Organometallic Chemistry

Synthesis and crystal and molecular structures of six-coordinate tin dibromides and diiodides containing lactamomethyl C,O-chelating ligands

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New (O—Sn)-bischelate bis(lactamomethyl)dibromo- and -diiodostannanes $[L^{(n)}]_2SnX_2$ (L is the bidentate lactamomethyl C,O-chelating ligand; *n* is the size of the lactam ring, 5—7; X = Br or I) were prepared both by the direct method from metallic tin and the corresponding *N*-(halomethyl)lactams and by the reactions of dichlorides $[L^{(n)}]_2SnCl_2$ with lithium halides. According to the data of X-ray diffraction analysis, the tin atom in $[L^{(n)}]_2SnBr_2$ (*n* = 5—7) and $[L^{(n)}]_2SnI_2$ (*n* = 5 or 6) adopts an octahedral configuration with the carbon atoms in *trans* positions and the coordinating oxygen and halogen atoms in *cis*-positions with respect to each other. A comparison with the structures of analogous lactamomethyl halide derivatives of five- and six-coordinate Si, Ge, and Sn demonstrates that the spatial structures of the hypervalent fragments containing six-coordinate atoms are less sensitive to the replacement of the halide ligands and the central atom. The covalence of the M—Hal bond increases and the covalence of the M—O bond decreases in the series M = Si, Ge, and Sn.

Key words: six-coordinate tin compounds, synthesis, multinuclear NMR spectroscopy, X-ray diffraction study.

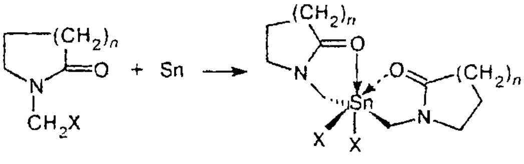
Recently, we have performed systematic studies of six-coordinate silicon, germanium, and tin compounds containing the amidomethyl and related C,O-chelating ligands.[1—4] These studies were an extension of investigations of analogous five-coordinate silicon[5,6] and germanium[7,8] derivatives. One of the major lines of investigation of the characteristic features of these compounds involves the elucidation of the properties of three-center hypervalent X—M—Y bonds, where M is an atom with an increased coordination number (Si, Ge, or Sn) and X and Y are electronegative atoms or groups (N—C=O, Hal, OTf, *etc.*). Investigations of tin derivatives as compounds containing six-coordinate atoms allow one to reveal the effects of the involvement of the M atom simultaneously in two hypervalent bonds and to follow the dependence of the properties of these bonds in the series M = Si, Ge, and Sn.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1988—1998, October, 1999.

In this work, we report the synthesis of previously unknown derivatives of five-, six-, and seven-membered lactams, *viz.*, (O—Sn)-bischelate bis(lactamomethyl)dibromo- and bis(lactamomethyl)diiodostannanes, and present the results of X-ray diffraction analysis of five of the synthesized compounds. In the cases of the five- and six-coordinate Si, Ge, and Sn atoms, the regularities of the structures of the hypervalent fragments in molecules of this type, which determine the chemical properties of the compounds, were revealed.

Results and Discussion

Synthesis and structures. Previously, we have found[4] that the reactions of *N*-(chloromethyl)lactams with metallic tin afforded (O—Sn)-bischelate dichlorostannanes $[L^{(n)}]_2SnCl_2$ (**1**) (L is a bidentate lactamomethyl C,O-chelating ligand and *n* is the size of the lactam ring). We demonstrated that these reactions can also be extended to other *N*-halomethyl derivatives. Thus, the reactions of *N*-(bromomethyl)- and *N*-(iodomethyl)-2-pyrrolidone with metallic tin yielded the previously unknown dibromide **2a** and diiodide **3a**.



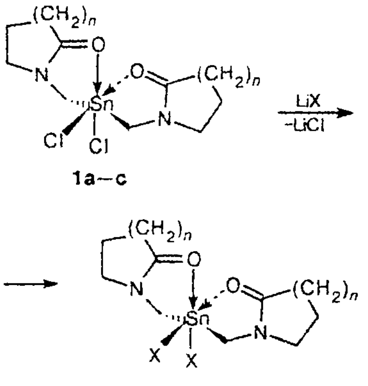
(1)

1a—c, 2a—c, 3a—c

X = Cl (**1**), Br (**2**), or I (**3**); *n* = 1 (**a**), 2 (**b**), or 3 (**c**)

Like dichlorides **1a—c**, compounds **2a** and **3a** were formed under rather mild conditions (refluxing of a mixture of the reagents in toluene for 2 h) and the target products were obtained in moderate yields (59 and 55%, respectively).

The reactivities of dichlorides **1a—c** toward nucleophilic reagents are rather high, which made it possible to perform the replacement of both Cl atoms by Br or I under the action of excess lithium bromide or iodide, respectively.



(2)

2a—c, 3a—c

The yields of the final products in reaction (2) (76—98%) were higher than those obtained in reaction (1). Taking into account that *N*-(chloromethyl)lactams are more readily available than the corresponding bromides and iodides and the fact that reaction (2) affords dihalides in higher yields, this reaction is a preferential procedure for the preparative synthesis of the compounds under consideration.

Table 1. Yields and the characteristics of (O—Sn)-bischelate bis(lactamomethyl)dibromo- and bis(lactamomethyl)diiodostannanes **2a—c** and **3a—c**

Compound	Reaction	Yield (%)	M.p.[a] /°C	IR,[b] ν/cm^{-1}	Found/Calculated (%) C	H	N	Molecular formula
2a	1	59	240—242	1510, 1615	24.95 25.30	3.22 3.40	5.87 5.90	$C_{10}H_{16}Br_2N_2O_2Sn$
	2	78	241—242					
2b	2	76	243—244	1505, 1605	28.31 28.67	3.88 4.01	5.61 5.57	$C_{12}H_{20}Br_2N_2O_2Sn$
2c	2	98	246—247	1505, 1580	31.54 31.68	4.45 4.56	5.39 5.28	$C_{14}H_{24}Br_2N_2O_2Sn$
3a	1	55	217—218	1505, 1610	20.88 21.12	2.63 2.84	4.58 4.93	$C_{10}H_{16}I_2N_2O_2Sn$
	2	93	217—218					
3b	2	77	214—215	1505, 1600	23.89 24.15	3.14 3.38	4.92 4.69	$C_{12}H_{20}I_2N_2O_2Sn$
3c	2	98	204—206	1505—1580	26.59 26.91	3.51 3.87	4.76 4.48	$C_{14}H_{24}I_2N_2O_2Sn$

[a] From acetonitrile.

[b] A solution in $CHCl_3$.

The formation of diiodies **3a—c** in reaction (2) was rather unexpected because the reactions of Ge analogs of compounds **1a—c**, *viz.*, dichlorides $[L^{(n)}]_2GeCl_2$, with iodine-containing nucleophiles resulted in the replacement of only one Cl atom and only mixed chloride-iodides $[L^{(n)}]_2Ge(Cl)I$ were isolated.[3] This difference is apparently associated with the nature of the central atom in the compounds under study. This effect is considered below in detail.

