

THE MUTUAL INFLUENCE OF LIGANDS AND THE NATURE OF CHEMICAL BONDS IN TIN(IV) OCTAHEDRAL COMPLEXES

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Summary

By considering the bond length Sn—Lig, determined by X-ray structure analysis in *cis*- and *trans*-complexes of general formula $(\text{CH}_3)_n\text{SnHal}_{4-n} \cdot 2\text{D}$, where $n = 0-2$, Hal = Cl or Br, D = hexamethylphosphoric triamide, dimethyl sulphoxide or dimethyl formamide, it was observed that in all complexes the tin atom is surrounded by ligands in a slightly deformed octahedral. The interactions of ligands in the considered complexes differ strongly from the interactions of ligands in octahedral and quadratic complexes of transition metals. All bond lengths are in good agreement with contributions from HV_{I} , HV_{II} hypervalent and covalent bonds in the formations of Sn—Lig bonds and also with the participation of the $5d$ -orbital of tin.

Introduction

The mutual influence of ligands in the quadratic and octahedral complexes of the transition metals has been studied and consists of two principle effects, *trans*- and *cis*-effects, which were revealed by Chernaev [1] and Grinberg and Kukushkin [2]. *Trans*-effect of the electron-donating ligand (D) on the electron-acceptor *trans*-partner (A) in transition metal (M) complexes is specifically demonstrated by the elongation of the interatomic distance M—A and contraction in the interatomic distance M—D in the linear trinuclear fragment D—M—A, compared with the distances between the same atoms in complexes which have linear trinuclear fragments A—M—A or D—M—D. One can well see this effect, for example, by comparing the interatomic distances in complexes $\text{MCl}_3 \cdot 3\text{L}$ and $\text{MCl}_4 \cdot 2\text{L}$ (M = W, Re, Os, Ir, Pt) [3].

The structure of non-transition metal complexes have not been so extensively studied. In the present work, to investigate the mutual influence of ligands in non-transition metal complexes, we used some tin(IV) octahedral compounds.

It is well known that the nature of the chemical bonds determines the chemical properties and the structures of complexes; one of the most interesting questions

concerning the structure of six-coordinated tin(IV) complexes is the nature of the chemical bond Sn—Lig.

The most popular interpretation for the six-coordinating bond of the tin atom is $5sp^3d^2$ -hybridisation. However, Tobias [4], considering the structures of anions $[(CH_3)_2SnHal_4]^{2-}$, believed that the vacant $5d$ -orbitals of the tin atom do not take an observed part in the formation of the bonds in those anions. From the NMR and IR spectra data, he concluded that in the tin—methyl group bonds tin contributes a $5s$ -orbital with one of the $5p$ -orbitals, since the tin—halogen bonds which lie in the equatorial plane (relative to the Sn—CH₃ bond), have the preferred character of the three-centre two-electron bond using σ -orbitals of halides and the remaining two $5p$ tin orbitals.

This agrees with the view of Pimentel [5] and Rundle [6] who introduced the concept of an orbital-deficient bond. These considerations were later generalized by Masher [7] who called orbital-deficient bonds hypervalent bonds. Orbital-deficient bonds, in which the s -character equals zero was called a hypervalent bond of the first kind (HV_I) and the hypervalent bond of the second kind (HV_{II}) is an orbital-deficient bond in which a pure p -orbital does not take part, but hybridised s - and p -orbitals do. It follows that the degree of orbital deficiency of HV_I bond is larger than HV_{II}. Therefore, in the Tobias model, the covalent bonds Sn—CH₃ are combined with the hypervalent bonds HV_I Sn—Cl.

In the anion complexes studied by Tobias [4], $[(CH_3)_2SnHal_4]^{2-}$, electronic structure and properties of ligands are quite different. On the one hand, methyl groups are strong electron-donor ligands which need a maximum contribution of s -orbital of tin atom, on the other hand the chlorine atoms are strong electron-acceptor ligands, which form the preferred bond with the p -orbital of tin.

