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Vibrational Study of Ionic Association in Aprotic Solvents. 11. Formation and Structure of Mixed Aggregates between Lithium Halides and Lithium Thiocyanate

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Mixed aggregates between LiX (X = Cl, Br) and LiSCN have been investigated by Fourier transform infrared spectroscopy in the ν(CN) region. In most weakly polar solvents separate salts are dimerized. In this case a mixed dimer Li_2XNCS is observed in the mixtures, and it has the same rhombic structure as pure dimers. The reactions of formation of mixed dimers from pure dimers are nearly athermic in tetrahydrofuran. In diethyl ether LiBr and LiSCN are tetramerized, and a mixed tetramer Li_4Br_3NCS is detected in mixed solutions. In some ethers mixed tetramers are also formed between LiI and LiSCN.

Introduction

Most alkali-metal halides and pseudohalides are soluble in some polar aprotic solvents. Vibrational spectroscopy has proved to be a valuable tool for the determination of the structure of these solutions.[2,3] In previous papers we established that when the polarity of the solvent is low, the salts are mostly in the form of labile neutral species $(MX)_n$.[4,5] This kind of molecule plays an important role in the mechanism of some carbanionic reactions.[6] Unfortunately spectrometric methods give little information on the nature and on the structure of species in alkali-metal halide solutions. This information must be obtained from more indirect methods: vapor pressure osmometry (VPO),[7] dielectric measurements,[8] and EXAFS.[9]

Owing to the great coordination capabilities of the SCN ligand,[10] an extensive vibrational investigation of alkali-metal thiocyanate solutions has been performed in our laboratory and in other groups.[11] The structure and the solvation of the most common and abundant aggregates, which are $(MNCS)_2$ (M = Li, Na, K) and $(LiNCS)_4$, has been determined.[12-14] We recently identified the mixed aggregate $LiNa(NCS)_2$ in tetrahydrofuran (THF) solutions.[5] Hence we decided to undertake a systematic investigation of another class of mixed aggregates of general formula $Li_{n+n'}X_n(NCS)_{n'}$ where X is an halogen atom (Cl, Br, I). These aggregates should fill the gap between lithium halide and lithium pseudohalide aggregates. Their spectroscopic investigation should also give some indirect information on lithium halide aggregates, which are somewhat elusive. After substitution of the ligand SCN in an alkali-metal halide aggregate this ligand can be used as a probe to investigate the original structure of the aggregate. The strong ν(CN) IR band has proved useful for the determination of the ionic environment.

When LiX and LiSCN are dissolved together in a given solvent, mixed aggregates are most likely to be formed between them if both salts are already aggregated. From existing data[7,15] lithium salts can be ordered as follows according to their increasing degree of aggregation in weakly polar solvents:

$$LiClO_4 \simeq LiI \ll LiSCN < LiBr \ll LiCl \qquad (1)$$

This order is the reverse of the order of the solubilities, and this fact can be easily explained: the salts that are the least soluble are those in which the interionic interactions are the strongest, and these intractions are also at the origin of the stability of small aggregates in solution.

In all solutions the major species which are formed from LiSCN are the free ions (I), the ion pair LiNCS (P), the dimer $(LiNCS)_2$ (D), and the tetramer $(LiNCS)_4$ (T). In some cases small amounts of other species are also observed.[11] Moreover, in a given solvent, at most two consecutive major species are found in the whole concentration range accessible by IR spectroscopy ($\sim 10^{-3}$–1 M). Hence, with the above abbreviations, solvents can be divided into three classes: IP, PD, and DT. For instance, in a solvent of the category PD, LiNCS and $(LiNCS)_2$—or only one of them—are observed in a given solution of LiSCN. Solvents belong to the category IP when their dielectric constant and their donor number DN_{SbCl_5} are sufficiently high. The following condition is fulfilled by solvents of this category:[16]

$$DN_{SbCl_5} + 105(\epsilon - 1)/(\epsilon + 2) > 65 \qquad (2)$$

The separation between classes PD and DT seems to depend essentially on the steric hindrance of the solvent molecules. At the present time all known DT solvents are ethers and tertiary amines. Among the salts that are studied here, those which can be dissolved in DT solvents are always lithium salts.

Our classification has been based on LiSCN for obvious reasons of experimental convenience. However different inorganic 1:1 salts generally exhibit the same qualitative behavior when they are dissolved in a given solvent. For instance LiSCN, LiCl, LiBr, NaBr, NaI, NaSCN and KSCN are all partly dimerized when they are in THF solution. Also LiSCN and LiBr are more or less tetramerized in Et_2O.

