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**X-RAY AND MÖSSBAUER STUDIES OF TRICYCLOHEXYLTIN(IV)
HALIDES. THE CRYSTAL STRUCTURES OF
(*cyclo-C₆H₁₁*)₃SnX (X = F, Br and I)**

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Summary

The structures of tricyclohexyltin fluoride (I), bromide (II) and iodide (III) have been determined by X-ray analysis. Compound I crystallizes in the space group $P2_1/m$ with $a = 10.422(6)$, $b = 17.238(9)$, $c = 5.769(3)$ Å, $\beta \doteq 104.6(1)^\circ$ and $Z = 2$. Compounds II and III crystallize in the space group $Pcmn$ with $a = 10.427(6)$, $b = 16.914(9)$, $c = 11.366(6)$ Å, $Z = 4$; and $a = 10.400(6)$, $b = 16.900(10)$, $c = 11.400(4)$ Å, $Z = 4$, respectively. All three structures consist of discrete tetrahedral (*cyclo-C₆H₁₁*)₃SnX units.

The temperature dependence of the Mössbauer resonance areas has been examined in order to obtain information about the relationship between chemical structure and lattice dynamics.

Introduction

The tricyclohexyltin(IV) halides (*cyclo-C₆H₁₁*)₃SnX (X = F, Cl, Br and I), have been subject of previous studies by Mössbauer spectroscopy [1,2]. The Mössbauer

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quadrupole splitting has been interpreted in terms of a coordination geometry intermediate between four and five for the bromine and iodine compounds, and in terms of a polymeric structure involving five-coordinate tin atoms for the fluoride and chloride [2]. Recently we showed by X-ray analysis that $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnCl}$ consists of discrete tetrahedral units, and its quadrupole splitting value ($\Delta = 3.49 \text{ mm s}^{-1}$) is consistent with such geometry if crystallographic data for the tin-coordination sphere are taken into account [3]. In order to gain more information about the influence of the bulky R groups and the halogens on the coordination of R_3SnX compounds, the crystal structures of the title compounds have been resolved. The temperature dependence of the Mössbauer resonance areas has been also examined.

Experimental

Tricyclohexyltin halides

Tricyclohexyltin halides $(\text{C}_6\text{H}_{11})_3\text{SnX}$, X = F, Br, I, were prepared as previously described [4]. Suitable crystals for X-ray analysis were obtained from glacial acetic acid, ethanol and ethanol/petroleum ether (30–60°C), respectively (X = F, dec., 260°C; Br, m.p. 76–77°C; I, m.p. 63–64°C. Lit. [4] 260, 77, 65°C, respectively).

Crystal and intensity data

Unit cell and space group data are listed in Table 1. Intensity data were collected by the θ – 2θ scan method with a Philips PW 1100 computer-controlled four-circle diffractometer with graphite-monochromated Mo-K_α radiation.

As with $(\text{C}_6\text{H}_{11})_3\text{SnCl}$ [3], these compounds were found to decompose in the X-ray beam; the intensities fell by 6–7% of the initial values during data collection. In all cases only one crystal was used, and no absorption corrections were made in view of the relatively small values of μR .

Data were collected from crystals of $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnF}$ (I), $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnBr}$ (II) and $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnI}$ (III) with dimensions $0.30 \times 0.30 \times 0.20$, $0.10 \times 0.10 \times 0.07$ and $0.20 \times 0.15 \times 0.10$ mm, respectively.

Systematic absences, and subsequent refinements, indicate space group $P2_1/m$ for I and $Pcmm$ for II and III. The intensities were corrected for Lorentz and polarization effects and scaled to give 1053, 545 and 579 independent F_{hkl} values with $I > 2\sigma(I)$ for I, II and III, respectively.

Solution and refinement of the structures

The structure solution was attempted for I using the coordinates of the isostructural $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnCl}$ [3], and for II and III, which are isostructural with each other, by three-dimensional Patterson methods. Full matrix least-squares refinement, with anisotropic temperature factors only for the heavy atoms, produced final R factors of 0.118, 0.125 and 0.149 for I, II and III, respectively. (Hydrogen atoms were not included in the calculations.) Unitary weight was used in all calculations. Atomic scattering factors were taken from Cromer and Weber [5,6]. Final atomic coordinates and thermal parameters are listed in Table 2. The most relevant bond lengths and angles are shown in Table 3. All calculations were carried out on a CDC Cyber 76 computer using the program of ref. 7.

