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Trans-STRENGTHENING IN TIN(IV) ANIONIC COMPLEXES

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Summary

X-Ray studies of $(NMe_4)_2EtSnCl_5$, $(NMe_4)_2BuSnBr_5$ and $(NMe_4)_2SnBr_6$ indicate octahedral geometry for all the tin atoms. In the first two complexes, under the influence of the alkyl group, the *cis*-Sn–Hal bonds are lengthened by 0.11 Å (Hal = Cl) and 0.09 Å (Hal = Br), while the *trans*-Sn–Hal bonds are shortened by 0.03 Å (Hal = Cl) and 0.05 Å (Hal = Br).

Introduction

During earlier X-ray studies of octahedral tin(IV) complexes of the general formula $Me_nSnHal_{4-n} \cdot 2HMPT$ ($n = 0, 1$; Hal = Cl, Br; HMPT = hexametapol), the phenomenon of strengthening of the Sn–Hal bond in the *trans*-position to the alkyl group was discovered [1]. The results of an X-ray study of $BuSnCl_3 \cdot PCI$ (PCI = *N'*-phenylpyridine-2-carbaldimine) [2], in which the *trans*-position to the alkyl group was occupied by an *N*-atom not by halogen, showed that *trans*-strengthening of the Sn–N bond did not occur.

In the work reported herein, the crystal and molecular structures of the anionic complexes $(NMe_4)_2EtSnCl_5$ (I), $(NMe_4)_2BuSnBr_5$ (II) and $(NME_4)_2SnBr_6$ (III) were determined. The fact that there were five identical ligands besides the alkyl group in complexes I and II guaranteed that the halogen-ligand was arranged *trans* to the alkyl group, unlike complexes of the general formula $RSnX_3 \cdot 2D$, where D is a neutral donor. Complex III served as a standard for comparison with complex II.

Experimental

Crystal preparation

Compounds I, II and III were obtained by mixing ethanol solutions of $EtSnCl_3$ with NMe_4Cl and $BuSnBr_3$, or $SnBr_4$ with NMe_4Br, in a molar ratio of 1/2. Crystals were obtained by slow cooling of solutions of I, II and III in a $H_2O/EtOH$ mixture. M.p. I 190°C (decomp.), II 175°C (decomp.).

TABLE 1

X-RAY CHARACTERISTICS OF THE STRUCTURES STUDIED

Substance	a (Å)	b (Å)	c (Å)	β, deg.	Space group	Z	Number of refl.	R
$(NMe_4)_2C_2H_5SnCl_5$	14.088(3)	11.237(5)	13.331(3)	90.97(2)	*Cc*	4	1136	0.045
$(NMe_4)_2C_4H_9SnBr_5$	14.277(4)	11.669(2)	14.163(3)	90.30(2)	*Cc*	4	1526	0.060
$(NMe_4)_2SnBr_6$	26.99(5)	–	–	90	*Fd*3*c*	32	184	0.079

Elemental analysis:

I: Found: C, 25.73; H, 6.08. $C_{10}H_{29}N_2Cl_5Sn$ calcd.: C, 25.24; H, 6.16%.

II: Found: C, 20.15; H, 4.67. $C_{12}H_{33}N_2Br_5Sn$ calcd.: C, 19.92; H, 4.60%.

III: Found: C, 13.40; H, 3.14. $C_8H_{24}N_2Br_6Sn$ calcd.: C, 12.87; H, 3.24%.

Data collection and reduction

The unit cell parameters, space groups and numbers of molecules per unit cell in the complexes investigated are listed in Table 1. Crystals of approximate dimensions 0.15 × 0.20 × 0.20 mm^3 (I) and 0.25 × 0.25 × 0.25 mm^3 (II and III) were used for data collection. Relative intensities up to θ 25.0° were collected with Mo-K_α radiation using a CAD-4 four-circle automatic diffractometer. The numbers of unique reflections with $I \geqslant 3\sigma(I)$ used for the subsequent analysis are listed in Table 1. Corrections were made for Lorentz and polarization effects, but no correction was applied for absorption.