As usual, the formula LiSCN will refer to the substance "lithium thiocyanate" without any structural assumption while LiNCS will refer to the ion pair that has an isothiocyanate structure.

Experimental Section

Tetrahydrofuran, dioxolane, and symmetrical ethers were distilled on a 20-plate column and stored on sodium wire. Unsymmetrical ethers were prepared according to a procedure described elsewhere.[13] Other solvents of the best commercial grade were dried on 4-Å molecular sieves. Infrared spectra were registered on a Bruker Fourier Transform IFS 85 spectrometer with CaF_2 cells. Enthalpies were measured by temperature variation between 15 and 45 °C. Temperatures were measured by a thermocouple in the IR cell. Equilibrium constants were calculated after decomposition of the spectra as a sum of two or three bands. Each band

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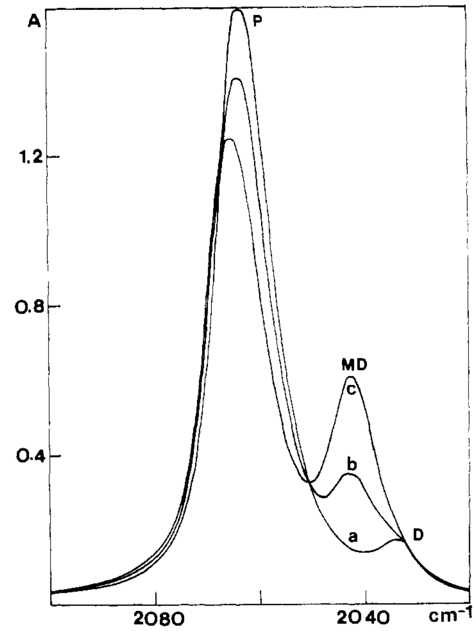


Figure 1. Infrared spectra of LiSCN–LiCl solutions in THF. The concentration in LiSCN is 0.2 M and the concentrations in LiCl are (a) 0 M, (b) 0.2 M, and (c) 0.6 M. P = LiNCS; D = $(LiNCS)_2$; MD = Li_2ClNCS. Cell thickness = 56 μm.

Table I. Infrared Frequencies (cm^{-1}) of Li_2XNCS in Various Solvents

solvent	X = Cl	X = Br
cyclopentanone	$2050._5$	2046
dimethyl carbonate	$2046._5$	2043
isopropyl acetate	$2045._5$	2043
diethyl carbonate	$2044._5$	2042
tetrahydrofuran	$2042._5$	2040
1,3-dioxolane	$2041._5$	2038
1,4-dioxane	$2039._5$	2036

was considered as a sum of Gaussian and Lorentzian contributions having the same bandwidth.

Results and Discussion

Mixed Dimers. It is unlikely to find mixed dimers in solvents of class IP because they are known to be ionizing solvents. Nevertheless we have studied mixed LiX–LiSCN solutions (X = Cl, Br) in three of these solvents: dimethylformamide, tetramethylurea, and propylene carbonate. As expected we found the same ν(CN) absorption bands in the mixtures as in pure LiSCN solutions.

The following solvents of class PD have been studied in this work: cyclopentanone, THF, 1,3-dioxolane, dioxane, and dimethyl and diethyl carbonates. These solvents cover a wide range of dielectric constants (~2–20) and dimerization constants (~ 0.2–200 M^{-1}). Attempts to find mixed LiI–LiSCN mixed aggregates failed, probably because of the low aggregation number of LiI. On the other hand the spectra of mixed LiX–LiSCN solutions (X = Cl, Br) exhibit a new IR band (Figure 1) between those of LiNCS (2064 cm^{-1} in THF) and $(LiNCS)_2$ (2034 cm^{-1}). As a reference, the band of SCN^- is found at 2052 cm^{-1} in Bu_4NSCN–THF solutions. The frequency of the new band is somewhat sensitive to the nature of the solvent (Table I). Its frequency variation is roughly the same as that in other SCN species. It depends on the Gutman acceptor number of the solvent or in most cases on its dielectric constant.[17]

The stoichiometry of the mixed aggregate in THF has been determined by Job's method. At the concentration that has been used the self association of LiNCS is completely negligible (K = 0.24 M^{-1}). On the contrary the dimerization of LiCl is nearly complete (K ~ 1000 M^{-1} according to VPO measurements[7]). This case falls into the field of application of Job's method because both oligomers LiNCS and Li_2Cl_2 are neither associated nor dissociated. The absorbance excess at 2043 cm^{-1} has been plotted in Figure 2 against the ratio of concentrations $x = c_{LiSCN}/(c_{LiCl} + c_{LiSCN})$. This plot being symmetrical, the new species is LiCl, LiNCS, or Li_2ClNCS. The same method has been applied to the LiSCN–LiBr system even though its application is somewhat more questionable here because LiBr is partly associated in THF. However, within the experimental uncertainties Job's plot is also symmetrical, which indicates the formation of Li_2BrNCS.