TABLE 1
UNIT CELL DATA

Compound	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	$U(\text{\AA}^3)$	Z	Space group	D_c (g cm^{-3})	μ (cm^{-1})	m.p. ($^{\circ}\text{C}$)
$(\text{C}_6\text{H}_{11})_3\text{SnF}$	10.422(6)	17.238(9)	5.769(3)	104.6(1)	1002.9	2	$P2_1/m$	1.28	12.93	
$(\text{C}_6\text{H}_{11})_3\text{SnCl}^a$	10.386(6)	17.195(9)	5.713(3)	104.3(1)	988.5	2	$P2_1/m$	1.36	14.07	127-128
$(\text{C}_6\text{H}_{11})_3\text{SnBr}$	10.427(6)	16.914(9)	11.366(3)		2004.5	4	$Pcnn$	1.48	33.69	76-77
$(\text{C}_6\text{H}_{11})_3\text{SnI}$	10.400(6)	16.900(10)	11.400(4)		2003.6	4	$Pcnn$	1.64	28.37	63-64

^a These data are taken from ref. 3 and reported for comparison.

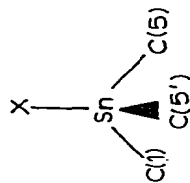
TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) OF $(C_6H_{11})_3SnF$ (I), $(C_6H_{11})_3SnBr$ (II) AND $(C_6H_{11})_3SnI$ (III) a,b

Com- pound	Atom	X	Y	Z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
I	Sn	369(3)	2500	2494(5)	77(2)	82(2)	98(3)	35(5)	31(2)	24(6)
	F	381(14)	2500	-1763(25)	59(4)					
	C(1)	-1760(36)	2500	2228(67)	92(11)					
	C(2)	-2427(56)	3144(30)	1022(90)	250(24)					
	C(3)	-4043(54)	3180(31)	1241(87)	234(22)					
	C(4)	-4552(30)	2500	-388(12)	178(28)					
	C(5)	1400(31)	3555(17)	3795(51)	111(9)					
	C(6)	871(55)	4280(88)	1894(101)	246(25)					
	C(7)	1685(30)	5025(34)	3745(96)	248(23)					
	C(8)	2933(47)	4922(27)	3123(78)	181(16)					
II	C(9)	3508(53)	4375(85)	5305(101)	245(23)					
	C(10)	2748(51)	3540(31)	4290(85)	214(20)					
	Sn	158(5)	2500	681(4)	117(5)	79(3)	100(4)	40(10)	0(4)	37(6)
	Br	640(13)	2500	-1494(8)	270(16)	221(13)	94(6)	-61(43)	-2(9)	0(40)
	C(1)	-1453(53)	2500	941(48)	77(18)					
	C(2)	-2850(80)	1720(46)	300(76)	262(40)					
	C(3)	-4012(43)	1791(25)	300(36)	91(13)					
	C(4)	-4134(64)	2500	-291(60)	114(22)					
	C(5)	1110(73)	1401(44)	1141(67)	195(29)					
	C(6)	757(69)	1080(50)	2267(59)	200(30)					
III	C(7)	1152(76)	244(50)	2490(71)	198(31)					
	C(8)	2198(81)	97(44)	2002(66)	198(31)					
	C(9)	2840(80)	430(52)	1041(77)	229(36)					
	C(10)	2305(88)	1320(40)	710(57)	172(24)					
	Sn	28(7)	2500	759(4)	172(7)	91(4)	65(3)	48(12)	11(5)	0(21)
	I	499(7)	2500	-1437(6)	154(3)	180(15)	132(10)	-20(16)	0(20)	29(30)
	C(1)	-2148(68)	2500	883(62)	94(23)					
	C(2)	-2716(57)	1709(30)	381(46)	116(17)					
	C(3)	-4314(80)	1719(34)	446(45)	129(20)					
	C(4)	-4696(73)	2500	-93(31)	126(23)					
C(5)	786(80)	1438(44)	1259(70)	166(27)						
C(6)	541(68)	1195(45)	2368(67)	162(27)						
C(7)	1161(81)	400(51)	2786(74)	190(33)						
C(8)	2002(89)	38(57)	2114(93)	223(41)						
C(9)	2499(88)	339(51)	1120(76)	189(31)						
C(10)	1945(90)	1213(55)	819(75)	204(37)						

