Synthesis, crystal structure and stereochemical non-rigidity of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes

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Previously unknown (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes have been synthesized by a direct method from metallic tin and *N*-chloromethyllactams. According to X-ray structural analysis data, in the solid state in these compounds the tin atom is hexacoordinated and has an octahedral configuration with the two carbon atoms in the *trans*-position, and both coordinating oxygen atoms and the two halogen atoms in the *cis*-position. A comparison to Ge-analogs indicates that the replacement of the central atom of the coordination unit $MCl_2O_2C_2$ has inconsistent effects on the parameters of the latter. According to ^1H and ^{119}Sn NMR data, the hexacoordination of tin and the geometry of the coordination unit are also retained in solution at low temperatures. At higher temperatures a dynamic process takes place resulting in isochronisms of the protons signals of the NCH_2Sn groups. Quantum-chemical calculations of isomeric bis(lactamomethyl)dichlorostannanes by MNDO and MNDO/PM3 methods have been discussed.

Key words: hexacoordinated tin compounds, synthesis; X-ray study; stereochemical non-rigidity; dynamic and multinuclear NMR spectroscopy; quantum-chemical calculations, MNDO, MNDO/PM3.

The interest in penta- and hexacoordinated organotin derivatives, in particular, in compounds with intramolecular coordination, is caused by their structural peculiarities, high reactivity, and also by the possibility of using them to study dynamic processes and model the pathway of nucleophilic substitution reactions at the tin atom. However, some types of hypervalent tin compounds have not yet been well investigated. So, at present, only a few examples of hexacoordinated tin derivatives with intramolecular O→Sn interaction have been described (see the review, Ref. 1, and references cited therein).

Recently we carried out the synthesis and X-ray study of bis(lactamomethyl) derivatives of hexacoordinated germanium,[2,3] which emphasized a comparison of the properties inside this uniform series of compounds. In particular, on the basis of the precise geometry of the coordination polyhedron a quantitative evaluation of the state of the hypervalent Ge atom was given.[4] For the purpose of comparing germanium compounds with their Sn-analogs (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes have been synthesized and three of them have been investigated by X-ray methods in this work. Quantum-chemical calculations of these compounds by the MNDO method and also by one of its recent modifications, MNDO/PM3, have been performed to reveal the probable reasons for the changes in the geometric characteristics that occur in going from the five-membered lactam derivatives to the seven-membered lactam derivatives and to evaluate of the relative thermodynamic stability of possible isomers of the compounds prepared. We also studied their stereochemical non-rigidity by dynamic NMR spectroscopy.

Results and Discussion

Synthesis and structure. We found that the interaction of *N*-(chloromethyl)lactams (**1a—d**) with metallic tin results in previously unknown (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes (**2a—d**).* The re-

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† Deceased.

* For the previous communication on the synthesis of dichlorides **2a**,**d**, see Ref. 5.

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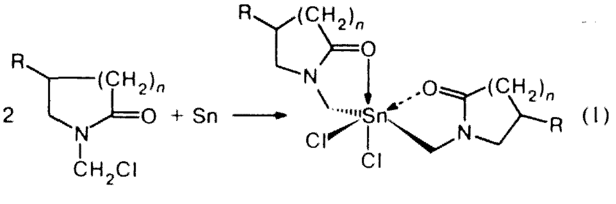
actions proceed under fairly mild conditions in nonpolar solvents (refluxing of reagents in toluene or *o*-xylene for 1—2 h) to give rather high yields of the final products (63—84 %).

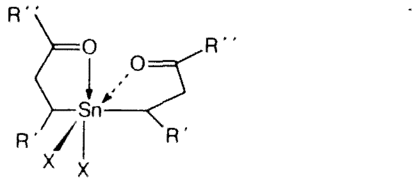


1a—d **2a—d**

a: n = 1, R = H; **b**: n = 1, R = Ph;
c: n = 2, R = H; **d**: n = 3, R = H

The formation of appreciable amounts of the monoorganotin and triorganotin derivatives, which are normal by-products in the direct synthesis of organotin compounds from alkyl halides and metal Sn,[6] was not observed in this reaction. This is likely connected with the relatively higher stability of the corresponding diorganotin derivatives with the hexacoordinated tin atom due to the two intramolecular O→Sn coordinate bonds (see below). The direct synthesis of the bis(lactamomethyl) derivatives of the group 14 elements, presented in this work using tin as an example, has doubtless preparative advantages over the previously described general method for synthesizing silicon[7] and germanium[2] compounds of a similar structure by the reaction of silylated lactams with $(ClCH_2)_2MCl_2$ (M = Si, Ge), as it allows one to avoid using the bis(halomethyl) derivatives, which are not easily accessible.

At present, a number of direct methods for the synthesis of hexacoordinate tin compounds having two C,O-chelating ligands have been described. However, as far as we know, *N*-(halomethyl)lactams have not been used in these reactions. In particular, the first hypervalent tin species containing a C,Y-chelating ligand (where Y is a coordinating atom, for example, O, N, *etc.*), *i.e.*, bis[1,2-bis(ethoxycarbonyl)ethyl]tin dibromide (**3**), for which the structure was established by X-ray analysis,[8] has been prepared by the reaction of metallic Sn with diethyl bromosuccinate.[9]



3: X = Br, R′ = COOEt, R′′ = OEt
4e: X = Cl, R′ = H, R′′ = OMe
4f: X = Cl, R′ = H, R′′ = NH_2

This compound and also the dichlorides **4e,f** have been synthesized by the interaction of metallic tin with the corresponding α,β-unsaturated carbonyl compounds in ether in the presence of HCl. The reaction is likely to proceed *via* a solvated chlorostannane intermediate of the type $H^+SnCl_3^- \cdot 2Et_2O$ (see the review, Ref. 1, and references cited therein).

Except for racemic 4-phenyl-2-pyrrolidone derivative **2b**, which is a viscous oil, the dichlorides **2** prepared in this work (Table 1) are crystal substances with high melting points. Their structures were established by elemental analysis and IR and NMR spectroscopy. The structures of compounds **2a,c,d** were confirmed by an X-ray investigation.

The IR spectroscopy data testify that the tin atom in the compounds prepared is hexacoordinated. Two strongly coupled ν(C=O) and ν(C=N) stretching vibrations of amide fragments are observed in the 1500—1700 cm^{-1} region (see Table 1).* The position and the inten-

Table 1. Conditions of syntheses, yields, and characteristics of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a—d**

Compound	Reaction conditions			Yield (%)	M.p.[a] /°C	IR spectrum, ν/cm^{-1}	Molecular formula	Found / Calculated (%)		
	Solvent	T/°C	τ/h					C	H	N
2a	Toluene	110	2	66	235—237	1510, 1615	$C_{10}H_{16}Cl_2N_2O_2Sn$	30.68 31.13	4.58 4.18	
2b	*o*-Xylene	144	1	72	Масло	1500[b] 1615	$C_{22}H_{24}Cl_2N_2O_2Sn$	49.20 49.11	4.42 4.50	
2c	Toluene	110	1	63	237—238	1505, 1585	$C_{12}H_{20}Cl_2N_2O_2Sn$	35.02 34.82	4.81 4.87	6.77 6.54
2d	*o*-Xylene	144	2	84	259—261	1500, 1580	$C_{14}H_{24}Cl_2N_2O_2Sn$	38.11 38.05	5.47 5.47	

[a] From acetonitrile. [b] An additional absorption band at 1510 cm^{-1} is present.

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* In the case of dichloride **2b**, two low-frequency absorption bands are observed at 1500 and 1510 cm^{-1} that may be due to the presence of several diastereomers in the sample of the compound.

