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Mixed aggregates between acetylenic lithium compounds and lithium thiocyanate in non-aqueous solutions

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Abstract

The following mixed aggregates between hexynyllithium $\text{BuC}\equiv\text{CLi}$ and lithium thiocyanate, LiNCS , have been characterized by infrared spectroscopy in the $\bar{\nu}(\text{C}\equiv\text{N})$ region: the mixed species $\text{Li}_2(\text{BuC}\equiv\text{C}(\text{NCS}))$ in tetrahydrofuran and dioxane and all three mixed tetranuclear species $\text{Li}_4(\text{BuC}\equiv\text{C})_3(\text{NCS})$, $\text{Li}_4(\text{BuC}\equiv\text{C})_2(\text{NCS})_2$, $\text{Li}_4(\text{BuC}\equiv\text{C})(\text{NCS})_3$ in triethylamine. In the same conditions similar species are formed between $\text{PhC}\equiv\text{CLi}$ and LiNCS .

1. Introduction

Organolithium compounds RLi and lithium alkoxydes ROLi generally form well defined aggregates in solution: dimers, tetramers and in some cases hexamers. During the past few years the investigation of the aggregates in relation to chemical reactivity has become more extensive [1–3]. Several recent reviews [4–7] have been devoted to the results obtained in solution by spectroscopic and by thermodynamic methods and also in the solid state. The structures of several new compounds have been determined and they give a more precise knowledge of similar species in solution.

Mixed aggregates between two different alkylolithiums RLi and $\text{R}'\text{Li}$ were first identified by NMR spectroscopy in 1966 [8]. The aggregation of lithium compounds in weakly polar solvents is not limited to lithium salts. In 1965 [9] we gave the first evidence of a tetrameric salt species $(\text{LiBr})_4$, in Et_2O and we later determined its structure by EXAFS [10]. Novak and Brown [11] characterized the mixed aggregate $\text{Li}_4(\text{CH}_3)_3\text{Br}$ between $(\text{LiBr})_4$ and $(\text{LiCH}_3)_4$ by NMR

spectroscopy. Quite recently Jackman *et al.* [12] identified the mixed aggregate $\text{Li}_4\text{P}_3\text{ClO}_4$ ($\text{P} = 3,5$ -dimethylphenolate) in diethyl ether solution and this result showed that even a slightly basic anion such as ClO_4^- can be introduced into mixed aggregates.

NMR spectroscopy does not give information of value when anion exchanges between aggregates are fast, as at room temperature. There is no such limitation with vibrational spectroscopy and aggregates in fast exchange can be detected provided that at least one frequency in the anions can be found which is sensitive to the aggregation state of the solute. By using $\bar{\nu}(\text{C}\equiv\text{N})$ of SCN^- we were able to identify the aggregates of alkali metal thiocyanates MSCN [4] in solution. We showed that M^+ is generally bonded to SCN^- through the nitrogen atom of SCN forming aggregates $(\text{MNCS})_p$. Consequently we will write lithium thiocyanate as LiNCS (“isothiocyanate”) although its molecular formula is commonly written as LiSCN .

We first investigated lithium mixed aggregates formed between Li_pX_p and $(\text{LiNCS})_q$ in LiX-LiNCS ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) solutions [13]. The SCN^- ion is a spectroscopic probe which is introduced into Li_pX_p . This method was then extended to the mixed RLi-LiNCS ($\text{R} = \text{alkyl}$) aggregates [14].

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In this work we investigated the series of mixed aggregates between LiNCS and $\text{RC}\equiv\text{CLi}$. The thiocyanate $\text{S}-\text{C}\equiv\text{N}^-$ and alkynyl $\text{RC}\equiv\text{C}^-$ anions have similar structures, but SCN^- is far less basic than $\text{RC}\equiv\text{C}^-$ because it shares its negative charge with the sulfur atom. As a consequence HNCS in water is nearly a strong acid whereas alk-1-yne have little acidic behaviour. The investigation of $\text{RC}\equiv\text{CLi}-\text{LiNCS}$ mixed aggregates should give some information on the aggregation of $\text{RC}\equiv\text{CLi}$ in solution.

2. Experimental section

Hexynyllithium and phenylethynyllithium were prepared by slow addition of an equivalent amount of hex-1-yne or phenylacetylene to a butyllithium solution in hexane (Aldrich, 2M) [15]. Here the lithiation is limited to the acetylenic proton while the lithiation of propyne goes on to C_3Li_4 in presence of an excess of butyllithium. The reaction was carried out under dinitrogen. Lithiation resulted in a cloudy colourless precipitate. Hexane was removed by evaporation under vacuum and the lithium compound remained as a very fine powder. It was nearly insoluble in open chain ethers and in triethylamine, but it could be dissolved in LiNCS solutions and in pure dioxane or tetrahydrofuran (THF).

