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Optical Stereoisomers of Geometric Isomers of the Octahedral Complex $TiF_4[Ph_2P(O)CH_2CH(OH)Me)]_2$ in CH_2Cl_2

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Abstract—Some peculiarities of the effect of enantiomers of the monodentate ligand on the stereoisomerism of the mixed octahedral tetrafluoride complexes of d^0-transition metals are established by the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR methods for the complex formation of TiF_4 with $Ph_2P(O)CH_2CH(OH)Me$ (L) having the asymmetric carbon atom in the aliphatic hydrocarbon radical and being a racemic mixture of enantiomers in CH_2Cl_2. The compositions of the complexes formed in solutions are determined. The conclusion about the relative stereochemical configuration of the chiral and *meso*-stereoisomers of the geometric isomers of the TiF_4L_2 octahedral complex is based on an analysis of the ^{19}F NMR spectra using the heterotropic concept.

Keywords: titanium tetrafluoride, complex formation, NMR, optical stereoisomerism

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INTRODUCTION

The reactions of TiF_4 with the simplest representatives of the new class of organophosphorus ligands, diphenylphosphorylalkanones $Ph_2P(O)CH_2C(O)Me$ (L^1) [1] and $Ph_2P(O)(CH_2)_2C(O)Me$ (L^2) [2], in CH_2Cl_2 have been studied earlier by the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR methods. It is shown that the ligands predominantly coordinate to the central ion through the P=O group to form the octahedral tetrafluoride complexes with the predominant *cis* configuration when a twofold excess of the ligands is added to the solution. The dimeric and polynuclear complexes containing fragments with three terminal *cis*-fluorine atoms and fluoride ions as bridges are formed in an equimolar TiF_4–L^2 solution. When a twofold excess of TiF_4 is applied, L^2 using the P=O and C=O groups acts as a bridge along with the F^- ions. The thermodynamic stability and the structures of the isomers of $TiF_4L^2_2$ and $[(\mu\text{-}F)(\mu\text{-}L^2_2)(TiF_3)_2]^+$ were calculated [2]. As for carbamoylphosphine oxides representing a class of compounds close to the discussed complexes, the reactions of TiF_4 with $Ph_2P(O)CH_2C(O)NBu_2$ (L^3) in toluene and dichloromethane [3] were studied by the ^{19}F and ^{31}P NMR methods. It was found that TiF_4 can coordinate one molecule of this ligand via the chelate mode to form $(\eta^2\text{-}L^3)TiF_4$ or can coordinate two molecules via the monodentate mode through the P=O group, which is stronger in basicity, to form *cis*-$Ti(L^3)_2F_4$. In addition to the molecular complexes, stereoisomers of the dimeric cation $\{(\mu\text{-}F[(\eta^2\text{-}L^3)TiF_3]_2\}^+$ were observed. These are two $[(\eta^2\text{-}L^3)TiF_3]^+$ moieties linked by the bridging fluoride ion and containing the ligand coordinated via the chelate mode [3]. The high chelating ability of the ligand retained as the length of the hydrocarbon bridge elongates on going to $Ph_2P(O)(CH_2)_2C(O)NMe_2$ (L^4). Conformational isomerism of the seven-membered heterocycle TiOPCCCO in the $(\eta^2\text{-}L^4)TiF_4$ complex at low temperatures was observed in a solution by the $^{19}F\{^1H\}$ and $^{13}P\{^1H\}$ NMR methods [4] and confirmed by the crystal structure [5]. Four crystallographically independent molecules $(\eta^2\text{-}L^4)TiF_4$ were found in the single crystal. They insignificantly differ in lengths of the bonds of the ligands with the Ti^{4+} ion and differ in geometry of the seven-membered metallocycle TiOPCCCO. An analysis of deviations of the metallocycles from the OTiO plane shows that the geometries of the chelate cycles almost coincide in pairs of the molecules and, hence, two conformers exist in both the crystal and solution. The quantum chemical calculations of the relative thermodynamic stability and optimization of the structures of all four molecules gave one theoretical structure nearly coinciding with one of the conformers [5].