Table 2. ^{1}H NMR chemical shifts and coupling constants ($^2J_{HH}$) of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a—d**

Compound	Solvent	δ ($^2J_{HH}$/Hz)					
		H(3)	H(4)	H(5)	H(6)	H(7)	NCH$_2$
2a	CDCl$_3$	2.58 t (7.3)	2.09 q (7.3)	3.65 t (7.3)			2.70[a] s
	(CD$_3$)$_2$CO	2.52 t (7.1)	2.10 q (7.1)	3.70 t (7.1)			2.68 br.s
2b[b]	CDCl$_3$	2.70 m	4.05 m	3.61 m			2.90 br.s
2c	CDCl$_3$	2.42 t (6.0)	1.82	1.84	3.45 (6.0)		2.74 br.s
	CD$_3$CN	2.41 t (6.1)	1.81	1.83	3.49 (6.1)		2.75 br.s
2d	CDCl$_3$[c]	2.61 t (6.0)	1.65	1.70	1.71	3.63 t (6.0)	2.97 br.s
	(CD$_3$)$_2$CO	2.68 t (6.3)	1.63	1.73	2.14	3.72 t (6.3)	2.83 br.s
	CD$_3$CN	2.59 t (6.3)	1.58	1.66	1.74	3.62 t (6.3)	2.81 br.s

[a] $^2J_{SnH}$ 86.4 Hz. [b] Signals of protons of the aromatic fragment are recorded as a multiplet at 7.2—7.4 ppm. [c] At −60°C the H(3)—H(7) signals are broadened, and signals of the NCH$_2$ grouping are recorded as an AB-pattern with $^1J_{HH}$ 12 Hz.

Table 3. ^{13}C NMR chemical shifts and coupling constants ($^nJ_{SnC}$) of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a—d**

Compound	Solvent	δ ($^nJ_{SnC}$/Hz)						
		C(3)	C(4)	C(5)	C(6)	C(7)	NCH$_2$	C=O
2a	CDCl$_3$	29.35	15.88	51.71 (84.2)			42.50 (1065)	177.35 (22.2)
	CDCl$_3$[a]	29.50	15.67	51.90 (85.5)			42.07 (1056)	177.59 (21.4)
2b[b]	CDCl$_3$	37.78	35.76	59.04 (82.2)			42.44 (1069)	176.60 (23.1)
2c	CDCl$_3$	29.90	20.37	22.52 (18.9)	51.54 (99.5)		45.76 (1128)	172.98 (29.7)
	CD$_3$CN	29.51	19.98	22.13 (18.4)	51.17 (98.7)		45.51 (1123)	173.21 (28.9)
2d	CDCl$_3$	29.42	22.23	26.04	34.38 (11.6)	53.73 (99.3)	48.16 (1084)	178.72 (25.5)

[a] The spectrum was recorded at −37 °C. [b] Chemical shifts of the aromatic fragment signals, ppm: 141.57 (C_{ipso}); 129.10 (C_{ortho}); 126.66 (C_{meta}); 127.47 (C_{para}).

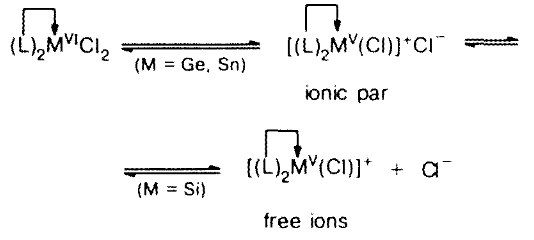
sity of these absorption bands in dichlorides **2a,c,d** are essentially the same as those observed for their Ge-analogs (Ge-**2a,c,d**).[2] The ν(C=O) absorption bands due to a non-chelated lactamo-*N*-methyl ligand are not present, which indicates that the O→Sn coordination is fairly strong.

The ^{1}H and ^{13}C NMR spectroscopy data for compounds **2a—d** confirming their structures are shown in Tables 2 and 3. For reliable assignment of the signals in the ^{1}H NMR spectra to various spin patterns, a method of homonuclear correlation of chemical shifts ^{1}H—^{1}H (COSY) was used. In some cases the signals of the quaternary carbon atoms in the ^{13}C NMR spectra were identified by the use of a special one-dimensional ^{13}C—^{13}C APT technique. Finally, using heteronuclear correlation spectroscopy data (a ^{1}H—^{13}C HETCOR $^1J_{CH}$ method),[10] the signals in the ^{1}H and ^{13}C NMR spectra were related to each other.

The significant upfield shifts of the signals of dichlorides **2a—d** in the ^{119}Sn NMR spectra in CDCl$_3$ (−194.6, −195.9, −270.2 and −256.2 ppm respectively) are indicative of hexacoordination of the tin atom,[11] *i.e.*, of the presence of two bidentate chelate ligands and two monodentate ligands. It should be noted that the ^{119}Sn signal for dichlorides **2a,b** is shifted upfield somewhat less than that for dichlorides **2c,d**, which suggests that the intramolecular interaction O→Sn is weaker in the case of the five-membered lactams derivatives than in their six-membered and seven-membered analogs. This result is in agreement with the similar influence of the size of the lactam cycle on the extent of coordination O→Si bonding in *N*-(dimethylchlorosilylmethyl) lactams established on the basis of ^{29}Si NMR data.[12]

Coupling interactions of tin with the carbonyl carbon atom and some carbon atoms of the lactam cycles are observed in the ^{13}C NMR spectra of the compounds under investigation (see Table 3). These interactions also occur at low temperatures. The magnitude of the $|J(^{13}C-^{119}Sn)|$ spin-spin coupling constant on the carbonyl atom increases as the extent of the coordination O→Sn interaction increases in the series **2a**, **2b** < **2d**, **2c**. For compound **2d**, which is characterized by the strongest O→Sn bond coordination, there is coupling interaction between the tin atom and the lactam cycle C(3) atom. These data probably indicate that for (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a—d** the coupling ^{13}C—^{119}Sn interaction occurs *via* a coordination bond. Previously, a similar result has been obtained for some fluorides of pentacoordinated silicon.[13]

We determined the electroconductivity of dichlorides **2a,d** in CH_2Cl_2. A comparison of the molar conductivity of these compounds and their Si- and Ge-analogs[14] (Table 4) indicates of a strengthening of the covalence of the metal—halogen bond in the dichloride-analogs Si < Ge <Sn. Moreover, there is an appreciable increase in the ionic character of the M—Cl bond when the five-membered lactam cycles are replaced by seven-membered cycles.



(2)

L is a lactamomethyl ligand

The quite low magnitudes of electroconductivity for tin dichlorides **2a,d** and their Ge-analogs (Ge-**2a,d**) suggest the existence of ionic pairs in solutions of these compounds in solvents with fairly low dielectric constants, such as CH_2Cl_2. The much higher molar conductivity of the corresponding silicon dichlorides Si-**2a,d** testifies evidently to the formation of free ions in their solutions.

X-ray structural investigation. The study of dichlorides **2a,c,d** showed that in these crystal compounds the tin atom, like the germanium atom in their recently investigated Ge-analogs Ge-**2a,c,d**,[2] has a somewhat distorted octahedral configuration, with the two carbon ligands in the *trans*-positions and both coordinating oxygen atoms and both halogen atoms in the *cis*-positions. Similar geometry is characteristic of the coordination unit of tin dihalides with two C,O-chelating ligands[7,15] and of the majority of their analogs having two C,N-chelating ligands (see review, Ref. 1, and references cited therein). At the same time it has been established that for {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)diiodostannane[16] and bis(thiolactimomethyl)dichlorogermanes[17] the same ligands are in the *trans*-orientation relative to the central atom.