Structure determination and refinement

Approximate coordinates of the tin and halogen atoms were determined by direct methods using the "MULTAN-82" program. The remaining atoms were located

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES IN $(NMe_4)_2C_2H_5SnCl_5$ ($\times 10^4$; for N and C, $\times 10^3$)

Atom	x	y	z
Sn	0	1980(1)	0
Cl(1)	345(3)	2091(6)	1865(4)
Cl(2)	–1728(4)	2042(8)	257(5)
Cl(3)	–30(10)	4119(4)	–26(10)
Cl(4)	–256(4)	2007(7)	–1859(4)
Cl(5)	1791(4)	2207(6)	–331(4)
N(1)	285(1)	–2(2)	–255(1)
N(2)	–289(1)	–4(2)	–250(1)
C(11)	209(2)	70(2)	–274(2)
C(12)	358(2)	94(2)	–202(3)
C(13)	261(2)	–78(2)	–171(2)
C(14)	313(2)	–81(2)	–339(2)
C(21)	–248(2)	80(3)	–338(2)
C(22)	–195(2)	–79(2)	–200(2)
C(23)	–367(1)	–67(2)	–284(2)
C(24)	–328(2)	63(2)	–159(2)
C(1)	–30(2)	2(2)	14(2)
C(2)	31(2)	–78(3)	–36(2)

TABLE 3

FINAL FRACTIONAL ATOMIC COORDINATES IN $(NMe_4)_2C_4H_9SnBr_5$ ($\times 10^4$; for N and C, $\times 10^3$)

Atom	x	y	z
Sn	0	2115(2)	0
Br(1)	317(3)	2152(4)	1877(3)
Br(2)	−1871(3)	2211(5)	277(3)
Br(3)	−80(4)	4312(3)	16(7)
Br(4)	−315(3)	2140(4)	−1887(3)
Br(5)	1843(3)	2281(4)	−336(3)
N(1)	−281(2)	−13(2)	−248(2)
N(2)	−225(2)	487(2)	−247(2)
C(11)	−207(3)	−86(4)	−213(3)
C(12)	−247(3)	84(3)	−324(3)
C(13)	−359(3)	−75(3)	−273(3)
C(14)	−301(3)	61(3)	−161(3)
C(21)	−242(3)	438(4)	−157(4)
C(22)	−312(3)	566(3)	−269(3)
C(23)	−143(4)	580(5)	−196(4)
C(24)	−188(3)	411(4)	−327(3)
C(1)	−27(3)	23(4)	11(4)
C(2) [b]	−34	−50	60
C(3) [a]	19	−178	34
C(4) [b]	37	−215	0
C(5) [b]	−59	−59	−9
C(6) [b]	20	−260	64

[a] Atoms were located by difference Fourier synthesis; coordinates were not refined by least-squares method; multiplicity = 1. [b] As above, multiplicity = 0.5.

from conventional and difference Fourier maps. All atoms (except the carbons of the ethyl group) in I; the Sn, bromine and nitrogen atoms in II; and the Sn and bromine atoms in III were given anisotropic temperature factors, and full matrix least-squares refinement gave the final *R*-values, listed in Table 1 (unit weights were applied for all reflections). All calculations were performed using the "Enraf–Nonius SDP" complex of programs. The scattering factors used were those for neutral atoms. Final fractional atomic coordinates, anisotropic thermal parameters, bond distances and angles, and some nonvalent contacts in complex I are given in Tables 2–10.