The resulting dihalides **2a—c** and **3a—c** (Table 1) are high-melting crystalline compounds. Their structures were established based on the data of elemental analysis and IR and NMR spectroscopy. The structures of all compounds (except for diiodide **3c**) were confirmed by X-ray diffraction analysis.

The six-coordinate state of the Sn atom in dihalides **2a—c** and **3a—c** is evidenced by the IR spectra (solutions in $CHCl_3$), which have two bands of strongly coupled ν(C=O) and ν(C=N) stretching vibrations of the amide fragments in the region of 1500—1700 cm^{-1} (see Table 1). The positions and intensities of these absorption bands (the medium intensity low-frequency band and the strong high-frequency band) in the spectra of the derivatives containing the identical lactamomethyl ligands are virtually independent both of the nature of the halogen atom and (when compared with the corresponding Ge analogs[3]) of the nature of the central atom. The ν(C=O) absorption bands of the nonchelated amide fragments are absent, which is indicative of rather strong O→Sn coordination.

The parameters of the ^1H, ^{13}C, and ^{119}Sn NMR spectra of dihalides **2a—c** and **3a—c**, which confirm their structures, are given in Tables 2 and 3. The signals in the ^1H NMR spectra of the valero- and caprlolactam derivatives were assigned to different spin systems with the use of the 2D $^1H—^1H$ COSY homonuclear correlation method. The multiplicities of the signals in the cases of the strongly coupled spin systems (compounds **2b,c** and **3b,c**) were determined by 2D *J*-resolved spectroscopy (HOM2DJ). The signals in the ^1H and ^{13}C NMR spectra were assigned based on the data of 2D heteronuclear correlation spectroscopy ($^1H—^{13}C$ HETCOR method, $^1J_{CH}$).[9]

The large upfield shifts of the signals in the ^{119}Sn NMR spectra in $CDCl_3$ (see Table 3) indicate that the tin atoms in the resulting dihalides exist in the six-coordinate state.[10] The ^{119}Sn signals for dihalides **2a,c** and **3a,c** are observed at lower field compared to those for compounds **2b** and **3b**, which may be indicative of a somewhat stronger intramolecular O→Sn interaction in the case of six-membered lactams. This result is consistent with the analogous effect of the size of the lactam ring on the degree of the coordination O→Si bonding in *N*-(dimethylchlorosilylmethyl)lactams $L^{(n)}SiMe_2Cl$, which was established based on the ^{29}Si NMR spectral data,[11] as well as with the data on six-coordinate tin dichlorides obtained previously.[4]

Analogously, the ^{13}C NMR spectra of compounds **2b** and **3b** have the signal of the C atom of the carbonyl group at higher field compared to those observed in the spectra of dihalides **2a,c** and **3a,c**.

Table 2. ^1H NMR chemical shifts and the spin-spin coupling constants ($^2J_{HH}$) for (O—Sn)-bischelate bis(lactamomethyl)dihalostannanes **2a—c** and **3a—c** (in $CDCl_3$)

Compound	δ ($^2J_{HH}$/Hz)					
	H(3)	H(4)	H(5)	H(6)	H(7)	NCH_2
2a	2.70 (t, *J* = 7.3)	2.09 (q, *J* = 7.3)	3.65 (t, *J* = 7.3)			2.57 (s)
2b	2.42 (t, *J* = 7.0)	1.82 (m)	1.86 (m)	3.46 (t)		2.85 (br.s)
2c	2.63 (t, *J* = 6.0)	1.62 (m)	1.82 (m)	1.85 (m)	3.64 (t, *J* = 6.0)	3.10 (br.s)
3a	2.59 (t, *J* = 6.1)	2.11 (m)	3.68 (m)			3.19 (br.s)
3b	2.41 (t, *J* = 6.0)	1.85 (m)	1.86 (m)	3.64 (t, *J* = 6.0)		3.10 (br.s)
3c	2.61 (t, *J* = 6.3)	1.65 (m)	1.78 (m)	1.80 (m)	3.63 (t, *J* = 6.3)	3.10 (br.s)

Table 3. ^{13}C ($^nJ_{SnC}$) and ^{119}Sn NMR chemical shifts for (O—Sn)-bischelate bis(lactamomethyl)dihalostannanes **2a—c** and **3a—c** (in $CDCl_3$)

Compound	δ							
	C(3)	C(4)	C(5)	C(6)	C(7)	NCH_2	C=O	^{119}Sn
2a	29.42	15.89	51.62 (*J* = 81.6)			44.92 (*J* = 1019)	177.29 (*J* = 21.9)	−241.3[*]
2b	30.01	20.33	22.51	51.47 (*J* = 91.9)		48.45 (*J* = 1077)	172.97 (*J* = 29.3)	−312.7
2c	29.55	22.08	26.00	34.45	53.62 (*J* = 99.1)	50.58 (*J* = 1048)	178.64 (*J* = 24.8)	−293.7
3a	29.70	16.10	51.41 (*J* = 82.2)			47.11 (*J* = 1069)	177.07 (*J* = 22.8)	−272.5
3b	30.32	20.29	22.44	51.39 (*J* = 84.6)		50.64 (*J* = 970)	172.98 (*J* = 23.1)	−336.5
3c	29.59	22.04	26.04	34.61	53.56	52.90	178.44	−294.5

Note. The $^nJ_{SnC}$ values (Hz) are given in parentheses. −244.6 at −50 °C.

In the ^{13}C NMR spectra of the tin dihalides under study, spin-spin coupling of the Sn atom with the carbonyl C atom and with some C atoms of the lactam rings is observed (see Table 3). The largest value of $J_{^{13}C-^{119}Sn}$ for the carbon atom of the carbonyl group is characteristic of dibromide **2b**. In this case, an increase in the $J_{^{13}C-^{119}Sn}$ value in parallel with the strength of the intramolecular coordination bond indicates that the transfer of the spin-spin $^{13}C-^{119}Sn$ coupling in dibromides **2a—c** occurs (as in dichlorides **2a—c** studied previously[4]) through the coordination bond. Note that the difference in the $J_{^{13}C-^{119}Sn}$ spin-spin coupling constants for compounds containing bidentate ligands of different sizes decreases on going from dibromides **2a—c** to diiodides **3a—c**. This is in agreement with the data of X-ray diffraction analysis, according to which the intramolecular coordination O→Sn bond lengths in diiodides **3a,b** are virtually equal (see below).

The conductivities of solutions of tin dihalides $[L^{(n)}]_2SnX_2$ (X = Cl, Br, or I; n = 5 or 7) are substantially lower than those of their Si analogs (data only for dichlorides are available), are slightly lower (in particular, as compared to dibromide $[L^{(7)}]_2GeBr_2$) than those of their germanium analogs (Table 4), and are close to the intrinsic conductivity of the solvent (CH_2Cl_2), which is indicative of an increase in the covalent character of the M—X bonds in dihalides $[L^{(n)}]_2MX_2$ (M = Si, Ge, or Sn) on going from silicon to germanium and then to tin compounds.