Table 4. Molar conductivity of (O—M)-bischelated bis(lactamomethyl)dichlorosilanes, -germanes, and -stannanes in CH_2Cl_2 at 25°C

Compound	C /mmol L^{-1}	Λ /mSm cm^2 mol^{-1}
Si-**2a**	10.4	2500
	1.9	4330
Si-**2d**	10.0	3660
	0.9	10900
	0.09	22700
Ge-**2a**	6.9	39
	5.0	261
Ge-**2d**	0.5	937
2a	6.9	22
2d	5.1	76
	0.5	194

It should be noted that in the case of 2-[(dimethylamino)methyl]phenyl-2′-(dimethylamino-1′-naphthyl)silicon difluoride, and also of bis[8-(dimethylamino)-1-naphthyl])silicon dihydride and hydride fluoride, the tetrahedral configuration of the central atom is largely retained. Thus, the geometry of a hexacoordinated Si atom is best described as a "bicapped" tetrahedron, formed at the expense of the two fairly weak N→Si coordination bonds.[18]

Compounds **2a** and **2d** are isostructural with their Ge-analogs Ge-**2a** and Ge-**2d**. This is true for the molecular packing (the sizes of the elementary cells of **2a** and **2d** are greater by 0.02—0.44 Å due to the fact that the covalent radius of the Sn atom is larger than that of the Ge atom), as well as for the structures of molecules having a characteristic *cis*-arrangement of the Cl-substituents at the central atom (Fig. 1). Compound **2c**, whose molecular geometry is also close to that in the Ge-**2c** analog, crystallizes in another spatial group because the structure **2c** does not contain solvate molecules, which are detected in crystals of its Ge-analog.[2] Thus, in the comparison of the geometric characteristics of at least molecules **2a** and **2d** with the corresponding Ge-derivatives, the influence of intermolecular interactions can be obviously neglected. This last circumstance is important, when it is taken into account that the two hypervalent fragments O—M—Cl (M = Sn, Ge), with bonds that are much weaker than the usual "tetrahedral" bonds, are present in both molecules. The lengths of the O—M and M—Cl bonds are longer than the standard values[19] by ~0.4 and ~0.2 Å, respectively.

As in the case of pentacoordinated germanium[20] and silicon[21] compounds, an increase in the size of the lactam cycle in molecules **2a,c,d** and Ge-**2a,c,d** somewhat strengthens the "coordination" M—O component of the hypervalent fragment (Table 5—7). Thus, in accordance with the hypervalent bond properties, the second M—Cl component of this bond becomes more "ionic", which is reflected in the fact that the electroconductivity of compounds **2d** and Ge-**2d** is appreciably greater than that of compounds **2a** and Ge-**2a** (see Table 4). However, the corresponding change in the average Sn—O distance for two hypervalent fragments is appreciably less than that of the Ge-analogs (0.03 against 0.09 Å) Hence, it may be suggested that the electronic system of the coordinative $SnCl_2O_2C_2$ unit is somewhat more rigid than that in the case of the structurally similar $GeCl_2O_2C_2$ unit. This conclusion is not consistent with the view that the electronic environment of the Sn atom is more polarizable than that of the Ge atom.

The deviation of the geometry of the coordination polyhedron of the hypervalent M atom from an ideal

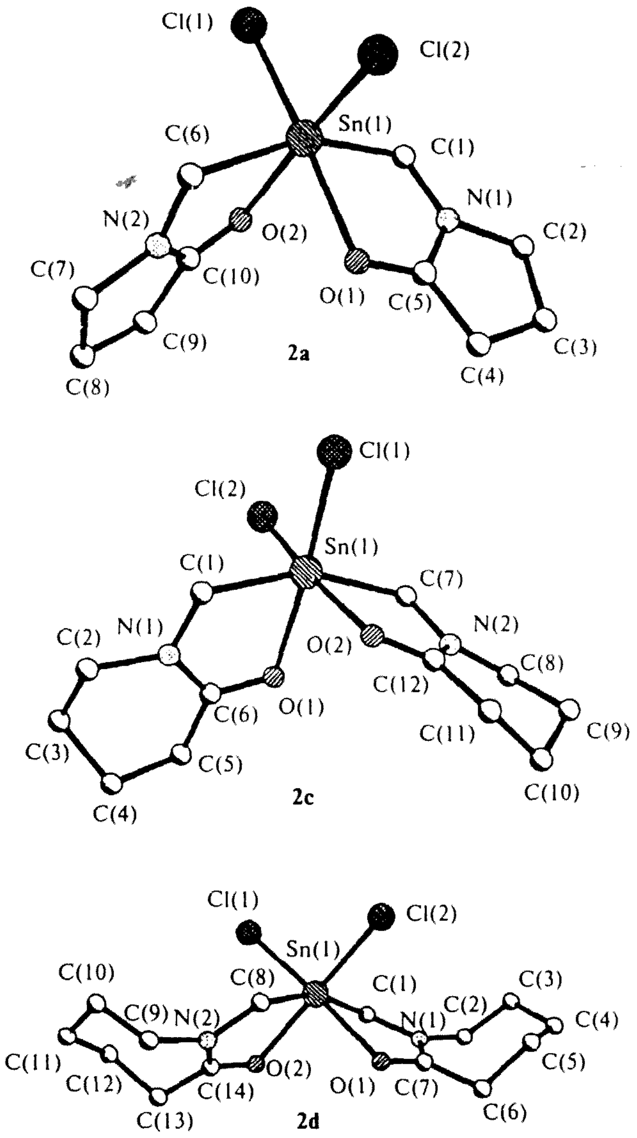


Fig. 1. General view of molecules **2a,c,d** in a crystal. The H atoms are not shown.

Table 5. Bond lengths in molecule **2a**

Bond	*d*/Å	Bond	*d*/Å
Sn(1)—Cl(1)	2.445(4)	N(1)—C(5)	1.33(1)
Sn(1)—Cl(2)	2.432(4)	N(2)—C(6)	1.48(2)
Sn(1)—O(1)	2.271(8)	N(2)—C(7)	1.44(2)
Sn(1)—O(2)	2.311(9)	N(2)—C(10)	1.30(1)
Sn(1)—C(1)	2.14(1)	C(2)—C(3)	1.52(2)
Sn(1)—C(6)	2.15(1)	C(3)—C(4)	1.51(2)
O(1)—C(5)	1.26(2)	C(4)—C(5)	1.47(2)
O(2)—C(10)	1.27(2)	C(7)—C(8)	1.52(2)
N(1)—C(1)	1.41(2)	C(8)—C(9)	1.53(2)
N(1)—C(2)	1.50(2)	C(9)—C(10)	1.49(2)

Table 6. Bond lengths in molecule **2c**

Bond	*d*/Å	Bond	*d*/Å
Sn(1)—Cl(1)	2.442(2)	N(2)—C(7)	1.48(1)
Sn(1)—Cl(2)	2.461(2)	N(2)—C(8)	1.46(1)
Sn(1)—O(1)	2.265(6)	N(2)—C(12)	1.303(9)
Sn(1)—O(2)	2.256(7)	C(2)—C(3)	1.50(1)
Sn(1)—C(1)	2.105(7)	C(3)—C(4)	1.54(2)
Sn(1)—C(7)	2.16(1)	C(4)—C(5)	1.50(1)
O(1)—C(6)	1.27(1)	C(5)—C(6)	1.48(1)
O(2)—C(12)	1.26(1)	C(8)—C(9)	1.49(2)
N(1)—C(1)	1.45(1)	C(9)—C(10)	1.51(2)
N(1)—C(2)	1.50(1)	C(10)—C(11)	1.53(2)
N(1)—C(6)	1.33(1)	C(11)—C(12)	1.51(1)

Table 7. Bond lengths in molecule **2d**

Bond	*d*/Å	Bond	*d*/Å
Sn(1)—Cl(1)	2.461(1)	N(2)—C(9)	1.480(4)
Sn(1)—Cl(2)	2.448(1)	N(2)—C(14)	1.334(3)
Sn(1)—O(1)	2.274(2)	C(2)—C(3)	1.509(5)
Sn(1)—O(2)	2.251(2)	C(3)—C(4)	1.522(6)
Sn(1)—C(1)	2.141(3)	C(4)—C(5)	1.520(5)
Sn(1)—C(8)	2.128(3)	C(5)—C(6)	1.532(5)
O(1)—C(7)	1.265(4)	C(6)—C(7)	1.504(4)
O(2)—C(14)	1.264(3)	C(9)—C(10)	1.523(5)
N(1)—C(1)	1.471(4)	C(10)—C(11)	1.516(5)
N(1)—C(2)	1.477(4)	C(11)—C(12)	1.521(5)
N(1)—C(7)	1.325(4)	C(12)—C(13)	1.540(5)
N(2)—C(8)	1.468(4)	C(13)—C(14)	1.501(4)