The purpose of this work is to study the effect on stereoisomerism of the mixed fluoride complexes of d^0-transition metals of the presence of the chiral center

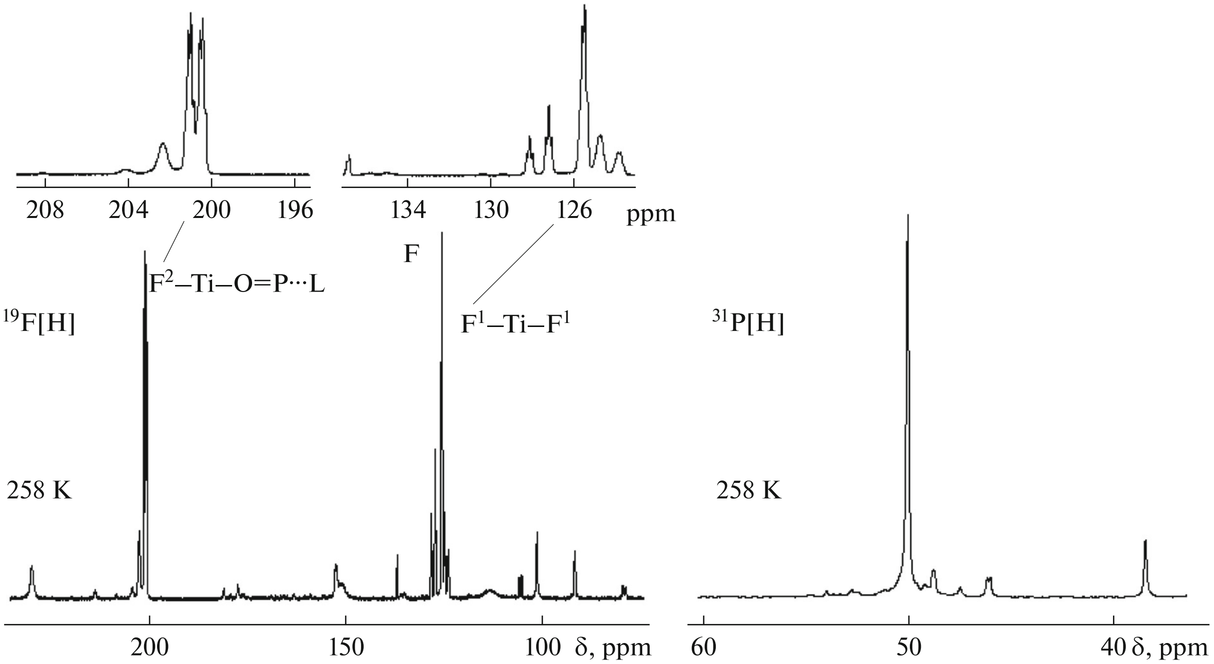


Fig. 1. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the solution with the ratio L : TiF_4 > 2 : 1 in CH_2Cl_2 at 258 K.

in the aliphatic hydrocarbon radical and to establish the possibility to identify optical isomers of the fluoride complexes using as an example the complex formation of TiF_4 with 1-diphenylphosphorylpropan-2-ol $Ph_2P(O)CH_2CH(OH)Me$ (L) having the asymmetric carbon atom in the hydrocarbon radical. Since the predominant formation of molecular complexes $TiF_4L_2^{1,2}$ in CH_2Cl_2 is observed upon the introduction of two ligands per mole of tetrafluoride [1, 2], the corresponding solution with an insignificant excess of ligand L was prepared and studied.

