	14.57	176 dec.
$C_{13}H_{15}N_3O_5$	(53.24)	(5.16)	(14.33)	
$Me_2Sn(BzTG)_2$	45.92	4.73	11.29	205 dec.
$C_{28}H_{34}N_6O_{10}Sn$	(45.86)	(4.67)	(11.46)	
$[n\text{-}Bu_2Sn(BzTG)]_2O$	46.78	6.05	7.74	126–127
$C_{42}H_{64}N_6O_{11}Sn_2$	(47.30)	(6.05)	(7.88)	
n-Bu_3Sn(BzTG)	51.70	7.29	7.34	145–147
$C_{25}H_{41}N_3O_5Sn$	(51.56)	(7.10)	(7.22)	
Ph_3Sn(BzTG)	58.02	4.75	6.75	248–250
$C_{31}H_{29}N_3O_5Sn$	(57.97)	(4.55)	(6.54)	
HAcTG	41.15	5.85	17.94	187 dec.
$C_8H_{13}N_3O_5$	(41.56)	(5.67)	(18.17)	
$Me_2Sn(AcTG)_2$	35.78	5.09	14.05	222 dec.
$C_{18}H_{30}N_6O_{10}Sn$	(35.49)	(4.96)	(13.80)	
$[n\text{-}Bu_2Sn(AcTG)]_2O$	40.82	6.62	8.70	168–170
$C_{32}H_{60}N_6O_{11}Sn_2$	(40.79)	(6.42)	(8.92)	
$[n\text{-}Oct_2Sn(AcTG)]_2O$	49.50	7.34	7.16	122–124
$C_{48}H_{92}N_6O_{11}Sn_2$	(49.41)	(7.95)	(7.20)	
n-Bu_3Sn(AcTG)	45.98	7.65	8.11	131–133
$C_{20}H_{39}N_3O_5Sn$	(46.17)	(7.56)	(8.08)	
Ph_3Sn(AcTG)	53.55	4.69	7.42	204 dec.
$C_{26}H_{27}N_3O_5Sn$	(53.82)	(4.69)	(7.24)	

[a] dec., decomposition.

6 h. The resulting cloudy solution was filtered: a white solid precipitated immediately, and was recrystallized from acetone.

$Me_2Sn(BzTG)_2$
A mixture of 1 mmol Me_2SnO and 1 mmol HBzTG in 25–30 cm^3 of methanol was stirred for 24 h at room temperature: the suspension was then filtered and the white solid was recrystallized from methanol. The same product was obtained on cooling the solution obtained by refluxing the reaction mixture for 50 min.

$[n\text{-}Bu_2Sn(BzTG)]_2O$
A mixture of 1 mmol $n\text{-}Bu_2SnO$ and 1 mmol HBzTG in 30 cm^3 of methanol was refluxed for 2 h. The clear solution obtained was evaporated to dryness. The suspension of the residue in acetone was refluxed for two days and was then filtered; on cooling a crystalline product was obtained.

$n\text{-}Bu_3Sn(AcTG)$
A mixture of 0.5 mmol $(n\text{-}Bu_3Sn)_2O$ and 1 mmol HAcTG in 30 cm^3 of methanol was refluxed for 6–7 h. The resulting cloudy solution was filtered and concentrated under reduced pressure: the oil that was obtained was dried, giving a white powder which was recrystallized from acetone.

$Ph_3Sn(AcTG)$
A mixture of 1 mmol Ph_3SnOH and 1 mmol HAcTG in 30 cm^3 of methanol was refluxed for 24 h. A cloudy solution resulted, which was filtered, concentrated under reduced pressure and stored in a refrigerator until a white solid was formed.

$Me_2Sn(AcTG)_2$
A mixture of 1 mmol Me_2SnO and 1 mmol HAcTG in 25–30 cm^3 of methanol was refluxed for 18 h; the solid residue was filtered off, washed with methanol and dried *in vacuo*. Alternatively, the product was obtained by refluxing a mixture of 1 mmol Me_2SnO and 1 mmol HAcTG in 50 cm^3 of acetone for two days. A cloudy solution was obtained which was filtered, concentrated under reduced pressure and stored at low temperature. After a few days a white solid precipitated.

$[n\text{-}Bu_2Sn(AcTG)]_2O$
A mixture of 1 mmol $n\text{-}Bu_2SnO$ and 1 mmol HAcTG in 30 cm^3 of acetone was refluxed for 48 h: the resulting white solid was separated by filtration, washed with hot acetone and dried.

$[n\text{-}Oct_2Sn(AcTG)]_2O$
A mixture of 1 mmol $n\text{-}Oct_2SnO$ and 1 mmol HAcTG in 30 cm^3 of methanol was refluxed for 1 h, the solid was then removed and the solution was evaporated to dryness *in vacuo*. Refluxing the residue in acetone for 1 h gave a cloudy solution which was filtered and stored in a refrigerator; a white solid precipitated after a few days.