Table 8. The main bond angles in molecule **2a**

Angle	ω/deg	Angle	ω/deg
Cl(1)—Sn(1)—Cl(2)	96.4(1)	C(2)—N(1)—C(5)	112.2(9)
Cl(1)—Sn(1)—O(1)	171.3(2)	C(6)—N(2)—C(7)	123.5(9)
Cl(2)—Sn(1)—O(1)	92.0(2)	C(6)—N(2)—C(10)	121(1)
Cl(1)—Sn(1)—O(2)	91.6(2)	C(7)—N(2)—C(10)	115(1)
Cl(2)—Sn(1)—O(2)	170.3(2)	Sn(1)—C(1)—N(1)	107.9(7)
O(1)—Sn(1)—O(2)	80.3(3)	N(1)—C(2)—C(3)	102(1)
Cl(1)—Sn(1)—C(1)	99.2(3)	C(2)—C(3)—C(4)	108(1)
Cl(2)—Sn(1)—C(1)	97.1(3)	C(3)—C(4)—C(5)	104(1)
O(1)—Sn(1)—C(1)	77.3(4)	O(1)—C(5)—N(1)	122(1)
O(2)—Sn(1)—C(1)	86.9(4)	O(1)—C(5)—C(4)	126(1)
Cl(1)—Sn(1)—C(6)	98.6(4)	N(1)—C(5)—C(4)	112(1)
Cl(2)—Sn(1)—C(6)	95.8(3)	Sn(1)—C(6)—N(2)	106.8(7)
O(1)—Sn(1)—C(6)	82.9(4)	N(2)—C(7)—C(8)	104(1)
O(2)—Sn(1)—C(6)	77.6(4)	C(7)—C(8)—C(9)	106(1)
C(1)—Sn(1)—C(6)	156.7(4)	C(8)—C(9)—C(10)	104(1)
Sn(1)—O(1)—C(5)	109.3(7)	O(2)—C(10)—N(2)	125(1)
Sn(1)—O(2)—C(10)	107.0(7)	O(2)—C(10)—C(9)	125(1)
C(1)—N(1)—C(2)	125.4(9)	N(2)—C(10)—C(9)	110(1)
C(1)—N(1)—C(5)	122(1)		

octahedron can be characterized by the value $\Delta\Omega = 2\pi - \Omega$, where Ω is the solid angle determined by the directions of the four bonds that are pseudoequatorial in relation to the hypervalent O—M—Cl fragment under consideration.[4] A comparison with the Ge-analogs shows that the distortion of the ideal octahedral configuration of the Sn atom is somewhat more than that of the Ge atom, other things being the same. The average $\Delta\Omega$ values in the **2a** and Ge-**2a**, **2d** and Ge-**2d** pairs are 42.5

and 29.5, and 48.5 and 38.5 degree of a solid angle. In analogs **2c** and Ge-**2c** these values are very nearly equal (42.5 and 41.5 degree). However, it is necessary to take into account the high experimental errors in the Ge-**2c** structure[2], which are apparently responsible for the proximity of the geometric parameters of the hypervalent fragments to those observed in the Ge-**2a** structure (five-membered lactam cycles). At the same time in compounds of pentacoordinated silicon, for example, the parameters under consideration, on the contrary, do not actually vary when the six-membered lactam cycle is replaced by a seven-membered cycle.[22] This is also observed in structures **2c** and **2d** (see Tables 6 and 7). It is not impossible that in the crystal the intermolecular interactions have some effect on the geometry of the Ge-**2c** molecules, and these interactions are different from the interactions in the Sn-analog **2c**, in which packing of the molecules is different.

The valent CMC angle is one more characteristic parameter reflecting the distortion of the octahedral coordination of the M atom. In previously investigated compounds of hexacoordinated Ge,[2,4] its magnitude correlated well with the $\Delta\Omega$ values. In the case of the Sn-derivatives (Tables 8—10), this angle is 2—5° less, which also points to greater deviation of the coordination polyhedron of the Sn atom from an octahedron.

The increase in the distortion of the octahedral coordination of the M atom in going from Ge derivatives to Sn derivatives reflects the growth of asymmetry of the hypervalent* O—M—Cl fragments caused by weaker bonding of the external electrons of the Sn atom with the nucleus. A similar increase in the distortion of the trigonal-bipyramidal environment of the Ge atom in comparison with the Si atom is observed in structures of their derivatives with pentacoordination.[20,21] However, in these structures the shortening of the O→M bonds in going from the five-membered lactam ligand to the seven-membered lactam is equal to 0.12 Å for the Ge atom and 0.10 Å for the Si atom, which is related to the greater mobility of the external electrons in the former.

It is unlikely that the contradictory character of the changes in the geometry of the coordination environment of the Sn atom in compounds **2a,c,d** is connected with the fact that the steric conditions in this environment are different from those of the Ge-analogs. In fact, an increase of the coordination number of an atom lengthens slightly its bonds (for example, see Ref. 19). Nevertheless, in structures of hexacoordinated germanium (Ge-**2a,d**) the lengths of the O→Ge bonds are 0.07—0.10 Å less than those in analogs with pentacoordination.[20] The increase in the average electronegativity of the "equatorial" substituents may only partially cause the reduction outlined above (within the limits of ~0.04 Å).[22]

Table 9. The main bond angles in molecule **2c**

Angle	ω/deg	Angle	ω/deg
Cl(1)—Sn(1)—Cl(2)	95.8(1)	C(7)—N(2)—C(8)	115.0(7)
Cl(1)—Sn(1)—O(1)	171.1(1)	C(7)—N(2)—C(12)	119.8(8)
Cl(2)—Sn(1)—O(1)	90.2(2)	C(8)—N(2)—C(12)	125.1(9)
Cl(1)—Sn(1)—O(2)	87.6(2)	Sn(1)—C(1)—N(1)	110.3(5)
Cl(2)—Sn(1)—O(2)	168.9(2)	N(1)—C(2)—C(3)	112.2(7)
O(1)—Sn(1)—O(2)	87.8(2)	C(2)—C(3)—C(4)	110.3(9)
Cl(1)—Sn(1)—C(1)	96.5(2)	C(3)—C(4)—C(5)	108.0(9)
Cl(2)—Sn(1)—C(1)	98.5(3)	C(4)—C(5)—C(6)	113.7(7)
O(1)—Sn(1)—C(1)	76.1(3)	O(1)—C(6)—N(1)	119.3(7)
O(2)—Sn(1)—C(1)	91.6(3)	O(1)—C(6)—C(5)	118.9(8)
Cl(1)—Sn(1)—C(7)	101.1(3)	N(1)—C(6)—C(5)	121.8(7)
Cl(2)—Sn(1)—C(7)	92.9(3)	Sn(1)—C(7)—N(2)	108.6(5)
O(1)—Sn(1)—C(7)	85.1(3)	N(2)—C(8)—C(9)	114.4(8)
O(2)—Sn(1)—C(7)	76.0(3)	C(8)—C(9)—C(10)	111(1)
C(1)—Sn(1)—C(7)	158.0(4)	C(9)—C(10)—C(11)	110(1)
Sn(1)—O(1)—C(6)	112.4(5)	C(10)—C(11)—C(12)	114.0(7)
Sn(1)—O(2)—C(12)	112.2(5)	O(2)—C(12)—N(2)	122.4(9)
C(1)—N(1)—C(2)	116.1(7)	O(2)—C(12)—C(11)	118.6(6)
C(1)—N(1)—C(6)	120.6(6)	N(2)—C(12)—C(11)	119.0(8)
C(2)—N(1)—C(6)	123.3(7)		