X-ray diffraction study. The configuration of the valence environment about the Sn atoms in dihalides **2a—c** and **3a,b** under study (the *cis* arrangement of the Hal and O atoms) is identical to that observed previously in six-coordinate tin[4,12] and germanium[13] dihalides containing the $MC_2O_2Hal_2$ coordination unit (M = Ge or Sn) with the intramolecular O→M coordination.

Interestingly, the replacement of the O atom by the N atom (the $MC_2N_2Hal_2$ coordination unit) leads to a change of the configuration to transoid.[14] Apparently, this is a manifestation of the difference in the donor properties of the O and N atoms. Note that both the *cis* (*i.e.*, like in dihalides **1—3**) and *trans* configurations of the like coordinating O and Hal atoms (*cis*-$Me_2SnCl_2\cdot2DMSO$, *cis*-$Me_2SnCl_2\cdot2DMF$, *trans*-$Me_2SnBr_2\cdot2DMSO$, and *trans*-$Me_2SnBr_2\cdot2HMPA$[15]) are observed in the structures containing the $SnC_2O_2Hal_2$ coordination unit with exclusively monodentate ligands.

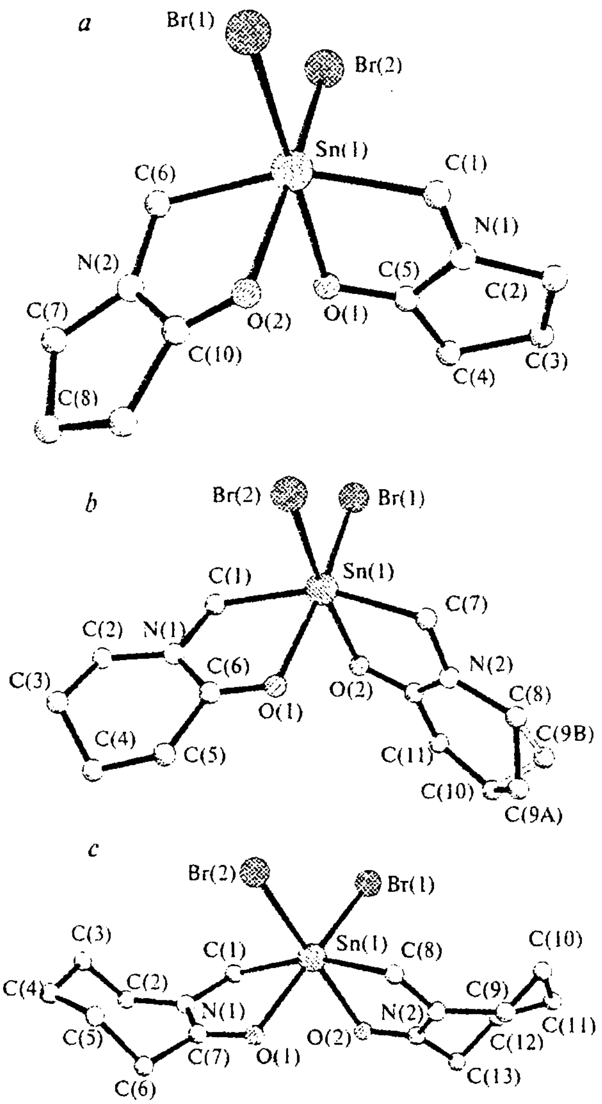


Fig. 1. Structures of molecules **2a** (*a*), **2b** (*b*), and **2c** (*c*) in the crystals. The H atoms are omitted.

Table 4. Molar conductivities (Λ) of solutions of (O—M)-bischelate bis(lactamomethyl)dihalosilanes, -germanes, and -stannanes in CH_2Cl_2 at 25 °C

Compound	C /mmol L^{-1}	Λ /mS cm^2 mol^{-1}
$[L^{(5)}]_2SiCl_2$	10.4	2500
	1.9	4330
$[L^{(7)}]_2SiCl_2$	10.0	3660
	0.9	10900
$[L^{(5)}]_2GeCl_2$	6.9	39
$[L^{(7)}]_2GeCl_2$	0.5	937
$[L^{(7)}]_2GeBr_2$	1.6	3220
1a	0.69	102
1c	5.1	76
	0.5	194
2a	5.7	18
3a	5.7	32

In the crystals not only of tin dibromides **2a—c** and diiodides **3a,b** (Figs. 1 and 2) but also of the analogous germanium dichlorides[13] and dibromides* $[L^{(n)}]_2GeX_2$

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* The complete data of X-ray structural analysis of dibromides $[L^{(n)}]_2GeBr_2$ (n = 5—7) and difluorides $[L^{(n)}]_2GeF_2$ (n = 5 or 6) will be published elsewhere. For the preliminary results, see Ref. 16.

(X = Cl or Br; $n = 5$—7) and tin dichlorides $[L^{(n)}]_2SnCl_2$ ($n = 5$—7).[4] which we have studied previously, the molecular conformations are virtually identical when the lactam rings in the lactamomethyl ligands are of the same size.

This is obvious in the case of molecules containing five- and six-membered lactam rings, whose flexibility is very limited. However, this fact is not evident in the case of seven-membered rings, whose sharply nonplanar geometry is responsible for the fact that bischelate $[L^{(7)}]_2M$ systems can adopt several different conformations. The flexibility of the lactam ring is limited by the presence of two sp^2-hybridized N and C atoms in this ring. As a result, the C—C—(O)—N—C fragment is always planar. The additional CH_2 group in the five-membered ring, which deviates from the above-mentioned plane, is rather labile. The dihedral angle between the corresponding C—C—C fragment and the planar portion of the ring can vary in the range of ±25°.[5,6] However, this fact affects only slightly the shape of the contact (van der Walls) surface of molecules of type **2**. The same is true for the six-membered lactam ring, which has the *twist* conformation with two additional CH_2 groups located on the opposite sides of the C—C—(O)—N—C plane. As for the seven-membered ring, which adopts a chair-like conformation in all known structures, if the orientation of the planar C—C(O)—N—C fragment is assumed to be fixed, the remaining portion of the ring is either above or below this plane. In this case, the conformation of the molecule can be substantially different, which, obviously, affects the molecular packing in the crystal.