Methyl/ethyl esters of the ligands

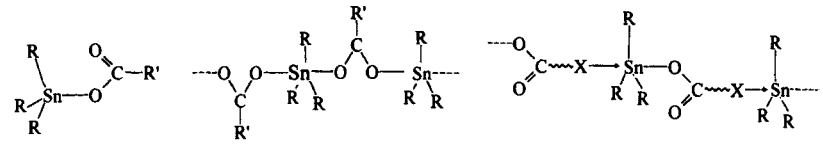
The methyl/ethyl ester of *N*-benzoyltriglycine was obtained by refluxing a mixture of 1 mmol Alk_2SnO (Alk=Me or n-Bu) and 1 mmol HBzTG in 30 cm^3 of methanol/absolute ethanol for 24 h. The resulting cloudy solution was then filtered and cooled. The white solid obtained was recrystallized from methanol/absolute ethanol. The esters of *N*-acetyltriglycine were prepared in a similar way, using 60–70 cm^3 of solvent and refluxing for seven days. It is noteworthy that any attempt to obtain the esters by reacting *N*-benzoyltriglycine or *N*-acetyltriglycine with the appropriate alcohol in the absence of the diorganotin(IV) oxide failed.

RESULTS AND DISCUSSION

Triorganotin(IV) derivatives

Triorganotin(IV) carboxylates may adopt in principle a tetrahedral structure (**A**), in which the carboxylate group of the ligand is monodentate, or a trigonal-bipyramidal structure in which planar R_3Sn^{IV} units are linked by bidentate carboxylate bridges (**B**) or by ligands with a monodentate carboxylate group and a donor group X present in the molecule of that ligand (**C**) (Fig. 1).

The values of the Mössbauer parameter quadrupole splitting (QS) for the compounds investigated (see Table 2) are typical of trigonal-bipyramidal structures with the organic groups bound to tin in the equatorial plane and with the electronegative ligands in the axial position.[10,11] Structure (**A**) can then be ruled out. However, on the basis of the Mössbauer data it is not possible to distinguish between structures (**B**) and (**C**). 'Point-charge' calculations[12] based on a regular trigonal-bipyramidal structure (see Fig. 2) give QS_{calc} values which are consistent with the experimental values, the difference $|QS_{calc} -$



(A) (B) (C)

Figure 1 Possible structures for triorganotin(IV) carboxylates.

QS_{exp}| being less than 0.4 mm s^{-1} for both structures.[13] The pqs (partial quadrupole splitting) values used were: $[Alk]^{tbe} = -1.13$ mm s^{-1};[10] $[Ph]^{tbe} = -0.98$ mm s^{-1};[10] $[COO_{monod.}]^{tba} = -0.10$ mm s^{-1};[14] $[COO_{deloc.}]^{tba} = 0.075$ mm s^{-1};[10] $[C{=}O]^{tba} = 0.16$ mm s^{-1};[10] $[NH]^{tba} = 0.01$ mm s^{-1}.[10]

Information on the nature of the tin–ligand bonds can be extracted from infrared absorption frequencies (Tables 3 and 4). In the spectra of triorganotin(IV) derivatives a strong absorption band is present in the range 1673–1691 cm^{-1}, which can be attributed to the (C=O) stretching vibration of the carboxylate group [often reported as the asymmetric stretching mode ν_{asym}(O–C–O)], indicating an ester–like tin–carboxylate bond. Since the geometry around tin is essentially trigonal-bipyramidal, as evidenced by Mössbauer quadrupole splitting values, the tin atom must be further coordinated by a donor group (such as amide C=O), as observed, for example, in organotin(IV) derivatives of *N*-acetylamino-acids,[6] *N*-formylglycine[3] and *N*-acetyldipeptides.[5] The involvement of this group, or possibly the NH group, should produce a variation in the Amide I frequency, essentially

Table 2 Mössbauer parameters, at 77 K, for organotin(IV) derivatives of *N*-benzoyltriglycine and *N*-acetyltriglycine

Compound	IS[a] (mm s^{-1})	QS[b] (mm s^{-1})	Γ_1[c] (mm s^{-1})	Γ_2[c] (mm s^{-1})	$(C{-}Sn{-}C)_{calcd}$ (°)
n-Bu_3Sn(BzTG)	1.47	3.44	0.79	0.86	140.5
20 mM soln in MeOH	1.47	3.55	0.77	0.82	144.1
Ph_3Sn(BzTG)	1.36	3.34	0.85	0.92	139.5
20 mM soln in MeOH	1.30	3.20	0.75	0.84	135.2
n-Bu_3Sn(AcTG)	1.52	3.65	0.77	0.84	147.6
20 mM soln in MeOH	1.48	3.60	0.67	0.82	145.8
Ph_3Sn(AcTG)	1.34	3.23	0.83	0.92	136.1
10 mM soln in MeOH	1.31	3.20	0.77	0.85	135.2
$Me_2Sn(BzTG)_2$	1.31	3.40	0.83	0.91	139.3
$Me_2Sn(AcTG)_2$	1.43	4.22	1.10	1.20	180.0
[n-Bu_2Sn(BzTG)]$_2O$[d]	1.24	2.85	0.84		123.5
	1.35	3.46	0.78		141.2
20 mM soln in MeOH[e]	1.24	2.98	0.75		127.1
	1.38	3.60	0.82		145.8
[n-Bu_2Sn(AcTG)]$_2O$[f]	1.26	3.21	0.81		133.6
	1.42	3.80	0.75		153.5
20 mM soln in MeOH[g]	1.15	3.03	0.74		128.5
	1.40	3.54	0.81		143.8
[n-Oct_2Sn(AcTG)]$_2O$[h]	1.38	3.65	0.77		147.6
	1.33	3.09	0.77		130.2
20 mM soln in MeOH[i]	1.36	3.44	0.81		140.5
	1.20	2.89	0.75		124.6

[a] Isomer shift relative to room-temperature $Ca^{119}SnO_3$. [b] Nuclear quadrupole splitting. [c] Full width at half height of the resonant peaks, at lower and higher velocity than the spectrum centroid, respectively. [d–i] Spectra fitted with two symmetric doublets. [d] $A_1 = 51.0\%$; $A_2 = 48.0\%$ (A_1 and A_2 are the relative areas of the doublets). [e] $A_1 = 50.0\%$; $A_2 = 50.0\%$. [f] $A_1 = 52.3\%$; $A_2 = 47.7\%$. [g] $A_1 = 49.9\%$; $A_2 = 50.1\%$. [h] $A_1 = 57.1\%$; $A_2 = 42.9\%$. [i] $A_1 = 62.1\%$; $A_2 = 37.9\%$.