TABLE 3
BOND LENGTHS AND BOND ANGLES INVOLVING TIN ATOM^a

X	Sn-X (Å)	Sn-C(1) (Å)	Sn-C(5) (Å)	X-Sn-C(1) (°)	X-Sn-C(5) (°)	C(1)-Sn-C(5) (°)	C(1)-Sn-C(6') (°)
F	2.45(1)	2.17(4)	2.15(3)	100(1)	103(1)	116(1)	121(2)
Cl ^b	2.41(1)	2.20(2)	2.14(2)	102(2)	101(1)	115(1)	118(2)
Br	2.52(1)	1.71(6)	2.17(7)	111(2)	99(2)	114(2)	118(2)
I	2.54(1)	2.27(7)	2.04(8)	104(3)	101(3)	115(3)	117(3)



^a The atoms are labelled according to the following scheme:

^b From ref. 3.

Tables of observed and calculated structure factors are available from the authors.

Mössbauer measurements

Mössbauer spectra were obtained by means of the apparatus and procedures previously described [8]. The measurements, performed with a prefixed number of up-down sweeps, showed statistically undetectable Mössbauer effect above 200 K. The average amount of ^{119}Sn in the polycrystalline samples was ca. 1 mg cm^{-2} .

The approximation relation for the high-temperature limit of the Debye model for solids, $a = d \ln A/dT = -1/\lambda d \langle x_i^2 \rangle/dT$, was employed; a is the temperature coefficient, A represents the Mössbauer resonance area normalized to 77.4 K, $\langle x_i^2 \rangle$ is the isotropic mean-square amplitude of vibration of the tin atom and $2\pi\lambda$ is the wavelength of the 23.9 keV ^{119}Sn transition [9–11].

As a first approximation, the isotropic mean-square amplitude of vibration of the tin atom was obtained by averaging the principal anisotropic temperature factors U_{11} , U_{22} and U_{33} of Table 2. These values were used to normalize to 298 K the temperature dependence of $\langle x_i^2 \rangle$.

Mössbauer data for various temperature, namely the isomer shift (δ), quadrupole splitting (Δ), full-width at half-height at lower (Γ_1) and higher energy (Γ_2), and the logarithm of the resonance area normalized to 77.4 K ($\ln A$) are given in Table 4.

TABLE 4
MÖSSBAUER DATA FOR $(\text{cyclo-C}_6\text{H}_{11})_3\text{SnX}$ COMPOUNDS

X	T(K)	δ ^{a,b}	Δ ^{a,b}	Γ_1 ^{b,c}	Γ_2 ^{b,c}	$\ln A$ ^d	$\langle x_i^2 \rangle$ ^e
I	77.4	1.60	2.76(−2.40 <i>f</i>)	0.78	0.75	0.000	0.085
	101	1.60	2.75	0.73	0.86	−0.380	0.087
	125	1.58	2.76	0.85	0.87	−0.766	0.090
	150	1.55	2.73	1.03	0.93	−1.168	0.093
	175	1.59	2.71	0.83	0.95	−1.570	0.095
	198	—	—	—	—	—	0.109
Br	77.4	1.60	2.90(−2.74 <i>f</i>)	0.90	0.93	0.000	0.074
	101	1.58	2.89	0.90	0.86	−0.378	0.077
	125	1.60	2.91	0.83	0.92	−0.757	0.080
	150	1.59	2.88	0.90	0.87	−1.190	0.082
	175	1.58	2.90	0.87	0.86	−1.601	0.085
	298	—	—	—	—	—	0.099
Cl	77.4	1.64	3.50(−3.64 <i>g</i>)	1.12	1.06	0.000	0.066
	101	1.65	3.59	1.01	0.94	−0.377	0.057
	125	1.62	3.57	0.98	0.96	−0.765	0.060
	150	1.61	3.60	0.97	1.09	−1.165	0.063
	175	1.66	3.54	1.02	1.14	−1.560	0.066
	298	—	—	—	—	—	0.079
F	77.4	1.55	3.95(−3.57 <i>g</i>)	1.00	0.90	—	—
	125	1.54	3.96	0.90	0.89	—	—
	298	—	—	—	—	—	0.086

^a Relative to SnO_2 . ^b $\pm 0.05 \text{ mm s}^{-1}$. ^c Full-widths at half-height at lower (Γ_1) and higher (Γ_2) energy. ^d Natural logarithm of the resonance area normalized to 77.4 K. ^e Amplitude of vibration of the tin atoms in Å^2 . ^f Assuming an ideal tetrahedral geometry. ^g Introducing the crystallographic data in the tetrahedral geometry.

