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Halogen exchange in complexes of hexacoordinate tin \((L^n CH_2)_2 SnX_2\)
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**Highlights**

1. Hypercoordinated complexes with octahedral structure.
2. Halogen exchange reactions between hexacoordinate tin dihalides produce mixed dihalides.
3. NMR \(^{119}\text{Sn}\) spectroscopy, electrical conductivity and quantum-chemical calculations for investigation of exchange reactions for hexacoordinated complexes.

**Graphical Abstract**

![Graphical Abstract Image]

**Abstract**

Halogen exchange reactions between hexacoordinate tin dihalides \((L^n\text{CH}_2)_2\text{SnX}_2\) and \((L^n\text{CH}_2)_2\text{SnY}_2\) \((L^n\text{CH}_2 = \text{C,O-chelate} \ n\text{-membered lactamomethyl ligand,} \ n = 5–7; X, Y = \text{Cl, Br, I})\) produce mixed dihalides \((L^n\text{CH}_2)_2\text{SnXY}\). Along with the signals of original complexes, NMR \(^{119}\text{Sn}\) spectra of solutions containing two different homodihalides show the third signal with a median chemical shift. The results of NMR monitoring studies, conductivity data and quantum-chemical calculations suggest that mixed dihalides readily form in solutions, although these complexes have not been isolated as individual compounds.

**Keywords:** hexacoordinated tin compounds, \(^{119}\text{Sn}\) NMR spectroscopy, quantum-chemical calculations, electrical conductivity.

**Introduction**

An important aspect of our ongoing studies on organic complexes of penta- and hexacoordinate (hypervalent) silicon, germanium and tin with C,O-chelating amidomethyl and lactamomethyl ligands
the coordination environment around the central atom. The results of these studies are discussed in reviews [1–4] and research papers [5–12].

In particular, the stoichiometric composition and spatial arrangement of mono- and bidentate ligands in bis(lactamomethyl)germanes (L"CH₂)₂GeXY depend on the nature of monodentate ligands [5, 13–15]. Reactions of dichlorides (L"CH₂)₂GeCl₂ with LiX, AgX and Me₂SiX (X = F, Br, I, OTf, ClO₄) yield disubstituted products cis-(L"CH₂)₂GeX₂ when the nucleofugacity of the entering group (F⁻ or Br⁻) is similar to that of the leaving group (Cl⁻). According to X-ray data, such products have the same configuration as the initial dichlorides, with carbon atoms in trans-positions and oxygen and halogen atoms in cis-positions. In contrast, good nucleofuges, such as F⁻, OTf⁻ and ClO₄⁻, favour the formation of monosubstituted products trans-(L"CH₂)₂Ge(Cl)X, in which carbon atoms, oxygen atoms and monodentate ligands occupy trans-positions with respect to each other.

The Ge–Cl bonds in both mono- and disubstituted complexes are largely covalent while the Ge–X bonds in monosubstituted complexes trans-(L"CH₂)₂Ge(Cl)X are predominantly ionic. The solutions of trans-(L"CH₂)₂GeCl₂ in dichloromethane have much higher electrical conductivity than solutions of cis-(L"CH₂)₂GeX₂ of the same concentration, which suggests that the former complexes can dissociate in a suitable solvent to produce germanium ions [(L"CH₂)₂GeCl]⁺ stabilised by intraionic O→Ge coordination [16]. A similar behaviour is observed for the complexes produced by the reactions of (L"CH₂)₂GeBr₂ with Me₃SiOTf and Me₃SiI [13].