ν(C=O), and in the Amide II frequency, ν(C–N)+δ(NH). Upon coordination of tin by oxygen of amide C=O, the frequency of the Amide I band would decrease and the frequency of Amide II would increase with respect to the values observed for the free groups; the opposite is expected in the case of coordination by the NH group.[6] In the spectra of *N*-acetyltriglycine derivatives (Fig. 3) a shift to lower frequencies of the Amide I band and a shift to higher frequencies of the Amide II band can be observed with respect to the spectrum of *N*-acetyltriglycine. As far as *N*-benzoyltriglycine derivatives are concerned, the spectra are characterized by a shift to lower frequencies of both Amide I and Amide II bands. We can then suppose that the amide C=O group coordinates to tin in all complexes, the anomalous shift of Amide II band in *N*-benzoyltriglycine derivatives being perhaps due to hydrogen bonds. The ν(N–H) frequencies of the ligands and of the triorganotin(IV) derivatives are found in the range characteristic for bonded NH groups and they do not give useful information.

In any case, the possibility must be considered that the interaction of amide C=O and tin may be weak, and that therefore the geometry of tin is probably better described as a distorted tetrahedron, as found for example in $[(CH_3)_2Sn(O_2CC_6H_4OH\text{-}o)]$,[1] where the OH group of the salicylate forms a weak intermolecular contact with a tin atom nearby, which is displaced 0.35 Å out of the plane defined by the CH_3 groups. The X–Sn–R bond angle, θ, in distorted tetrahedral structures R_3SnX may be evaluated from the Mössbauer quadrupole splitting value by means of Eqn [1].[15]

$$QS = 2[X]^{tet} - 3[R]^{tet}(1 - 3\cos^2\theta) \qquad [1]$$

Using literature pqs values,[12] $[X]^{tet} = [COO_{monod.}]^{tet} = -0.15$ mm s^{-1}, $[Alk]^{tet} = -1.37$ mm s^{-1} and $[Ph]^{tet} = -1.26$ mm s^{-1}, X–Sn–C bond angles of 100.0°, 96.4°, 96.1° and 98.7° were calculated for n-Bu_3Sn(BzTG), Ph_3Sn(BzTG), n-Bu_3Sn(AcTG) and Ph_3Sn(AcTG) respectively, which are intermediate between the tetrahedral angle and 90°, suggesting in effect a long Sn–O contact.

Studies in the solution phase were carried out by means of NMR and Mössbauer spectroscopy. ^{1}H NMR spectra were recorded from CD_3OD and DMSO-d_6 solutions, using TMS as internal standard; ^{13}C NMR spectra were also recorded for *N*-benzoyltriglycine derivatives in CD_3OD. The Mössbauer spectra were taken using methanol solutions frozen by immersion in liquid nitrogen. The Mössbauer parameters (Table 2) are practically coincident with those relating to the solid-state complexes, indicating that the geometry of tin is maintained in methanol solution. ^{1}H NMR spectral data are collected in Tables 5 and 6. The assignments of the methylene and NH signals were made according to Rabenstein.[16]

The ^{1}H NMR spectrum of n-Bu_3Sn(BzTG) in CD_3OD (Table 5) is characterized by an upfield shift of the α-CH_2 signal (3.95→3.83 ppm), indicating that the tin is bonded to the deprotonated carboxylate group; the β- and γ-CH_2 signals are instead practically unchanged (β-CH_2, 3.95→3.93 ppm; γ-CH_2, 4.08→4.07 ppm). In the case of Ph_3Sn(BzTG) we observe a larger shift of the α-CH_2 signal; also, the γ-CH_2 and, mainly, the β-CH_2 signals are shifted upfield: α-CH_2, 3.95→3.78 ppm; β-CH_2, 3.95→3.85 ppm; γ-CH_2, 4.08→4.02 ppm. The shifts of β-CH_2 and γ-CH_2 signals are however very similar to those observed in the spectrum of the methyl ester and it is not possible

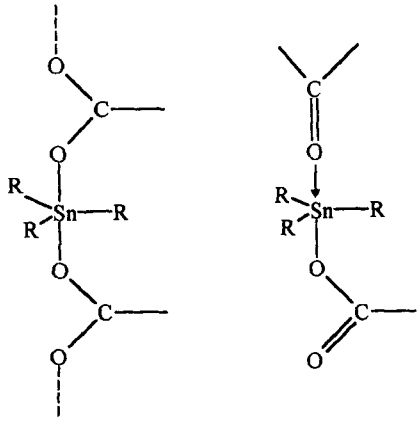


Figure 2 Point-charge calculations for triorganotin(IV) carboxylates with planar R_3Sn^{IV} units bridged by bidentate carboxylate groups (**I**) and bonded by a monodentate carboxylate and an amide C=O group (**II**). Regular trigonal-bipyramidal structures are assumed. The pqs values used are reported in the Results and Discussion section.