Results and discussion

Crystal structures

The most relevant structural features involve the coordination geometry about the tin atom. As shown in Table 3, all the corresponding angles (except for $C(1)-Sn-Br = 111^\circ$) are almost identical within the standard deviations, including those found for $(C_6H_{11})_3SnCl$ [3], which has a distorted tetrahedral coordination. Thus the geometry around the tin atom is also the same in all cases.

The $Sn-Br$ (2.52 Å), $Sn-Cl$ (2.41 Å) [3] and $Sn-C$ (except for $Sn-C(1)$ of III) bond lengths all fall within the range of accepted values [12]. However the $Sn-F$ (2.45 Å) and $Sn-I$ (2.54 Å) bond lengths are longer and shorter, respectively, than the expected values [12]. Not too much significance should be attached to these results because of the particular experimental conditions under which the crystals were examined; these are also responsible for the relatively high final R factors and for the rough geometry of the cyclohexyl groups.

The structures of $(C_6H_{11})_3SnF$ and of $(C_6H_{11})_3SnCl$ [3] consist of layers of *iso*-oriented molecules orthogonal to c^* , with spacing of about 5.62 Å. The molecules appear piled along the c axis with non-bonded intermolecular $Sn\cdots F$ distances of 3.32 Å (compare 3.30 Å for $Sn\cdots Cl$ in $(C_6H_{11})_3SnCl$, (see Fig. 1A).

The structures of II and III consist of layers of alternately *iso*- and *anti*-oriented molecules (with respect to the a axis); the layers are still orthogonal to c^* ($\equiv c$) with spacings of 5.68 and 5.70 Å respectively. These layers are alternately shifted by $a/2$, giving a molecular packing in which no intermolecular $Sn\cdots X$ contact distances shorter than 5 Å are present (see Fig. 1B). It is noteworthy that the relatively short $Sn\cdots X$ contact distances in the case of the chlorine and the fluorine derivatives do not affect the main molecular geometry, which remains almost identical with that in the bromine and iodine derivatives.

Mössbauer data

There is good agreement between our data and those previously reported [1,2]. The isomer shift values do not change within the experimental error when the halogen is varied; this reflects the constancy of the total s -electron density at the tin nucleus, as previously noted and explained for many organotin halides [13].

The following points can be made about the Δ -values (cf. Table 4). The component V_{ZZ} of the electric field gradient (EFG) tensor is due to a predominant valence contribution, q_v , arising from an anisotropic population in the valence shell of the σ -bonding orbitals rather than π -bondings [14], and to a small lattice contribution, q_l , arising from an anisotropic distribution of the lattice charges [15]. Therefore q_v and q_l have opposite signs with $|q_v| \gg |q_l|$ [16]. In our compounds the valence anisotropy arises from differences in the tin p -electrons involved in the $Sn-C$ and $Sn-X$ bonds. On going from the iodo to the fluoroderivative the Δ -values increase with the valence anisotropy. A local pseudo-symmetry C_{3v} , with the ternary axis nearly coincident with the EFG axis, may be assumed. With the further assumption that the p -electron density of the $Sn-C$ bonds is larger than that of the $Sn-X$ bonds, V_{ZZ} proves to be po-