In contrast to germanium complexes, the reaction of organotin dichlorides cis-(L"CH₂)₂SnCl₂ with lithium halides produces structurally similar cis-dihalides (L"CH₂)₂SnX₂ (X = Br, I) [13, 17]. An attempt to synthesise a monosubstituted product with trans-configuration of monodentate ligands by the reaction of [L"CH₂]₂SnCl₂ with AgBF₄ was unsuccessful and led to a dinuclear cationic complex 1 as a result of partial hydrolysis [18]. To some extent, the latter complex was structurally similar to cationic disiloxanes [(L"CH₂)₂SiOSi(CH₂L")-]²⁺ · X⁻ (X = HgCl₂⁻, Hg₂Cl₆⁻), which contained disilicenium dications stabilised by intraionic O→Si coordination [19].

\[
(L"CH₂)₂SnCl₂ + AgBF₄ \xrightarrow{H_2O} \begin{cases} \text{[cis-(L"CH₂)₂SnCl₂]} & \text{2+} \\ \text{H} & \text{O} \\ \text{Sn(CH₂L"-)} & \text{2BF₄⁻} \end{cases}
\]

In the present work, our studies of anion exchange reactions between different dihalides of hexacoordinate tin are reported. The formation of mixed dihalides (L"CH₂)₂SnXY (X ≠ Y; X, Y = Cl, Br, I) in solutions was detected by \[^{119}\text{Sn}\] NMR monitoring and supported by electrical conductivity data.

The synthesis, structure, and spectra of initial homodihalides (L"CH₂)₂SnX₂ (X = Cl, Br, I) have been reported in review [13] and research papers [17, 20].

**Discussion**

**NMR spectroscopy and electrical conductivity**

The properties of mixed organotin dihalides (L"CH₂)₂SnXY could be studied only in solution, as these complexes have not been isolated as individual compounds. The formation of mixed dihalides in
monitored by the $^{119}$Sn NMR spectroscopy method, which turned out to be more informative compared to $^1$H and $^{13}$C NMR (Table 1).

Table 1. Chemical shifts of $^{119}$Sn ($\delta$, 20 °C, CDCl$_3$) and electrical conductivity ($\lambda$, in CH$_2$Cl$_2$, $c = 5.7$ mmol dm$^-3$) of complexes 2–9 and their mixtures in solutions

<table>
<thead>
<tr>
<th>Complex A</th>
<th>$\delta$(119Sn), ppm/$\lambda$, mS cm$^2$ mol$^{-1}$</th>
<th>Complex B</th>
<th>$\delta$(119Sn), ppm/$\lambda$, mS cm$^2$ mol$^{-1}$</th>
<th>Complex C</th>
<th>$\delta$(119Sn), ppm</th>
<th>$\lambda$, mS cm$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, X = Cl, n = 5</td>
<td>–194.6/21</td>
<td>5, Y = Br, n = 5</td>
<td>–241.8/18</td>
<td>2 + 5</td>
<td>–217.8</td>
<td>52.6</td>
</tr>
<tr>
<td>2, X = Cl, n = 5</td>
<td>–194.6/21</td>
<td>8, Y = I, n = 5</td>
<td>–272.8/32</td>
<td>2 + 8</td>
<td>–233.8</td>
<td>65.0</td>
</tr>
<tr>
<td>3, X = Cl, n = 6</td>
<td>–270.1</td>
<td>6, Y = Br, n = 6</td>
<td>–312.4</td>
<td>3 + 6</td>
<td>–291.3</td>
<td>–</td>
</tr>
<tr>
<td>4, X = Cl, n = 7</td>
<td>–255.9</td>
<td>7, Y = Br, n = 7</td>
<td>–294.5</td>
<td>4 + 7</td>
<td>–275.7</td>
<td>–</td>
</tr>
<tr>
<td>5, X = Br, n = 5</td>
<td>–241.8/18</td>
<td>8, Y = I, n = 5</td>
<td>–272.8/32</td>
<td>5 + 8</td>
<td>–257.3</td>
<td>65.0</td>
</tr>
<tr>
<td>7, X = Br, n = 7</td>
<td>–294.5</td>
<td>9, Y = I, n = 7</td>
<td>–382.9</td>
<td>7 + 9</td>
<td>–338.9</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Immediately after mixing the reactants. $^b$ In two hours after mixing the reactants.

For each pair of reactants, stoichiometric amounts (~0.01 mmol) of complexes A and B were dissolved in CDCl$_3$ and placed in the NMR tube. The $^1$H, $^{13}$C and $^{119}$Sn NMR spectra were studied.