Table 10. The main bond angles in molecule **2d**

Angle	ω/deg	Angle	ω/deg
Cl(1)—Sn(1)—Cl(2)	97.0(1)	C(8)—N(2)—C(14)	119.4(2)
Cl(1)—Sn(1)—O(1)	172.8(1)	C(9)—N(2)—C(14)	122.8(2)
Cl(2)—Sn(1)—O(1)	88.1(1)	Sn(1)—C(1)—N(1)	107.5(2)
Cl(1)—Sn(1)—O(2)	87.2(1)	N(1)—C(2)—C(3)	113.9(3)
Cl(2)—Sn(1)—O(2)	172.4(1)	C(2)—C(3)—C(4)	115.2(4)
O(1)—Sn(1)—O(2)	88.4(1)	C(3)—C(4)—C(5)	114.1(3)
Cl(1)—Sn(1)—C(1)	98.9(1)	C(4)—C(5)—C(6)	114.1(3)
Cl(2)—Sn(1)—C(1)	95.2(1)	C(5)—C(6)—C(7)	112.6(3)
O(1)—Sn(1)—C(1)	75.4(1)	O(1)—C(7)—N(1)1	20.6(3)
O(2)—Sn(1)—C(1)	90.4(1)	O(1)—C(7)—C(6)	119.4(3)
Cl(1)—Sn(1)—C(8)	95.1(1)	N(1)—C(7)—C(6)	119.9(3)
Cl(2)—Sn(1)—C(8)	96.8(1)	Sn(1)—C(8)—N(2)	108.7(2)
O(1)—Sn(1)—C(8)	89.3(1)	N(2)—C(9)—C(10)	112.5(3)
O(2)—Sn(1)—C(8)	76.4(1)	C(9)—C(10)—C(11)	113.8(3)
C(1)—Sn(1)—C(8)	160.2(1)	C(10)—C(11)—C(12)	116.0(3)
Sn(1)—O(1)—C(7)	110.1(2)	C(11)—C(12)—C(13)	113.7(3)
Sn(1)—O(2)—C(14)	111.0(2)	C(12)—C(13)—C(14)	112.0(3)
C(1)—N(1)—C(2)	117.5(3)	O(2)—C(14)—N(2)	120.8(3)
C(1)—N(1)—C(7)	119.6(2)	O(2)—C(14)—C(13)	119.2(2)
C(2)—N(1)—C(7)	122.9(3)	N(2)—C(14)—C(13)	119.9(2)
C(8)—N(2)—C(9)	117.5(2)		

Hence, even the introduction of an additional sixth bond in the coordination environment of the central atom does not increase (on the contrary, it more likely reduces) the length of the components of the hypervalent bond. The insignificant reduction in the steric repulsion of the ligands when Ge is replaced by Sn should not result in the observed abnormal shortening of the O→Sn bonds in the series of compounds **2a** → **2c** → **2d**. The results of semiempirical calculations of the geometry of molecules **2a—d** presented below also do not give the answer to this question.

Note that the increase in the electroconductivity of a solution of dichloride **2d** over that of dichloride **2a** is

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* For more detail about the hypervalence model, see Ref. 12.

considerably less than in the corresponding germanium derivatives (see Table 4). Thus, the considered effect takes place not only in the crystal.

Quantum-chemical investigation. As has been previously established,[23] in the case of 1-(dimethylfluorosilylmethyl)- and 1-(dimethylchlorosilylmethyl)-2-pyrrolidones quantum-chemical calculations by the semiempirical MNDO method reflect the changes in the geometric characteristics rather adequately, which is an indication of preference for the conformations of molecules with the coordination O→Si bond, *i.e.*, with a pentacoordinate silicon atom. Taking into account the results of the X-ray investigation presented above, we performed quantum-chemical calculations by the MNDO method using the appropriate parameters of the MOPAC set of programs adapted for an IBM PC with full geometry optimization over all of the independent parameters,[24] and also using one of the last modifications of the MNDO method, *i.e.*, the PM3 method within the same program,[25] with the aim of elucidating the reasons for the variation of the geometric characteristics in going from five-membered lactam derivatives to seven-membered lactam derivatives and to estimate the relative thermodynamic stability of the possible isomers of dichlorides **2a,c,d**.

The quantum-chemical calculations by the MNDO method suggest that the stable conformation with a coordination bond for the 2-pyrrolidone derivative **2a**, *i.e.*, for the compound in which, according to the X-ray data, the coordination O→Sn interaction is weaker than that in six- and seven-membered lactam derivatives does not occur. The calculation results in a structure in which the Sn—O distances are equal to 4.02 and 4.26 Å. By contrast, in the case of dichlorides **2c,d** the MNDO method allows such conformations to be fixed (Table 11). With the use of the PM3 method, the optimized geometry of all three dichlorides **2a,c,d** corresponds to *cis*-isomer structures that are essentially no different in conformation from those observed in the crystal (see Fig. 1). Thus, from here on we present results obtained by the latter method. It should be noted that the calculations of compounds **2c,d** were performed for the conformations of lactam cycles in real molecules.

The calculated lengths of the Sn—O and Sn—Cl bonds in a series of five-, six- and seven-membered lactam derivatives change in parallel with those in real molecules (compare the data from Tables 11 and 5—7), which means the calculations adequately reflect the tendencies observed in these compounds. It is necessary to note that quantum-chemical calculations result in symmetric geometric characteristics of molecules, and the real geometry of the molecules is different from the calculated data by virtue of possible intermolecular interactions in the crystal.

Table 11. The Sn—O and Sn—Cl bond lengths (*d*/Å) for the *cis*-isomers of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a,c,d** according to data calculated by the MNDO and PM3 methods

Bond	**2a**	**2c**		**2d**	
	PM3	MNDO	PM3	MNDO	PM3
Sn—O(1)	2.478	2.400	2.168	2.354	2.161
Sn—O(2)	2.477	2.386	2.164	2.361	2.162
Sn—Cl(1)	2.381	2.352	2.396	2.357	2.400
Sn—Cl(2)	2.382	2.353	2.398	2.356	2.400

Parallel changes in the series of compounds **2a,c,d** were also observed for the charges on the heteroatoms of the coordination unit and on the nitrogen atoms calculated by the PM3 method for the observed geometries of molecules in a crystal and for the geometries taken from the data of calculations (Table 12). In the calculation of the charges on atoms using the real geometries of molecules the positions of the hydrogen atoms not determined by X-ray analysis were optimized with fixed coordinates of the other atoms obtained in the course of the X-ray investigation. It should be noted that the least separation of the charges took place in the case of the five-membered lactam derivative **2a**, *i.e.*, the compound with the weakest coordination O→Sn interaction.

The PM3 method was also used for calculating the optimum geometric parameters and for determinating the relative thermodynamic stabilities of the possible isomers of compounds **2a,c,d**.

