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Stereochemical nonrigidity of (O—Ge)-chelate bis[(2-oxo-1-hexahydroazepinyl)methyl]dichlorogermane: substantiation of the dissociative mechanism of chelating ligand exchange

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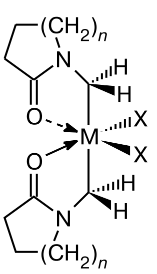
Stereochemical nonrigidity of the hexacoordinated (O—Ge)-chelate bis(2-oxo-1-hexahydroazepinylmethyl)dichlorogermane in $CDCl_3$ was studied by dynamic NMR. The activation parameters of the intramolecular rearrangement at the coordination center are $\Delta G^{\neq}{}_{298}$ = 12.3±0.2 kcal mol^{-1}, $\Delta H^{\neq}$ = 16.9±0.2 kcal mol^{-1}, and $\Delta S^{\neq}$ = 15.3±0.7 cal mol^{-1} K^{-1}. The dissociative mechanism of ligand exchange involving the cleavage of the O→Ge coordination bond is discussed based on the positive entropy of activation.

Key words: germanium, hexacoordination, intramolecular exchange, dissociative mechanism, dynamic NMR, activation parameters.

The characteristic feature of hexacoordinated silicon,[1,2] germanium, and tin[3—5] compounds is their stereochemical nonrigidity resulting in an easy ligand exchange. According to the results of X-ray diffraction analysis, neutral bischelate bis(lactamomethyl)dihalogermanes (**1**) and -stannanes (**2**),[6—11] *i.e.*, hexacoordinated C,O-bischelate complexes of the general formula L_2MX_2, exist as one isomer containing two linear hypervalent O→M—X fragments and *trans*-arranged carbon atoms. In solutions of these compounds, ligand exchange takes place,[4] which can be observed by dynamic NMR (DNMR). Results of earlier calculations[4] and analysis of $\Delta G^{\neq}$ for this process by the DNMR method based on the coalescence temperature did not allow us to elucidate the mechanism of this process primarily because of the lack of data on $\Delta H^{\neq}$ and $\Delta S^{\neq}$.[4]



1, **1a**, **2**

Compound	M	X	*n*
1	Ge	Cl, Br	1—3
1a	Ge	Cl	3
2	Sn	Cl, Br, I	1—3

In the present study, we investigated the stereochemical nonrigidity of the (O—Ge)-chelate bis[(2-oxo-1-hexahydroazepinyl)methyl]dichlorogermane (**1a**). In the crystal of **1a**, the germanium atom adopts an octahedral configuration[6] due to formation of two O→Ge—Cl hypervalent fragments (174.5 and 174.1°). In these fragments, the lengths of the O→Ge coordination bonds (2.113 and 2.137 Å) are substantially smaller than the sum of the van der Waals radii of the oxygen and germanium atoms (3.67 Å). The presence of intramolecular O→Ge coordination interaction in compound **1a** both in the solid state and solution is evident from the IR spectra, which show two characteristic absorption bands at 1576 and 1508 cm^{-1} (KBr pellets) or at 1584 and 1512 cm^{-1} (chloroform solution). Earlier, it has been demonstrated[12] that these bands correspond to mixed stretching vibrations of the N—C—O fragment of the lactamomethyl ligand coordinated to the Ge atom.[13] The occurrence of the intramolecular O→Ge coordination in solution is also evidenced by additional deshielding of the carbonyl carbon atom (δ 177.61) with respect to the noncoordinated model *N*-(benzyldimethylgermyl)hexahydroazepin-2-one (**3**) (δ 174.77).[14]

The chirality of molecule **1a** is makes the methylene protons of the $GeCH_2$ groups diastereotopic. In the ^1H NMR spectrum, these protons appear as a broadened singlet at room temperature and as two doublets of an AB system at temperatures below 268 K. The spectrum restores its original shape with increasing temperature.

