A Study of *cis*-octahedral Compounds of Tin(IV) Halides with Thiourea or Urea Type Ligands

S. CALOGERO*
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti 4, 35100 Padua, Italy

U. RUSSO
Istituto di Chimica Generale ed Inorganica, Università di Padova, Via Loredan 4, 35100 Padua, Italy

G. VALLE
Centro di Ricerca sui Biopolimeri del C.N.R., Via Marzolo 1, 35100 Padua, Italy

P. W. C. BARNARD
Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX U.K.

and J. D. DONALDSON
Department of Chemistry, The City University, Northampton Square, London EC1 V OHB, U.K.

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Twenty five six coordinate compounds of the type $SnX_4 2L$, with X = Cl, Br or I and L = thiourea or urea derivatives, have been prepared and characterized. The crystal structures of two of the compounds are reported. $SnCl_4$ 2(1,3-diethylthiourea) is trigonal with a *= 18.679(4),* c *= 33.402(6) Å, space group R3c and Z = 18. The tin is in a* cis*-octahedral environment with four bonds to chlorine and two to sulphur atoms. The crystal structure determination of $SnBr_4$ 2(1,3-diethylurea) has been limited to the nearest atoms of the tin centre. $SnBr_4$ 2(1,3-diethylurea) is tetragonal with* a *= 15.832(3),* c *= 17.095(4) Å, space group $P4_2/mbc$ and Z = 8. The tin is in a distorted* cis*-octahedral site with four bonds to chlorine and two to oxygen atoms. The ^{119}Sn Mössbauer and infrared data are explained in terms of* cis*-octahedral geometry around the tin atoms.*

Introduction

There are few reports of molecular adducts of SnX_4 [1, 2] or SnX_2 [3, 4] with thiourea or urea derivatives. For tin(IV) only a small number of this type of compounds has been prepared and characterized. No crystal structures have been reported and the Mössbauer spectra of only a few of the compounds have been obtained [5, 6]. The lack of crystal structure and Mössbauer information [7, 8] prevents a full description of the nature of the bonds and of the factors affecting the tin(IV) coordination geometry.

As a part of our continuing research on thiourea and urea type derivatives of transition and non-transition elements a large number of compounds of general formula $SnX_4 2L$ has been prepared and characterized (X = Cl, Br, or I; L = urea, 1,3-dimethylthiourea (dmtu), 1,3-dimethylurea (dmu), 1,1-dimethylurea (dmua), 1,3-diethylthiourea (detu), 1,3-diethylurea (deu), 1,1-diethylurea (deua), tetramethylthiourea (tmtu), tetramethylurea (tmu), 1,3-dicyclohexylthiourea (dchtu), 1,3-dicyclohexylurea (dchu), 1,3-diisopropylthiourea (diptu), acetylthiourea (actu), 1,3-dibenzylthiourea (dbetu) and 1,3-diphenylthiourea (dphtu)).

Experimental

All of the compounds were prepared by the same procedure: 8.5 mmol of the ligand dissolved in a suitable solvent (CH_2Cl_2, $CHCl_3$ or CCl_4) were added dropwise to a solution of 4.2 mmol of $SnBr_4$ or SnI_4 in the same solvent, or to liquid $SnCl_4$. The solid products were generally obtained by stirring or adding diethyl ether, hexane or petroleum ether but in the cases where a viscous layer was obtained crystallization was achieved by vigorous stirring, or dissolving the oil in acetone or $MeNO_2$, and adding ether or hexane. The compounds, whose stability decreased in the order chloro-, bromo-, iodo-derivative, were filtered, washed, dried under vacuum and recrystallized to constant analysis. Analytical data

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical Data.