In the $^1$H NMR spectra, the position and shape of the signals of the lactam cycle of complexes A and B coincide, while the NCH$_2$ signals are observed as a broadened multiplet (Fig. 1a).

Figure 1. $^1$H (a), $^{119}$Sn (b) NMR spectra mixture of (L$^5$CH$_2$)$_2$SnCl$_2$ (2) and (L$^5$CH$_2$)$_2$SnBr$_2$ (5) (Varian VXR-400, CDCl$_3$, room temperature)

In each case, three $^{119}$Sn NMR signals were detected (Fig. 1b). The reversible dynamic nature of the observed process is indicated by characteristic spectral changes in the NMR spectra. Indeed, as the temperature rises to 55 °C, the signals in the NMR spectra narrow, and as the temperature decreases, the spectral picture is restored (Fig. 2).
Two signals corresponded to the initial homodihalides A and B while the third signal of the mixed complex C had a median chemical shift (Table 1). Over a period of two hours, the integral intensity of signals A, B and C gradually changed from ~10 : 3 : 10 to ~1 : 2 : 1. After that point, no further change in integral intensity was detected at temperatures up to +60 °C.

The median values of δ(119Sn) for complexes C suggest that mixed dihalides of hexacoordinate tin are likely to have the same cis-configuration of mono- and bidentate ligands as that in initial homodihalides 2–9. Indeed, the rearrangement of ligands from cis- to trans-configuration in structurally similar complexes of hexacoordinate silicon shifts the δ(29Si) signals downfield, from –110 ± –120 ppm in cis-(L^7CH_2)_2SiX_2 to –50 ± –60 ppm in trans-(L^7CH_2)_2SiXY [1, 4].

The same conclusion could be drawn from the analysis of 1H NMR spectra of complexes A, B and C at equilibrium. In all cases, three overlapping sets of signals were observed, and all signals of the same type were detected within a narrow range of chemical shifts. In particular, at ambient temperature, the signals of non-equivalent protons H_a and H_b in NCH_2 groups (Scheme 1) of the three complexes in each mixture appeared as a superposition of three broad singlets.

Scheme 1. Halogen exchange between (L^7CH_2)_2SnX_2 and (L^7CH_2)_2SnY_2 in solution

Further evidence for the cis-configuration of mixed dihalides (L^7CH_2)_2SnXY was provided by the electrical conductivity of their solutions in CH_2Cl_2 (52.6–96.5 mS cm^2 mol^-1 at 5.7 mmol dm^-3), which was only marginally higher than that of initial homodihalides 2, 5 and 9 (18–32 mS cm^2 mol^-1 at the same concentration, Table 1). In contrast, the conductivity of Ge- and Si-analogues of complexes 2–9 was much higher (40–3000 and 4000–100000 mS cm^2 mol^-1, respectively) within the concentration range 1–10 mmol dm^-3 [20]. The observed trend in electrical conductivity of structurally similar organic dihalides of Si, Ge and Sn reflected the increasing covalent character of the M–X bond in heavier Group 14 elements.
Relative stability of cis- and trans-isomers of complexes \((L^nCH_2)_2SnX_2\) and \((L^nCH_2)_2SnXY\) \((X = Cl, Br, I; n = 5, 7)\) was evaluated by quantum-chemical calculations (Table 1S in ESI). The molecules of both types had similar calculated geometries, with a distorted octahedral environment of the tin atom. Cis-isomers contained two almost linear O–Sn–Hal moieties while in trans-isomers the two halogen atoms were located at the opposite sides of the plane formed by carbon and oxygen atoms.

The most noticeable differences between the complexes with \(L^5CH_2\) and \(L^7CH_2\) ligands were the Sn–O and Sn–Hal bond lengths. In the case of \(L^5CH_2\) complexes, the Sn–O distances were consistently shorter (by 0.02–0.03 Å) than those in \(L^7CH_2\) complexes while the Sn–Hal distances in the former complexes were consistently longer (by up to 0.1 Å). These differences could be related to electron-donating properties of five- and seven-membered lactam rings.