EXPERIMENTAL

Titanium tetrafluoride TiF_4 was synthesized by the fluorination of the powdered metal with elemental fluorine in a quartz system. 1-Diphenylphosphorylpropan-2-ol, $Ph_2P(O)CH_2CH(OH)Me$ (L), was synthesized at the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences). A solution in CH_2Cl_2 with the ratio L : TiF_4 > 2 : 1 was prepared for testing in order to the TiF_4L_2 complex would be the major moiety in the solution. The calculated amount of TiF_4 was introduced into a solution of L in CH_2Cl_2, and the mixture was magnetically stirred for 30 min at room temperature. The complete dissolution of TiF_4 was observed. All procedures were conducted under anhydrous nitrogen. The $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra in a range of 298–213 K were recorded on a Bruker AVANCE 300 spectrometer at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences). The ^{19}F and ^{31}P NMR chemical shifts were measured relative to CCl_3F and 85% H_3PO_4, respectively.

RESULTS AND DISCUSSION

In the $^{19}F\{^1H\}$ NMR spectrum of a solution of TiF_4 with an insignificant excess of ligand L at 258 K (Fig. 1), the major signals are two groups of lines in ranges of 123–129 and 200–201.5 ppm manifesting a fine structure. The position of these signals [1, 2] and their equal total relative intensities indicate, in our opinion, the presence of different *cis*-tetrafluorotitanium complexes TiF_4L_2. Based on a comparison of the chemical shift ranges with the earlier obtained data [1, 2], we assigned the lines in the high field to the resonance signals of the fluorine atoms F^1 arranged in the *trans* position to each other on the ordinate F–Ti–F. The signals in a weaker field at 200–201.5 ppm were attributed to the fluorine atoms F^2 in the *trans* position to the P=O groups on the ordinates F–Ti–OP···L. In the $^{31}P\{^1H\}$ NMR spectrum at 258 K (Fig. 1), the intense singlet line at 50 ppm corresponded to the phosphorus atoms of the ligands coordinated in the *cis*-TiF_4L_2 complexes.

The first-order ^{19}F NMR spectra of the TiF_4X_2 *cis*-tetrafluoride complexes with the monodentate ligands represent two triplets of equal intensities corresponding to two pairs of nonequivalent fluorine atoms lying on the ordinates F^1–Ti–F^1 and F^2–Ti–X of the octa-