	M.P.[a] (°C)	Analysis (%)[b]				Colour	Λ (ohm^{-1} cm^2 mol^{-1})
		C	H	N	X		
$SnCl_4$ 2detu	155	23.2(22.9)	4.6(4.6)	10.6(10.7)	27.4(27.0)	yellow	8
$SnCl_4$ 2actu	188	14.5(14.5)	2.5(2.4)	10.9(11.3)	28.6(28.6)	white	9
$SnCl_4$ 2tmtu	198	22.5(22.9)	4.4(4.6)	10.4(10.7)	28.2(27.0)	yellow	14
$SnCl_4$ 2dmtu	202	15.5(15.4)	3.4(3.4)	11.9(11.9)	30.4(30.2)	yellow	18
$SnCl_4$ 2diptu	205	28.8(28.9)	5.4(5.5)	9.6(9.6)	24.6(24.4)	yellow	7
$SnCl_4$ 2dchtu	231	40.5(42.1)	6.6(6.5)	7.3(7.6)	18.7(19.1)	white	13
$SnCl_4$ 2dbetu	178	45.6(46.6)	4.2(4.2)	7.0(7.2)	18.7(18.3)	yellow	9
$SnCl_4$ 2dphtu	159	43.2(43.5)	3.2(3.4)	7.7(7.8)	20.0(19.8)	white	16
$SnCl_4$ 2dmu	208	16.4(16.5)	3.6(3.7)	12.4(12.8)	33.6(32.5)	white	13
$SnCl_4$ 2deua	114	24.7(24.4)	5.1(4.9)	11.1(11.4)	28.4(28.8)	white	10
$SnCl_4$ 2dmua	177	16.1(16.5)	3.5(3.7)	12.3(12.8)	33.0(32.5)	white	17
$SnCl_4$ 2dchu	205	43.7(44.0)	7.1(6.8)	7.8(7.9)	19.4(20.0)	white	9
$SnCl_4$ 2tmu	203	23.6(24.4)	4.8(4.9)	11.0(11.4)	28.9(28.8)	white	36
$SnCl_4$ 2deu	84	23.7(24.4)	4.9(4.9)	11.2(11.4)	28.5(28.8)	white	9
$SnCl_4$ 2urea	175	6.1(6.3)	2.1(2.1)	14.3(14.7)	38.6(37.3)	white	14
$SnBr_4$ 2detu	139	17.5(17.1)	3.6(3.4)	8.0(8.0)	45.4(45.5)	yellow	23
$SnBr_4$ 2dbetu	195	37.7(37.9)	3.5(3.4)	5.8(5.9)	34.4(33.6)	yellow	16
$SnBr_4$ 2dmtu	192	11.8(11.1)	2.6(2.5)	8.6(8.7)	49.9(49.4)	yellow	25
$SnBr_4$ 2diptu	188	22.2(22.2)	4.2(4.3)	7.4(7.4)	42.5(42.1)	yellow	22
$SnBr_4$ 2dchu	190	34.8(35.2)	5.2(5.5)	6.2(6.3)	36.2(36.0)	white	10
$SnBr_4$ 2deu	136	18.0(17.9)	3.6(3.6)	8.3(8.4)	48.2(47.7)	white	13
$SnBr_4$ 2tmu	178	17.8(17.9)	3.6(3.6)	8.2(8.4)	48.0(47.7)	brown	10
SnI_4 2tmu	–	14.0(14.0)	3.0(2.8)	6.1(6.5)	59.3(59.1)	brown	14
SnI_4 2dmtu	109	9.0(8.7)	2.1(1.9)	6.8(6.7)	60.2(60.8)	brown	12
SnI_4 2detu	135	14.0(13.5)	2.9(2.7)	6.1(6.3)	59.2(59.1)	brown	15

[a] Melting points were determined under vacuum and are uncorrected. [b] Calculated values are given in parentheses.

TABLE II. Some Relevant IR Bands (values in parentheses are the shifts from the free ligands) in cm^{-1}.