It can be supposed that in those tin(IV) complexes in which ligand properties differ greatly, such as in $[(CH_3)_2SnHal_4]^{2-}$, each of the two models sp^3d^2 hybridization and HV_I hypervalent bonds, do not quite describe the true structure of the complexes. It is important to know what is the mutual influence of ligands in complexes with different contributions of hypervalent bonds. We therefore carried out systematic X-ray crystal and molecular structure studies on some methyltin halide complex compounds with electron-donor molecules (D) having the general formula $(CH_3)_nSnHal_{4-n} \cdot 2D$, where $n = 0-2$, Hal = Cl or Br, D = hexamethylphosphoric triamide (HMPT), dimethyl sulphoxide (DMSO) or dimethylformamide (DMF).

Preliminary studies involved the synthesis [8], NQR [9], Mössbauer [10] and NMR [11] spectra of these compounds.

Experimental

Diffraction reflection intensities for single crystals of all compounds were collected by means of four-circles single crystal automatic diffractometer Hilger & Wats Y 290. Structures have been determined by the heavy-atom method and refined by the least square method.

Detailed information about the unit cell parameters, space groups and refinements of all the structures studied will be published separately [12]. Here we shall discuss only the stereochemical results.

Data on complexes investigated together with the necessary literature data for

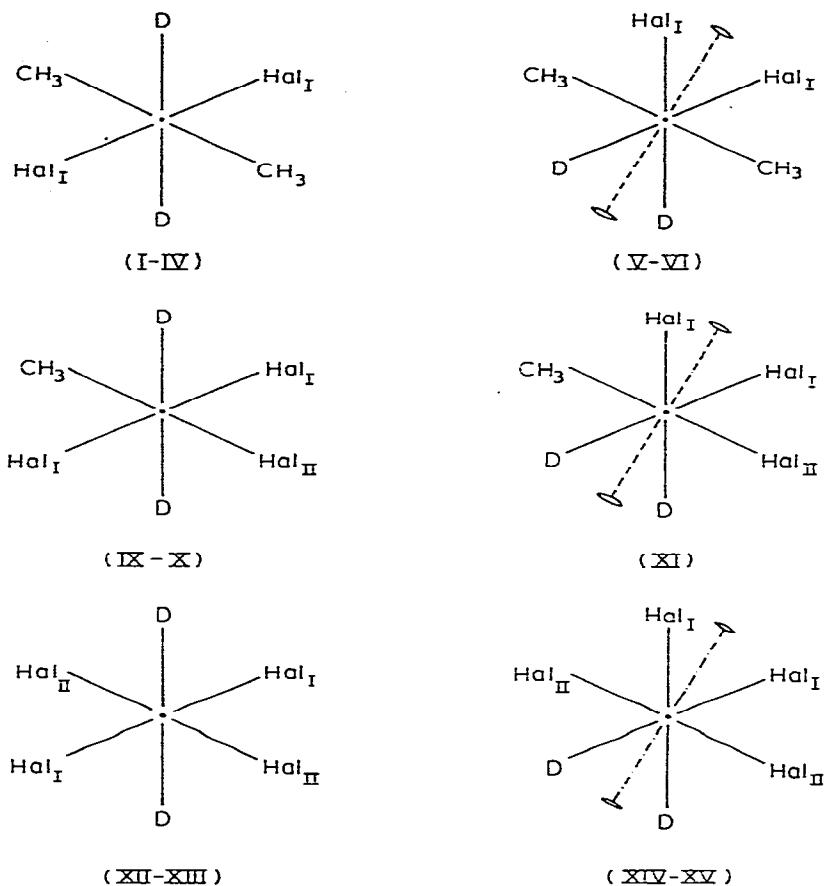


Fig. 1. Structures of investigated complexes.

the discussion are listed in Table 1; structures of the compounds studied are represented in Fig. 1.