Earlier,[4] the exchange process for compounds **1** and **2** resulting in the interconversion of enantiomers was stud-

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ied by DNMR at the temperature of coalescence of the signals for the protons of the NCH_2Ge group, and the activation energies of this process were calculated according to the Eyring equation[15] (10—14 kcal mol^{-1}). The calculated activation energies for the germanium complexes are, on the average, 2—3 kcal mol^{-1} lower than those for their Sn analogs. For compound **1a**, $\Delta G^{\neq}$ for enantiomerization at the coalescence point[14] (268 K) is 12.7±0.1 kcal mol^{-1}. However, the mechanism of enantiomerization was an open question. In particular, it remained unclear whether or not the coordination bonds are cleaved in the course of intramolecular ligand exchange.

In the present study, we carried out complete analysis of the overall line shapes of the signals for the protons of the NCH_2Ge group in the DNMR spectra of compound **1a** in $CDCl_3$ with the use of the Bloch equation modified for chemical exchange processes.[16] The evaluated activation parameters of permutational isomerization are $\Delta G^{\neq}_{298} = 12.3\pm0.2$ kcal mol^{-1}, $\Delta H^{\neq} = 16.9\pm0.2$ kcal mol^{-1}, and $\Delta S^{\neq} = 15.3\pm0.7$ cal mol^{-1} K^{-1} ($r = 0.999$). In different solvents, $\Delta G^{\neq}_{298}$ remains virtually unchanged (12.6±0.3 in CD_3CN, 12.3±0.3 in $(CD_3)_2CO$, and 12.3±0.6 kcal mol^{-1} in CD_3CD_5). The parameter $\Delta S^{\neq}$ is only slightly affected by the nature of the solvent (11.5±1.1 in CD_3CN and acetonitrile-d_3, 15.2±0.9 in $(CD_3)_2CO$, and 16.6±2.0 cal mol^{-1} K^{-1} in CD_3CD_5). The activation parameters are independent of the concentration (in the range from 1 to 10 mol L^{-1}), which indicates that the intermolecular (associative) mechanism of exchange is highly improbable.

It was found that the inversion of the seven-membered lactam rings has no effect on the observed averaging of the signals. Earlier, we have demonstrated that inversion of the seven-membered lactam ring in **3** (in a 1 : 1 mixture of $CDCl_3$ and CD_2Cl_2) slows down at lower temperature (T = 194 K, $\Delta G^{\neq}_{194} = 9.4\pm0.2$ kcal mol^{-1}).[14] Cooling of compound **1a** (in a 1 : 1 mixture of $CDCl_3$ and CD_2Cl_2 or in toluene) below 210 K leads to further broadening of all signals of the methylene protons due to inhibition of inversion of the lactam ring.

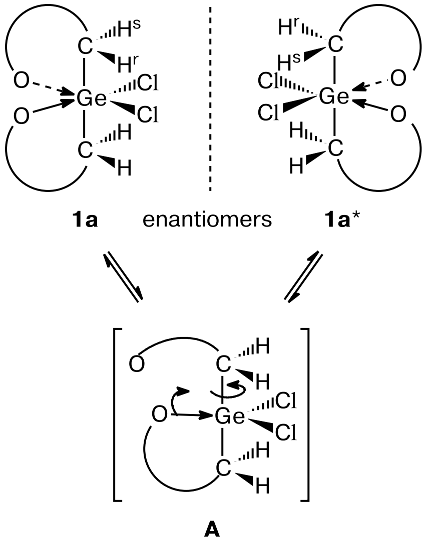
Possible mechanisms of averaging of the signals of the methylene protons for compounds **1** and **2** can be divided into two groups: nondissociative (regular) mechanisms, the so-called trigonal[17,18] and digonal (which are also referred to as 1,2-shift)[19] twists proceeding with retention of all bonds in complexes, and dissociative (irregular) mechanisms[20] involving the cleavage of coordination bonds followed by their recovery. In our opinion, the mechanism involving the cleavage of the Ge—Cl covalent bonds is highly improbable for covalent dichlorogermanes **1**, as evidenced by a substantially lower electrical conductivity of their solutions in chloroform (40—260 mS cm^2 mol^{-1}) compared to that of cation-anion complexes of the $L_2Ge(Cl)OTf$ type, in which one the halogen atom is replaced by the triflate group (1000—2000 mS cm^2 mol^{-1}).[21]