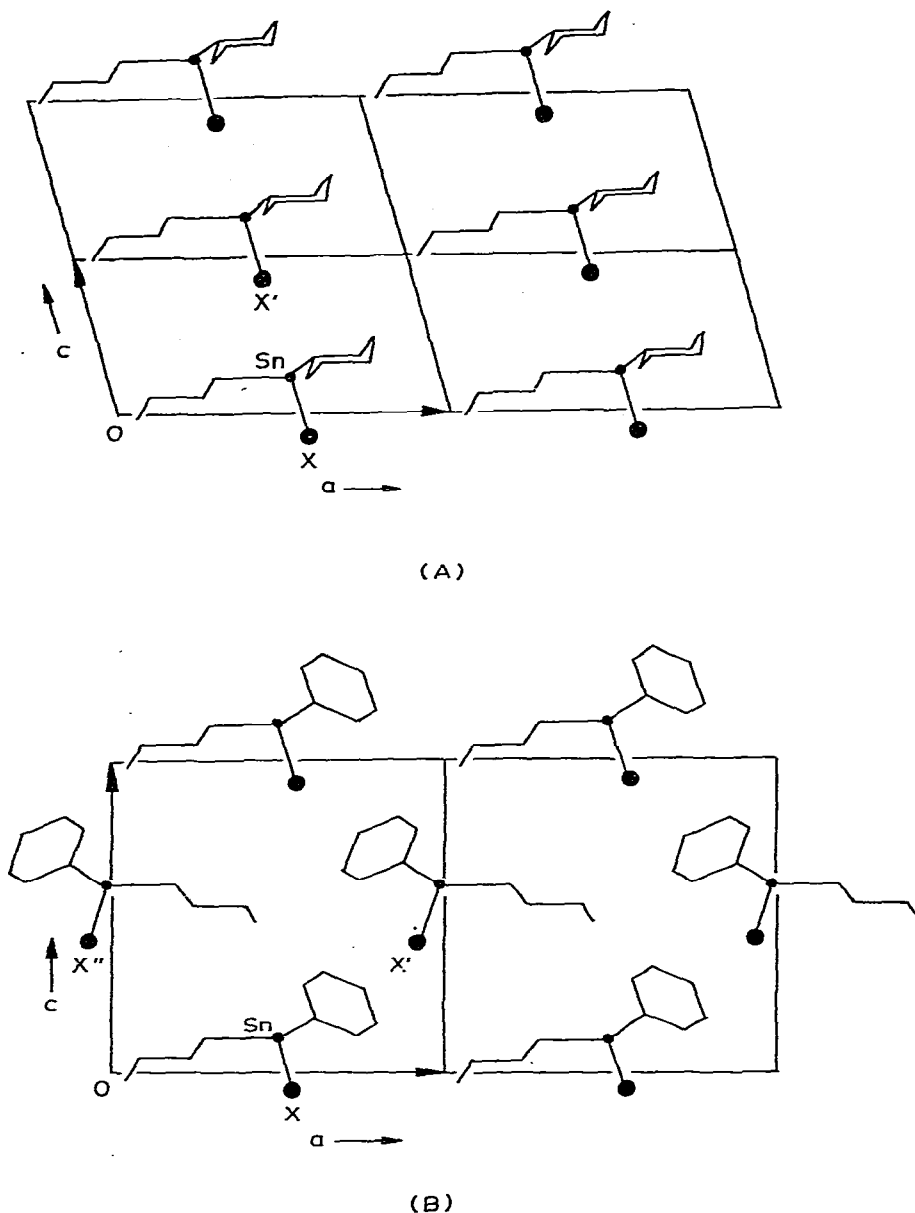


Fig. 1. Schematic representation of the structures of the tricyclohexyltin halides as viewed along the b axis. A) $X, X' = F$ or Cl . B) $X, X', X'' = Br$ or I .

sitive for $q_v > 0$ and $q_l < 0$. Q is negative for ^{119}Sn , consequently the quadrupole coupling constant, e^2QV_{ZZ} , is negative, which is in agreement with the sign of the Δ -values of the cyclohexyltin halides, as calculated by the point-charge model and using the data available for tetrahedral organotin(IV) compounds [13].

Calculations of the Δ -values for the cyclohexyltin halides were performed assuming the simple point-charge model and the modified model including distortions [3]: the calculated values are shown in Table 4.

The temperature coefficients a derived from Mössbauer resonance areas normalized to 77.4 K (see Table 4), are ca. $-1.6 \times 10^{-2} \text{ K}^{-1}$. They represent a measure of the strength of the bonds between tin and its nearest neighbour atoms [17–21]. These values are similar to those for non-interacting monomeric molecules ($-1.8 \times 10^{-2} \text{ K}^{-1}$) [21].

The correlation between the X-ray thermal vibration coefficients $\langle x_i^2 \rangle$, for tin atoms and the temperature dependence of the Mössbauer resonance areas, $\ln A$ (see Table 4), shows that the strength of the bonds between the tin and its nearest atoms are almost constant. This appears to indicate that there are no variations in the bond strength within the series of halogen derivatives.