In all the investigated six-coordinated complexes ligands are arranged around Sn^{IV} atom at the apices of slightly distorted octahedral, i.e., electron-donor molecules D are oriented both *trans* and *cis* to each other. All the *trans*-complexes have C_i symmetry in crystals; the centres of symmetry are customarily occupied by the tin atoms. It is known from the literature [13] that the six-coordinated *trans*-complex $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{pyo}$, where pyo = pyridine oxide, also has C_i symmetry. The following *cis*-complexes have been investigated and have different symmetry: C_1 , $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{DMSO}$ [14]; C_2 , $\text{SnCl}_4 \cdot 2 \text{OSeCl}_2$ [15]; C_2 , $\text{SnCl}_4 \cdot 2 \text{NCCH}_3$ [16]; and C_v , $\text{SnCl}_4 \cdot 2 \text{OPCl}_3$ [17]; VI and XI *cis*-complexes have C_2 symmetry.

In spite of the impossibility for the methyltin trihalide complexes to have a centre of symmetry in the *trans*- or the *cis*-complexes and two-fold axis in the crystals of IX, X and XI tin atoms are located in a special position. This being in centres of symmetry and on the two-fold axes, i.e. the halogen atom Hal_{II} and methyl groups, Fig. 1, which are arranged in *trans*-position, are statis-

TABLE I
THE INTERATOMIC DISTANCES IN $(\text{CH}_3)_n\text{SnHal}_{4-n} \cdot 2 \text{ D COMPLEXES}$

No.	n	Hal	D	Type of the con-figuration	r(Sn-C) (Å)	r(Sn-O) (Å)	r(Sn-Hal) (Å)	r(Sn-Hal) (Å)	Ref.
I	2	Br	DMSO	Trans	2.15(4)	2.22(2)	2.75(2)	Present paper	
II	2	Br	HMPT	Trans	2.14(1)	2.23(1)	2.74(1)	Present paper	
III	2	Cl	Pyo	Trans	2.22(2)	2.25(2)	2.58(1)	13	
IV	2	Cl	HMPT	Trans	2.14(1)	2.26(2)	2.57(1)	Present paper	
V	2	Cl	DMSO	Cis	2.12(2); 2.13(2)	2.27(1); 2.31(1)	2.53(1); 2.49(1)	Present paper	
VI	2	Cl	DMF	Cis	2.13(2)	2.39(2)	2.47(1)	Present paper	
VII	2	Br	bis(1,2-dieoxy-1-carbonyl-ethyl) MO-DIF,	Cis	2.26(5); 2.26(5)	2.44(3); 2.46(3)	2.588(6); 2.516(6)	18	
VIII	2	Br	bis(1,2-dieoxy-1-carbonyl-ethyl) MO-DIF,	Cis	2.24(3)	2.49(2)	2.504(5)	19	
IX	1	Br	HMPT	Trans		2.16(1)	2.65(1)	2.40(1) ^a	
X	1	Cl	HMPT	Trans		2.18(1)	2.46(1)	2.31(1) ^a	
XI	1	Cl	DMF	Cis		2.22(2)	2.43(1)	2.35(1) ^a	
XII	0	Br	HMPT	Trans		2.09(1)	2.56(1)	2.54(1)	
XIII	0	Cl	HMPT	Trans		2.13(2)	2.40(1) and 2.36(1) ^b	Present paper	
XIV	0	Cl	OPCl ₃	Cis		2.25(5); 2.30(4)	2.31(2); 2.32(2)	2.33(2); 2.33(2)	
XV	0	Cl	OSeCl ₂	Cis		2.121(16)	2.360(7)	2.409(6)	

^a The distance between tin atom and $(\text{Hal})_2 + \text{CH}_3$ superimposed peak; see experimental mark. ^b $\text{SnCl}_4 \cdot 2 \text{ HMPT}$ and $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{ HMPT}$ are not isostructural, therefore, it is not known, which of the chlorine atoms in $\text{SnCl}_4 \cdot 2 \text{ HMPT}$ is Hal_I and which Hal_{II} .

tically replacing each other. Therefore, IX, X, XI must be considered as pseudo-centrosymmetrical.