High positive entropies of activation are indicative of a larger number of degrees of freedom of a transition state or an intermediate compared to the starting compound,[22] which can be attributable to the cleavage of the O→Ge coordination bond. The processes occurring without bond cleavage, for example, those proceeding through trigonal-prismatic transition states, are characterized by a negative entropy of activation.[23] Hence, these processes can be excluded from consideration.

The ligand exchange in the neutral hexacoordinated trischelate complex $(1,2\text{-}O_2C_6H_4)Si[O(Ph)C{=}NNMe_2]_2$ (**4**) is also characterized by a positive entropy of activation ($\Delta S^{\neq}$ = 5.4 cal mol^{-1} K^{-1}).[24] For this compound, the following two mechanisms of ligand exchange are discussed: the exchange of two hydrazide chelate rings through the (O,O)-1,2-shift[25] and dissociation—recombination of the N→Si bond. In our opinion, the parameter $\Delta S^{\neq}$ determined in the cited study corresponds to the (O,O)-1,2-shift.

The results of the present study (in particular, the higher entropy of activation compared to that of trischelate complex **4**) provide evidence that the dissociative mechanism is most probable for the intramolecular rearrangement in dichloride **1a**. This mechanism involves the cleavage of the O→Ge coordination bond resulting in equivalence of the diastereotopic methylene protons of the NCH_2Ge group (Scheme 1).

Scheme 1



Note. The diastereotopic methylene protons of the NCH_2Ge group are labeled by the superscripts r (*pro*-R) and s (*pro*-S).

After completion of the sequence of steps **1a** → **A** → **1a***, the proton H^r of enantiomer **1a** occupies the position H^r in enantiomer **1a***. The latter position is a mirror reflection of the position of the proton H^s in enantiomer **1a**. Therefore, the protons H^r and H^s become magnetically equivalent due to exchange.

It should be noted that the germanium atom in the transition state **A** formed after cleavage of one coordination bond in enantiomer **1a** or **1a*** is pentacoordinated. It is known[5] that, according to X-ray diffraction data, the coordination bond and the most electronegative substituent occupy the apical positions in stable trigonal-bipyramidal germanium compounds (as well as in compounds of other Group 14 elements). Taking into account this fact, it is also not inconceivable that intermediates with the linear hypervalent O→Ge—Cl fragment are involved in the enantiomerization process.

To study preferable processes resulting in averaging of signals of diastereotopic atoms or groups in dihalides **1** and **2** and related compounds, we are carrying out quantum-chemical calculations and additional investigations for other objects.

Experimental

The ^1H NMR spectra were recorded on Bruker AM300 and Bruker DRX500 spectrometers operating at 300.13 and 500.13 MHz, respectively, in $CDCl_3$. The results were processed using the standard Bruker software (DISNMR on ASPECT-3000 under Adakos and XWINNMR 2.6 on a Silicon Graphics Station under IRIX 6.4). Complete analysis of the line shapes was performed based on the ^1H signals of the NCH_2Ge group taking into account the temperature dependence of the resonance frequencies of exchanging signals with the use of an external standard for temperature calibration[26] on a spectrometer. The activation parameters were calculated using eight spectra recorded at different temperatures in the temperature range from –25 to +20 °C. Calculations were carried out using the DNMR-SIM[27] and DNMR5[28] programs for simulation and iteration of resonance frequencies of exchanging signals, respectively. The relaxation times were measured at each temperature point.

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