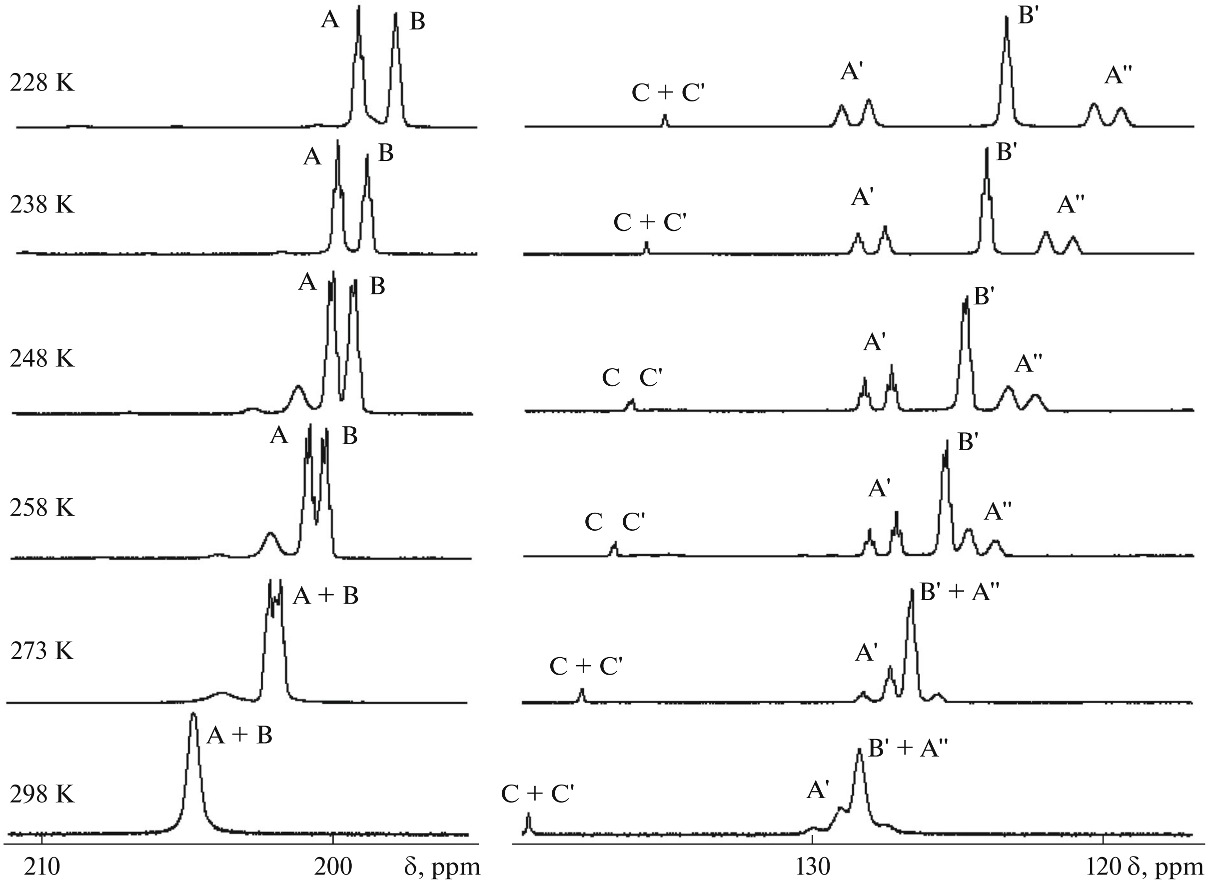


Fig. 2. Temperature dependences of the $^{19}F\{^1H\}$ NMR spectra of the solution with the ratio L : $TiF_4 > 2$ in CH_2Cl_2: A, A', and A'' designate F^2, F^1, and $F^{1'}$ from *cis*-$TiF_4L_RL_S$; B and B' designate F^2 and F^1 from *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$; C designates F^1 from *trans*-$TiF_4L_RL_S$; and C' designates F^1 from *trans*-$TiF_4L_RL_R$ and *trans*-$TiF_4L_SL_S$.

hedron [1, 2, 5]. In our opinion, many multiplet resonance lines in the ranges corresponding to the nonequivalent fluorine atoms indicate the presence of stereoisomers of the tetrafluoride complex *cis*-TiF_4L_2 in the solution. The formation of the stereoisomers can be related to the existence of ligand L with the asymmetric carbon atom as a racemic mixture of *R* and *S* enantiomers. The possibility of the presence of conformers of this complex due to the retarded rotation of the coordinated ligands cannot be excluded. To assign the observed resonance lines and to establish the nature of the unusual groups of resonance signals, it seemed reasonable to study the temperature dependence of the ^{19}F NMR spectra of this solution (Fig. 2).