The Sn–Hal bond lengths in all studied complexes exceeded their typical values for tetracoordinate tin compounds by at least 0.25 Å, which facilitated the dissociation of these bonds in solution. This trend was similar to that observed for hexacoordinated organogermanium complexes [10, 11], in which the energies of Ge–Cl and Ge–Br bonds were also much lower than those in tetracoordinate germanium compounds.

According to our calculations, the total energies of cis-isomers were lower than those of trans-isomers with the same molecular composition. This difference was more pronounced in complexes with \(L^5CH_2\) ligands \((-3 \pm 3.5\) kcal mol\(^{-1}\)) than in complexes with \(L^7CH_2\) ligands \((-1 \pm 1.5\) kcal mol\(^{-1}\)). The only exception was \((L^5CH_2)_2SnCl\) and \((L^5CH_2)_2SnBr\) compounds, for which the differences in total energy between cis- and trans-isomers were negligible (less than 0.5 kcal mol\(^{-1}\)), so the equilibrium ratio of these isomers in solutions could be nearly stoichiometric.

In addition to isomerisation, the hydrolysis of the studied complexes in solution was also considered. This process could be induced by trace amounts of water in the solvent \((CH_2Cl_2)\) used in conductivity studies, which could produce a range of dinuclear neutral and ionic species. Possible structures of such species containing \(L^nCH_2\) \((n = 5, 7)\) ligands and iodine atoms were studied using quantum-chemical calculations (Scheme 2).

![Scheme 2. Hydrolysis intermediates \([(L^5CH_2)_2SnOSn(CH_2L^n)_2]_2\) and \([(L^5CH_2)_2Sn(OH)_2Sn(CH_2L^n)_2]_2\) \([n = 5, 7; R_1, R_2 = (CH_2)_3, (CH_2)_5]\).](image)

The dissociation of Sn–I bonds in the presence of water can produce mononuclear cations with a weak Sn...I coordination. The dinuclear complexes can be produced by the hydrolysis of two Sn–I bonds. According to our calculations, there are two possible types of dinuclear complexes, both existing
[(L^	ext{5} \text{CH}_2)_2\text{SnOSn(L}^\text{5} \text{CH}_2)_2]I_2$, contains two pentacoordinate tin atoms and can be formally described as a product of hydrolytic dimerisation of two [(L^	ext{5} \text{CH}_2)_2\text{SnI}^+] cations with subsequent elimination of both iodide anions. The second type, [(L^	ext{7} \text{CH}_2)_2\text{Sn(OH)Sn(L}^\text{7} \text{CH}_2)_2]I_2$, contains two hexacoordinate tin atoms and is a possible intermediate on the hydrolysis reaction pathway between the [(L^	ext{5} \text{CH}_2)_2\text{SnI}]^+ cation and [(L^	ext{7} \text{CH}_2)_2\text{SnOSn(L}^\text{7} \text{CH}_2)_2]^2+ dication. In all dinuclear complexes the lengths of O→Sn coordination bonds formed by L^7CH_2 ligands were longer than those in corresponding mononuclear complexes. In addition, the lengths of these bonds formed by L^5CH_2 ligands exceeded the respective values for L^5CH_2 ligands by ~0.03 Å. At the same time, the lengths of Sn–O bonds involving bridging oxygen atoms in [(L^	ext{5} \text{CH}_2)_2\text{Sn(OH)Sn(L}^\text{5} \text{CH}_2)_2]I_2 complexes were longer than those in [(L^	ext{5} \text{CH}_2)_2\text{SnOSn(L}^\text{5} \text{CH}_2)_2]^2+ dications by 0.18 Å.

The calculation of $^{119}$Sn NMR chemical shifts with quantum-chemical methods could be potentially used for the study of the structure of (L^5CH_2)_2SnX_2 in solution. However, it suffers from the inaccuracy of computational schemes, as the large number of core electrons in the tin atom complicates the calculations due to relativistic effects. Even in the case of simple tetracoordinated compounds of tin, post Hartree-Fock methods and carefully selected basis sets are necessary to achieve quantitative agreement between experimental and calculated values [21].