Table 3 Characteristic IR spectral data (cm^{-1}) for *N*-benzoyltriglycine and organotin(IV) derivatives

HBzTG	NaBzTG	MeBzTG	EtBzTG	$Ph_3SnBzTG$	$n\text{-}Bu_3SnBzTG$	$Me_2Sn(BzTG)_2$	$[n\text{-}Bu_2Sn(BzTG)]_2O$	Assignments
3305vs,br	3495s	3556m	3412m,br	3285s,br	3295s,br	3284vs,br	3278vs,br	ν(NH)
3081s	3420s	3303vs,br	3301vs,br	3066s	3061m	3077m	3060s	
	3326vs	3078m	3080m					
	3262s							
	3075m							
1701vs		1744vs	1741vs	1690vs	1673vs			ν(C=O) (carboxylate)
1658vs	1670vs	1675s	1671vs	1658vs	1630vs,br	1688s	1642vs,br	Amide I
1647vs	1631vs	1638vs,br	1641vs	1642vs		1662vs		
1631vs			1632vs	1624vs		1642vs		
	1599vs					1611s	1596s,br	ν_{asym}(OCO)
1576s	1588vs	1579vs	1551vs,br	1572vs,br	1563vs, br	1580s	1535vs,br	Amide II
1553vs	1553vs	1553vs,br			1525vs,br	1562sh		
1537vs	1537vs					1546vs		
	1406vs					1384m	1396s	ν_{sym}(OCO)
				450s				$\nu(B_1)$[a]
				279m		512w	584m	ν(Sn–C)
						426w	430w	ν(Sn–O)
							639s	ν(Sn–O–Sn)

[a] Characteristic of the Ph–Sn group.[28]

Abbreviations: w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder.

Table 4 Characteristic IR spectral data (cm^{-1}) for *N*-acetyltriglycine and organotin(IV) derivatives

HAcTG	NaAcTG	MeAcTG	EtAcTG	$Ph_3SnAcTG$	$n\text{-}Bu_3SnAcTG$	$Me_2Sn(AcTG)_2$	$[n\text{-}Bu_2Sn(AcTG)]_2O$	$[n\text{-}Oct_2Sn(AcTG)]_2O$	Assignments
3321s,br	3303vs,br	3303vs,br	3309vs,br	3281s	3289s	3300vs,br	3306vs,br	3291vs,br	ν(NH)
3079m	3084s	3227s	3078s	3093m	3089m	3079m	3090m	3083s	
		3075s							
1725vs		1747vs	1742s	1689s	1691s		1693s		ν(C=O) (carboxylate)
1667vs	1642vs,br	1675s	1641vs,br	1658vs	1659vs	1679m	1658vs	1665vs,br	Amide I
1649vs		1640vs		1623vs	1647vs	1641vs,br	1640vs		
1624vs					1624vs		1631vs		
	1607vs						1587vs,br	1594vs	ν_{asym}(OCO)
1561vs,br	1562vs,br	1566vs,br	1565s,br	1565s,br	1569vs,br	1553vs,br	1523vs,br	1552vs,br	Amide II
1550vs,br									
	1395s					1393m	1400s,sh	1396vs	ν_{sym}(OCO)
				455m					$\nu(B_1)$[a]
				275m	503m	546m	508m	551m	ν(Sn–C)
								427m	ν(Sn–O)
							597s,br	639s	ν(Sn–O–Sn)

[a] Characteristic of the Ph–Sn group.[28]
Abbreviations as in Table 3.

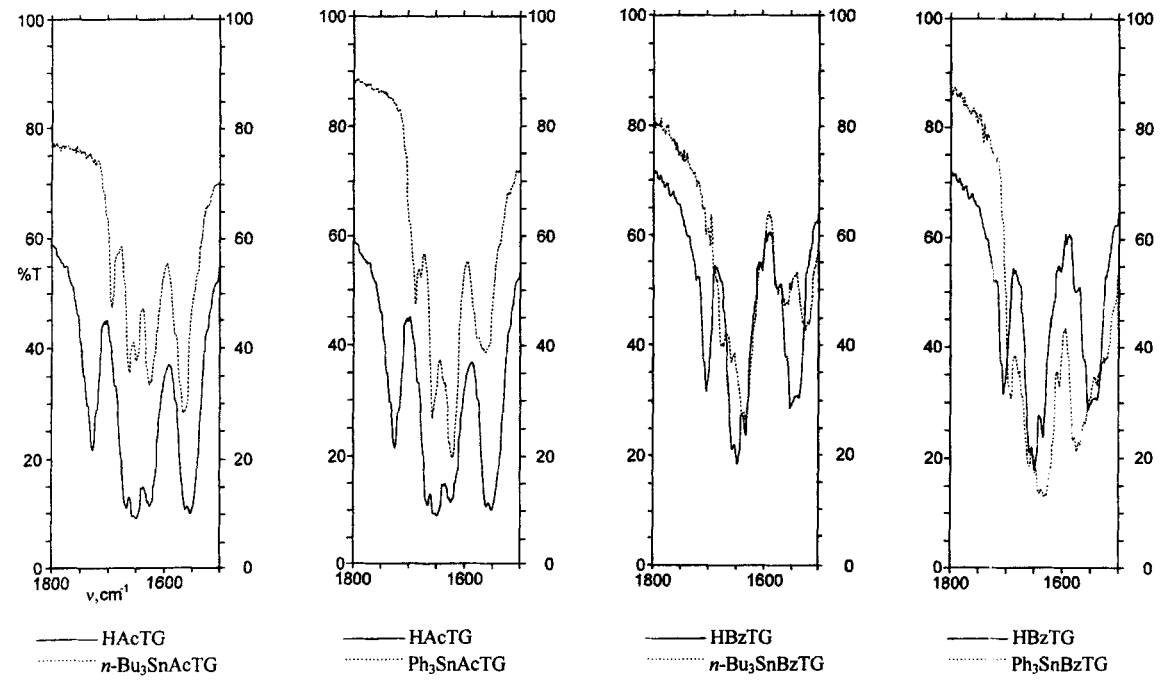


Figure 3 Infrared spectra of *N*-acetyltriglycine, *N*-benzoyltriglycine and their triorganotin derivatives in the range 1500–1800 cm^{-1}.