In Table 13 are given the calculated heats of formation (ΔH^0_f), dipole moments, Sn—O distances, and charges on tin atom for the symmetric *cis*-isomers forming a crystal (s-*cis*, see Fig. 2) and for other isomers containing two coordination O→Sn bonds, *i.e.*, *cis*-isomers with an alternate arrangement of the substituents in the octahedral coordination unit (O...Cl, C...Cl, C...O) (as-*cis*), isomers with a *trans*-arrangement of the same atoms (O...O, C...C, Cl...Cl) (s-*trans*), and isomers with the chlorine atoms in the *trans*-position and the carbon and oxygen atoms in the *cis*-position (C...O, C...O, Cl...Cl) (as-*trans*) (Fig. 2, the other possible isomers of these compounds were not investigated), and also for isomers with a pentacoordinated tin (Sn^V) atom, *i.e.*, (O—Sn)-monochelated bis(lactamomethyl)dichlorostannanes (Sn^V-**2a,c**), and finally isomers with a

Table 12. Charges on the Sn, O, Cl and N atoms for the observed (by X-ray analysis) and calculated (PM3) geometry of the *cis*-isomers of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes **2a,c,d**

Compound	X-ray			PM3		
	2a	**2c**	**2d**	**2a**	**2c**	**2d**
Sn	1.432	1.472	1.466	1.354	1.544	1.543
Cl(1)	−0.529	−0.547	−0.579	−0.519	−0.581	−0.589
Cl(2)	−0.558	−0.576	−0.583	−0.519	−0.585	−0.589
O(1)	−0.453	−0.463	−0.457	−0.420	−0.472	−0.464
O(2)	−0.450	−0.481	−0.450	−0.421	−0.470	−0.465
N(1)	0.174	0.192	0.159	0.053	0.147	0.134
N(2)	0.187	0.207	0.175	0.054	0.145	0.136

Table 13. Heats of formation (ΔH^0_f/kcal · mole^{-1}), dipole moments (μ/D), the Sn—O distance (l/ Å) and charges (q) on the tin atom for isomers of bis(lactamomethyl)dichlorostannanes **2a,c,d** according to the PM3 method

Isomer	$-\Delta H^0_f$	μ	l(Sn—O^1)	l(Sn—O^2)	q(Sn)
(s-*cis*)-**2a**	139.2	9.67	2.478	2.477	1.354
(as-*cis*)-**2a**	136.0	7.60	2.504	2.538	1.285
(s-*trans*)-**2a**	137.8	0.19	2.142	2.131	1.566
(as-*trans*)-**2a**	136.7	1.29	2.130	2.132	1.556
Sn^{V}-**2a**	138.3	6.76	2.491	4.332	1.099
Sn^{IV}-**2a**	134.6	2.86	4.466	4.402	0.793
(s-*cis*)*-**5a**	106.1	10.90	3.122	3.124	1.255
(s-*cis*)**-**6a**	123.1	10.02	3.106	2.539	1.280
(s-*cis*)-**2c**	151.7	11.43	2.168	2.164	1.544
(as-*cis*)-**2c**	148.4	10.12	2.107	2.352	1.508
(s-*trans*)-**2c**	152.6	0.18	2.089	2.086	1.635
(as-*trans*) **2c**	151.4	0.85	2.084	2.082	1.630
Sn^{V}-**2c**	147.4	8.41	2.186	4.225	1.238
Sn^{IV}-**2c**	142.1	3.11	4.459	4.484	0.848
(s-*cis*)-**2d**	157.8	10.39	2.161	2.162	1.543
(as-*cis*)-**2d**	154.1	10.16	2.200	2.103	1.547
(s-*trans*)-**2d**	158.4	0.11	2.087	2.086	1.634
(as-*trans*)-**2d**	157.2	0.99	2.083	2.081	1.631

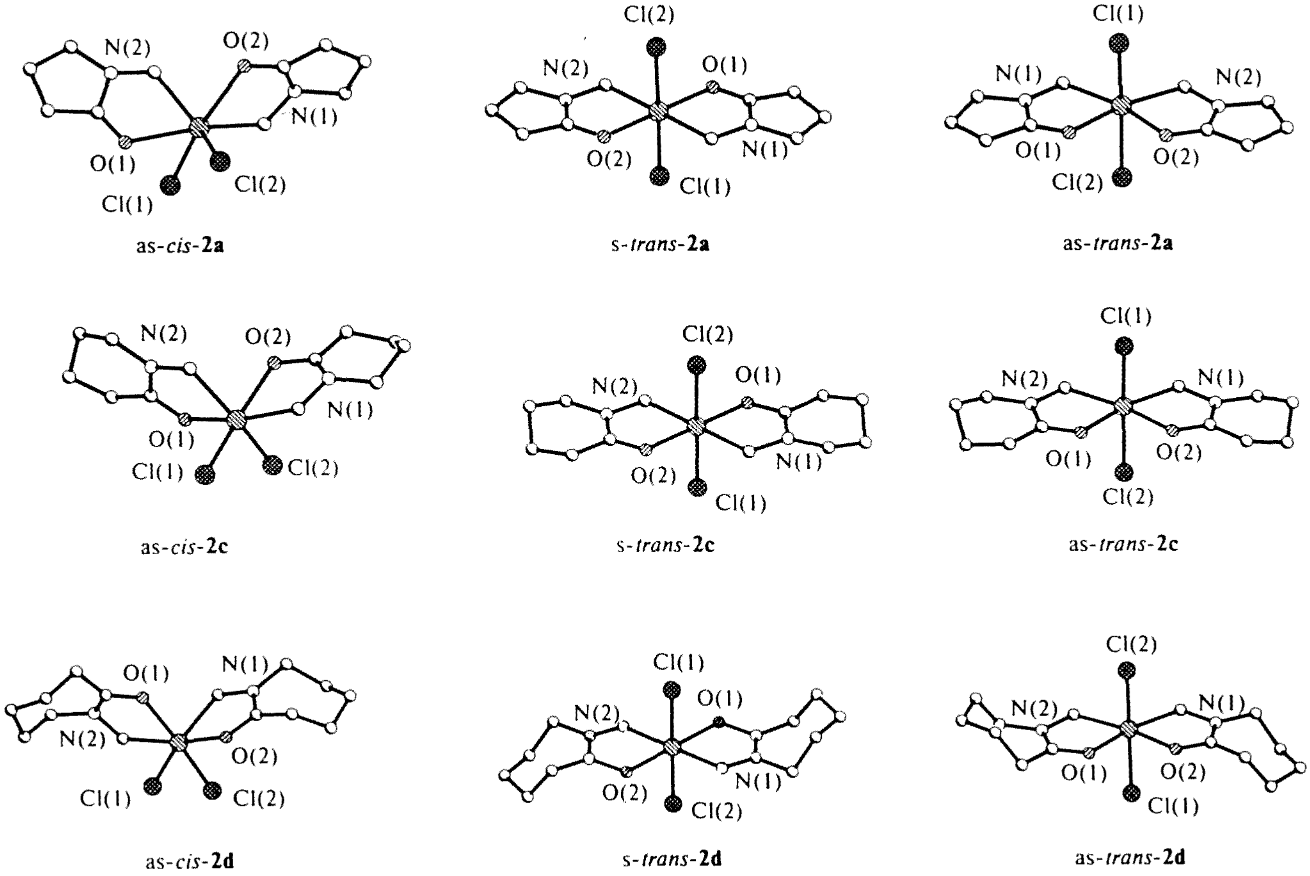
* N→Sn bond lengths 2.443 and 2.444 Å. ** N→Sn bond lengths 2.410 Å, Sn...N distance 3.052 Å.

tetracoordinated tin (Sn^{IV}) atom, *i.e.*, non-chelated bis(lactamomethyl)dichlorostannanes (Sn^{IV}-**2a,c**) containing no coordination bonds.

Above all, the similarity of the heats of formation of all of the hexacoordinated isomers of compounds **2a,c,d** should be noted. This indicates that there is a definite probability that some of them participate in the processes recorded by dynamic ^{1}H NMR (see below).

A comparison of the heats of formation of the isomeric derivatives containing tetra-, penta- and hexacoordinated tin atoms (for example, of the series of compounds: Sn^{IV}-**2a**, Sn^{V}-**2a**, s-*cis*-**2a**; Sn^{IV}-**2c**, Sn^{V}-**2c**, s-*cis*-**2c**) allows one to propose that the thermodynamic stability of the hexacoordinated species is greater than that of the pentacoordinated species, and is still greater than that of the tetracoordinated species, which contains no hypervalent bonds. Thus, the difference in ΔH^0_f between the penta- and hexacoordinated species in the case of the five-membered lactam derivatives is substantially less than that of the corresponding six-membered lactam derivatives, since in the former the coordination O→Sn interaction is fairly weak in the hexacoordinated s-*cis*-**2a** isomer (see above).

As expected, the calculated dipole moments of hexacoordinated isomers differ widely. They are maxi-



as-*cis*-**2a** s-*trans*-**2a** as-*trans*-**2a**

as-*cis*-**2c** s-*trans*-**2c** as-*trans*-**2c**

as-*cis*-**2d** s-*trans*-**2d** as-*trans*-**2d**

Fig. 2. Structures of the hexacoordinated isomers of compounds **2a,c,d** calculated by the PM3 method.