TABLE 4

FINAL FRACTIONAL ATOMIC COORDINATES IN $(NMe_4)_2SnBr_6$ ($\times 10^4$; for N and C, $\times 10^3$)

Atom	x	y	z
Sn	0	0	0
Br	958(2)	−87(3)	83(3)
N(1)	125	125	125
N(2)	875	125	125
C(1)	156(1)	156(2)	156(1)

TABLE 5

FINAL ANISOTROPIC THERMAL PARAMETERS IN $(NMe_4)_2C_2H_5SnCl_5$, $(NMe_4)_2C_4H_9SnBr_5$ AND $(NMe_4)_2SnBr_6$ (for Sn and Cl(Br) only) [a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$(NMe_4)_2C_2H_5SnCl_5$						
Sn	5.66(5)	10.29(9)	7.06(6)	0.6(6)	−1.4(1)	0.1(7)
Cl(1)	4.9(2)	16.9(6)	5.9(3)	−2.8(8)	−1.1(5)	2.5(9)
Cl(2)	5.6(3)	24.8(9)	10.5(5)	−5(1)	0.7(6)	9(1)
Cl(3)	7.4(2)	10.0(4)	9.0(3)	1(2)	−0.4(5)	1(2)
Cl(4)	10.6(4)	13.3(6)	7.9(4)	−3(1)	1.9(7)	−2(1)
Cl(5)	5.9(3)	16.1(7)	7.1(3)	3.7(8)	−1.5(5)	−2.8(9)
$(NMe_4)_2C_4H_9SnBr_5$						
Sn	2.92(7)	5.0(1)	3.77(8)	−0.5(6)	0.5(1)	−0.4(8)
Br(1)	3.4(2)	9.7(3)	3.4(2)	1.0(4)	−0.5(3)	2.5(5)
Br(2)	3.3(2)	13.6(5)	5.3(2)	−2.3(5)	1.0(3)	2.3(6)
Br(3)	4.2(2)	5.1(2)	6.1(2)	−0.1(7)	2.1(3)	0(1)
Br(4)	3.9(2)	10.7(4)	4.7(2)	−0.2(5)	1.7(3)	−0.2(5)
Br(5)	3.5(2)	10.2(4)	3.7(2)	2.0(5)	0.7(3)	−1.3(5)
$(NMe_4)_2SnBr_6$						
Sn	1.57(9)	β_{11}	β_{11}	0	0	0
Br	1.6(3)	3.0(2)	2.6(1)	−0.2(4)	−0.4(5)	0.0(8)

[a] β_{ij} are of the form $10^3 \times \exp[-(\beta_{11} \times h^2 + \beta_{22} \times k^2 + \beta_{33} \times l^2 + \beta_{12} \times h \times k + \beta_{13} \times h \times l + \beta_{23} \times k \times l)]$.

Results and discussion

The complex anions I, II and III are mononuclear; the environment of the tin atoms is octahedral, although slightly distorted. The NMe_4^+ cations are disordered, so the estimated standard deviations of the N–C bond distances are rather large. The reliability of the Sn–C bond distances in complexes I and II is also insufficient:

TABLE 6

BOND DISTANCES (Å) IN $(NMe_4)_2C_2H_5SnCl_5$

Atoms	Distance
Sn–Cl(1)	2.527(9)
Sn–Cl(2)	2.460(10)
Sn–Cl(3)	2.407(3)
Sn–Cl(4)	2.503(11)
Sn–Cl(5)	2.587(9)
Sn–C(1)	2.23(2)
C(1)–C(2)	1.42(3)
N(1)–C(11)	1.36(4)
N(1)–C(12)	1.65(4)
N(1)–C(13)	1.45(4)
N(1)–C(14)	1.50(4)
N(2)–C(21)	1.62(4)
N(2)–C(22)	1.69(3)
N(2)–C(23)	1.38(4)
N(2)–C(24)	1.53(4)

TABLE 7

BOND DISTANCES (Å) IN $(NMe_4)_2C_4H_9SnBr_5$

Atoms	Distance
Sn–Br(1)	2.694(5)
Sn–Br(2)	2.704(4)
Sn–Br(3)	2.566(2)
Sn–Br(4)	2.707(6)
Sn–Br(5)	2.690(4)
Sn–C(1)	2.24(2)
N(1)–C(11)	1.45(3)
N(1)–C(12)	1.64(3)
N(1)–C(13)	1.37(3)
N(1)–C(14)	1.53(3)
N(2)–C(21)	1.42(4)
N(2)–C(22)	1.58(3)
N(2)–C(23)	1.74(4)
N(2)–C(24)	1.53(4)