Statistical replacement of the methyl group and Hal_{II} atom in IX, X and XI complexes makes it difficult to determine the bond distances Sn—Hal_{II} and Sn—CH₃. In all methyltin trihalide complexes studied we have not established the coordinates of the carbon atom of the methyl group and Hal_{II}. The coordinates determined are the summation of the two peaks (Hal_{II} + CH₃).

As the chlorine atom has a higher atomic number than carbon, it can be considered that the distance between Sn and the superimposed peak (Hal_{II} + CH₃) is nearer to the value of the Sn—Hal_{II} distance.

Among the complexes investigated, two groups of isomeric structures can be separated: II, IV, IX, XII and X, XIII. Essential differences in the atomic coordinates and the unit cell parameters were observed in the VI and XI complexes, therefore, they may be cautiously regarded as isomers. All complexes are mononuclear. The electron-donor molecules are bonded to tin through the oxygen atom. The distances between atoms of different complexes exceed 3 Å which are normal for crystals of complexes under the influence of Van der Waals interactions.

Results and discussion

The mutual influence of the ligands in the octahedral tin(IV) complexes leads to two consequences, firstly, the formation of *trans*- and *cis*-isomers, and secondly, regular changes in the interatomic distances Sn—Lig depending on the relative location of the ligands and their electrical (donor, acceptor) properties.

Earlier [20] it was expressed that the formation of *trans*- or *cis*-isomers depends on the size of the electron-donating ligand D; the isomer formed was that which ensured minimum spatial difficulties inside the complexes.

All the investigated structures confirmed this hypothesis. On the other hand going from chloride [14] to bromide I a change from *cis*- to *trans*-configuration occurs. It must be remembered also that SnI₄ · 2 HMPT (NQR method [9]) has a *cis*-configuration.

Apparently, the formation of *cis*- or *trans*-isomer not only depends on the size of the electron-donating ligand D, but also on the other ligands in the complexes, i.e., this principle must be extended to all the ligands of tin(IV) octahedral complexes. From the two possible configurations, *cis* or *trans*, only those are realized which ensure the minimum spatial difficulties between all the ligands of the complex. This conclusion is general for tin(IV) octahedral complexes containing any set of ligands but, as will be discussed later, the mutual influence of the ligands within a complex determined configuration depends on their properties and their relative arrangement. Therefore, for further consideration, all the investigated compounds are suitably collected in groups according to their compositions and we shall consider the essential characteristics of the structures of these complexes.

(CH₃)₂SnHal₂ · 2 D complexes

Table 1 contains beside (CH₃)₂SnHal₂ · 2 D complexes, two forms of bis(1,2-diethoxycarbonyl)tin dibromide [18,19]. In one, both metallic

cycles of each mononuclear complex belong to *d*- or *l*-form (I), while in the other each complex contains metallic cycles such as *d*- and *l*-form (II). These complexes have approximately an octahedral structure and carbon atoms are *trans* to each other.

The distances $r(\text{Sn}-\text{CH}_3)$ in four of the six complexes shown in Table 1, approximate to 2.14 Å. The exceptions to this are in: in $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{ DMSO}$, 2.07(6), 2.08(5) Å [14] and $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{ pyo}$, 2.22(2) Å [13].

These differences in the Sn-CH₃ bond lengths provide evidence for the rehybridisation of the tin atom orbitals, which act on the all bounds in the complex. Therefore, the structure $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{ DMSO}$ was refined by us, to reduce the values of the standard deviations for the all bond distances, especially $r(\text{Sn}-\text{CH}_3)$.