	ν(CO)	ν(CS)	ν(CN)
$SnCl_4$ 2detu		796m(−2)	1601s(+34)
$SnCl_4$ 2tmtu			1573s(+62)
$SnCl_4$ 2dmtu		717m(−5)	1605s(+39)
$SnCl_4$ 2diptu		735m(−7)	1594s(+31)
$SnCl_4$ 2dchtu		760m(−12)	
$SnCl_4$ 2dbetu		730m(−10)	1598s(+43)
$SnCl_4$ 2dphtu		691s(−7)	
$SnCl_4$ 2dmu	1616s(−15)		
$SnCl_4$ 2deua	1624s(−22)		
$SnCl_4$ 2dmua	1629s(−30)		
$SnCl_4$ 2dchu	1602s(−23)		1526s(+22)
$SnCl_4$ 2tmu	1581s(−63)		1526s(+22)
$SnCl_4$ 2deu	1619s(−11)		1578sh(+49)
$SnCl_4$ 2urea	1658s(−13)		1511m(+45)
$SnBr_4$ 2detu		795m(−2)	1602s(+35)
$SnBr_4$ 2dbetu		728m(−12)	1594s(+39)
$SnBr_4$ 2dmtu		716m(−6)	1604s(+38)
$SnBr_4$ 2diptu		735m(−7)	1594s(+31)
$SnBr_4$ 2dchu	1597s(−28)		
$SnBr_4$ 2deu	1621s(−9)		1575sh(+46)
$SnBr_4$ 2tmu	1576s(−68)		1524s(+20)
SnI_4 2dmtu		714m(−8)	1603s(+37)
SnI_4 2detu		796m(−1)	1600s(+33)

for the compounds are in Table I, along with melting points and conductivity data. The melting points decrease on going from chloro to iodo-derivatives. The conductivity values were obtained using a LKB

TABLE III. Infrared Bands Tributable to ν(Sn–X) in cm^{-1}.

$SnCl_4$2detu	296s	350w	360sh	
$SnCl_4$2ctu	287m			
$SnCl_4$2tmtu	282m			
$SnCl_4$2dmtu	289s	346sh		
$SnCl_4$2diptu	296s	320sh	384w	
$SnCl_4$2dchtu	292m			
$SnCl_4$2dbetu	266s	306s	381m	
$SnCl_4$2dphtu	277m	305m		
$SnCl_4$2dmu	329s			
$SnCl_4$2deua	301m	343m		
$SnCl_4$2dmua	303m	338m	373w	380sh
$SnCl_4$2dchu	275w	315s	371w	395m
$SnCl_4$2tmu	323s	361m	386sh	
$SnCl_4$2deu	284sh	316s	385sh	393m
$SnCl_4$2urea	295sh	316m		
$SnBr_4$2detu	219s			
$SnBr_4$2dbetu	216s			
$SnBr_4$2dmtu	210s			
$SnBr_4$2diptu	204s			
$SnBr_4$2dceu	206s	225s		
$SnBr_4$2deu	203m			

3216B bridge at 25 °C on 10^{-3} mol dm^{-3} solutions in $MeNO_2$. The i.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer using KBr pellets and nujol mulls. Some relevant i.r. bands are in Tables II and III.

Mössbauer spectra were obtained using a constant acceleration spectrometer. The source, $Ca^{119}SnO_3$, nominal strength 15 mCi, was kept at 95 K in a cryostat with vertical beam geometry. Constant temperature (±0.5 K), controlled by a gold–iron thermocouple, was obtained by a continuous flow of exchange gas. The measurements were performed with a fixed number of up-down sweeps. The average amount of ^{119}Sn in the powdered samples was *ca.* 0.5 mg cm^{-2}. Mössbauer parameters for some compounds are in Table IV.

TABLE IV. Mössbauer Parameters.