TABLE 8

ANGLES (°) IN $(NMe_4)_2C_2H_5SnCl_5$

Atoms	Angle	Atoms	Angle
Cl(1)–Sn–Cl(2)	92.2(3)	Cl(5)–Sn–C(1)	106.9(6)
Cl(1)–Sn–Cl(3)	88.2(4)	Sn–C(1)–C(2)	118(1)
Cl(1)–Sn–Cl(4)	175.4(3)	C(11)–N(1)–C(12)	100(3)
Cl(1)–Sn–Cl(5)	89.5(3)	C(11)–N(1)–C(13)	108(2)
Cl(1)–Sn–C(1)	90.0(7)	C(11)–N(1)–C(14)	116(3)
Cl(2)–Sn–Cl(3)	87.5(4)	C(12)–N(1)–C(13)	103(2)
Cl(2)–Sn–Cl(4)	90.7(4)	C(12)–N(1)–C(14)	123(3)
Cl(2)–Sn–Cl(5)	172.5(2)	C(13)–N(1)–C(14)	106(3)
Cl(2)–Sn–C(1)	80.4(6)	C(21)–N(2)–C(22)	107(2)
Cl(3)–Sn–Cl(4)	88.4(4)	C(21)–N(2)–C(23)	111(3)
Cl(3)–Sn–Cl(5)	85.2(4)	C(21)–N(2)–C(24)	115(3)
Cl(3)–Sn–C(1)	167.8(6)	C(22)–N(2)–C(23)	119(3)
Cl(4)–Sn–Cl(5)	87.2(3)	C(22)–N(2)–C(24)	103(2)
Cl(4)–Sn–C(1)	94.0(7)	C(23)–N(2)–C(24)	102(2)

TABLE 9

ANGLES (°) IN $(NMe_4)_2C_4H_9SnBr_5$

Atoms	Angle	Atoms	Angle
Br(1)–Sn–Br(2)	91.0(1)	Br(5)–Sn–C(1)	104.6(5)
Br(1)–Sn–Br(3)	89.0(2)	C(11)–N(1)–C(12)	114(2)
Br(1)–Sn–Br(4)	178.5(1)	C(11)–N(1)–C(13)	111(2)
Br(1)–Sn–Br(5)	90.8(1)	C(11)–N(1)–C(14)	101(2)
Br(1)–Sn–C(1)	88.5(7)	C(12)–N(1)–C(13)	116(2)
Br(2)–Sn–Br(3)	85.0(2)	C(12)–N(1)–C(14)	102(2)
Br(2)–Sn–Br(4)	89.1(1)	C(13)–N(1)–C(14)	111(2)
Br(2)–Sn–Br(5)	173.2(1)	C(21)–N(2)–C(22)	106(2)
Br(2)–Sn–C(1)	82.0(5)	C(21)–N(2)–C(23)	90(2)
Br(3)–Sn–Br(4)	89.5(2)	C(21)–N(2)–C(24)	119(2)
Br(3)–Sn–Br(5)	88.5(1)	C(22)–N(2)–C(23)	104(2)
Br(3)–Sn–C(1)	166.7(5)	C(22)–N(2)–C(24)	117(2)
Br(4)–Sn–Br(5)	89.0(1)	C(23)–N(2)–C(24)	116(2)
Br(4)–Sn–C(1)	93.0(7)		

TABLE 10

THE SHORTEST CATION–ANION CONTACTS (Å) IN $(NMe_4)_2C_2H_5SnCl_5$ [a]

Cation	Anion				
	Cl(1)	Cl(2)	Cl(3)	Cl(4)	Cl(5)
N(1)	4.892	5.023	4.567	4.373	4.166
N(1)′	4.288	4.494	4.604	5.027	4.677
N(2)	4.225	4.631	4.616	4.432	4.270
N(2)′	5.187	4.107	4.604	4.800	4.955

[a] Symmetry code: none *x*, $-y$, *z*; (′) *x*, *y*, $1/2+z$.