The bond distances $r(\text{Sn}-\text{CH}_3)$, determined after the refinement by 1211 independent reflections ($R = 0.076$), are 2.12(2) and 2.13(2) Å, slightly different from the mean $r(\text{Sn}-\text{CH}_3)$ (2.14 Å) for the above mentioned four compounds. In this case, the distance $r(\text{Sn}-\text{CH}_3)$ in $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{ pyo}$ complex is the single exception from the rule. The uniformity of the bond distance Sn-CH₃ for the all investigated complexes $(\text{CH}_3)_2\text{SnHal}_2 \cdot 2 \text{ D}$ indicates that the contribution by s-orbitals of tin in formation of the Sn-CH₃ bond is constant. It is supposed that the electronegativity of the oxygen atom of any of the electron-donating molecules D used entering into the inner sphere of Sn(IV), essentially larger than that of the methyl group. Therefore, it may be that the 5s-orbital of tin is hybridised with one of the 5p orbitals to give two equivalent orbitals to form the Sn-CH₃ bond, while the two remaining 5p orbitals of the Sn^{IV} can be bonded through orbitals of oxygen atoms or halide ions (Cl⁻, Br⁻) to form hypervalent bonds of the first group (O-Sn-O, Hal-Sn-Hal and O-Sn-Hal). In this case, Tobias' model can be justified for $(\text{CH}_3)_2\text{SnHal}_2 \cdot 2 \text{ D}$ complexes.

Now let us consider the X-ray crystal and molecular structure analysis of the methyltin halide complexes (Table 1) incorporating the idea of the co-existence of the covalent and hypervalent bonds in those complexes. The bond distances $r(\text{Sn}-\text{O})$ in *cis*-complexes are longer than those in *trans*-complexes, while the opposite is true for the distances $r(\text{Sn}-\text{Hal})$. The differences between the distances are rather essential, i.e. $r_{\text{max}}(\text{Sn}-\text{O}) - r_{\text{min}}(\text{Sn}-\text{O}) = 0.27 \text{ Å}$, $r_{\text{max}}(\text{Sn}-\text{Hal}) - r_{\text{min}}(\text{Sn}-\text{Hal}) = 0.25 \text{ Å}$. In the linear trinuclear fragment Hal-Sn-Hal $r(\text{Sn}-\text{Hal})$ is a maximum, and is reduced when one of the halogens is replaced by an oxygen atom of the electron-donor molecule (Hal-Sn-O). On the other hand, the distance $r(\text{Sn}-\text{O})$ has a minimum value when there are only two oxygen atoms in the linear trinuclear fragment beside the tin atom (O-Sn-O). This increases when a halogen is arranged *trans* relative to the oxygen atom (O-Sn-Hal).

These empirical regularities in the alteration of the bond lengths can be explained on the basis of the consideration of the electron-donating ability of the molecules entering into the inner sphere of the complex and the electron-accepting properties of the halide ions. It is well known that the shorter the bond distance, the higher is the electron density between the bonded atoms in the internuclear space.

In the linear trinuclear fragment Hal-Sn-Hal both atoms at the extremity accept electrons from the internuclear space, reducing the concentration of electrons between tin and halogen atoms, which leads to a maximum bond dis-

tance Sn—Hal among all the Sn—Hal bonds. In the linear trinuclear fragment O—Sn—O oxygen atoms donate electrons to the internuclear space, therefore, the electron concentration will be increased and the bond distance Sn—O becomes a minimum among all the Sn—O bonds. In the case of the mixed linear trinuclear fragment O—Sn—Hal, due to the compensation between the donated electrons from the oxygen atom and the accepted electrons by the halogen atom in the internuclear spaces, the resulting electron density in the internuclear space O—Sn is decreased relative to the O—Sn—O fragment and at the same time, the electron density in the internuclear space Sn—Hal becomes higher than in the Hal—Sn—Hal linear trinuclear fragment. This leads to the elongation in O—Sn and reduction of the Sn—Hal bond lengths.