Conclusion

The X-ray and Mössbauer results both indicate that tricyclohexyltin halides are characterized by discrete tetrahedral units in the crystals. The “secondary bonding” which was suggested for other similar cases [22–26] would require significantly different conformational distortions in the interacting molecules. A remarkable fact is that the molar volumes do not vary on going from fluoride to iodide derivative (see Table 1); these molar volumes seem to be mainly controlled by the large bulk of the cyclohexyl groups; and so the interactions between molecules in the crystals should be similar, in agreement with the temperature variation of the Mössbauer data.

It is noteworthy that for $R_3\text{SnX}$ compounds (X = halogen) the bulky groups, such as cyclohexyl and phenyl, give rise to a tetrahedral geometry about the tin atom [3,12], whereas polymeric pentacoordinated structures are generally encountered for smaller R groups [22].

The interpretation of the fact that the quadrupole splittings for the fluoride and chloride derivatives are higher than those for the bromide and iodide in terms of polymeric structures or a mixed coordination number is unsatisfactory. The structural information in the present paper indicates that the quadrupole splitting values may well be associated with differences in the crystal packing of the molecules.

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References

- 1 R.H. Platt, *J. Organometal. Chem.*, **24** (1970) C23.
- 2 A.G. Maddock and R.H. Platt, *J. Chem. Soc. A*, (1971) 1191.
- 3 S. Calogero, P. Ganis, V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.*, **179** (1979) 145.
- 4 E. Krause and R. Pohland, *Ber.*, **57** (1924) 532.
- 5 D.T. Cromer and J.T. Weber, *Acta Cryst.*, **18** (1965) 104.
- 6 D.T. Cromer, *Acta Cryst.*, **18** (1965) 17.
- 7 G. Sheldrick, *Shelx 76 system of computing programs*, University of Cambridge, 1976.
- 8 S. Calogero, P. Ganis, V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.*, **191** (1980) 381.
- 9 P.G. Harrison, K. Molloy and E.W. Thornton, *Inorg. Chim. Acta*, **33** (1979) 137.
- 10 P.G. Harrison, M.G. Begley and K.C. Molloy, *J. Organometal. Chem.*, **186** (1980) 213.
- 11 B.Y.K. Ho, K.C. Molloy, J.J. Zuckermann, F. Reidinger and J.A. Zubieta, *J. Organometal. Chem.*, **187** (1980) 213.
- 12 J.A. Zubieta and J.J. Zuckermann, in S.J. Lippard (Ed.), *Progress in Inorganic Chemistry*, Vol. 24, Wiley, New York, 1978, and references therein.

- 13 R.V. Parish, in S.J. Lippard (Ed.), *Progress in Inorganic Chemistry*, Vol. 15, Wiley, New York, 1972.
- 14 J. Devooght, M. Gielen and S. Lejeune, *J. Organometal. Chem.*, 21 (1970) 333.
- 15 M.G. Clark, in A.J. Buckingham (Ed.), *Molecular Structures and Properties*, Vol. 2, Butterworths, London, 1975.
- 16 R.V. Parish and C.E. Johnson, *J. Chem. Soc. A*, (1971) 1906.
- 17 Y. Hazony and R.H. Herber, in I.J. Gruverman and C.W. Seidel (Ed.), *Mössbauer Effect Methodology*, Vol. 8, Plenum Press, New York, 1973, p. 107.
- 18 R.H. Herber, *J. Chem. Phys.*, 54 (1971) 3755.
- 19 R.H. Herber and M.F. Lealhy, in J.J. Zuckermann (Ed.), *Organotin Compounds — New Chemistry and Applications*, *Advances in Chemistry series*, American Chemical Society, Washington, 1976, p. 10.
- 20 P.G. Harrison, *ibid.*, p. 258.
- 21 K.C. Molloy, J.J. Zuckermann and H. Schumann, *Inorg. Chem.*, 19 (1980) 1089.
- 22 N.W. Alcock and R.E. Timms, *J. Chem. Soc. A*, (1968) 1873.
- 23 N.W. Alcock and R.E. Timms, *J. Chem. Soc. A*, (1968) 1876.
- 24 N.W. Alcock, *Advan. Inorg. Chem. Radiochem.*, 15 (1972) 1.
- 25 N.W. Alcock and R.M. Countryman, *J. Chem. Soc. Dalton*, (1977) 217.
- 26 N.W. Alcock and J.F. Sawyer, *J. Chem. Soc. Dalton*, (1977) 1090.