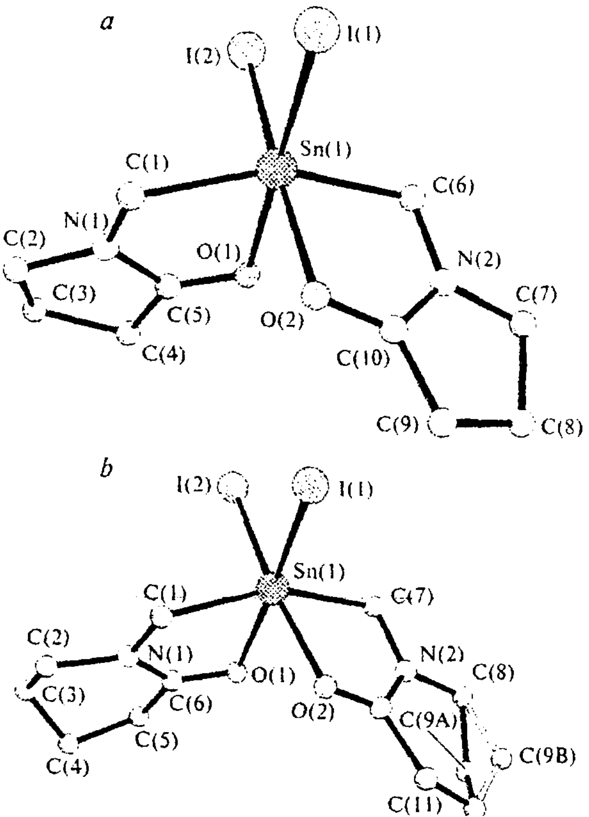


Fig. 2. Structure of molecules **3a** (*a*) and **3b** (*b*) in the crystals. The H atoms are omitted.

Actually, the orientations of the lactam rings and the molecular packing in the crystal of difluoride $[L^{(7)}]_2GeF_2$[17] (Fig. 3) are quite different from those observed in dichlorides, dibromides, and diiodides with the $L^{(7)}$ rings under consideration.

Therefore, the fact that these compounds containing the corresponding lactamomethyl ligands are isostructural (the linear and angular unit cell parameters vary within rather narrow ranges of <1 Å and <1.6°, respectively) is determined, among other things, by the adjustment of the molecular conformation to the most favorable molecular packing, whose type is not too sensitive to changes in the shape of the molecule of up to ~0.5 Å. The exception is the crystal of dichloride $[L^{(6)}]_2GeCl_2$[13] containing molecules of solvation. Difluorides $[L^{(n)}]_2GeF_2$ ($n = 5$—7), including those which are similar in conformation to other analogous dihalides ($n = 5$ or 6), crystallize in other space groups as well.[17] The disorder of the CH_2 group in one of the lactam rings in dibromide $[L^{(6)}]_2GeBr_2$ (**2b**) and in diiodide **3b** (see Figs. 1 and 2) is also indicative of the stability of the observed molecular packing with respect to noticeable changes in the shape of the molecule. The observed isomorphism of the structures makes it possible to assign even small differences in the spatial structures of the molecules of analogous compounds exclusively to the difference in the chemical structure and to rule out the effect of intermolecular interactions, which are approximately identical in these crystals.

In all the studied compounds of the $[L^{(n)}]_2MHal_2$ type (M = Ge or Sn; $n = 5$—7), the six-coordinate M atom is involved in two hypervalent O—M—Hal bonds. As in dichlorostannanes **1a—c** described previously, the O—Sn and Sn—Hal bond lengths in dibromides **2a—c** and diiodides **3a,b** are larger (by ~0.4 and ~0.15 Å, respectively) than the standard values[18,19] for the usual "tetrahedral" bonds.

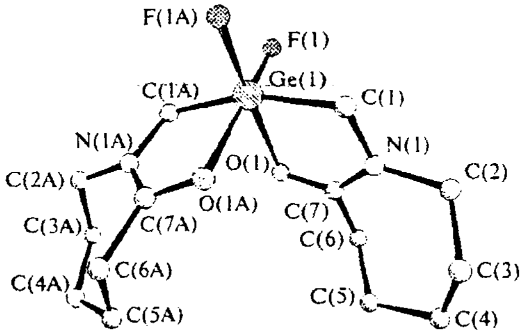


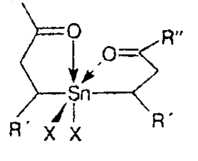
Fig. 3. Overall view of the $[L^{(7)}]_2GeF_2$ molecule in the crystal. The H atoms are omitted.

When treating hypervalent O—M—Hal bonds independently, the components of this hypervalent bond, *viz.*, M—O and M—Hal, in the distorted octahedral coordination environment about the M atom can be considered as "axial," and the remaining bonds, including the components of the second hypervalent bond, can be considered as "equatorial." The state of this hypervalent bond is characterized by the generalized parameter of the deviation of this bond from the "symmetrical" form (when the directions of the equatorial bonds about the M atom are in a single plane perpendicular to the line of the hypervalent bond). Previously,[2] we have demonstrated that it is convenient to use $\Delta\Omega = 2\pi - \Omega$ (where Ω is a solid angle determined by the directions of the equatorial bonds) as such a parameter. The deviation of the central atom from the plane through the equatorial substituents (Δ_M) is an alternative parameter, which is often used in the case of five-coordinate compounds (see, for example, Ref. 5).

Previously, it has been found[6] that the dependences of the lengths of the components of the hypervalent bond (d(Si—O) and d(Si—X)) on $\Delta\Omega$ for the trigonal-bipyramidal hypervalent O—SiC_3—X units (X = Hal or OR) are one-valued functions if the series under consideration consists of compounds of the same kind. The uniformity of the series implies primarily the similarity of steric conditions in which the axial O and X atoms occur. In particular, the dependences $d(\Delta\Omega)$ are substantially different for the O atoms involved in the chelate $SiCH_2NC(O)$ ring and for the O atoms belonging to "free" OR groups (R = O_2SCF_3, Ph, *etc.*).

The situation becomes more complicated on going from the trigonal-bipyramidal hypervalent unit to the octahedral unit with two hypervalent O(1)—M—X(1) and O(2)—M—X(2) bonds. Actually, a change in the state of the second hypervalent bond should be accompanied by a change in the type of the coordination polyhedron about the M atom and thereby should affect the parameters of the first hypervalent bond. To a first approximation, this effect is insignificant, as follows from a comparison of the experimental data on the five- and six-coordinate germanium compounds.[20] However, the mutual effect of the hypervalent bonds can also occur through alternative mechanisms. In the case of trigonal-bipyramidal coordination, a pronounced effect of the total electronegativity of the equatorial substituents on the hypervalent bond is observed (see, for example, Ref. 21). Apparently, this effect should also take place in the case of octahedral coordination. In this case, the average electronegativity of the O(2) and X(2) atoms of the second hypervalent bond fulfills the role of the electronegativity of the third equatorial substituent. Clearly, the latter value depends on the degree of involvement of both atoms in this bond, *i.e.*, on the ratio between the covalences of the M—O(2) and M—X(2) components. Finally, yet another substantial difference between the six-coordinate and five-coordinate states is determined by the well-known purely steric effects and is not associated with hypervalent interactions. Thus, the mutual repulsion of even not-too-bulky ligands leads to a more unique distribution of these ligands over the coordination sphere about the M atom and to somewhat of an increase in the M—X distance.[22]

Let us compare the structures of the hypervalent units in molecules **2a—c** and **3a,b** and in their direct analogs **1a—c** [4] and $[L^{(n)}]_2GeX_2$ (X = F, Cl, or Br; n = 5—7)[13,20] by including the published data on compounds **4—6**,[12] whose hypervalent units are similar to a large extent to those described above.