This hypothetical mechanism of the ligands interaction in the linear trinuclear fragment Lig—Sn—Lig supposes the ability of tin atom to translate the electron density from one half of the linear trinuclear fragment to the other under the electron-donation and electron-acceptance characters of ligands. It can be considered that the tricentral orbital of the hypervalent bond of the first kind acts as a "canal", through which the transportation of electrons from one half of the linear trinuclear fragment to the other takes place.

SnHal₄ · 2 D complexes

By comparing the interatomic distances Sn—Lig in SnHal₄ · 2 HMTP and (CH₃)₂SnHal₂ · 2 HMTP complexes, it is indicated that, in the absence of a methyl group, the bond distances Sn—O and Sn—Hal become shorter in both *trans*- and *cis*-configurations. This provides evidence for the increasing *s*-character of these bonds [21]. While in (CH₃)₂SnHal₂ · 2 HMTP the *s*-orbital of the tin atom contributes to form an *sp*-hybridised orbital, it contributes to form a second type of hypervalent bond or *sp³d²*-hybridised orbital in SnHal₄ · 2 HMTP complexes. Both cases lead to equal distribution of the contributed 5*s*-orbital on the Sn—Lig bond. The degree of orbital deficiency in the HV_{II} is smaller than in HV_I, but the orbital-deficiency of the bond which is formed from *sp³d²*-hybridisation is quite absent. Accordingly, on going from HV_I to HV_{II} and further to *sp³d²*-hybridised bonds the electron density between the nuclei must be increased, and the bond length must be decreased. Thus, from the fact of decreasing bond length for Sn—Lig on going from (CH₃)₂SnHal₂ · 2 HMTP to SnHal₄ · 2 HMTP, it can be concluded that the bonding in the latter complex contains a contribution from a second type of hypervalent bond or *sp³d²*-hybridised bond or both.

In considering the contributions to the *cis*-complex SnCl₄ · 2 OSeCl₂ [15], the very short distances Sn—O (2.121(16) Å) indicates that the OSeCl₂ molecule is a relatively strong electron-donating ligand. The interatomic distances Sn—Cl in the linear trinuclear fragment O—Sn—Cl and Cl—Sn—Cl are equal to 2.360(7) and 2.409(6) Å respectively, which means that in the *trans*-position to the electron-donating ligand a reduction in the Sn—Cl bond length takes place, and not elongation such as is observed in the case of transition metal complexes. This leads us to conclude that the character of the chemical bond of tin(IV) complexes and of the octahedral transition metal complexes are essentially different. Since the chemical bonds in the latter are represented by *sp³d²*-hybridised orbital of the metal atom, then it can be concluded that the chemical bonds in SnHal₄ · 2 D complexes have a considerable contribution from the second type

of hypervalent orbital, while the contribution from sp^3d^2 -hybridised orbital is negligible. Owing to the slight inequality of the distances Sn—Cl_I and Sn—Cl_{II} for SnCl₄ · 2 OSeCl₂ (Table 1) it can be concluded that the contribution from 5s orbital is slightly unequally distributed in the linear trinuclear fragments Lig—Sn—Lig. In the fragments containing the electron-donating ligand, the contribution of the 5s-orbital of tin atom is greater than in the fragment Cl_{II}—Sn—Cl_{II}, therefore the fragment O—Sn—Cl_I has a covalent constitution and in Cl_{II}—Sn—Cl_{II} hypervalent contribution of the first type.