In our case, we discuss formally hexacoordinated compounds of tin calculated with DFT (meta-GGA TPSS level). Hence, the discrepancy between calculated and experimental $\delta(^{119}\text{Sn})$ can be significant, so it is difficult to distinguish trans and cis isomers. Quantum-chemical calculations show that $\delta(^{119}\text{Sn})$ for trans-isomers are more upfield than those for cis isomers (Table 3S). The dependency between the lactam ring size and $\delta(^{119}\text{Sn})$ is also reproduced by quantum-chemical calculations. According to our calculations (Fig. 3), the values of $\delta(^{119}\text{Sn})$ for trans-(L^5CH_2)_2SnX_2 are in better agreement with experiment than those for cis-isomers. The best agreement between experiment and calculation is observed for Hal = Cl, Br (n = 5) and Hal = Cl (n = 7).

**Figure 3.** Experimental vs calculated $\delta(^{119}\text{Sn})$ for L^5 and L^7 ligands (a and b, respectively). The values for trans- and cis-isomers are shown by magenta boxes and green circles, respectively.

In the case of Hal = I, the calculated $\delta(^{119}\text{Sn})$ differ significantly from the experimental values. Compounds (L^7CH_2)_2SnI_2 have highly negative $\delta(^{119}\text{Sn})$ values (Table 1), which suggests that their structures do not correspond to the (L^5CH_2)_2SnI_2 formula. In particular, the experimental $^{119}$Sn chemical
[(L^7CH_2)_2Sn(OH)_2Sn(L^7CH_2)_2]I_2 (–326.1 ppm, Table 4S). The most negative calculated δ(^119Sn) value is observed for trans-(L^5CH_2)_2SnCl_2 (–256.4 ppm), which is close to the experimental value for (L^5CH_2)_2SnI_2 (–272.6 ppm). Therefore, the structures of (L^5CH_2)_2SnI_2 species can be affected by halogen exchange and/or hydrolysis reactions in solutions.

Conclusion

The ^1H and ^119Sn NMR monitoring studies, electrical conductivity data and quantum-chemical calculations reported in this work suggest that exchange reactions between C,O-bischelate bis(lactamomethyl)tin homodihalides (L^6CH_2)_2SnX_2 and (L^6CH_2)_2SnY_2 (n = 5–7, X, Y = Cl, Br, I) in solutions produce mixed dihalides (L^6CH_2)_2SnXY with cis-configuration of the central atom.

Experimental

^1H, ^13C and ^119Sn NMR spectra of all compounds were recorded on a "Varian VXR-400" instrument (400.1, 100.6 and 149.2 MHz, respectively) in pulse mode with subsequent Fourier transformation and ^2H stabilization of the resonance conditions. Chemical shifts in ^1H and ^13C spectra were measured using Me_3Si as internal reference. The ^119Sn chemical shifts were measured using Me_4Sn as external reference.

The conductivities of 10^-1 ÷ 10^-5 mol dm^-3 solutions in dichloromethane were measured on a Radelkis OK-102/1 instrument equipped with OK-9023 electrodes with three platinum rings at ~20 °C and the AC frequency 80 Hz–3 kHz. The relative error of specific conductivity was ±1%.

Quantum-chemical calculations were carried out using Orca 4.2.0 program [22]. The structures for subsequent optimization were constructed using X-ray data from CSD [23] and Chemcraft software [24]. On initial stage the geometry was optimized using meta-GGA functional TPSS and SVP all-electron basis set. The structures were further optimized using all-electron TZVPP basis set in conjunction with CPCM model to take into account the solvation effects. Zero-order relativistic approximation (ZORA) was utilized to account for significant relativistic effects in tin and iodine atoms. Local minima of potential energy hypersurface were determined by calculating the hessian matrix for all optimized structures. NMR properties were calculated in terms of GIAO method using relativistic aug-cc-pVQZ-DK basis set for Sn and old-ZORA-TZVPP basis set for I. The molecule of SnMe_4 calculated on the same level of theory was used as standard to calculate ^119Sn chemical shifts.

Declaration of Competing Interest

None

Acknowledgements

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