Infrared spectra were recorded on a IRFT Bruker IFS 85 spectrometer with a resolution of 2 cm^{-1} . Calcium fluoride windows were chosen because of their chemical inertness although they are transparent only beyond 1000 cm^{-1} . The spectra of solids were obtained in Nujol mulls. Dielectric measurements were performed on a DM01 dipolmeter from WTW with a DFL1 cell.

3. Hexynyllithium and phenylethynyllithium

Before lithiation, acetylenic hydrocarbons show a weak infrared $\bar{\nu}(\text{C}\equiv\text{C})$ band at 2117 cm^{-1} ($\epsilon = 7.7\text{ mol}^{-1}\text{ l cm}^{-1}$) in hex-1-yne and at 2110 cm^{-1} ($\epsilon = 6.8\text{ mol}^{-1}\text{ l cm}^{-1}$) in phenylacetylene. In their solid lithium derivatives this band remains weak but it shifts to lower wavenumbers, 2046 cm^{-1} ($\text{BuC}\equiv\text{CLi}$) and 2034 cm^{-1} ($\text{PhC}\equiv\text{CLi}$). The value of $\bar{\nu}(\text{C}\equiv\text{C})$ in $\text{BuC}\equiv\text{CLi}$ is the same as in propynyllithium [15]. The electronic structure of this compound has been investigated by *ab initio* methods [16]. The shift to lower wavenumbers with lithiation can be explained by the electron displacement from the CH bond to the $\text{C}\equiv\text{C}$ group which

increases the interelectronic repulsions within this group. In dioxane or THF solutions the bands of the lithium derivatives shift by $4-6\text{ cm}^{-1}$ to higher wavenumbers relative to the value in the solid compounds. The bandwidth of $\bar{\nu}(\text{C}\equiv\text{C})$ before and after lithiation is $15 \pm 1\text{ cm}^{-1}$.

In solutions, as in solid solvates, the solvating molecules play an important role in setting up a dimeric or a tetrameric state of aggregation. A minor change in the solvent geometry, especially in its shape and bulk is often sufficient to change this. For instance LiNCS is dimeric in open chain ethers and tetrameric in branched ethers [17]. Solid $\text{PhC}\equiv\text{CLi}$ solvated by $\text{Me}_2\text{N}(\text{CH}_2)_n\text{NMe}_2$ is dimeric when $n = 2$ [18] and tetrameric when $n = 6$ [19].

In THF solutions at -108°C it has been shown by cryoscopy that $\text{PhC}\equiv\text{CLi}$ is a dimer [20] while $^1\text{BuC}\equiv\text{CLi}$ seems to be in part tetrameric. Hässig and Seebach [21] confirmed the dimeric state of $\text{PhC}\equiv\text{CLi}$ by ^{13}C and ^6Li NMR spectroscopy at low temperature and they identified the mixed species $\text{BuPhC}\equiv\text{CLi}_2$ and one mixed tetranuclear species $\text{Bu}_3\text{PhC}\equiv\text{CLi}_4$ by progressive addition of BuLi.

Usually a temperature increase favours the aggregation of lithium compounds [22,23]. Consequently they are at least dimeric and probably in part tetrameric at room temperature in tetrahydrofuran (THF). It is the same in dioxane, which is a slightly more associating solvent towards LiNCS. The hexynyl and phenylethynyllithium solutions in these solvents exhibit one $\bar{\nu}(\text{C}\equiv\text{C})$ band. However this is not sufficient to show that there is only one species because it is rather broad and because the sensitivity of $\bar{\nu}(\text{C}\equiv\text{C})$ to the coordination mode of carbon with lithium is not known.

The Raman spectrum of $\text{BuC}\equiv\text{CLi}$ shows one $\bar{\nu}(\text{C}\equiv\text{C})$ band at the same wavenumber as in infrared spectrum, while there are two $\bar{\nu}(\text{C}\equiv\text{N})$ bands in $(\text{LiNCS})_4$. It seems that, due to the deformability of the Bu groups, the aggregates are not so symmetrical as in $(\text{LiNCS})_4$. When $\text{BuC}\equiv\text{CLi}$ was synthesized in presence of Et_2O a solid etherate precipitated. Its $\bar{\nu}(\text{C}\equiv\text{C})$ band was shifted slightly to lower wavenumbers (2036 cm^{-1}) and it was much narrower than in the other cases ($\Delta\bar{\nu}_{1/2} = 4.3\text{ cm}^{-1}$). The only similar case of such a narrow band is that from $\bar{\nu}(\text{C}\equiv\text{N})$ in $(\text{LiNCS})_4$ of T_d symmetry [17] and this also indicates tetrahedral symmetry.