The molecule OPCl₃ has less electron-donating character than OSeCl₂ according to the values of the interatomic distances Sn—O 2.25(5) and 2.30(4) Å in *cis*-complex SnCl₄ · 2 OPCl₃ [17]. But in both SnCl₄ · 2 OPCl₃ and SnCl₄ · 2 OSeCl₂, the distances Sn—Cl_I *trans* to the electron-donating molecule are equivalent, within the limit of the standard deviations (Table I), and the *cis*-ligand (Cl_{II}) is nearer to the tin atom in the presence of the weaker electron-donating ligands. This mutual influence of the ligands also has no analogy in the transition metal complexes, but it may be explained on the basis of the existence of the second type of hypervalent bonds. Apparently, the contribution of the tin atom 5s orbital in the presence of relatively weak electron-donating ligands is distributed more equally in all the bonds of the complex, and therefore all the bond lengths are equivalent. The bond lengths Sn—Lig in the complexes of the type SnCl₄ · 2 D, which have equally (in strength) electron donating molecules, e.g. HMPT and OSeCl₂, are practically equal and consequently do not depend on whether the complexes are *cis* or *trans*. This also substantiates the existence of the second type of hypervalent bond in SnHal₄ · 2 D complexes, which must ensure enough equal distribution of the contributing 5s-orbital of the tin atom over all the Sn—Lig bonds. So, for the interpretation of the bond length Sn—Lig in complexes of the type SnHal₄ · 2 D, differing in configuration and composition, it is necessary to consider the value of contributions of the second type of hypervalent bond and covalent bond for all the bonds of the complex which in the linear trinuclear fragment Lig—Sn—Lig, and not in the separate Sn—Lig bonds.

CH₃SnHal₃ · 2 D complexes

We will consider two specific peculiarities of structures of these complexes.

Firstly, where the interatomic distances Sn—O and Sn—Hal_I in the *trans*-complexes have an intermediate value between similar interatomic distances in the (CH₃)₂SnHal₂ · 2 D and SnHal₄ · 2 D complexes. In the *cis*-complexes CH₃SnHal₃ · 2 D the interatomic distances Sn—Hal_I have an intermediate value between the corresponding interatomic distances in the (CH₃)₂SnHal₂ · 2 D and SnHal₄ · 2 D complexes. The same tendency in the *cis*-complexes are observed for the interatomic distance Sn—O, with the exception of the SnCl₄ · 2 OPCl₃ complex, in which the interatomic distances Sn—O increases to 2.25(5) and 2.30(4) Å. This can be explained by the weakness of the electron-donating ability of OPCl₃ molecule. Accordingly, all these facts indicate that the nature of the chemical bond in the CH₃SnHal₃ · 2 D complexes is intermediate in nature between the bond in (CH₃)₂SnHal₂ · 2 D and that in the SnHal₄ · 2 D, i.e. in all the Sn—Lig bonds of the CH₃SnHal₃ · 2 D complexes contributions from the first and second type of hypervalent bonds together with the covalent.

Secondly, in the linear trinuclear fragment CH₃—Sn—Hal_{II}, which only exists

in this type of complex, the distance Sn—Hal_{II} was the shortest of all the Sn—Hal distances measured in our work, which would be expected for two reasons. On one hand, the contribution of HV_I in the linear trinuclear fragment CH₃—Sn—Hal_{II} bonds and the strong methyl electron-donating ligand leads to the natural influence of ligands which was considered above. On the other hand, the contribution of the covalency and hypervalency (HV_{II}) which are induced in the chemical bonds of the linear trinuclear fragment CH₃—Sn—Hal_{II}, increase the s-character of the Sn—Hal_{II} bond, i.e. do much to reduce Sn—Hal_{II} distance to a minimal value.

If we had succeeded to fix the coordination of the carbon atom, evidently, the Sn—CH₃ bond length in the trinuclear fragment CH₃—Sn—Hal_{II}, due to the two above reasons, will result in a shorter bond length than that of Sn—CH₃ in the (CH₃)₂SnHal₂ · 2 D complexes. The CH₃—Sn bond in CH₃SnHal₃ · 2 D really has not a pure covalent character, such as was considered for the (CH₃)₂SnHal₂ · 2 D complexes, but contain also HV_I and HV_{II} contributions.