to relate such shifts to a possible tin–amide group interaction.

The spectra measured in DMSO-d_6 can be commented upon in a similar manner: the α-CH_2 signals of n-Bu_3Sn(BzTG) and Ph_3Sn(BzTG) are shifted upfield with respect to the signals of the ligand and a larger shift is observed for the α-NH signals: from 8.16 (8.24) to 7.91 ppm for n-Bu_3Sn(BzTG), while the α-NH signal of the triphenyltin(IV) derivative appears below 7.95 ppm, overlapping with the signals of the benzoyl *ortho*-protons. The other signals are

Table 5 ^1H NMR spectral data[a] for *N*-benzoyltriglycine[b] and organotin(IV) derivatives in CD_3OD and DMSO-d_6

Compound	Solvent	α-CH_2	β-CH_2	γ-CH_2	α-NH	β-NH	γ-NH	*o*-Ph	*m,p*-Ph	Other signals	
HBzTG	CD_3OD	3.95	3.95	4.08				7.87–7.91	7.43–7.59		
	DMSO-d_6	3.77d	3.77d	3.93d	8.16t	8.24t	8.80t	7.88–7.91	7.44–7.57	OH	12.47b
NaBzTG	CD_3OD	3.78	3.93	4.10				7.88–7.92	7.43–7.58		
	DMSO-d_6	3.34d	3.76d	3.99d	7.37t	8.40t	8.99t	7.94–7.98	7.52–7.66		
MeBzTG	CD_3OD	3.84	3.88	3.97				7.77–7.80	7.34–7.46	O–CH_3	3.61
	DMSO-d_6	3.77d	3.87d	3.92d	8.24–8.30		8.79t	7.88–7.91	7.44–7.54		3.63
EtBzTG	CD_3OD	3.88	3.90	4.01				7.80–7.84	7.37–7.49	O–CH_2–	4.11q
										–CH_3	1.19t
	DMSO-d_6	3.84d	3.92d	3.99d	8.30–8.36		8.87t	7.94–7.98	7.52–7.63	O–CH_2–	4.16q
										–CH_3	1.26t
n-Bu_3SnBzTG	CD_3OD	3.83	3.93	4.07				7.89d	7.44–7.58	Sn–Bu^n	0.88–1.74
	DMSO-d_6	3.64d	3.78d	3.97d	7.91t	8.21t	8.83t	7.94d	7.50–7.60		0.88–1.67
Ph_3SnBzTG	CD_3OD	3.78	3.85	4.02				7.68–7.96	7.36–7.56		
	DMSO-d_6	3.62d	3.70d	3.91d	n.a.*	8.11t	8.74t	7.66–7.95	7.36–7.54		
[n-Bu_2SnBzTG]$_2$O	CD_3OD	3.88	3.94	4.07				7.85–7.91	7.43–7.55	Sn–Bu^n	0.88–1.71

[a] Chemical shifts (ppm) downfield from internal TMS. [b] *N*-Benzoyltriglycine: C_6H_5–CO–$^{\gamma}$NH–$^{\gamma}CH_2$–CO–$^{\beta}$NH–$^{\beta}CH_2$–CO–$^{\alpha}$NH–$^{\alpha}CH_2$–COOH

Abbreviations. d, doublet; t, triplet; q, quartet; b, broad; n.a., not assigned; * the signal is hidden by the *o*-Ph signals.

Table 6 ^{1}H NMR spectral data[a] for *N*-acetyltriglycine[b] and organotin(IV) derivatives in CD_3OD and DMSO-d_6

Compound	Solvent	α-CH_2	β-CH_2	γ-CH_2	α-NH	β-NH	γ-NH	CH_3	Other signals	
HAcTG	CD_3OD	3.87	3.92	3.92				2.01		
	DMSO-d_6		3.76–3.83		8.21t	8.21t	8.21t	1.92	OH	12.5b
NaAcTG	CD_3OD	3.78	3.89	3.91				2.03		
	DMSO-d_6		3.67–3.73		7.34t	8.29t	8.29t	1.87		
MeAcTG	CD_3OD	3.86	3.92	3.96				2.02	(O)–CH_3	3.72
	DMSO-d_6	3.63–3.73		3.84d	8.15–8.30			1.86	(O)–CH_3	3.63
EtAcTG	CD_3OD	3.87	3.92	3.95				2.02	(O)–CH_2–	4.18q
									–CH_3	1.24t
	DMSO-d_6	3.69–3.75		3.83d	8.14–8.18		8.25t	1.86	(O)–CH_2–	4.09q
									–CH_3	1.20t
n-Bu_3Sn(AcTG)	CD_3OD	3.82	3.87	3.91				2.01	(Sn)–Bu^n	0.89–1.67
	DMSO-d_6	3.59d	3.70d	373d	7.79t	8.06t; 8.11t		1.87	(Sn)–Bu^n	0.84–1.59
Ph_3Sn(AcTG)	CD_3OD	3.81	3.84	3.86				1.98	Ph	7.43–7.95
	DMSO-d_6	3.65d	3.72–3.74		n.a.*	8.11t; 8.16t		1.90	Ph	7.43–7.86
[n-Bu_2Sn(AcTG)]$_2O$	CD_3OD	3.68	3.68	3.92				2.03	(Sn)–Bu^n	0.90–1.67
[n-Oct_2Sn(AcTG)]$_2O$	CD_3OD	3.87	3.87	3.92				2.02	(Sn)–Oct^n	0.85–1.75