Compound	T (K)	$\delta^{a,b}$	$\Gamma/2^b$	A^c
$SnCl_4$^{d}		0.85		
$SnCl_4$2detu	77	0.31	0.74	5.6
	100	0.34	0.70	3.6
	125	0.38	0.76	2.2
	150	0.39	0.80	1.4
	175	0.42	0.90	0.9
$SnBr_4$^{d}		1.05		
$SnBr_4$2detu	77	0.39	0.76	5.5
	100	0.39	0.80	3.5
	125	0.40	0.78	2.1
	150	0.43	0.78	1.3
	175	0.42	0.79	0.8
$SnBr_4$2dmtu	77	0.40	0.83	5.4
	100	0.41	0.80	3.6
	125	0.42	0.79	2.4
	150	0.44	0.81	1.6
	175	0.44	0.79	1.0
	200	0.43	0.71	0.7
SnI_4^{d}		1.55		
$SnI_4$2dmtu	77	0.41	0.86	6.3

[a] Relative to SnO_2. [b] ± 0.03 mm s^{-1}. [c] Resonance area %. [d] From Ref. 25.

Crystal and Intensity Data

Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 50°$ with Mo-K_α radiation (λ = 0.71069 Å). Using the criterion $I > 3\sigma(I)$, 1017 of the 1997 recorded intensities for $SnCl_4$2detu, and 909 of the 1370 recorded intensities for $SnBr_4$2deu, were independent and observable. Lorentz and polarization corrections were applied.

Tetrachlorobis(1,3-diethylthiourea)tin(IV), $SnCl_4$2detu, $C_{10}H_{24}Cl_4N_4S_2Sn$, M = 524.96, trigonal, a = 18.679(4), c = 33.402(6) Å, D_c = 1.54 g cm^{-3}, D_m = 1.52 (by flotation), Z = 18, U = 10093(4) $Å^3$, F(000) = 4761, space group $R\bar{3}c$, crystal dimensions 0.30 × 0.25 × 0.60 mm.

Tetrabromobis(1,3-diethylurea)tin(IV), $SnBr_4$2deu, $C_{10}H_{24}Br_4N_4O_2Sn$, M = 670.65, tetragonal P, a = 15.832(3), c = 17.095(4) Å, D_c = 2.07 g cm^{-3}, D_m = 2.08 (by flotation), Z = 8, U = 4285(2) $Å^3$, F(000) = 2.544, space group $P4_2/mbc$, crystal dimensions 0.25 × 0.25 × 0.40 mm.

Solution and Refinement of the Structures

The structures were solved using three-dimensional Patterson-Fourier syntheses locating first the Sn, Cl or Br, S or O atoms and then the C and N atoms. A full-matrix least-squares refinement on F was computed and the function $\Sigma w||F_o|-|F_c||^2$, in which w = 1, was minimized. The SHELX 76 program and the usual scattering factors were used [9, 10]. Only the atoms Sn, Cl, S, N(1), N(2), C(1) and C(2) for $SnCl_4$2detu, and Sn and Br for $SnBr_4$2deu, were refined anisotropically. The final R values were 0.085 for $SnCl_4$2detu and 0.19 for $SnBr_4$2deu. The X-ray analysis for $SnBr_4$2deu was limited to the nearest atoms of the tin site in order to clarify its co-ordination geometry. The stereochemical arrangement of $SnCl_4$2detu is shown in Fig. 1. The final atomic coordinates, bond angles and distances are listed respectively in Tables V and VI. The anomalous values for some distances and angles found in both the structures are due to a wide crystalline disorder: in fact all the crystals examined are intimately mixed

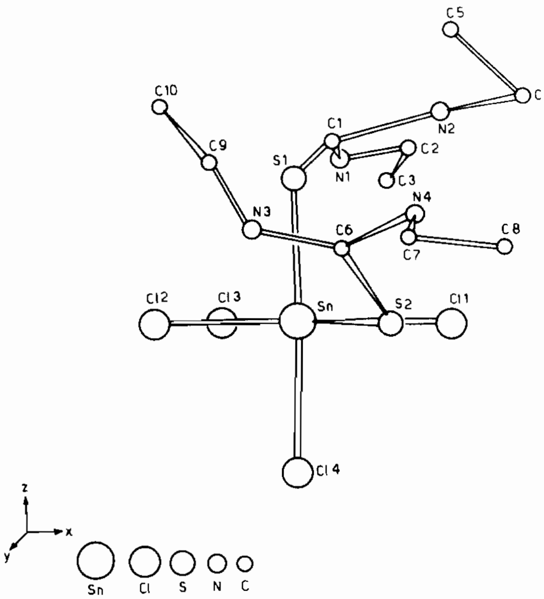

Fig. 1. Perspective view of SnCl$_4$2detu with the atom numbering scheme.