4: X = Cl, R′ = H, R″ = OMe
5: X = Cl, R′ = H, R″ = NH_2
6: X = Br, R′ = COOEt, R″ = OEt

Since the states of the pairs of the hypervalent O—M—Hal bonds in all the molecules under consideration are virtually identical (see, for example, Tables 5 and 6), it is convenient to estimate the distortion of the coordination environment about the M atom from the ideal octahedron using the parameter $\Delta\Omega$

Table 5. Principal bond lengths (d) in the hypervalent fragments of molecules **2a—c** (X = Br) and **3a,b** (X = I)

Molecule	d/Å				
	2a	**2b**	**2c**	**3a**	**3b**
Sn—X(1)	2.606(3)	2.579(1)	2.613(1)	2.798(2)	2.753(2)
Sn—X(2)	2.595(3)	2.613(1)	2.591(1)	2.744(2)	2.815(1)
Sn—O(1)	2.26(1)	2.272(7)	2.266(4)	2.24(1)	2.28(1)
Sn—O(2)	2.31(1)	2.250(6)	2.255(4)	2.27(1)	2.26(1)
Sn—C(1)	2.17(2)	2.17(1)	2.143(6)	2.15(2)	2.13(1)
Sn—C(m)*	2.16(2)	2.15(1)	2.130(6)	2.17(2)	2.16(1)

* m = 6 (**a**), 7 (**b**), or 8 (**c**).

Table 6. Principal bond angles (ω) in the hypervalent fragments of molecules **2a—c** (X = Br) and **3a,b** (X = I)

Molecule	ω/deg				
	2a	**2b**	**2c**	**3a**	**3b**
X(1)—Sn—X(2)	96.46(9)	96.22(4)	97.67(4)	96.1(1)	96.42(4)
X(1)—Sn—O(1)	172.0(3)	170.4(2)	172.8(1)	173.2(3)	170.5(3)
X(1)—Sn—O(2)	90.4(3)	88.7(2)	87.7(1)	90.4(3)	89.1(3)
X(1)—Sn—C(1)	99.2(4)	96.6(3)	99.5(1)	99.1(5)	96.3(3)
X(1)—Sn—C(m)*	97.6(5)	101.7(3)	94.3(2)	98.7(4)	103.0(4)
X(2)—Sn—O(1)	91.3(4)	89.5(2)	95.4(2)	90.3(3)	90.1(3)
X(2)—Sn—O(2)	170.9(3)	169.2(2)	170.9(1)	172.0(3)	169.5(2)
X(2)—Sn—C(1)	95.9(6)	97.4(3)	95.4(2)	95.1(6)	97.1(4)
X(2)—Sn—C(m)*	96.7(4)	94.0(3)	95.9(2)	96.5(4)	94.3(3)
O(1)—Sn—O(2)	82.2(5)	86.9(3)	87.8(2)	83.4(4)	85.6(4)
O(1)—Sn—C(1)	77.7(5)	74.9(3)	74.9(2)	78.0(6)	76.0(4)
O(1)—Sn—C(m)*	83.6(5)	85.5(3)	90.2(2)	82.6(5)	83.4(5)
O(2)—Sn—C(1)	88.9(7)	90.9(3)	91.0(2)	88.4(6)	91.2(4)
O(2)—Sn—C(m)*	76.3(5)	76.2(3)	76.2(2)	77.9(5)	75.7(4)
C(1)—Sn—C(m)*	157.6(7)	157.2(4)	160.8(2)	157.5(6)	156.4(5)

* m = 6 (**a**), 7 (**b**), or 8 (**c**).

Table 7. Parameters of the hypervalent units in dihalides **1**—**6** and related compounds containing the $SnO_2C_2X_2$ coordination unit (X = Cl or Br) (averaged over two hypervalent O—M—Hal bonds)

Compound	*d*/Å		ΔΩ/deg
	Sn—O	Sn—X	
1a	2.29	2.44	49
1b	2.26	2.45	40
1c	2.26	2.45	39
2a	2.28	2.60	46
2b	2.26	2.60	42
2c	2.26	2.60	38
3a	2.25	2.77	45
3b	2.27	2.78	44
4	2.53	2.41	60
5	2.33	2.46	41
6	2.49	2.51	68
cis-$Me_2SnCl_2 \cdot 2DMSO$	2.29	2.51	22
cis-$Me_2SnCl_2 \cdot 2DMF$	2.39	2.47	31

averaged over these two bonds. The parameters of the hypervalent units in compounds **1**—**6** are given in Table 7.

Of special note is the fact that this parameter depends only weakly on the type of the halogen ligands and on the nature of the central atom. Thus, for all the lactamomethyl derivatives $[L^{(n)}]_2MX_2$ (M = Ge or Sn) studied by us, the ΔΩ value varies within 27—52° (π steradians is taken to be equal to 180° of the solid angle) and depends primarily on the size of the lactam ring, *i.e.*, on the state of the carbonyl O atom. The replacement of the Ge atom by the Sn atom leads to a decrease in the range over which the ΔΩ value varies (from 12—15° to 8—10°) as the size of the lactam rings changes as well as to somewhat of an increase in the distortion from ideal octahedral coordination (on the average, by 8°). In all cases, the above-mentioned distortion can be described as a deviation of the M atom from the plane through the "equatorial" ligands toward the Hal atoms, *i.e.*, the M—X components of the hypervalent bonds are characterized by a larger degree of covalence than the M—O components. The $d_{M-O}(\Delta\Omega)$ correlation is pronounced in the series of germanium compounds, while this correlation is virtually absent in the case of Sn analogs. In the case of germanium derivatives, this dependence is also not manifested for more covalent and rigid M—X components within such a small range of change in ΔΩ. The Ge—O distances decrease by ~0.08 Å in magnitude on going from the five- to seven-membered lactamomethyl ligands.

The hypervalent units in dihalides **4** and **6** are more substantially distorted (see Table 7) than those in molecules **1**—**3**. It is reasonable to attribute the noticeable difference in the distortion of the octahedral coordination in compounds **4** and **6** to the higher donor ability of the O atom of the aminocarbonyl group compared to that of the alkoxycarbonyl group.

At the same time, the data available in the Cambridge Structural Database* on compounds which contain the hypervalent $SnHal_2O_2C_2$ unit with *cis* arrangement of the Hal atoms with respect to the O atoms that are not involved in the chelate ring (about 20 structures) extend the ranges of the changes in the ΔΩ (19—70°) and *d*(Sn—O) (2.27—2.78 Å) values. However, in this case, too, we failed to reveal an unambiguous dependence $d_{Sn-O}(\Delta\Omega)$, apparently due to the fact that these structures belong to different types. The Cambridge Structural Database contains also data on structures with the hypervalent $SnCl_2N_2C_2$ units, in which the O atom is replaced by the N atom. The Sn—N bond lengths (*d*(Sn—N)) in these structures vary in the range of 2.32—2.96 Å.