As the dipole moment of dioxane is close to zero it is easy to determine whether the dissolved species are polar or not by measuring the dielectric constant ϵ of solutions. We obtained low values $\Delta\epsilon/c$ (between 0.15 and 0.25 M^{-1}) between 0.015 and 0.07 M. This shows that the dipole moments of the aggregates are close to zero. For instance monomeric lithium salt ion pairs LiX give $\Delta\epsilon/c \sim 5-10\text{ M}^{-1}$ [24,25].

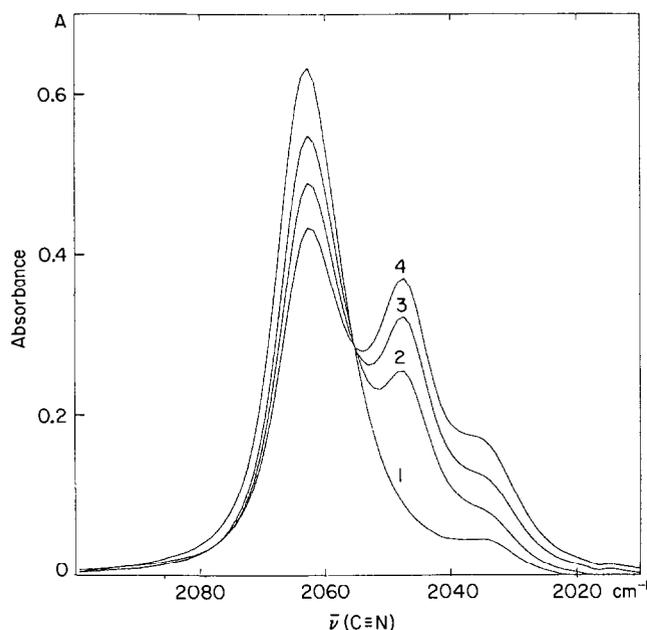


Fig. 1. Infrared spectra of $\text{BuC}\equiv\text{CLi}(c)\text{-LiNCS}$ (0.1 M) solutions in THF. Concentration of $\text{BuC}\equiv\text{CLi}$ (M): (1) 0; (2) 0.1; (3) 0.2; (4) 0.4.

4. Mixed aggregates

Mixed aggregates $\text{BuC}\equiv\text{CLi-LiNCS}$ were studied by using the $\bar{\nu}(\text{C}\equiv\text{N})$ of NCS in the 2000–2050 cm^{-1} region, the same region as for $\bar{\nu}(\text{C}\equiv\text{C})$ in $\text{BuC}\equiv\text{CLi}$. As the molar extinction of $\bar{\nu}(\text{C}\equiv\text{N})$ is roughly a hundred times higher than that of $\bar{\nu}(\text{C}\equiv\text{C})$, the adsorption of the $\text{BuC}\equiv\text{C}$ group is negligible in comparison to that of $\bar{\nu}(\text{C}\equiv\text{N})$ in $\text{SC}\equiv\text{N}$ and $\bar{\nu}(\text{C}\equiv\text{C})$ could not be observed in mixed aggregates with LiNCS.

In our earlier work [17] we showed that the $\bar{\nu}(\text{C}\equiv\text{N})$ value of NCS in $(\text{LiNCS})_p$ and in mixed species is determined mainly by the number of lithiums on each nitrogen atom of NCS: one ($N\text{-}\mu_1$ coordination in LiNCS) $\sim 2060\text{ cm}^{-1}$ (LiNCS), two ($N\text{-}\mu_2$ in $(\text{LiNCS})_2$) $\sim 2040\text{ cm}^{-1}$, three ($N\text{-}\mu_3$ coordination) $\sim 2000\text{--}2020\text{ cm}^{-1}$.