[a] Chemical shifts (ppm) downfield from internal TMS. [b] *N*-Acetyltriglycine: CH_3–CO–$^{\gamma}$NH–$^{\gamma}CH_2$–CO–$^{\beta}$NH–$^{\beta}CH_2$–CO–$^{\alpha}$NH–$^{\alpha}CH_2$–COOH

Abbreviations as in Table 5.

essentially coincident with the signals of the ligand.

The spectra of the *N*-acetyltriglycine derivatives in CD_3OD solution are characterized by similar trends, though the changes in the position of the peaks with respect to HAcTG are rather small. However, in the spectra measured in DMSO-d_6 an upfield shift of α-CH_2 and α-NH signals is quite evident (Table 6). From the data it may be inferred that in both solvents the triorganotin(IV)–carboxylate bond is maintained, while there is no evidence regarding the coordination of tin by amide C=O or by amide NH.

The ^{13}C NMR spectral data of *N*-benzoyltriglycine derivatives (Table 7) do not give further information, the carbonyl chemical shifts being very close to those observed in the spectrum of the sodium salt.

Diorganotin(IV) derivatives

Reaction of R_2SnO with HAcTG and HBzTG, respectively, in methanol or ethanol affords

Table 7 ^{13}C NMR spectral data[a] for triorganotin(IV) derivatives of *N*-benzoyltriglycine[b]

Compound	$\delta(C_6H_5)$	δ(C=O) (amide)	δ(C=O) (carboxylate)	$\delta(CH_2)$	δ(R)
NaBzTG	134.78	172.27	176.28	44.26	
	132.88	171.15		43.48	
	129.46	170.61			
	128.51				
n-Bu_3SnBzTG	134.76	172.25	175.78	44.34	29.00
	132.89	171.62		43.37	28.04
	129.45	170.74		43.05	18.35
	128.48				14.05
Ph_3SnBzTG	134.60	171.94	175.10	44.14	141.53
	132.77	171.31		43.22	137.35
	129.45	170.42		42.96	130.28
	128.34				129.36

[a] Chemical shifts (ppm) downfield from internal TMS. [b] R_3Sn(BzTG): C_6H_5–CO–NH–CH_2–CO–NH–CH_2–CO–NH–CH_2–$COOSnR_3$.

essentially two products. Depending on the reaction time, either the diorganotin dicarboxylate $R_2Sn(O_2CR')_2$ or the tetraorganodistannoxane $[R_2Sn(O_2CR')]_2O$ is obtained in addition to the methyl ester (in methanol solution) or the ethyl ester (in ethanol solution) of the ligand. Fortunately, the esterification reaction is slower, especially in the case of *N*-acetyltriglycine. $Me_2Sn(AcTG)_2$ was also obtained using acetone as solvent. Five species were isolated, the two diorganotin(IV) dicarboxylates, $Me_2Sn(BzTG)_2$ and $Me_2Sn(AcTG)_2$, and three tetraorganodistannoxanes, $[n\text{-}Bu_2Sn(BzTG)]_2O$, $[n\text{-}Bu_2Sn(AcTG)]_2O$ and $[n\text{-}Oct_2Sn(AcTG)]_2O$ (Table 1).

Diorganotin(IV) dicarboxylates

In the compounds of the general formula $R_2Sn(O_2CR')_2$ characterized by X-ray diffraction studies to date, the Sn atoms exist in skew trapezoidal-bipyramidal geometries with the basal plane being defined by two asymmetrically chelating carboxylate groups. The axial positions are occupied by the two organo substituents in such a way that the R groups are disposed over the longer Sn–O vectors with the C–Sn–C bond angles ranging from 130° to 152°.[1,17–20]

The degree of the distortion in these structures is reflected in the value of the Mössbauer parameter quadrupole splitting. In five- and six-coordinate diorganotin(IV) compounds this parameter is largely determined by the highly covalent Sn–C bonds, and normally the contribution of the other ligands to the electric field gradient may be neglected; with this approximation the quadrupole splitting may be calculated using Eqn [2].[15]