Note that in the complex with monodentate ligands, *viz.*, *cis*-$Me_2SnCl_2 \cdot 2DMF$,[15] in which the environment about the Sn atom is similar to that in dichlorides **1a**—**c** studied by us, the average lengths of the hypervalent O—Sn and Sn—Cl bonds and the ΔΩ value (see Table 7) are 2.39 Å, 2.47 Å, and 31°, respectively, *i.e.*, the O—Sn bond is ~0.1 Å longer than the corresponding bonds in dichlorides **1a**—**c**, which indicates that complexation plays an important role in this case.

The above-mentioned characteristic features of the behavior of the hypervalent O—M—Hal bonds are also observed in the structures of lactamomethyl derivatives of five-coordinate Si, Ge, and Sn though some substantial differences exist. The size of the lactam ring in the $L^{(n)}MMe_2Cl$ molecules (M = Si or Ge)[5,7,23] has approximately the same effect on the ΔΩ value, which decreases by 16—18° in going from $L^{(5)}$ to $L^{(7)}$. However, the absolute value of the deviation from ideal trigonal-bipyramidal coordination in five-coordinate germanium chlorides $L^{(n)}GeMe_2Cl$ (ΔΩ = 46—63°) is substantially larger than that in the analogous six-coordinate germanium compounds $[L^{(n)}]_2GeCl_2$ (ΔΩ = 30—43°, *n* = 5—7). The ΔΩ value also decreases from 55 to 40° in going from the five-coordinate to the six-coordinate state in the case of monochloride $L^{(6)}SnMe_2Cl$** and dichloride $[L^{(6)}]_2SnCl_2$ (**1b**).

Unlike compounds with six-coordinate M atoms, the replacement of the Hal atom, which is involved in the hypervalent bond, in the case of the five-coordinate silicon and germanium compounds affects substantially the geometry of the trigonal-bipyramidal environment. In the lactamomethyl compounds $L^{(n)}SiMe_2Hal$ and amidomethyl silicon derivatives **7** and **8**,[25] which are similar in parameters to the former compounds, the F→Cl, Cl→Br, and Br→I replacements lead to a decrease in the ΔΩ value by 50—60°, ~90° (with inversion of the configuration of the trigonal bipyramid), and 40°, respectively.[26] In the germanium derivatives, the decrease in the ΔΩ value in going from Cl to Br (in the

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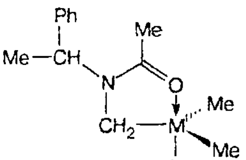
* Cambridge Crystallographic Database, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

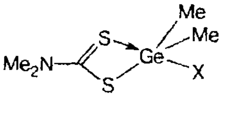
** The complete data for the structure of $L^{(6)}SnMe_2Cl$, studied by us recently, will be published elsewhere. For the preliminary results, see Ref. 24.

case of chloride **9** and bromide **10**) is ~20°.* In going from Br to I, the decrease in the ΔΩ value is ~25° [28] (a comparison was made for the hypervalent S—Ge—Hal bonds in compounds **11** with the use of the ΔΩ values corresponding to the series of structures under consideration).



7—10

M = Si; X = F (**7**), Cl (**8**);
M = Ge; X = Cl (**9**), Br (**10**)

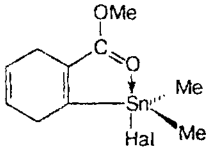


11

X = Br, I (**11**)

There is a series of five-coordinate tin structures **12** of the same type with C,O-coordinating ligands, in which Cl→Br→I replacements have virtually no effect on the geometry of the trigonal bipyramid (ΔΩ = 90, 93, and 90°, respectively).[19] Therefore, even taking into account the specific features of the chelate ring in halides **12**, the effect of the nature of the axial halogen atom on the geometry of the hypervalent unit is sharply weakened in the case of five-coordinate tin.

The replacement of the five-coordinate atom in the Si→Ge→Sn series substantially affects the distortion of its trigonal-bipyramidal environment. Thus, the ΔΩ values are 19, 45, and 55° in chlorides $L^{(6)}MMe_2Cl$. In chlorides **8** and **9**, which are similar in parameters to the above-mentioned chlorides, the ΔΩ values are 10 and 39°, respectivly. In the cases of bromides and iodides, this replacement can lead to a change in the configuration of the central atom in the coordination polyhedron. For example, the replacement of the chlorine atom in $L^{(6)}SiMe_2Cl$ (ΔΩ = 19°) by a bromine atom leads to the inversion of the configuration of the central atom (ΔΩ = −69°). At the same time, the sign of ΔΩ remains unchanged in going from germylchloride **9** to germylbromide **10** (ΔΩ are 39 and 19°, respectively).



12

Based on the aforesaid, the following conclusions can be made. In the case of the six-coordinate state and two identical hypervalent O—M—Hal bonds, the angular characteristics of the coordination polyhedra about the Ge and Sn atoms are more stable (rigid) with respect to the replacement of the halogen atoms (Cl, Br, or I) or the central atoms of the hypervalent unit than the corresponding characteristics in the analogous compounds with five-coordinate Ge and Sn atoms, which form one hypervalent bond. A change in the donor properties of the O atoms (the lactamomethyl ligands containing lactam rings of different sizes) exerts an analogous effect on the coordination of five- and six-coordinate Ge and Sn atoms, namely, the lengths of the O—M components of the hypervalent bonds decrease, while the M—Hal bond lengths increase as the donor ability of the O atoms increases, *i.e.*, in going from derivatives of five-membered lactams to derivatives of six- and seven-membered lactams. In this case, the coordination about the tin atom becomes more rigid.

Noticeable changes in the spatial structure of the hypervalent unit as the central atom changes (Si→Ge→Sn in the case of five-coordinate compounds and Ge→Sn in the case of six-coordinate compounds) indicate that the degree of covalence and the degree of ionicity of the O—M and M—Hal components of the hypervalent O—M—Hal bond strongly depend on the nature of the M atom. Whether or not a particular atom in the series F, Cl, Br, and I can invert the configuration of the trigonal bipyramid is also determined by the nature of the central atom. This fact or, more precisely, the characteristic features of hypervalent bonding can be responsible for the substantial difference in the reactivity of the analogous organosilicon, organogermanium, and organotin compounds.

In particular, the above-mentioned difference in the chemical behavior of germanium and tin dichlorides $[L^{(n)}]_2MCl_2$ (M = Ge or Sn) with respect to iodine-containing nucleophiles, in our opinion, is associated with the characteristic features of the hypervalent bonding in the central coordination units of these compounds and, primarily, with an increase in the size and polarizability of the central atom in going from germanium to tin, which is favorable for a comfortable arrangement of the bulky ligands about the metal atom and thereby for the retention of the hypervalent O—Sn—Hal fragments.