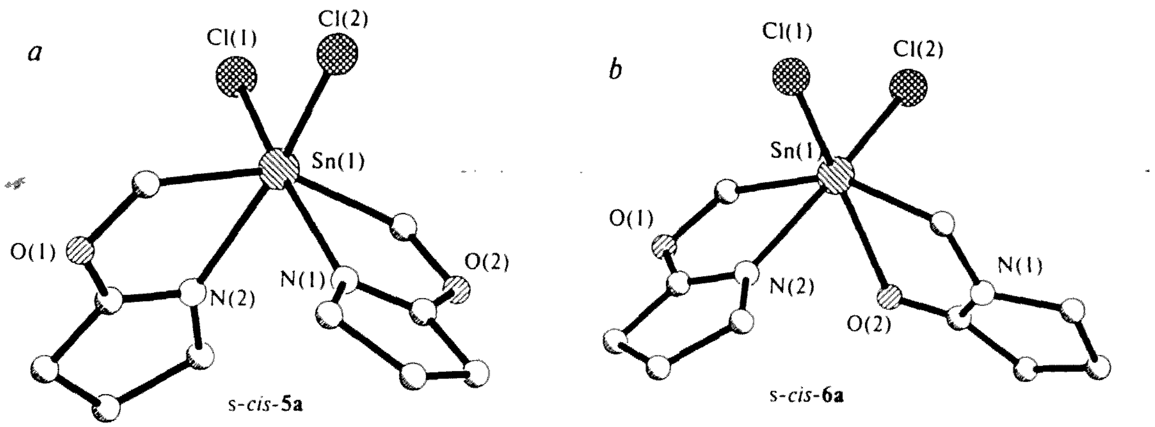


Fig. 3. Structures of molecules of lactim ethers (s-*cis*)-**5a** (*a*) and (s-*cis*)-**6a** (*b*) calculated by the PM3 method.

mum for the symmetric (s-*cis*) isomers, and minimum for the symmetric (s-*trans*) isomers. The maximum charge on the tin atoms is observed in the symmetric *trans*-isomers (s-*trans*), and generally it tends to increase as the coordination O→Sn interaction strengthens. This increase can be estimated as a first approximation by the shortening of the hypervalent Sn—O bonds.

The calculations for the probable isomers with N→Sn coordination for the derivatives of 2-pyrrolidone, *i.e.*, (N—Sn)-bischelated bis[(1-pyrrolin-2-yl)oxymethyl]dichlorostannane (s-*cis*-**5a**), (N—Sn, O—Sn)-bischelated [(1-pyrrolin-2-yl)oxymethyl][(2-oxo-1-pyrrolidinyl)methyl]dichlorostannane (s-*cis*-**6a**) (Fig. 3) indicate that they are less thermodynamically stable.

Dynamic ^{1}H NMR. The geometry of the coordination unit in dichlorides **2a,c,d** as found by X-ray structural analysis in the solid state are also retained in solution at low temperatures. Thus, in these compounds at temperatures below −30 °C, in the ^{1}H NMR spectra the protons of the two prochiral methylene NCH_2 groups are chemically non-equivalent pairs and appear as a quartet with an AB pattern.

Increasing the temperature of a solution results in consecutive broadening and coalescence of the signal, and then the formation of an average singlet of the diastereotopic methylene groups. A typical dynamic NMR (DNMR) spectrum is given in Fig. 4.

DNMR spectra of the reported type are characteristic of stereochemical non-rigid chelate complexes of metals, for which processes involving inversion of a chiral center take place in solution. The values of the $\Delta G^{\#}$ for compounds **2a,c,d** calculated by dynamic ^{1}H NMR spectroscopy are equal to 13.6±0.1, 13.6±0.1 and 13.9±0.1 kcal $\cdot$ mol^{-1}, respectively. It was found that in the investigated range of concentrations the $\Delta G^{\#}$ values are independent of the concentration of the solution, which indicates that the process under observation is intramolecular.

The magnitude of the chemical shift of the ^{119}Sn signal in compounds **2a,c,d** depends little on temperature (as the temperature decreases to −30 °C the upfield shielding is equal to no more than 3 ppm). This allows one to consider dissociative mechanisms of the stereodynamic process under observation (with fission of the coordination O→Sn bond or dissociation of one monodentate ligand) that decrease the coordination number of the Sn atom to be very improbable. The low electroconductivity of dichlorides **2a,d** discussed above also argues against a dissociative mechanism that forms a chloride ion and a stannacenium cation containing a pentacoordinated tin atom stabilized by two coordination O→Sn bonds.

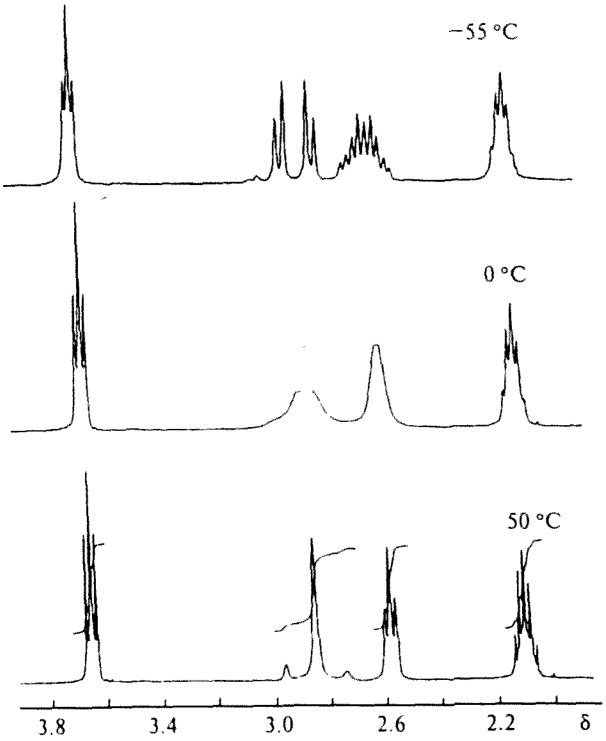


Fig. 4. The temperature dependent ^{1}H NMR spectra of compound **2a** in $CDCl_3$.

Table 14. Crystal data and main characteristics of the X-ray diffraction experiments for compounds **2a,c,d**

Parameter	**2a**	**2c**	**2d**
Molecular formula	$C_{10}H_{16}N_2O_2SnCl_2$	$C_{12}H_{20}N_2O_2SnCl_2$	$C_{14}H_{24}N_2O_2SnCl_2$
T/K	185	190	180
$2\theta_{max}$/deg	52	54	52
a/Å	15.205(2)	9.673(2)	6.352(2)
b/Å	7.923(3)	9.673(2)	19.085(3)
c/Å	11.841(4)	28.401(3)	14.786(4)
α/deg	90	90	90
β/deg	102.37(2)	90	100.18(2)
γ/deg	90	120	90
V/Å^3	1393(1)	2301(1)	1764(1)
Space group (Z)	$P2_1/c$ (4)	$P6_5$ (6)	$P2_1/n$ (4)
d_{calc}/g cm^{-3}	1.839	1.792	1.664
N_{refl}	3048	3658	3447
N_{refl} (least squares)	2183 $I > 3\sigma(I)$	1506 $I > 2.5\sigma(I)$	2687 $I > 3\sigma(I)$
R, R_w	0.083; 0.093	0.035; 0.033	0.022; 0.021

