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## Abstract

## Full Text

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# STUDY OF THE STRUCTURE OF COMPLEXES OF ALIPHATIC ORGANOLITHIUM COMPOUNDS

In work ([1]) the possibility was indicated of the formation of lithium bonds C—Li . . . C and O—Li . . . O, and the question of their nature was considered. The formation of these bonds is the cause of complex formation in organolithium compounds. The study of IR spectra, together with cryoscopic measurements, made it possible to establish the presence of two types of complexes of organolithium compounds—dimers and hexamers.

It was necessary to prove which of the observed frequencies are directly associated with the C—Li groups in dimers and hexamers. For this purpose, in the present work the IR spectra of a number of isotopically substituted aliphatic organolithium compounds were studied: $C_2H_5Li^6$, $n$-$C_5H_{11}Li^6$ (enrichment with the isotope $Li^6$ 92.5%) and $CH_3CD_2Li^7$ (content of $CH_3CD_2Li^7$ 95%), etc., in the region of NaCl, KBr, and CsJ prisms.

Comparison of the spectra of these compounds with spectra obtained by us earlier of ordinary organolithium compounds of the type $C_2H_5Li^7$, etc., again showed the dependence of the intensity of the bands in the region 870-1120 $cm^{-1}$ on the concentration of the solutions and on the solvents. However, the expected shift of these bands upon replacement of $Li^7$ by $Li^6$ did not occur. On the other hand, a very intense band in the region 530-550 $cm^{-1}$, though only slightly sensitive to changes in concentration, shifts toward shorter wavelengths by approximately 20 $cm^{-1}$ upon replacement of $Li^7$ by $Li^6$ (Table 1, Fig. 1), which agrees with approximate calculations of the isotopic shift for the C—Li bond. In the longer-wavelength part of the spectrum (CsJ prism) a band is observed near 370 $cm^{-1}$, also shifting somewhat upon isotopic substitution.

*Table 1*

| Substance | Solvent | $Li^7$ | $Li^6$ | $CH_3CD_2Li^7$ |
|---|---|---|---|---|
| Frequencies C—Li . . ., in $cm^{-1}$ | | | | |
| $C_2H_5Li$ | Hexane | 532 | 550 | 514 |
| $C_2H_5Li$ | Benzene | 530 | 545 | 512 |
| $n$-$C_5H_{11}Li$ | Hexane | 548 | 569 | — |
| $n$-$C_5H_{11}Li$ | Cyclohexane | 550 | — | — |
| $n$-$C_{12}H_{25}Li$ | Hexane | 550 | — | — |
| $n$-$C_{12}H_{25}Li$ | Benzene | 545 | — | — |

Thus, these data make it possible to assign the bands in the regions 530-550 and 370-385 cm$^{-1}$ to vibrations of the C—Li groups, which introduces corrections into the assignment of frequencies in the region 870-1200 cm$^{-1}$. However, measurements of molecular weight kindly carried out by O. A. Nogina and V. A. Dubovitskii by the cryoscopic method for $C_2H_5Li^7$ in benzene and cyclohexane and $n$-$C_{12}H_{25}Li^7$ in benzene showed that even in dilute solutions these compounds are associated ($C_2H_5Li$ is a hexamer, and $n$-$C_{12}H_{25}Li$ a dimer). In the IR spectra of these solutions there are bands at 375, 532, and 919 cm$^{-1}$ for $C_2H_5Li^7$ and at 382 and 545 cm$^{-1}$ for $n$-$C_{12}H_{25}Li^7$.

Hence it may be concluded that the bands in the regions 370-390 and 530-550 cm$^{-1}$ correspond to vibrations not of free C—Li groups, but of groups participating in the formation of complexes. Apparently, to the valence vibration of the groups

C—Li$^7$ ... in the dimeric complex corresponds to a band at about 550 cm$^{-1}$ (570 cm$^{-1}$ for Li$^6$), which is also observed in the spectrum of $n$-$C_{12}H_{25}Li^7$; the lowering of the C—Li ... absorption band in the spectrum of $C_2H_5Li^7$ to 522 cm$^{-1}$ (550 cm$^{-1}$ for Li$^6$), with the simultaneous appearance of a band at about 920 cm$^{-1}$, is evidently connected with the formation of more complex complexes (hexamers, etc.). Indeed, upon dilution of hexane and benzene solutions of $C_2H_5Li^7$, as the band at about 920 cm$^{-1}$ weakens and the intensities of the bands at about 870, 1050, and 1100 cm$^{-1}$ increase, the band assigned by us to vibration of the C—Li ... group, at about 522 cm$^{-1}$, gradually shifts into the shorter-wavelength region.

(Figure: Figure 1. Infrared spectra of organolithium compounds. KBr prism, d = 50 $\mu$. 1 —n-C5H11Li7 in hexane, C = 0.95 N; 2 —n-C5H11Li6 in hexane, C = 0.93 N)

**Fig. 1.** Infrared spectra of organolithium compounds. KBr prism, $d = 50\,\mu$. **1** —$n$-$C_5H_{11}Li^7$ in hexane, $C = 0.95\,N$; **2** —$n$-$C_5H_{11}Li^6$ in hexane, $C = 0.93\,N$.

The observed facts can be explained on the assumption that the hexamer is formed from three dimers oriented in parallel ( “bookcase” type) through the formation of more complex multicenter electron orbitals, analogous to the tetramer $[Pt_2(CH_3)_8]_2$ (2).