In THF LiNCS is mostly found as the LiNCS monomer ($\bar{\nu} = 2063\text{ cm}^{-1}$) in equilibrium with some rhombic dimer $(\text{LiNCS})_2$ ($\bar{\nu} = 2034\text{ cm}^{-1}$). When an increasing amount of $\text{BuC}\equiv\text{CLi}$ was added to a 0.1 M solution of LiNCS a new band was observed at 2047 cm^{-1} (Fig. 1). Job's method [28] was applied to this system at a total concentration of 0.15 M. The curve (Fig. 2(a)) represents the deviation from additivity ΔA of the absorbance at 2047 cm^{-1} as a function of the mole fraction of LiNCS in the solute. As this curve is symmetrical the mixed species is $\text{RC}\equiv\text{CLi-LiNCS}$ or $\text{Li}_2(\text{RC}\equiv\text{C})\text{NCS}$. The $\bar{\nu}(\text{C}\equiv\text{N})$ value is also typical of $N\text{-}\mu_2$ bonding. Consequently the mixed species is formed by simple replacement of one $\text{SC}\equiv\text{N}$ group by $\text{RC}\equiv\text{C}$ in $(\text{LiNCS})_2$. A similar result has also been observed in dioxane. Whereas $(\text{LiNCS})_2$ is mostly dissociated in LiNCS, the mixed dimer is fairly stable in agreement with the fact that $\text{BuC}\equiv\text{CLi}$ is at least dimeric.

In triethylamine (TEA) LiNCS is almost entirely in the form of $(\text{LiNCS})_4$, whereas in open chain ethers it is found mostly as $(\text{LiNCS})_2$. Consequently TEA is the best solvent for observing mixed tetramers. The addition of LiNCS strongly increases the solubility of $\text{BuC}\equiv\text{CLi}$. The development of the spectrum of a 0.1 M solution of LiNCS in TEA near addition of $\text{BuC}\equiv\text{CLi}$ from 0.02 M to 0.5 M is represented on Fig. 3. The

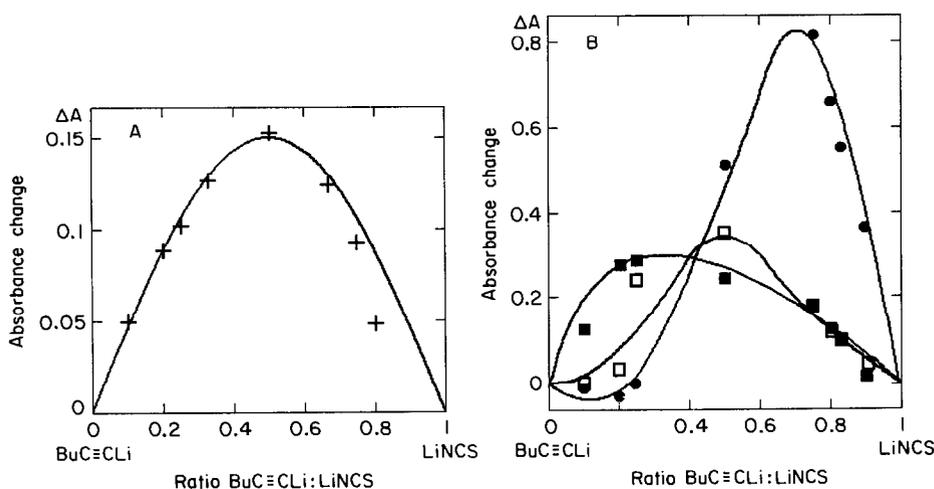


Fig. 2. Job's curves in $\text{BuC}\equiv\text{CLi-LiNCS}$ solutions at a total concentration c . (A) In THF; $c = 0.15\text{ M}$; 2047 cm^{-1} . (B) In TEA; $c = 0.25\text{ M}$; \blacksquare 2020 cm^{-1} , \square 2006 cm^{-1} , \bullet 1999 cm^{-1} .

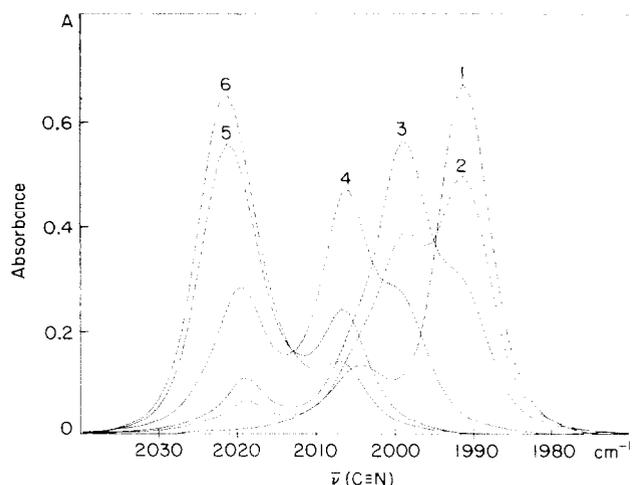


Fig. 3. Infrared spectra of $\text{BuC}\equiv\text{CLi(c)}\text{-LiNCS}$ (0.1 M) solutions in TEA. Concentration of $\text{BuC}\equiv\text{CLi}$ (M): (1) 0; (2) 0.02; (3) 0.03; (4) 0.1; (5) 0.3; (6) 0.5.