We can summarize our conclusions in the following:

The mutual influence of the ligands arranged *trans* to each other in the octahedral tin(IV) complexes is directly opposite to that which was observed in the quadratic and octahedral complexes of the transition metals. Since, in the transition metal octahedral complexes the contribution by *sp*³*d*²-hybridisation orbitals are undoubtable, in the tin(IV) complexes the opposition of the mutual influence of the ligands indicates that the 5*d*-orbitals of tin in the bond formation in the octahedral complexes do not take any part. By considering the chemical bonds in the linear trinuclear fragment Lig—Sn—Lig a good opportunity arises to discuss the values of the contributions of the covalent, HV_I and HV_{II}, in the interatomic distance Sn—Lig. Therefore, the hypervalent bond contributions actually exist in the octahedral tin complexes, and together with the covalent component determine their constructions and properties.

Since the inert gas compounds and the polyhalide compounds are formed with the aid of those hypervalent bonds, it can be argued that the coordinated compounds of all the elements between Xe and Sn also contain hypervalent bonds. Moreover, as the contribution of the hypervalent bonds in the formation of tin(IV) octahedral complexes is so great, this gives reason to assume the existence of hypervalent bonds in the Cd and In octahedral complexes, i.e. for the all non-transition elements.

References

- 1 I.I. Chernjaev, *Izv. Inst. Plating*, 4 (1923) 213.
- 2 A.A. Grinberg and Yu. N. Kukushkin, *Zh. Neorg. Khim.*, 2 (1957) 106.
- 3 L. Aslanov, R. Mason, A.G. Wheeler and P.O. Whimp, *Chem. Commun.*, (1970) 30.
- 4 R.S. Tobias, *Inorg. Chem.*, 2 (1970) 1296.
- 5 G.C. Pimentel, *J. Chem. Phys.*, 19 (1951) 446.
- 6 R.J. Hack and R.E. Rundle, *J. Amer. Chem. Soc.*, 73 (1951) 432.
- 7 R.E. Rundle, *J. Amer. Chem. Soc.*, 85 (1963) 112.
- 8 J.I. Musher, *Angew. Chem. Int. Ed.*, 8 (1969) 54.
- 9 V.S. Petrosyan, N.S. Yashina and O.A. Reutov, *J. Organometal. Chem.*, 52 (1973) 315.
- 10 V.S. Petrosyan, N.S. Yashina, O.A. Reutov, E.V. Bryuchova and G.K. Semin, *J. Organometal. Chem.*, 52 (1973) 321.
- 11 V.S. Petrosyan, N.S. Yashina, S.G. Sacharov, O.A. Reutov, V. Ya. Rochev and V.I. Gol'danskii, *J. Organometal. Chem.*, 52 (1973) 333.

- 11 V.S. Petrosyan, N.S. Yashina, V.I. Bakhmutov, A.B. Permin and O.A. Reutov, *J. Organometal. Chem.*, **72** (1974) 71.
- 12 L.A. Aslanov, V.M. Ionov, W.M. Attia, A.B. Permin and V.S. Petrosyan, *Zh. Struct. Khim.*, in press.
- 13 E.A. Blom, B.R. Penfold and W.T. Robinson, *J. Chem. Soc. A*, (1969) 913.
- 14 N.W. Isaacs and C.H.L. Kennard, *J. Chem. Soc. A*, (1970) 1257.
- 15 I. Hermodsson, *Acta Crystallogr.*, **13** (1960) 656.
- 16 M. Webster and H.E. Blayden, *J. Chem. Soc. A*, (1969) 2443.
- 17 C.I. Bränden, *Acta Chem. Scand.*, **17** (1963) 759.
- 18 M. Yoshida, T. Ueki, N. Yasuoka, N. Kasai, M. Karudo, I. Omae, S. Kikkawa and S. Natsuda, *Bull. Chem. Soc. Japan*, **41** (1968) 1113.
- 19 T. Kimura, T. Ueki, N. Yasuoka, N. Kasai and M. Kakudo, *Bull. Chem. Soc. Japan*, **42** (1969) 2479.
- 20 Y.K. Ho and J.J. Zuckerman, *J. Organometal. Chem.*, **49** (1973) 1.
- 21 H.A. Bent, *Chem. Rev.*, **61** (1961) 275.