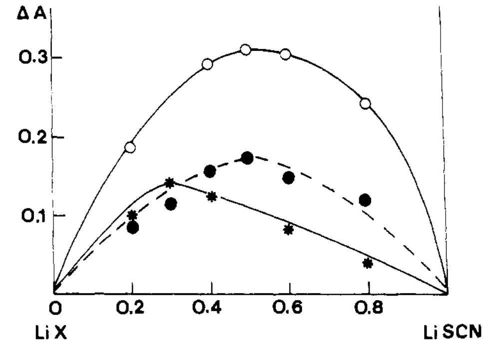
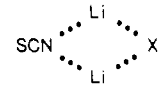


Figure 2. Job's plot of LiX–LiSCN solutions at a total concentration of 0.4 M: (○) X = Cl in THF (2042 cm^{-1}); (●) X = Br in THF (2040 cm^{-1}); (*) X = Br in Et_2O (2004 cm^{-1}).

In our previous work[13] we established that three kinds of coordination of SCN can be found in LiSCN solutions μ_1 (monodentate through N), μ_2 (bidentate through N) and μ_3 (tridentate through N). These categories are readily distinguished by their ν(CN) frequencies μ_1 ~ 2064 cm^{-1}, μ_2 ~ 2040 cm^{-1}, and μ_3 ~ 2000 cm^{-1}. If there are several vibrations due to a mechanical coupling between several SCN groups, the above values refer to the weighed average of the corresponding frequencies. For instance $(LiNCS)_2$ has two ν(CN) vibrations: 2034 cm^{-1} (IR) and 2051 cm^{-1} (Raman). Their average (2042.5 cm^{-1}) is nearly the same as in Li_2ClNCS (2043 cm^{-1}) or in Li_2BrNCS (2040 cm^{-1}). Hence the SCN bonding is the same in all dimers (μ_2) and their structures are similar:



X=NCS, Cl, Br

The equilibrium constant of the reaction LiCl + LiNCS = Li_2ClNCS in THF has been determined by IR spectroscopy and found equal to 30 M^{-1}. Its value is intermediate between the dimerization constants of LiNCS (0.24 M^{-1}) and of LiCl (estimated to be ~1000 M^{-1}).

The enthalpies of the following reactions (X = Cl, Br), in which ligands are exchanged between pure dimers, have been also evaluated from the temperature variations of their equilibrium constants (Figure 3):

$$\tfrac{1}{2}Li_2X_2 + \tfrac{1}{2}(LiNCS)_2 = Li_2XNCS \qquad (3)$$

In order to increase the extent of the dimerization of LiX we have used a mixture of THF (33% in volume) and C_6H_6 as a solvent instead of pure THF. For instance the dimerization constant of LiNCS is about 20 times larger in the mixture than in pure THF. In the calculation it is assumed that LiX is completely dimerized in the mixed solvent. Even for LiBr this assumption is quite reasonable because this salt is already in part dimerized in pure THF.[7] Both reactions have been found to be athermic within experimental uncertainties that come mainly from systematic uncertainties on ε values ($\Delta H°$ = –0.4 ± 1 kcal/mol for Cl and $\Delta H°$ = –0.7 kcal/mol for Br). On the other hand the dimerization reaction of LiNCS is endothermic. The dimerization enthalpy is nearly the same in pure THF (5.5 kcal/mol) and in the mixed solvent (5.7 kcal/mol). Calorimetric measurements[18]

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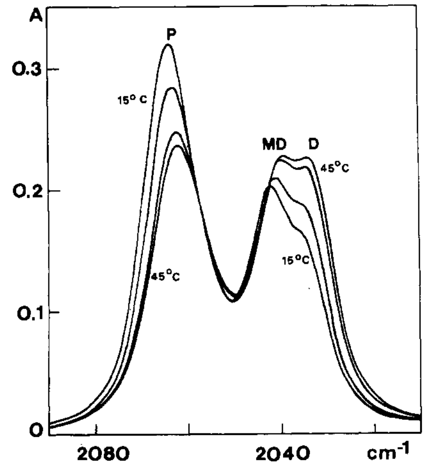

Figure 3. Infrared spectra of a LiCl (0.053 M)–LiSCN (0.036 M) solution in THF (33%) + benzene at temperatures of 15, 25, 35, and 45 °C. Cell thickness = 56 μm.

indicate that the dimerization enthalpy of LiCl in THF is about 1 kcal/mol, which is in agreement with a stability of Li_2Cl_2 greater than that of $(LiNCS)_2$. From these results it can be concluded that the bonding is the same in pure and in mixed dimers and that lithium halide and thiocyanate aggregates are quite similar.