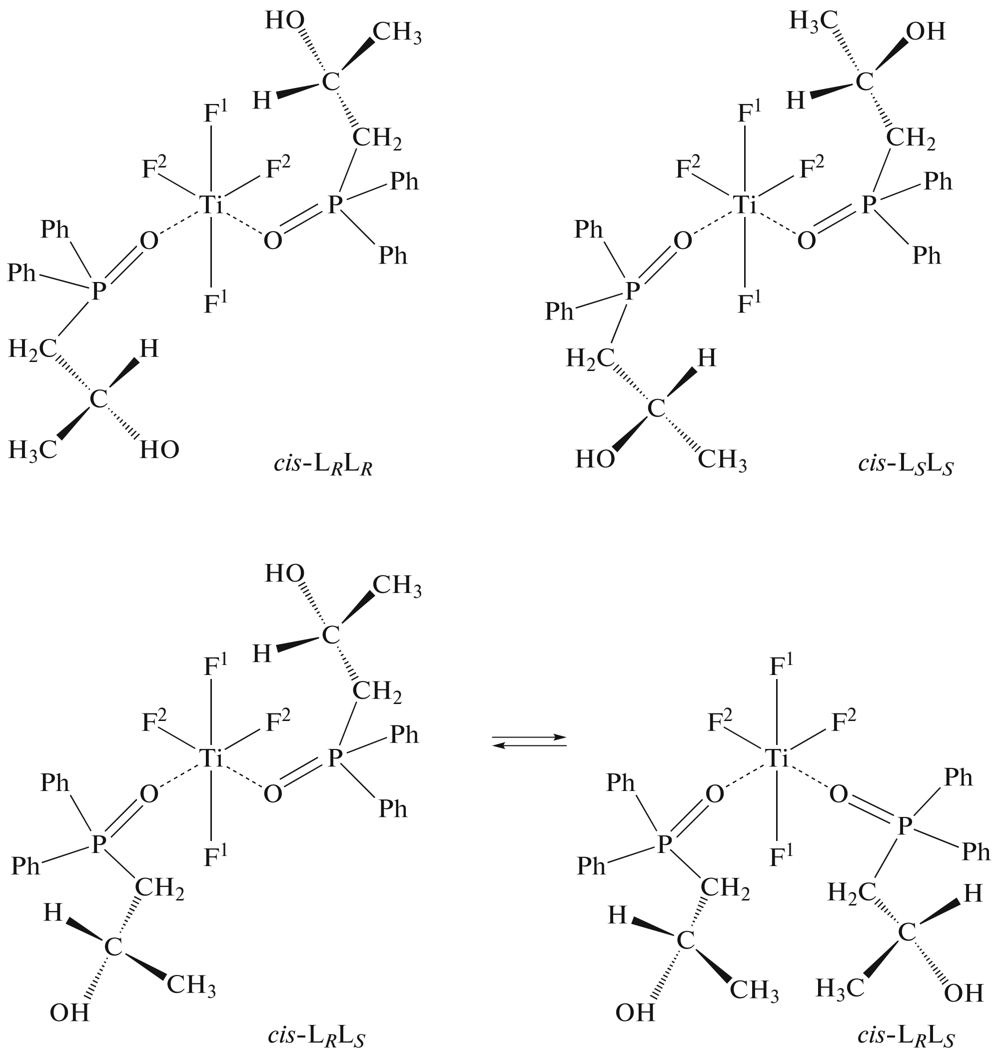
The range of the resonance ^{19}F NMR lines of the F^1 fluorine atoms arranged in the *trans* position to each other in the *cis*-TiF_4L_2 complexes at room temperature exhibits a group of broad overlapped resonance lines A', B', and A'', whereas a broad exchange signal is observed at 204.8 ppm in the range of signals of the F^2 fluorine atoms located in the *trans* position to the P=O groups (Fig. 2). This indicates that intramolecular ligand exchange processes occur in the solution. As the temperature decreased to 273 K, the resonance line began to split and some of them manifested a fine structure (Fig. 2).