To clarify the nature of the bands in the 870—1100 cm$^{-1}$ region in the spectra of $C_2H_5Li$ solutions, we studied the spectra of $CH_3CD_2Li^7$ in various solvents. It was found that the bands at about 530 and 920 cm$^{-1}$ (for $C_2H_5Li^7$) in the spectrum of $CH_3CD_2Li^7$ shift to 514 and 910 cm$^{-1}$, respectively, which can be explained by a change in the effective mass at the $\alpha$-carbon atom due to replacement of hydrogen by deuterium. The bands most sensitive in the spectra of $C_2H_5Li^7$ and $C_2H_5Li^6$ to solvents, concentration, and other parameters are altogether absent in the spectrum of $CH_3CD_2Li^7$. Instead, in the spectra of $CH_3CD_2Li^7$ solutions, bands at about 979 and 1163 cm$^{-1}$ were found, behaving similarly to the bands at 875, 1050, and 1100 cm$^{-1}$ in the spectra of $C_2H_5Li$, i.e., increasing in intensity as the band at about 910 cm$^{-1}$ weakens. At the same time, the band at about 979 $cm^{-1}$ shifts to 1000 $cm^{-1}$. Thus, the bands in the 870–1200 $cm^{-1}$ region should apparently be assigned to deformation vibrations of the $\alpha$-$CH_2$ group. The sensitivity of these bands to dilution and to the solvent is evidently associated with the participation of $CH_2$ or $CD_2$ groups in the formation of complex associates and is caused by deformation of the angles and bonds in these groups.

The spectra of $C_2H_5Li$ and $CH_3CD_2Li$ in the region of stretching vibrations of C–H and C–D bonds also confirm the participation of $CH_2$ and $CD_2$ groups in the formation of associates. Thus, in the spectra of benzene solutions of these compounds, a strong lowering of the vibrational frequencies of the $CH_2$ groups (2810, 2782, 2740 $cm^{-1}$) and $CD_2$ groups (2075, 2033 $cm^{-1}$) is observed, with retention of the frequencies characteristic of vibrations of $CH_3$ groups.

When the concentration of the substance is lowered, when the intensity of the band near 910 $cm^{-1}$ decreases, there is a weakening of the shifted bands at 2782 and 2740 $cm^{-1}$ (in the spectrum of $CH_3CH_2Li^7$) and at 2075 $cm^{-1}$ (for $CH_3CD_2Li^7$), with a simultaneous increase in the intensity of higher-frequency bands (2810 $cm^{-1}$ for the first compound and 2135 $cm^{-1}$ for the second).

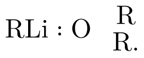
We next studied solutions of these same organolithium compounds in other solvents capable of forming complexes with the lithium atom by means of the unshared electron pairs of oxygen and nitrogen atoms: $(C_2H_5)_2O$; $(n\text{-}C_4H_9)_2O$; $(\text{iso-}C_5H_{11})_2O$; $(C_2H_5)_3N$.

**Table 2**

| Substance | Solvent | Frequencies of C—Li···, in $cm^{-1}$ | | |
|---|---|---:|---:|---:|
| | | $Li^7$ | $Li^6$ | $CH_3CD_2Li^7$ |
| $C_2H_5Li$ | $(C_2H_5)_2O$ | 492 | – | – |
| $C_2H_5Li$ | $(n\text{-}C_4H_9)_2O$ | 512; 568 | 533, 605 | 479, 570 |
| $C_2H_5Li$ | benzene + $(C_2H_5)_2O$ | 511 | – | – |
| $C_2H_5Li$ | benzene + $(\text{iso-}C_5H_{11})_2O$ | 515 | – | – |
| $C_2H_5Li$ | benzene + $(C_2H_5)_3N$ | 520 | – | – |
| $C_2H_5Li$ | $(\text{iso-}C_5H_{11})_2O$ | 530, 573 | 529, 600 | – |

It was found that in all the solvents listed there is a lowering of the frequency of the C—Li··· vibration (Table 2), owing to the formation of acceptor–donor complexes with the solvent. The relatively small shift in most of the solvents investigated is apparently connected with the formation of complexes with the solvent without rupture of the original dimeric complex, as was observed by Wittig for phenyllithium in diethyl ether (3).

With an increase in the concentration of the solvent in the system R—Li + ($n$-$C_4H_9$)$_2$O or (iso-$C_5H_{11}$)$_2$O, along with the preservation of bands in the region 530—550 cm$^{-1}$, weak bands with higher frequencies appear, retaining the corresponding isotopic shift among themselves ($C_2H_5Li^7$ 568 cm$^{-1}$; $C_2H_5Li^6$ 605 cm$^{-1}$; $CH_3CD_2Li^7$ 570 cm$^{-1}$). The appearance of these bands may be connected with partial disruption of the dimeric complex and the formation of a simpler complex of the type



$$RLi : O \begin{matrix} R \\ R. \end{matrix}$$

Under the action of ethers and amines, the deformation and stretching vibrations of C—H and C—D behave analogously to what was described above upon dilution with benzene or hexane, but at considerably smaller dilutions with the donor solvent.

Thus, in the infrared spectra of solutions of organolithium compounds, frequencies are observed which characterize the formation of hexameric and dimeric complexes. For the dimeric complex, the characteristic frequencies are those of stretching vibrations of the C—Li groups in the region 530—570 cm$^{-1}$. In the case of the hexameric complex, the frequencies of the dimeric complex are retained, though somewhat shifted toward longer wavelengths; in addition, an additional frequency at 920 cm$^{-1}$ is observed, as well as bands in the region 870—1100 cm$^{-1}$; the latter may be assigned to deformation vibrations of the $\alpha$-$CH_2$ groups of molecules participating in the formation of complex aggregates.

The deformation vibrations of the C—Li··· groups in the complex apparently lie in a more long-wavelength region of the spectrum; their study will make it possible to investigate the structure of these complexes more deeply.

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*Note: Figure translations are in progress. See original paper for figures.*

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