TABLE V. Final Fractional Atomic Coordinates for SnCl$_4$-2detu (above) and SnBr$_4$2deu (below if available) with Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c
Sn	0.2516(3)	0.0005(6)	0.2500
	0.2296(5)	0.1758(5)	0.0000
L(1)^a	0.248(1)	0.007(1)	0.3243(4)
	0.336(6)	0.270(6)	0.0000
L(2)^a	0.335(2)	0.156(1)	0.2465(5)
	0.169(7)	0.292(6)	0.0000
X(1)^b	0.390(1)	0.003(2)	0.2484(8)
	0.2319(7)	0.1799(7)	0.1501(7)
X(2)^b	0.120(1)	0.003(2)	0.2480(7)
	0.2319(7)	0.1799(7)	−0.1501(7)
X(3)^b	0.181(2)	−0.155(1)	0.2507(8)
	0.3246(8)	0.0453(8)	0.0000
X(4)^b	0.246(1)	0.006(1)	0.1731(6)
	0.0863(6)	0.1062(7)	0.0000
N(1)	0.295(2)	−0.109(2)	0.333(1)
N(2)	0.388(5)	0.020(5)	0.363(3)
N(3)	0.211(4)	0.171(3)	0.300(2)
N(4)	0.360(6)	0.266(6)	0.305(3)
C(1)	0.312(3)	−0.034(3)	0.341(1)
C(2)	0.356(5)	−0.131(5)	0.339(2)
C(3)	0.334(3)	−0.213(3)	0.320(2)
C(4)	0.466(8)	0.138(7)	0.364(4)
C(5)	0.397(9)	0.136(9)	0.400(5)
C(6)	0.294(5)	0.195(5)	0.288(2)
C(7)	0.356(9)	0.339(9)	0.295(5)
C(8)	0.464(6)	0.381(6)	0.291(3)
C(9)	0.174(8)	0.183(8)	0.333(4)
C(10)	0.130(7)	0.122(8)	0.362(3)

^{a}L = S above, L = O below. ^{b}X = Cl above, L = Br below.

TABLE VI. Bond Distances (Å) and Angles (°) for SnCl$_4$-2detu and SnBr$_4$2deu with Standard Deviations in Parentheses.

	SnCl$_4$2detu^a	SnBr$_4$2deu^b
Bond distances		
Sn–L(1)	2.49(1)	2.36(9)
Sn–L(2)	2.52(2)	2.09(7)
Sn–X(1)	2.55(3)	2.56(1)
Sn–X(2)	2.48(3)	2.56(1)^c
Sn–X(3)	2.51(2)	2.59(2)
Sn–X(4)	2.58(2)	2.55(1)
Bond angles		
X(1)–Sn–L(2)	86.9(9)	89.4(3)
X(1)–Sn–X(2)	176.8(8)	180.0^c
X(1)–Sn–X(3)	87.7(9)	90.4(3)
X(2)–Sn–L(2)	91(1)	81.4(3)^c
X(2)–Sn–X(3)	94(1)	90.4(3)^c
X(3)–Sn–L(2)	174.2(5)	174(2)
X(1)–Sn–L(1)	94.2(7)	88.5(3)
L(1)–Sn–X(2)	88.5(7)	88.5(3)^c
L(1)–Sn–X(3)	92.0(7)	96(2)
L(1)–Sn–L(2)	90.4(7)	78(3)
X(1)–Sn–X(4)	92.4(7)	91.4(3)
X(2)–Sn–X(4)	84.8(7)	91.4(3)^c
X(3)–Sn–X(4)	92.7(8)	99.9(4)
X(4)–Sn–L(2)	85.5(6)	86(2)
X(4)–Sn–L(1)	172.1(6)	164(2)

^{a}For SnCl$_4$2detu L = S, X = Cl. ^{b}For SnBr$_4$2deu L = O, X = Br ^{c}Br(2) is related to Br(1) by equivalent position x, y, $\bar{z}$.

with amorphous powder and in no case were good data collections possible. Observed and calculated structure factors together with the thermal parameters may be obtained on request.