Five multiplet resonance lines appeared in the range of signals of the F^1 fluorine atoms at 258 K and with the further temperature decrease: two pairs of multiplets A' and A'' of equal intensities and multiplet B', whose intensity (within inaccuracy) was equal to the sum of intensities A' and A'' (Fig. 2). Multiplets A' represented triplets (or doublets of doublets) due to the spin-spin coupling of the F^1 fluorine nuclei with the nuclei of two F^2 fluorine atoms ($J_{F^1F^2} = 39.0$ Hz), whereas multiplets A'' underwent an additional doublet splitting ($J_{F^1F^2} = 36.6$ Hz). The peculiarities of the temperature behavior of the pairs of signals A' and A" are noteworthy: the shift in opposite directions with the temperature decrease and the retention of the difference in resonance frequencies $\Delta\nu = 260.1$ Hz with the multiplets in pairs A' and A" and a decrease in the differences in their relative intensities. These factors and equal total integrated intensities of the pairs of lines A' and A" make it possible to assign them to the resonance lines of the XY components of the ^{19}F NMR spectra of the second order of the A_2XY or ABXY type of the *cis*-TiF_4L_2 octahedral tetrafluoride complex in which the fluorine atoms localized in the *trans* position to each other are nonequivalent: F^1–Ti–$F^{1'}$. We hypothetically designated this complex as stereoisomer **I** of the *cis*-TiF_4L_2 complex. The assignment of the pairs of multiplets A' and A" to the spectral components of the second order is also confirmed by the observed decrease in the differences (equalization) in the relative intensities of the "external" and "internal" components of the pairs of multiplets A' and A" with an increase in the difference of the chemical shifts between them, i.e., approaching the first-order spectrum: two doublets with equal intensities. The difference in the resonance frequencies between the multiplets in pairs A' and A" remains unchanged with the temperature decrease and was attributed to the spin-spin coupling constant (SSCC) of the nuclei of the nonequivalent fluorine atoms lying on the same ordinate: $J_{F^1F^{1'}} = 260.1$ Hz. Thus, two pairs of multiplets A' and A" were assigned to the nonequivalent fluorine atoms F^1 and $F^{1'}$ of stereoisomer **I** of the *cis*-TiF_4L_2 complex.

On the basis of the study of the temperature behavior of the resonance lines (Fig. 2), of two low-field signals A and B of equal intensities and equal multiplicities, signal A was attributed to the F^2 fluorine atoms of stereoisomer **I** localized in the *trans* position to the P=O groups of ligands L. In our opinion, this multiplet represents a doublet of doublets of doublets instead of the assumed doublet of doublets due to the spin-spin coupling of the nuclei of the F^2 atoms with the F^1 and $F^{1'}$ nuclei ($J_{F^2F^1} = J_{F^2F^{1'}} = 39.0$ Hz). The additional splitting of line A ($J_{F^2F^{2'}} = 39.0$ Hz) indicates steric nonequivalence of the F^2 and $F^{2'}$ fluorine atoms existing in the *trans* position to ligands L, which can be related to the conformational isomerism of L due to the possibility of retarded rotation or differences in the geometry of the chiral centers L_R or L_S. Since both nonequivalent fluorine atoms F^1 and $F^{1'}$ exist in the *cis* position toward F^2 and $F^{2'}$, the SSCC between the *cis*-arranged fluorine atoms ($J_{F^2F^{2'}}$, $J_{F^2F^1}$, $J_{F^2F^{1'}}$, $J_{F^{2'}F^{1'}}$, and $J_{F^{2'}F^{1'}}$) are substantially lower than those between the nonequivalent fluorine atoms lying on the same ordinate ($J_{F^1F^{1'}}$) and having different chemical shifts. The latter ($J_{F^1F^{1'}}$) substantially exceeds the SSCC observed between the terminal fluorine atom and bridging fluorine atom arranged in the *trans* position to the terminal atom in the ^{19}F NMR spectra of the dimeric complexes $[M_2F_{11}]^-$ (M = Nb, Ta, Sb, Ti) [6–9] and $M_2F_{10}L$ (M = Nb, Ta) [10] ranging from 150 to 175 Hz. This confirms the predominant character of the interligand interactions in the octahedral d^0-transition metal complexes between the ligands lying in the *trans* position to each other through the central atom [11].