Table 15. Coordinates of atoms (×10^4) in structure **2a**

Atom	x	y	z
Sn(1)	2441.5(6)	1157.1(8)	3647.8(6)
Cl(1)	3251(2)	3826(3)	4085(3)
Cl(2)	1022(2)	2383(4)	2642(3)
O(1)	1862(6)	−1494(10)	3449(7)
O(2)	3729(7)	−378(11)	4384(7)
N(1)	1559(7)	−756(12)	5178(7)
N(2)	3610(7)	−800(12)	2453(8)
C(1)	2071(9)	743(14)	5269(9)
C(2)	1110(11)	−1446(15)	6097(11)
C(3)	675(9)	−3052(15)	5539(10)
C(4)	1045(9)	−3394(15)	4473(9)
C(5)	1503(7)	−1819(13)	4290(9)
C(6)	2906(9)	494(16)	2112(10)
C(7)	3993(10)	−1749(16)	1634(12)
C(8)	4628(9)	−2984(17)	2387(12)
C(9)	4654(9)	−2454(14)	3636(12)
C(10)	3951(9)	−1120(12)	3536(10)

In our opinion, the most likely mechanism of permutational isomerization involves the trigonal twist mechanism with a trigonal prismatic transition state[26] that has been widely discussed in the case of stereochemical non-rigid octahedral complexes.[27] In particular, this stereoisomerization mechanism has been proposed for bis[(2-dimethylaminomethyl)phenyl]dibromostannane[28] and also for triorganotin halides containing two C,N-chelating 8-dimethylamino-1-naphthyl ligands.[29]

Table 16. Coordinates of atoms (×10^4) in structure **2c**

Atom	x	y	z
Sn(1)	5339.8(5)	1103.5(5)	0
Cl(1)	2726(2)	79(3)	368(1)
Cl(2)	5965(3)	3900(2)	−38(1)
O(1)	7568(6)	1734(7)	−420(2)
O(2)	5123(7)	−1289(6)	147(2)
N(1)	5828(8)	1003(7)	−1019(2)
N(2)	6966(8)	98(8)	700(2)
C(1)	4497(9)	421(10)	−693(3)
C(2)	5412(11)	845(12)	−1531(3)
C(3)	6849(12)	1780(12)	−1835(3)
C(4)	8210(10)	1499(11)	−1680(4)
C(5)	8683(10)	2129(10)	−1187(3)
C(6)	7311(10)	1600(9)	−862(3)
C(7)	6837(12)	1533(10)	611(3)
C(8)	8214(12)	323(12)	1033(4)
C(9)	8034(16)	−1189(14)	1229(4)
C(10)	7613(13)	−2410(13)	846(4)
C(11)	6082(11)	−2715(10)	601(3)
C(12)	6058(9)	−1213(9)	469(3)

Experimental

IR spectra in ~5% $CHCl_3$ solutions were measured with a Specord IR-75 instrument in KBr cells.

The ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Varian XL-400 spectrometer at 400.1, 100.6 and 149.2 MHz, respectively, in a pulsing mode with the subsequent Fourier transformation. The ^1H and ^{13}C chemical shifts were measured using tetramethylsilane as internal reference. The ^{119}Sn chemical shifts were recorded using Me_4Sn as external reference.

Table 17. Coordinates of atoms (×10^4, ×10^3 for H atoms) in struture **2d**

Atom	*x*	*y*	*z*
Sn(1)	1517.0(3)	1541.8(1)	3441.3(1)
Cl(1)	2981(1)	984.7(5)	2185.4(5)
Cl(2)	−101(1)	2554.2(4)	2566.1(6)
O(1)	569(4)	2030(1)	4714(1)
O(2)	2567(3)	581(1)	4284(1)
N(1)	3640(4)	2617(1)	4708(2)
N(2)	−697(4)	202(1)	3601(2)
C(1)	4320(5)	2089(2)	4093(2)
C(2)	5066(6)	3223(2)	4966(3)
C(3)	4149(6)	3911(2)	4575(3)
C(4)	2517(7)	4245(2)	5082(3)
C(5)	555(6)	3794(2)	5107(2)
C(6)	1046(5)	3089(2)	5594(2)
C(7)	1777(5)	2544(2)	4983(2)
C(8)	−1292(5)	913(2)	3273(2)
C(9)	−2269(5)	−365(2)	3323(2)
C(10)	−1641(7)	−838(2)	2585(2)
C(11)	44(7)	−1377(2)	2953(3)
C(12)	2168(6)	−1089(2)	3452(3)
C(13)	1977(5)	−655(2)	4311(2)
C(14)	1263(5)	82(2)	4071(2)
H(1A)	495(5)	231(2)	362(2)
H(1B)	533(6)	176(2)	448(2)
H(2A)	529(7)	325(2)	555(3)
H(2B)	642(7)	309(2)	472(3)
H(3A)	347(7)	381(2)	393(3)
H(3B)	524(8)	424(3)	455(3)
H(4A)	329(7)	435(2)	572(3)
H(4B)	211(7)	468(2)	482(3)
H(5A)	−34(7)	405(2)	544(3)
H(5B)	−20(7)	368(2)	447(3)
H(6A)	209(6)	314(2)	616(3)
H(6B)	−24(6)	290(2)	583(2)
H(8A)	−199(6)	84(2)	259(3)
H(8B)	−231(7)	110(2)	361(3)
H(9A)	−240(6)	−64(2)	387(2)
H(9B)	−365(6)	−11(2)	309(2)
H(10A)	−113(6)	−55(2)	217(3)
H(10B)	−299(6)	−103(2)	230(3)
H(11A)	−57(6)	−164(2)	336(3)
H(11B)	36(7)	−169(2)	248(3)
H(12A)	287(6)	−78(2)	302(3)
H(12B)	302(7)	−149(2)	364(3)
H(13A)	99(5)	−91(2)	461(2)
H(13B)	330(6)	−60(2)	470(2)

The two-dimensional NMR experiments were carried out using the standard set of programs. Activation energies for the permutation isomerization were calculated from the Eyring equation.[10]

Conductometric measurements were performed with an OK-102/1 conductometer (Radelkis Company, Hungary) with OK-9023 electrodes consisting of three Pt rings in a CH_2Cl_2 solution (concentrations 10^{-1}—10^{-5} mole · l^{-1}) at ~20 °C. The frequency of alternating current was from 80 Hz to 3 kHz. The relative error of measurement of specific electroconductivity was ±1%.

The initial *N*-(chloromethyl)lactams **1a—d** were synthesized according to procedures described previously.[30]

General procedure for preparation of (O—Sn)-bischelated bis(lactamomethyl)dichlorostannanes 2a—d. A double quantity of *N*-(chloromethyl)lactam was added dropwise with intense stirring to a suspension of tin powder (10—25 mmoles) activated by 0.1 ml H_2O in about 15—50 ml of boiling toluene or *o*-xylene and the reaction mixture was refluxed for 1—2 h. After evaporation of the solvent, a crude product was purified by recrystallization from acetonitrile. The data of elemental analysis, yields, and physical constants of dichlorides **2a—d** are given in Table 1.

X-Ray investigation of dichlorides 2a,c,d. The crystal data and the X-ray diffraction characteristics of compounds **2a,c,d** are given in Table 14. The experiments were carried out on a four-circle automatic Syntex $P2_1$ diffractometer (λMo-*K*α-radiation, θ/2θ-scanning). The structures were solved by the direct method and refined by the full-matrix least-squares technique in the anisotropic approximation for nonhydrogen atoms. The H atoms in structure **2d** were located by a difference synthesis and were refined isotropically. The H atoms in structures **2a** and **2c** were placed in the calculated positions and were refined with fixed C—H distances of 0.96 Å and thermal parameters U = 0.08 Å^2. For crystals **2c** an absolute structure was determined. The refinement in the space group $P6_5$ gave R = 0.0348, R_w = 0.0332, S = 1.0126 as compared to R = 0.0366, R_w = 0.0343, S = 1.0321 for an inverted structure in the space group $P6_1$. According to the Hamilton test, the first structure is true with a probability exceeding 0.995. All calculations were carried out with an IBM PC/AT computer using the SHELXTL PLUS programs.[31] The atomic coordinates in structures **2a,c,d** are listed in Tables 15—17; the bond lengths and the valent angles are given in Tables 5—10.

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