Results and Discussion

To the best of our knowledge the crystal structures of SnCl$_4$2detu and SnBr$_4$2deu are the first examples of structures of tin(IV) bonded to thiourea or urea derivatives to be determined. They consist of discrete covalent SnX$_4$2(Ligand) moieties. For the compounds of Table I, the discrete structures are consistent with previous cryoscopic measurements [1] and the low conductivity values (Table I) are in agreement with previous reports [1].

As shown in Fig. 1, the tin atom in SnCl$_4$2detu is surrounded by four chlorine atoms and two S-bonded detu molecules. The i.r. spectrum of the complex is consistent with the bond through the sulphur atom because the ν(CN) band is found at 1601 cm^{-1} with a positive shift of 34 cm^{-1} from the free detu value, while the ν(CS) has a negative shift [1, 2]. All of the thiourea type compounds in Table II show this trend and are presumably all containing S-bonded ligands. $SnCl_4$2detu presents a slightly distorted octahedral geometry around the tin atom with two *cis*-S-atoms from detu molecules. The average bond lengths and angles are: Sn–Cl, 2.53 Å; Sn–S, 2.50 Å; Cl–Sn–Cl, 90° and S–Sn–S, 90.4°. A *cis*-octahedral geometry also explains the far i.r. spectrum, because this geometry requires four bands due to ν(Sn–Cl), while the *trans* requires only one. $SnCl_4$2detu has three bands at 296, 350 and 360 cm^{-1}, attributable to ν(Sn–Cl), and the fourth may be hidden by absorptions due to the thioureas [11–13]. The infrared spectra of the chloride compounds listed in Table III are similar and for this reason we also assign *cis*-octahedral configurations to them.

A partial crystal structure of $SnBr_4$2deu shows that the tin atoms are in a distorted *cis*-octahedral geometry with four bromine atoms and two O-bonded deu molecules. The average bond lengths and angles are: Sn–Br, 2.56 Å; Sn–O, 2.33 Å; Br–Sn–Br, 92.7° and O–Sn–O, 77.6°. Bonding through the oxygen atom is consistent with the i.r. spectrum of the compound, and because of similar i.r. data this bonding mode is extended to all the urea type compounds of Table II.

The presence of more than one i.r. band in the 400–200 cm^{-1} region for most of the chloride compounds in Table III, and the present crystal structure information on $SnBr_4$2deu, suggests that all of the compounds in Table III have *cis*-octahedral geometry. The presence of only one of the four bands in the 400–200 cm^{-1} region for some of the compounds in Table III presumably means that the other Sn–X bands are outside the range of the spectrometer used.

Zahrobsky's model [14], which gives the most probable configurations, provides a mean to overcome the instrumental limit. In fact, for the compounds of Table I the *cis*-configuration presents a calculated overlap between adjacent van der Waals surfaces less than that for the *trans* one. This result was verified assuming literature covalent and van der Waals radii [15] to calculate the steric angles of ligands atoms in three normal planes through the tin. The present crystal structures are consistent with the suggestion that the *cis*-octahedral environment is preferred in $SnX_4$2L type compounds when a monodentate ligand is present, with groups not directly linked to the donor atom, (L = thiourea or urea derivative, $OPCl_3$ [16], $OSeCl_2$ [17, 18], NCMe [19] and $OSMe_2$ [20]). This is true even if (in the compounds of Table I) branched ligands are present because they may easily twist to adapt themselves to a *cis*-tin configuration. The non-rigid nature of the thioureic ligands is also evidenced in the lone-pair affected series $SbCl_3$2L [21], and $[TeL_4]Cl_2$ [22] for which X-ray diffraction or Mössbauer data point to an octahedral geometry.