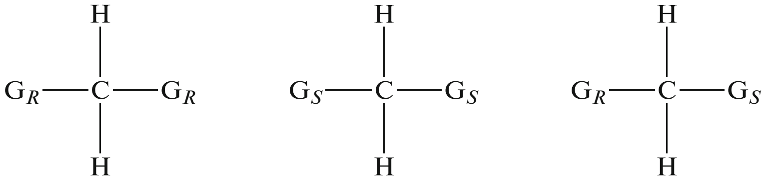
Two multiplet lines B and B' of equal intensities and equal multiplicities, being doublets of doublets of doublets (doublets of triplets) were attributed to stereoisomer **II** of the *cis*-TiF_4L_2 complex. Multiplet B in a low field corresponds to the F^2 fluorine atoms in the *trans* position to the P=O group of the ligand (F^2–Ti–OP···L), and multiplet B' corresponds to the F^1 atoms on the ordinate F^1–Ti–F^1. The additional splitting of lines B and B' instead of the assumed two triplets due to the spin-spin coupling between the nuclei of the nonequivalent atoms F^1 and F^2 indicates their steric nonequivalence. As already mentioned, this can be related to the conformational isomerism of L due to the possibility of their retarded rotation or to the possible formation of a hydrogen bond between the OH group of the ligand and the fluorine atoms. In our opinion, the formation of stereoisomers **I** and **II** of the *cis*-TiF_4L_2 complex in the solution is associated with the existence of ligand L as a racemic mixture of two optically active *R* and *S* isomers.

Complex *cis*-TiF_4L_2 can form three optical stereoisomers: *cis*-$TiF_4L_RL_R$, *cis*-$TiF_4L_SL_S$, and *cis*-$TiF_4L_RL_S$ (Scheme 1). Taking into account that the ligand exists as a racemic mixture of enantiomers, we can consider the observed equal total intensities of the resonance lines in the ^{19}F NMR spectrum of isomers **I** and **II** and, hence, their equal concentrations as an indirect confirmation of three stereoisomers of the *cis*-TiF_4L_2 complex existing in the solution. According to the theory of equiprobable ligand distribution [12], the random probability of the formation of optical stereoisomers containing two right-handed or left-handed ligand molecules *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$ is by two times lower than that of *cis*-$TiF_4L_RL_S$ and, therefore, the total concentration of the former two stereoisomers should be equal to the concentration of the latter, which is observed experimentally (Fig. 2).



Scheme 1.

The fundamental works on the determination of the stereochemical configuration of chiral molecules of organic compounds by NMR spectroscopy [13, 14], in particular, the consideration of organic molecules bearing two asymmetric centers separated by one carbon atom, were used as a basis to assign the groups of lines A, A', A'' and B, B' in the ^{19}F NMR spectra to possible stereoisomers of the *cis*-TiF_4L_2 complex. The molecules containing symmetrically arranged chiral groups (G_R, G_S) can exist in two forms named *meso*-isomer or optically inactive isomer and racemic isomers (Scheme 2) [13]. It was assumed for these molecules [15] that the symmetry relations between the protons would allow one to discern *meso*- and racemic isomers by the NMR method.



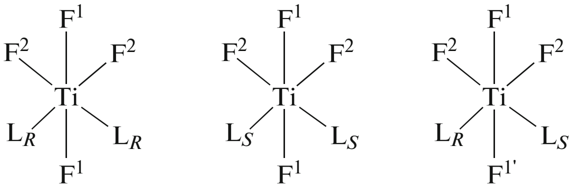
Racemic isomers of molecule *meso*-isomer

Scheme 2.

Two chiral groups in the racemic isomers (G_R or G_S) have the same absolute configurations, whereas they have opposite configurations in the *meso*-isomer [13]. Therefore, in the racemic isomers two protons of the bridging carbon atom can exchange the symmetry procedure C_2 and, hence, should be isochronous [13].

The protons at the bridging carbon atom in the *meso*-isomer cannot be superposed by any symmetry procedure: they are diastereotopic and should be anisochronous [13].

In our opinion, this consideration can also be applied to possible optical stereoisomers **I** and **II** of the octahedral *cis*-TiF_4L_2 complexes if the carbon atom is replaced by the titanium atom and the hydrogen atoms are replaced by the axial fluorine atoms F^1 (Scheme 3).



Racemic isomers *meso*-isomer
of complex *cis*-TiF_4L_2

Scheme 3.