$$QS = 4[R]\sqrt{1 - \frac{3}{4}\sin^2\theta} \qquad [2]$$

where [R] is the pqs value for the alkyl group, -1.03 mm s^{-1},[21] and θ is the C–Sn–C bond angle. The soundness of this correlation was essentially confirmed by a number of structural data; for example, the compounds $n\text{-}Bu_2Sn(O_2CC_6H_4OH\text{-}o)_2$ and $n\text{-}Bu_2Sn(O_2CC_6H_4Cl\text{-}o)_2$[17] are characterized by C–Sn–C bond angles of 143.9° and 140.4° respectively. The observed quadrupole splitting values are 3.57 and 3.53 mm s^{-1}, which give calculated C–Sn–C bond angles of 144.8° and 143.5° respectively. However, it must be pointed out that, although all the structures reported in the literature are quite distorted, more regular structures may be hypothesized for some diorganotin(IV) dicarboxylates which are characterized, like some diorganotin(IV) bis(trimethoxybenzoate)s reported by Gielen,[22] by quadrupole splitting values up to 4.32 mm s^{-1}, typical for octahedral *trans*-R_2Sn structures. The Mössbauer parameters and the C–Sn–C bond angles calculated by means of Eqn [2] are reported in Table 2. From this table we can see that, while the C–Sn–C bond angle (139.3°) of the first compound falls in the range observed for the diorganotin(IV) dicarboxylates, $Me_2Sn(AcTG)_2$ seems to have a more regular geometry. The relatively large linewidths of the Mössbauer peaks in the spectrum of $Me_2Sn(AcTG)_2$ may indicate the presence of two tin atoms with a slightly different chemical environment.

The spectra of the dimethyltin(IV) derivatives are characterized by the absence of the carboxylate stretching frequency ν(C=O), which indicates that tin is bonded to this group. Moreover, two intense bands are present in the spectrum of $Me_2Sn(BzTG)_2$, at 1611 and 1384 cm^{-1}, which can be assigned to the asymmetric and symmetric O–C–O stretching modes, respectively. In the spectrum of $Me_2Sn(AcTG)_2$ only the absorption band of the symmetric stretching mode is recognizable, at 1393 cm^{-1}. The asymmetric stretching frequency is probably masked by the broad band centred at 1641 cm^{-1}, which can be assigned, together with the band at 1679 cm^{-1}, to the ν(C=O) stretching of the amide groups (Amide I band). The position of these bands is similar to that observed in the spectra of the sodium salts of the ligands, indicating the presence of a delocalized carboxylate group. The very large QS value which characterizes the *N*-acetyltriglycine derivative could originate from more symmetric, that is to say bridging, bidentate behaviour of the carboxylate. Alternatively, it has been demonstrated[23,24] that when tin adopts skew trapezoidal-bipyramidal geometry it can, with relative ease, expand its coordination number to seven, thus causing a decisive increase in the C–Sn–C bond angle. Thus it is possible that the mode of bidentate behaviour is the same for the ligands of both complexes but that, in the case of $Me_2Sn(AcTG)_2$, tin forms an additional bond as a result of an associated structure or as a result of it being a hydrate with the water coordinated to tin.

methanol, ethanol, dimethyl sulphoxide and other common solvents did not allow us to study their behaviour in the solution phase.

Tetraorganodistannoxanes

The structure of tetraorganodistannoxanes, $\{[R_2Sn(O_2CR')]_2O\}_2$, is built up around a planar $(Sn–O)_2$ unit, with two exocyclic Sn atoms connected to the bridging O atoms of the $(Sn–O)_2$ unit. The coordination mode of the carboxylate ligand defines up to five structural types,[1,25] but the geometry of tin is not always well defined, the coordination number ranging from five to six. Also, the nature of the carboxylate-tin bond cannot be clearly described in all cases due to possible interactions of the tin atoms with neighbouring oxygen atoms. Normally, Mössbauer spectra do not reveal the presence of tin atoms with different coordination numbers in such compounds: the spectra of the tetraorganodistannoxanes are characterized by a symmetric doublet whose quadrupole splitting may be related rather to the mean value of the C–Sn–C bond angle in the dimer.[26] Spectra containing two doublets were also reported.[22]

The Mössbauer spectra of the complexes $[n\text{-}Bu_2Sn(BzTG)]_2O$, $[n\text{-}Bu_2Sn(AcTG)]_2O$ and $[n\text{-}Oct_2Sn(AcTG)]_2O$ (Table 2) are quite asymmetric, and fitted well with two symmetric doublets with similar areas. Two tin environments are then present in each dimer. The C–Sn–C bond angles which were calculated with Eqn [2] are listed in Table 2. From these values it is inferred that four- and six-coordination of tin can be excluded, but that the tin atoms are formally five-coordinated. It is suggested that, as in comparable distannoxanes,[1] weak interactions with the neighbouring oxygen atoms exist.