since the alkyl groups are disordered, the carbon atoms have been poorly refined by the least-squares method. The structures of complexes I, II and III, similar to those of some other octahedral tin(IV) anionic complexes such as $(NH_2Me_2)_2SnBr_6$ [3], K_2SnBr_6 [4], and M_2SnCl_6 (M = K, Rb, Cs, NH_4, NMe_4, NH_2Me_2) [5–7], belong to the K_2PtCl_6 structural type. The structures of I and II are distorted by compression of the cube along the *b*-axis (see Table 1) and by displacement of the cation from tetrahedral hole centres, also along the *b*-axis. In the structure of III, the ideal packing of K_2PtCl_6 is destroyed by the disorientation of the $SnBr_6^{2-}$ octahedra, which causes the doubling of the unit cell parameters. Figure 1 shows the anion $RSnX_5^{2-}$ and its cationic environment.

In complex I the shortest Cl...Cl distance between neighbouring anions is equal to 4.992 Å, which is 1.4 Å longer than the sum of the Van der Waals' radii of two chlorine atoms (3.60 Å). Consequently, similar to the complex $(NMe_4)_2SnCl_6$ [5], the unit cell dimensions are determined by anion-cation contacts. As for complexes II and III, this is also justifiable for them, because the Br...Br distance between

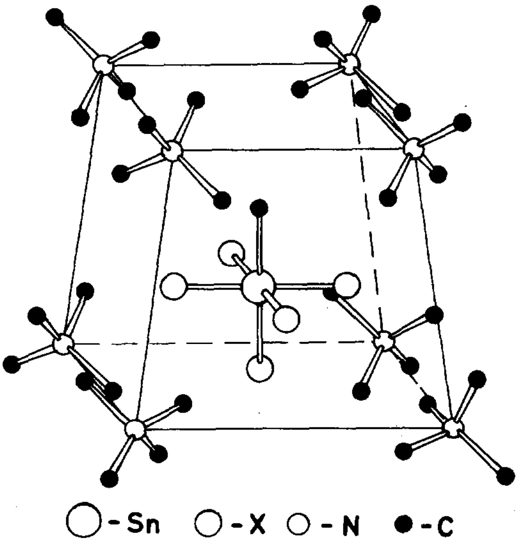

Fig. 1. $RSnX_5^{2-}$ anion and its cationic environment (I: R = Et, X = Cl, II: R = Bu, X = Br).

neighbouring anions is equal to 5.384 Å (II) and to 5.918 Å (III) and the sum of the Van der Waals' radii of two Br atoms is 3.90 Å.

In complex II all the *cis*-Sn–Br bond distances are practically equivalent (see Table 7). This is in accordance with the fact that all the Br-cation contacts are almost equivalent. In complex I the *cis*-Sn–Cl bond distances are non-equivalent. In the linear fragment Cl(1)–Sn–Cl(4), the Sn–Cl bond distances are almost equal to each other. However, in the linear fragment Cl(2)–Sn–Cl(5), significant lengthening of the Sn–Cl(5) bond is observed; simultaneously, the Sn–Cl(2) bond is shortened so that the average Sn–Cl bond length in both linear fragments is practically the same: 2.515 Å in Cl(1)–Sn–Cl(4) and 2.524 Å in Cl(2)–Sn–Cl(5). At the same time, Cl(5) has the shortest contacts with the nitrogen atoms of the cations (see Table 10); besides this, Cl(5) has five contacts with the carbon atoms of the cationic methyl groups which are shorter than the sum of the Van der Waals' radii of Me and Cl (3.80 Å). Other equatorial chlorine ligands have only one such contact.