Mössbauer Spectra

The Mössbauer spectra of thiourea type compounds are characterized by the presence of single Lorentzian lines, as shown in Table IV by the half-widths at half-maximum, Γ/2 [23].

The lower pseudo-symmetry C_{2v} assumed for the tin site in our thioureic compounds, on the basis of Zahrobsky's model and structural data, agrees with a small Mössbauer splitting in the framework of the point-charge model. In fact if the following partial quadrupole splittings, in mm s^{-1}, are assumed: Cl = Br = 0.00, I = –0.14 and –0.25, *i.e.* the value for ½$\{S_2CNR_2\}$, for all the thioureic ligands [24], the quadrupole splitting is small and its value ranges from –0.5 to –0.2 mm s^{-1} implying a little excess of negative charge in p_x and p_y ortibals.

The undetectable electric field gradient at the tin nucleus in $SnCl_4$2detu is both consistent with the nearly regular *cis*-octahedral geometry about the tin atom (*cf.* bond lengths and angles in Table VI), and with a valence contribution arising from a nearly isotropic population in the valence shell of the σ-bonding orbitals [8], if the valence contribution is comparable in magnitude but opposite in sign to the lattice one. On the contrary the *cis*-octahedral geometry about the tin atom in $SnBr_4$2deu is more distorted (*cf.* bond lengths and angles in Table VI). This might imply anisotropy among the σ-bonding orbitals and then a small electric field gradient at the tin nucleus. The imbalance in electron density would be a p-imbalance, and would arise from small differences in the tin p-electron involvement in the Sn–Br and Sn–O bonds. Here it is interesting to note that detectable splittings have been reported for $SnX_4$2tmu (X = Cl and Br) [6]. Further studies are in progress to verify if the splitting is entirely due to σ-bonding and structural effects.

On going from tetrahedral SnX_4 to *cis*-octahedral $SnX_4$2L compounds, the s-electron density at the tin nucleus decreases (Table IV) [25]. This agrees very well with an increase in the coordination number and a decrease in the covalency of tin(IV) bonding on adduct formation. The lengthening of the Sn–X bonds can be seen on comparing the bond lengths of $SnCl_4$ [26] or $SnBr_4$ [27] with those of $SnCl_4$2detu or $SnBr_4$2deu. On going from the chloride to the bromide or iodide compounds, the isomer shift increases slightly because a decrease in the halide electronegativity increases the s-electron density at the tin nucleus [23].

δ and Γ/2 do not show significant changes with temperature, instead the fast temperature decrease of the resonance absorption results in an undetectable resonance above 200 K. Information about the lattice dynamics at the tin site may come from the temperature coefficient values, *a*, derived from the variation of the logarithm of the Mössbauer resonance areas, normalized at 77 K. These coefficients, −1.9, −2.0 and −1.7 10^{-2} K^{-1} for $SnCl_4 2detu$, $SnBr_4 2detu$ and $SnBr_4 2dmtu$ respectively, are near to −1.8 10^{-2} K^{-1}, the value exhibited from non-interacting discrete molecules [28].

In order to correlate the strength of the tin bonds with the tin mean-square amplitude of vibrations, the relation $a = d\ln A/dT = -1/\chi \, d\langle x_i^2\rangle/dT$ was tentatively employed for $SnCl_4$ 2detu in the approximation of the high-temperature limit of the Debye model [29]. The tin isotropic mean-square amplitude of vibration, $\langle x_i^2\rangle$, at room temperature was obtained averaging the anisotropic temperature factors U_{ii} (i = 1, 2 and 3) of $SnCl_4 2detu$, 0.051, 0.056 and 0.060 Å^2 respectively. Thus at room temperature and at 77 K, the tin root-mean-square amplitudes of vibrations, $\langle x_i^2\rangle^{1/2}$, are 0.23 and 0.16 Å respectively, implying, though semiquantitatively, a fast decrease in the bond strength with increasing temperature.

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