In the IR spectra of the three complexes (Tables 3 and 4), two strong bands that are present near 1600 and 1400 cm^{-1} can be attributed to the asymmetric and symmetric stretching frequencies of the carboxylate group, respectively. They strictly correspond to appropriate bands observed in the spectrum of the sodium salt and suggest the presence of symmetric (bridging) carboxylate groups. A strong band, characteristic of the tetraorganodistannoxanes and attributed to the $(Sn–O)_2$ ring vibration, is present in the spectra near 600 cm^{-1}. Tentative assignments of Sn–C and Sn–O stretching frequencies are also reported in Tables 3 and 4. In the IR spectrum of $[n\text{-}Bu_2Sn(AcTG)]_2O$ an additional strong band is present at 1693 cm^{-1}, which can be attributed to ν(C=O) of a carboxylate group which, then, is bonded to tin in a monodentate (ester-type) way. Apparently, $[n\text{-}Bu_2Sn(AcTG)]_2O$ contains both monodentate and bridging bidentate carboxylate groups, whereas the other distannoxanes contain only bridging bidentate carboxylate groups. However, it must be pointed out that the ν(C=O) frequency would be lowered by intermolecular hydrogen bonds,[27] and then ester-like bonds in $[n\text{-}Bu_2Sn(BzTG)]_2O$ and $[n\text{-}Oct_2Sn(AcTG)]_2O$ cannot be excluded. The molecular geometry of the compounds in methanol solution was investigated by means of Mössbauer and ^1H NMR spectroscopy; it was not possible to record well-resolved NMR spectra in DMSO-d_6. The Mössbauer spectra, obtained from solutions frozen by immersion in liquid nitrogen, are very similar to those of solid samples, indicating that the complexes retain essentially the solid-state configuration in this solvent. The ^1H NMR spectrum of $[n\text{-}Bu_2Sn(BzTG)]_2O$, like that of the other derivatives of *N*-benzoyltriglycine (Table 5), is characterized by an upfield shift of the α-CH_2 signal, indicating the presence of a tin–carboxylate bond. As far as the spectra of the *N*-acetyltriglycine derivatives are concerned, a marked upfield shift is observed for both α- and β-CH_2 groups in $[n\text{-}Bu_2Sn(AcTG)]_2O$, while the spectrum of $[n\text{-}Oct_2Sn(AcTG)]_2O$ shows only a small variation with respect to the spectrum of the ligand: however, it should be kept in mind that the chemical shift values are very similar so that the assignments of the signals are merely tentative. Nevertheless, the NMR data, like the Mössbauer data (see above), indicate that the complexes essentially retain their solid-state structure in methanol solution.

Acknowledgements Financial support by the Ministero per l'Università e la Ricerca Scientifica e Tecnologica, Roma, and by the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. E. R. T. Tiekink, *Appl. Organomet. Chem.* **5**, 1 (1991).
2. G. Ruisi and M. T. Lo Giudice, *Appl. Organomet. Chem.* **5**, 385 (1991).

3. G. Roge, F. Huber, A. Silvestri and R. Barbieri, *Z. Naturforsch. Teil B.* **37**, 1456 (1982).
4. Y. K. Ho, K. C. Molloy, J. J. Zuckerman, F. Reidinger and J. A. Zubieta, *J. Organomet. Chem.* **187**, 213 (1980).
5. F. Huber, M. Vornefeld, G. Ruisi and R. Barbieri, *Appl. Organomet. Chem.* **7**, 243 (1993).
6. G. Roge, F. Huber, H. Preut, A. Silvestri and R. Barbieri, *J. Chem. Soc., Dalton Trans.* 595 (1983).
7. M. W. Williams and G. T. Young, *J. Chem. Soc.* 881 (1961).
8. A. H. Blatt (ed.), *Organic Syntheses*, Coll. Vol. 2, John Wiley, New York, 1950, p. 11.
9. G. Longworth, Spectral data reduction and refinement, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Long, G. J. (ed.), Plenum Press, New York, 1984, Vol. 1, p. 43.
10. G. M. Bancroft, V. G. Kumar Das, T. K. Sham and M. G. Clark, *J. Chem. Soc., Dalton Trans.* 643 (1976).
11. J. J. Zuckerman, *Chemical Mössbauer Spectroscopy*, Plenum Press, New York, 1984, p. 167.
12. G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.* **15**, 59 (1972).
13. M. G. Clark, A. G. Maddock and R. H. Platt, *J. Chem. Soc., Dalton Trans.* 281 (1972).
14. R. Barbieri, A. Silvestri, F. Huber and C.-D. Hager, *Can. J. Spectrosc.* **26**, 194 (1981).
15. R. V. Parish, Structure and bonding in tin compounds, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Long, G. J. (ed.), Plenum Press, New York, 1984, Vol. 1, pp. 544–548.
16. D. L. Rabenstein and S. Libich, *Inorg. Chem.* **11**, 2960 (1972).
17. S. P. Narula, Shashi K. Bharadwaj, Y. Sharda, R. O. Day, L. Howe and R. R. Holmes, *Organometallics* **11**, 2206 (1992).
18. M. Gielen, M. Bouâlam, B. Mahieu and E. T. Tiekink, *Appl. Organomet. Chem.* **8**, 19 (1994).
19. E. R. T. Tiekink, *J. Organomet. Chem.* **408**, 323 (1991).
20. C. Vatsa, V. K. Jain, T. Kesavadas and E. R. T. Tiekink, *J. Organomet. Chem.* **410**, 135 (1991).
21. T. K. Sham and G. M. Bancroft, *Inorg. Chem.* **14**, 2281 (1975).
22. M. Gielen, J. Meunier-Piret, M. Biesemans, R. Willem and A. El Khloufi, *Appl. Organomet. Chem.* **6**, 59 (1992).
23. T. P. Lockhart, J. C. Calabrese and F. Davidson, *Organometallics* **6**, 2479 (1987).
24. B. Clarke, D. Cunningham, J. F. Gallagher, T. Higgins, P. McArdle, J. McGinley, M. N. Cholchúin and D. Sheerin, *J. Chem. Soc., Dalton Trans.* 2473 (1994).
25. C. Vatsa, V. K. Jain, T. K. Das and E. T. Tiekink, *J. Organomet. Chem.* **421**, 21 (1991).
26. S. P. Narula, S. K. Bharadwaj, H. K. Sharma, G. Mairesse, P. Barbier and G. Nowogrowcki, *J. Chem. Soc., Dalton Trans.* 1719 (1988).
27. V. B. Mokal, V. K. Jain and E. R. T. Tiekink, *J. Organomet. Chem.* **431**, 283 (1992).
28. R. C. Poller, *Spectrochim. Acta* **22**, 935 (1966).