Experimental

The IR spectra of ~5% solutions of the compound in $CHCl_3$ were recorded on a Specord IR-75 instrument in KBr cells.

The ^1H, ^{13}C, and ^{119}Sn NMR spectra were obtained on a Varian XL-400 spectrometer (at 400.1, 100.6, and 149.2 MHz, respectively) in the pulsed mode followed by the Fourier transform. The ^1H and ^{13}C chemical shifts were measured relative to the internal standard (Me_4Si). The ^{119}Sn chemical shifts were measured relative to the external standard (Me_4Sn).

The conductivities of solutions of the compounds (the concentrations were 10^{-1}—10^{-5} mol L^{-1}) in CH_2Cl_2 were measured on a Radelkis OK-102/1 conductivity meter (Hungary) equipped with OK-9023 electrodes with three platinum rings at ~20 °C; the frequency of the alternating current was 80 Hz—3 kHz. The relative error of the determination of the specific conductivity was ~1%.

The initial tin dichlorides **1a—c**[4] and *N*-(halomethyl)-lactams[29] were synthesized according to procedures reported previously.

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* The complete data of X-ray structural analysis of these compounds will be published elsewhere. For the preliminary results, see Ref. 27.

Table 8. Principal parameters of X-ray diffraction studies and crystal-structural data for compounds **2a—c** and **3a**,**b**

Parameter	**2a**	**2b**	**2c**	**3a**	**3b**
Molecular formula	$C_{10}H_{16}Br_2N_2O_2Sn$	$C_{12}H_{20}Br_2N_2O_2Sn$	$C_{14}H_{24}Br_2N_2O_2Sn$	$C_{10}H_{16}I_2N_2O_2Sn$	$C_{12}H_{20}I_2N_2O_2Sn$
a/Å	15.76(1)	9.861(1)	6.414(3)	16.147(2)	10.159(2)
b/Å	7.943(6)	9.861(1)	19.161(8)	7.948(3)	10.159(2)
c/Å	11.892(9)	28.383(6)	15.027(6)	11.953(4)	28.348(7)
α/deg	90	90	90	90	90
β/deg	101.49(6)	90	99.88(3)	101.04(2)	90
γ/deg	90	120	90	90	120
$V/Å^3$	1459(2)	2390.3(7)	1819(1)	1506(1)	2533.8(9)
d_{calc}/g cm^{-3}	2.162	2.096	1.938	2.509	2.347
Space group (*Z*)	$P2_1/c$ (4)	$P6_1$ (6)	$P2_1/n$ (4)	$P2_1/c$ (4)	$P6_5$ (6)
Number of measured reflections	3637	1968	4373	3873	2517
Number of reflections in the least-squares refinement	3392	1935	4367	2727(I>8δ(I))	2489
Number of refinable parameters	154	171	286	154	181
Absorption coefficient (cm^{-1})	72.2	66.2	58.0	57.6	51.7
$R_1(I > 2\delta(I))$	0.098	0.039	0.046	0.089(I>8δ(I))	0.048
wR_2 (based on all reflections, R_w for **3a**)	0.392	0.233	0.114	0.116(I>8δ(I))	0.081

(O—Sn)-Bischelate bis[1-(2-oxopyrrolidinyl)methyl]dibromostannane (2a). *A* (reaction 1). *N*-(Bromomethyl)-2-pyrrolidone (3.56 g, 20 mmol) was added dropwise with intense stirring to a suspension of powdered tin (1.18 g, 10 mmol) activated with H_2O (0.1 mL) in boiling toluene (20 mL). The reaction mixture was heated to boiling for 2 h. Then the solvent was removed *in vacuo*. Dibromide **2a** was obtained in a yield of 2.8 g (59%).

B (reaction 2). A solution of dichloride **1a** (1.93 g, 5 mmol) and $LiBr \cdot 2H_2O$ (12.28 g, 0.1 mol) in MeCN (30 mL) was heated to boiling for 3 h. The crystals that precipitated after cooling were filtered off and dibromide **2a** was obtained in a yield of 1.85 g (78%).

(O—Sn)-Bischelate bis[1-(2-oxopiperidinyl)methyl]dibromostannane (2b) was prepared analogously to dibromide **2a** by method *B* from dichloride **1b** (1.66 g, 4 mmol) and $LiBr \cdot 2H_2O$ (9.82 g, 80 mmol) in MeCN (20 mL) in a yield of 1.53 g (76%).

(O—Sn)-Bischelate bis[1-(2-oxohexahydroazepinyl)methyl]dibromostannane (2c) was prepared analogously to dibromide **2a** according to method *B* from dichloride **1c** (3.09 g, 7 mmol) and $LiBr \cdot 2H_2O$ (17.20 g, 0.14 mol) in MeCN (80 mL) in a yield of 3.63 g (98%).

(O—Sn)-Bischelate bis[1-(2-oxopyrrolidinyl)methyl]diiodostannane (3a) was prepared analogously to dibromide **2a** by method *A* from powdered Sn (1.18 g, 10 mmol) and *N*-(iodomethyl)-2-pyrrolidone (4.50 g, 20 mmol) in toluene (25 mL) in a yield of 3.1 g (55%).

Diiodide **3a** was also obtained according to method *B* from dichloride **1a** (3.09 g, 8 mmol) and $LiI \cdot H_2O$ (24.29 g, 0.16 mol) in MeCN (60 mL) in a yield of 3.57 g (93%).

(O—Sn)-Bischelate bis[1-(2-oxopiperidinyl)methyl]diiodostannane (3b) was prepared analogously to dibromide **2a** by method *B* from dichloride **1b** (1.45 g, 3.5 mmol) and $LiI \cdot H_2O$ (10.63 g, 70 mmol) in MeCN (15 mL) in a yield of 1.61 g (77%).

(O—Sn)-Bischelate bis[1-(2-oxohexahydroazepinyl)methyl]diiodostannane (3c) was prepared analogously to dibromide **2a** according to method *B* from dichloride **1c** (1.77 g, 4 mmol) and $LiI \cdot H_2O$ (12.14 g, 80 mol) in MeCN (35 mL) in a yield of 1.95 g (98%).

The constants, yields, and data of elemental analysis and IR spectroscopy are given in Table 1. The ^1H, ^{13}C, and ^{119}Sn NMR spectral data are summarized in Tables 2 and 3.