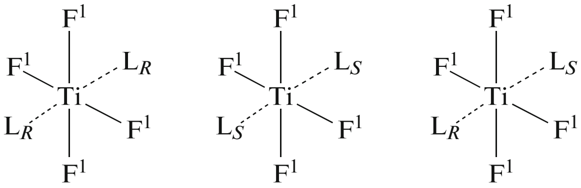
In the *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$ racemic stereoisomers of the octahedral complex containing symmetrically arranged L_R or L_S ligands, the axial fluorine atoms can be superimposed by rotation around the C_2 axis, bisector of the OTiO angle (Scheme 1), lying in the equatorial plane of the octahedron perpendicular to the F^1–Ti–F^1 ordinate. Therefore, under the conditions of the same absolute configurations of the coordinated ligands L, the F^1 fluorine atoms in the racemic isomers should be isochronous and their chemical shifts in the NMR spectra are indiscernible.

In the *meso*-stereoisomer of the octahedral complex *cis*-$TiF_4L_RL_S$, the ligands coordinated to the central ion have opposite configurations and the axial fluorine atoms are not bound by any symmetry procedure, and hence, can differ in chemical shifts.

Taking into account the aforesaid, we can assert that stereoisomer **I** (in which the axial F^1 and $F^{1'}$ fluorine atoms arranged in the *trans* position to each other are sterically nonequivalent and differ in chemical shifts and to which lines A, A', and A'' correspond in the ^{19}F NMR spectrum) is a *meso*-stereoisomer *cis*-$TiF_4L_RL_S$ of the octahedral tetrafluoride complex (Scheme 3).

Two multiplets B and B' of equal intensities and equal multiplicities were assigned to the F^1 and F^2 fluorine atoms of racemic stereoisomer **II**. Since the axial F^1 atoms are equivalent and the geometric arrangement of ligands L relative to these atoms is symmetric, they are isochronous and indiscernible in the ^{19}F NMR spectrum. Multiplets B and B' correspond to the F^1 and F^2 atoms of the optically active racemic stereoisomers *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$, which are present in the solution in equal concentrations, i.e., as a racemic mixture. According to the theory of random ligand distribution [12], their total concentration should be equal to the concentration of *meso-cis*-$TiF_4L_RL_S$, which is observed indeed.

The low-intense and narrow at room temperature signal B at 139.4 ppm (Fig. 2) was attributed to the presence of *trans*-TiF_4L_2 in an insignificant concentration. As the temperature decreases, this signal splits into overlapped resonance lines: at 248 K the narrow (136.12 ppm) and broad (136.24 ppm) components are observed, which were assigned to the presence in the solution of possible stereoisomers: a racemic mixture of *trans*-$TiF_4L_RL_R$ and *trans*-$TiF_4L_SL_S$ and *meso-trans*-$TiF_4L_RL_S$, respectively (Scheme 4).



Racemic isomers *meso*-isomer
of complex *trans*-TiF_4L_2

Scheme 4.

We failed to observe nonequivalent equatorial fluorine atoms in the ^{19}F NMR spectra of the stereoisomers *trans*-TiF_4L_2 present in the solution in an insignificant concentration. This can be related to a high rotation rate of chiral ligands L for their geometric arrangement on the same ordinate of the octahedron in the *trans* position to each other.

Thus, the conclusion about the relative stereochemical heterotropism of the chiral and optical *meso*-stereoisomers of the geometric isomers of the octahedral TiF_4L_2 complex was made on the basis of an analysis of the ^{19}F NMR spectra using the heterotropic concept. In the *meso*-stereoisomers *cis*-$TiF_4L_RL_S$ (**I**), the fluorine atoms lying on the same ordinate of the octahedron in the *trans* position to each other, F^1 and $F^{1'}$, are sterically nonequivalent, their chemical shifts differ, and the SSCC $J_{F^1F^{1'}}$ is observed between them.

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