($\text{C}\equiv\text{N}$) bands of the three possible mixed tetranuclear species are clearly seen and their stoichiometry was confirmed by Job's method (Fig. 2(b)). The $\bar{\nu}(\text{C}\equiv\text{N})$ values of mixed tetramers and of $(\text{LiNCS})_4$ are reported in Table 1.

As expected for tetrahedral structures the infrared spectra do not show any sign of isomerism of $\text{Li}_2\text{X}_2\text{Y}_2$. There is a regular decrease in $\bar{\nu}(\text{C}\equiv\text{N})$ on replacement of SCN^- by $\text{RC}\equiv\text{C}^-$ and it becomes closer and closer to its value in free SCN^- ($\approx 2050 \text{ cm}^{-1}$). Consequently the strength of the Li-N bond decreases. This is rationalized by the large negative charge on the terminal carbon atom in $\text{RC}\equiv\text{C}^-$. The substitution of SCN^- by $\text{RC}\equiv\text{C}^-$ causes an increase of the repulsions exerted on the remaining SCN^- anions and a weakening in the Li-NCS bond. This is consistent with the mainly ionic character of the lithium bond [26] even if it has some covalent character [27].

The mixed species with $\text{PhC}\equiv\text{CLi}$ was identified in dioxane by its $\bar{\nu}(\text{C}\equiv\text{N})$ at 2042.5 cm^{-1} . In Bu_2O , LiNCS is mostly dimerized with a small proportion of tetramer. The bands of the first two mixed tetramers were observed at 2002 and 2010 cm^{-1} . The band of the third, $\text{Li}_4\text{Y}_3\text{NCS}$ is close to 2025 cm^{-1} but it overlaps with that of $(\text{LiNCS})_2$ at 2028 cm^{-1} . The mixed te-

TABLE 1. $\bar{\nu}(\text{C}\equiv\text{N})$ (cm^{-1}) in $(\text{LiNCS})_4$ and in mixed tetramers

Tetramer	$(\text{LiNCS})_4$	$\text{Li}_4(\text{NCS})_3\text{Y}$	$\text{Li}_4(\text{NCS})_2\text{Y}_2$	Li_4NCSY_3
$\text{Y} = \text{BuC}\equiv\text{C}^a$	1992	2000	2006	2020
$\text{Y} = \text{PhC}\equiv\text{C}^b$	1992	~ 2000	2006	2020
$\text{Y} = \text{Bu}$ [14]	1992	2005	2013	
$\text{Y} = \text{Br}$ [13]	1992			2005

^a In TEA. ^b in Bu_2O .

tramers of $\text{PhC}\equiv\text{CLi}$ were also investigated in Bu_2O and the corresponding spectra are reported in Table 1. The wavenumbers are nearly the same as in $\text{BuC}\equiv\text{CLi}$ mixed tetramer but $\text{Li}_4\text{PhC}\equiv\text{C}(\text{NCS})_3$ gives a weak band of uncertain position (Table 1).

5. Conclusion

The mixed dimer and all three mixed tetramers between $(\text{LiNCS})_p$ and $(\text{RC}\equiv\text{CLi})_q$ have been characterized by their $\bar{\nu}(\text{C}\equiv\text{N})$ values. In earlier papers only the 3-1 compound $\text{Li}_4\text{R}_3\text{X}$ between an organolithium compound RLi and a lithium salt LiX was detected by NMR spectroscopy. This is probably due to the greater lability of the other mixed tetramers. The mixed aggregates are more stable than those from pure $(\text{LiNCS})_p$. This is probably true for those of $\text{RC}\equiv\text{CLi}$ which are difficult to investigate directly by infrared spectroscopy. LiNCS gives mixed aggregates with many different lithium compounds: LiCl , LiBr , $\text{RC}\equiv\text{CLi}$ and RLi . The great variability of bonds to lithium bond is probably related to its large ionic character even in organolithium compounds. As lithium salt aggregates are known to play a role in organic synthesis [1-3] more attention should be given to LiNCS as a complexing agent which is soluble in many organic solvents.

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