X-ray diffraction studies of dibromides 2a—c and diiodides 3a,b. The crystal-structural parameters and the principal characteristics of X-ray diffraction analysis for compounds **2a—c** and **3a**,**b** are given in Table 8. The X-ray data were collected on an automated four-circle Syntex $P2_1$ diffractometer (λ(Mo-Kα) radiation, θ/2θ scanning technique, $2\theta_{max}$ = 56°) at 190 K. The structures were solved by the direct method and refined by the full-matrix least-squares method based on F^2 (the structure of **3a** was refined based on F) with anisotropic thermal parameters for nonhydrogen bonds (in the structure of **2b**, the C(9a) and C(9b) atoms were refined isotropically). The H atoms in structures **2a**,**b** and **3a**,**b** were placed in calculated positions and refined using the riding model with fixed values of thermal parameters (U = 0.08 Å for **2a** and **3a**; $1.2U_C$ for **2b** and **3b**; U_C is the equivalent thermal parameter of the corresponding carbon atom). In the structure of **2c**, the positions of the H atoms were located from the difference electron density synthesis and refined isotropically. In the structures of **2b** and **3b**, the C(9) atoms are disordered over two sites, which were refined with occupancies of 1/3 and 2/3 in structure **2b** and with occupancies of 0.5 and 0.5 in structure **3b**. The absolute structures of **2b** and **3b** were determined using Flack's parameter[30] (0.01(2) for **2b** and 0.05(8) for **3b**). Absorption corrections were applied using the DIFABS program.[31] All calculations were carried out on an IBM PC using the SHELXTL PLUS program package[32,33] (versions 4.0 and 5.0). The atomic coordinates in the structures of **2a**,**b**,**c** and **3a**,**b** are given in Table 9. The principal

Table 9. Atomic coordinates ($\times 10^4$) in the structures of **2a—c**, **3a**, and **3b**

Atom	*x*	*y*	*z*
		Structure **2a**	
Sn(1)	7522(1)	1017(1)	6338(1)
Br(1)	6740(1)	3913(2)	5969(2)
Br(2)	9004(1)	2198(3)	7389(2)
O(1)	8047(9)	−1629(14)	6469(10)
O(2)	6235(8)	−354(17)	5623(9)
N(1)	8395(10)	−824(18)	4783(12)
N(2)	6364(10)	−831(19)	7519(11)
C(1)	7896(14)	681(24)	4694(15)
C(2)	8865(14)	−1351(24)	3915(15)
C(3)	9350(17)	−3038(29)	4452(21)
C(4)	8918(12)	−3423(24)	5463(16)
C(5)	8395(12)	−1902(20)	5625(12)
C(6)	7047(12)	323(19)	7856(12)
C(7)	5950(14)	−1819(26)	8314(18)
C(8)	5282(16)	−2856(28)	7563(19)
C(9)	5289(11)	−2310(24)	6366(17)
C(10)	6017(10)	−1120(19)	6408(13)
		Structure **2b**	
Sn(1)	5591.4(7)	986.3(7)	0
Br(1)	7253(1)	−78(1)	376.7(5)
Br(2)	7842(1)	3900(1)	−52.9(5)
O(1)	4024(8)	1608(9)	−424(3)
O(2)	3445(8)	−1357(7)	130(3)
N(1)	5029(9)	939(9)	−1038(3)
N(2)	3011(9)	7(9)	693(3)
C(1)	5741(12)	327(13)	−718(4)
C(2)	5294(13)	834(14)	−1539(4)
C(3)	4824(17)	1862(16)	−1822(5)
C(4)	3315(14)	1586(13)	−1676(5)
C(5)	3384(15)	2125(14)	−1176(4)
C(6)	4197(11)	1545(10)	−840(4)
C(7)	4534(11)	1378(11)	609(4)
C(8)	1982(12)	206(14)	1034(4)
C(9A)	326(17)	−855(17)	952(14)
C(9B)	668(17)	−1261(13)	1196(6)
C(10)	−76(16)	−2445(16)	833(6)
C(11)	1079(11)	−2712(12)	568(5)
C(12)	2607(10)	−1282(10)	456(4)
		Structure **2c**	
Sn(1)	1542(1)	1530(1)	3466(1)
Br(1)	3059(1)	923(1)	2157(1)
Br(2)	−242(1)	2581(1)	2549(1)
O(1)	630(7)	2031(2)	4710(3)
O(2)	2583(6)	585(2)	4321(2)
N(1)	3618(7)	2621(3)	4687(3)
N(2)	−603(7)	189(3)	3641(3)
C(1)	4298(9)	2094(3)	4083(4)
C(2)	5021(12)	3225(4)	4929(5)
C(3)	4126(13)	3898(5)	4536(6)
C(4)	2476(14)	4236(4)	5014(6)
C(5)	548(11)	3791(4)	5038(4)
C(6)	1038(11)	3096(4)	5536(4)
C(7)	1795(9)	2546(3)	4958(3)
C(8)	−1221(9)	895(3)	3312(4)
C(9)	−2073(10)	−382(4)	3343(4)
C(10)	−1360(13)	−845(4)	2628(4)
C(11)	318(12)	−1372(3)	3011(4)
C(12)	2332(12)	−1074(4)	3521(5)
C(13)	2074(10)	−641(3)	4351(4)
C(14)	1334(9)	78(3)	4115(3)
		Structure **3a**	
Sn(1)	2504.7(7)	890(1)	6346.0(8)
I(1)	1724(1)	4044(1)	6057(1)
I(2)	4056(1)	2046(2)	7417(1)
O(1)	3005(9)	−1742(16)	6414(10)
O(2)	1260(8)	−382(12)	5624(9)
N(1)	3395(8)	−860(14)	4786(10)
N(2)	1318(8)	−922(15)	7509(11)
C(1)	2845(14)	635(23)	4696(15)
C(2)	3884(14)	−1437(25)	3928(14)
C(3)	4336(18)	−2947(24)	4464(22)
C(4)	3881(17)	−3487(31)	5434(20)
C(5)	3380(11)	−2012(21)	5608(12)
C(6)	2076(9)	108(19)	7875(11)
C(7)	909(10)	−1749(21)	8273(13)
C(8)	282(14)	−2910(21)	7523(14)
C(9)	211(9)	−2213(20)	6246(14)
(10)	980(9)	−1148(17)	6415(11)
		Structure **3b**	
Sn(1)	5363(1)	826(1)	0
I(1)	7120(1)	−268(1)	−382(1)
I(2)	7691(1)	3884(1)	58(1)
O(1)	3768(11)	1399(13)	400(4)
O(2)	3279(11)	−1462(11)	−131(3)
N(1)	4845(14)	927(13)	1023(4)
N(2)	2870(13)	−122(13)	−679(4)
C(1)	5495(15)	223(16)	711(5)
C(2)	5137(19)	904(18)	1536(5)
C(3)	4700(21)	1891(19)	1803(5)
C(4)	3226(23)	1705(25)	1662(7)
C(5)	3310(20)	2127(19)	1160(6)
C(6)	4002(15)	1447(15)	832(5)
C(7)	4315(14)	1181(14)	−613(4)
C(8)	1849(14)	85(16)	−1014(5)
C(9A)	315(25)	−973(20)	−895(14)
C(9B)	451(34)	−1240(27)	−1130(17)
C(10)	−117(21)	−2524(22)	−826(7)
C(11)	969(15)	−2803(17)	−562(5)
C(12)	2457(15)	−1375(15)	−429(5)

bond lengths and bond angles are listed in Tables 5 and 6, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-32718, 96-07-89187, 96-15-97367, and 97-03-33783).

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Received November 11, 1998;
in revised form February 19, 1999