In complex III the tin atom occupies a position with multiplicity 32; it is surrounded by six crystallographically equivalent bromine atoms (multiplicity 192). The $SnBr_6^{2-}$ anion is almost ideally octahedral, the deviations of the angles from 90° not exceeding 0.7°. The Sn–Br bond distance is equal to 2.605(1) Å. The NMe_4^+ cations occupy positions in tetrahedral hole centres with multiplicity 16 (N(1)) and 48 (N(2)). The N(1)–C(1) bond distance is equal to 1.43(3) Å; we did not succeed in revealing the carbon atoms of Me near N(2), probably because of the disorder of the cation. For the Sn–Hal bond distances in complexes I–III and for some complexes described in the literature, thermal motion correction has been applied using the "riding" model of Busing and Levy [9]. The results are listed in Table 11.

TABLE 11

Sn–X BOND DISTANCES (Å) IN ANIONIC TIN(IV) COMPLEXES (X = Cl, Br)

Substance	*d*(Sn–X)	*d* (Sn–X) with thermal motion correction applied [a]	Ref.
$(NMe_4)_2EtSnCl_5$-*cis*:	2.527(9); 2.460(10) 2.503(11); 2.587(9)	2.533; 2.486; 2.517; 2.594	this work
$(NMe_4)_2EtSnCl_5$-*trans*:	2.407(3)	2.414	
$(NMe_4)_2BuSnBr_5$-*cis*:	2.694(5); 2.704(4); 2.707(6); 2.690(4)	2.701; 2.718; 2.715; 2.696	this work
$(NMe_4)_2BuSnBr_5$-*trans*:	2.566(2)	2.573	
$(NMe_4)_2SnBr_6$	2.605(1)	2.622	this work
$(NMe_4)_2SnCl_6$	2.402(3)	2.446	[5]
K_2SnCl_6 (*a*)	2.411(2)	2.433	[5]
K_2SnCl_6 (*b*)	2.409(2)	2.426 [b]	[7]
$(NH_4)_2SnCl_6$ (*a*)	2.421(1)	2.430	[5]
$(NH_4)_2SnCl_6$ (*b*)	2.421(1)	2.428 [b]	[7]
$(NH_2Me_2)_2SnCl_6$		2.437; 2.450 [b]	[6]
$(NH_2Me_2)_2SnBr_6$	2.601(2); 2.609(3)	2.610; 2.625	[3]
K_2SnBr_6	2.590(3); 2.591(3); 2.597(3)		[4]
$(PyH)_2Me_2SnCl_6$	2.603(2); 2.625(3)		[8]

[a] Thermal motion correction was applied using the "riding" model [9]. [b] Libration correction was applied.

In complex I the average value of the *cis*-Sn–Cl bond distance is equal to 2.519(10) Å, this is 0.11 Å longer than the Sn–Cl bond distance in $(NMe_4)_2SnCl_6$ [5]. It should be noted that the presence of the second alkyl group in the anionic complex causes the Sn–Cl bond distance in $(PyH)_2Me_2SnCl_4$ [8] to lengthen by an additional 0.10 Å. In complex II the average value of the *cis*-Sn–Br bond is equal to 2.699(5) Å, this is 0.09 Å longer than the Sn–Br bond distance in complex III (2.605(1) Å). Complexes of the general formula $R_2SnBr_4^{2-}$, similar to complex III [8], are not described in the literature, as far as we know. After thermal motion correction the character of the change of the bond distances remains the same.

In complex I, without the thermal motion correction, the *trans*-Sn–Cl bond distance is equal to the Sn–Cl bond length in $(NMe_4)_2SnCl_6$ in the limits of estimated standard deviations, but after taking the thermal motion correction into consideration the *trans*-Sn–Cl bond distance appears to be 0.03 Å shorter than the Sn–Cl bond in $(NMe_4)_2SnCl_6$ and also shorter than those in other complexes containing the $SnCl_6^{2-}$ anion (Table 11). As for complex II, the *trans*-Sn–Br bond distance is 0.04 Å shorter than the Sn–Br bond in complex III (after taking the thermal motion correction into consideration, it is 0.05 Å shorter).

Thus the experimental data discussed above give additional evidence of the correctness of the conclusion made earlier [1] about the existence of *trans*-strengthening in tin(IV) bromine-containing complexes. In addition, structural evidence of *trans*-strengthening in tin(IV) chlorine-containing complexes has been found in complex I.

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