Mixed Tetramers. The investigation of mixed aggregates has also been performed in ethers. These solvents belong to the solvent class that has been called DT (dimer–tetramer). The equilibrium constant of the tetramerization reaction $2(LiNCS)_2 = (LiNCS)_4$ is strongly dependent on the steric hindrance of the alkyl residues R and R′ of the solvent ROR′.[11b,13] When both R and R′ are unbranched (Et_2O, Bu_2O) or when R′ is a methyl group (*t*-BuMeO) the tetramerization constant is very low (~0.1 M^{-1}). Lithium chloride is insoluble in ethers while lithium bromide is moderately soluble. It is completely tetramerized in Et_2O.[4] The tetramers Li_4Br_4 and $(LiNCS)_4$ have the same cubane-like structure.[9,13] Lithium iodide, as well as lithium perchlorate,[19] is highly soluble in ethers and probably less aggregated than LiBr.

LiBr–LiSCN solutions have been investigated in the five above ethers. In all cases a new band is observed at 2003 ± 1 cm^{-1}. This value is very close to the mean ν(CN) frequency in $(LiNCS)_4$:

$$\nu(\mathrm{CN}) = \tfrac{1}{4}\nu(\mathrm{A}_1) + \tfrac{3}{4}\nu(\mathrm{T}_2) = \tfrac{1}{4}2022 + \tfrac{3}{4}1993 = 2000\ \mathrm{cm}^{-1} \qquad (4)$$

Hence in both cases the SCN groups are bonded in the same manner (μ_3). Job's method has been applied to LiBr–LiSCN solutions in Et_2O (Figure 2). Both LiSCN and LiBr are in well-defined states of aggregation: $(LiNCS)_2$ and Li_4Br_4. The maximum of Job's plot is located at the composition 3LiBr, LiSCN. Consequently, in the concentration range that has been used only two tetramers are found in equilibrium: Li_4Br_4 and Li_4Br_3NCS. This behavior is consistent with a decrease in the stability of aggregates from Li_4Br_4 to $(LiNCS)_4$. Finally LiI–LiSCN solutions have been investigated in ethers. In Et_2O we did not find any new absorption band, but one or two such bands were found between 2001 and 2006 cm^{-1} in Bu_2O, *s*-BuEtO, and *i*-PrPrO. These frequencies are in agreement with a μ_3 bonding of SCN, and they are attributed to mixed tetramers $Li_4I_p(NCS)_{4-p}$. The finding of these species in the most associating ethers only is in agreement with a weak aggregation of LiI.

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Neutral Water-Soluble Post-Transition-Metal Chelate Complexes of Medical Interest: Aluminum and Gallium Tris(3-hydroxy-4-pyronates)

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A series of tris(3-hydroxy-4-pyronato)aluminum(III) and -gallium(III) complexes have been prepared with the pyrones pyromeconic acid (Hpa), maltol (Hma), kojic acid (Hka), and chlorokojic acid (Hck). They have been characterized by their IR, UV, ^1H and ^{27}Al NMR, and fast atom bombardment (FAB) mass spectra. The complexes of Hma and Hka are water-soluble (2–60 mM) but retain their neutral charge in water according to conductivity measurements. Variable-pH ^{27}Al NMR spectra demonstrate that $Al(ma)_3$ and $Al(ka)_3$ are stable to hydrolysis in pH 4.5–8 solutions while *n*-octanol/water partition coefficients show that the most water-soluble complexes—$Al(ma)_3$ (60 mM) and $Ga(ma)_3$ (31 mM)—are also the most lipophilic. Preliminary toxicity studies show that $Al(ma)_3$ is extremely neurotoxic.

Introduction

Active investigations, in the past 30 years, of the role that metal ions play in biological processes[1] have been supplemented more recently by studies directed toward the use of metal complexes for medical applications, both therapeutic and diagnostic.[2] In this manner, the bioinorganic chemistry of rarer metals such as technetium, platinum, and plutonium is gradually being integrated with that of the commonly occurring metals such as iron, copper, and zinc to afford a cohesive overview of the varied biological and medical roles that may be played by all the elements in the periodic table. A new, directed approach to the coordination chemistry of many metals results where the basic chemistry is explored with ligands that may either direct the metal in vivo or impart certain desired properties to the resulting complex for subsequent in vivo study.

As recently as 1974, aluminum was regarded as a generally benign element,[3] however, a considerable body of evidence[4-10] has

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