Ionic aggregates of 1-1 salts in non-aqueous solutions: structure, thermodynamics and solvation

Martial Chabanel

Laboratoire de Spectrochimie des Ions, 2 Rue de la Houssinière, 44072 Nantes Cedex, France

<u>Abstract</u> - The field of ionic aggregates finds its place at the boundary between more classical topics in chemistry such as ion, fused salt, coordination and organometallic chemistry. Ionic aggregates are found in very different situations : unsolvated in the gas state, solvated in solid solvates and in solution. In the case of model compounds like LiBr and LiSCN we now have a complete knowledge on the structure and the properties of aggregates in solution. Differences between unsolvated and solvated aggregates arise from the fact that in solvated aggregates the coordination number of lithium is usually equal to 4. As a consequence two main states of aggregation beyond ion pairs are predominent in solution : dimers and tetramers while trimers have not been identified. Ion pairs are strongly polar while dimers and tetramers are non polar. A cubane like structure is the rule in tetramers. Dimerization equilibria are non ideal because there are strong dipole dipole interactions between ion pairs. The three steps of aggregation are entropy driven reactions. Each reaction is a competition between solvent and anion in the first solvation shell of the cation. The solvation numbers of lithium have been measured by infrared in solvent-benzene mixtures. Dimerization equilibria of NaNCS and KNCS are closely similar to those of LiNCS. The coordination modes of SCN in dimers and in $(LiNCS)_4$ are unusual for that ligand (nitrogen μ_2 and μ_3). Ionic and organolithium aggregates are similar although organolithium compounds are even more associated and often give hexamers. Ionic aggregates intermingle with organolithium aggregates to give mixed species. Although underestimated for a long time the role that is played by all these species in organic chemistry is now more and more recognized.

INTRODUCTION

The concept of ion pairing was introduced by Bjerrum in 1926 (Ref. 1) to interpret the activity coefficients of salts of multivalent ions in water and of 1-1 salts in non aqueous solutions. The formation of triple ions was then postulated to explain the rise in conductivity at high concentrations of associated salts (Ref. 2). Later it was proved by vibrational spectroscopy that ion pairs between polyatomic anions and alkali cations have a well defined molecular structure which is testified by their spectroscopic fingerprint.

Ionic association of alkali salts is a part of coordination chemistry of non transition ions although the vocabulary is different. There are no essential differences between an ion pair like CsNCS[‡] and a 1-1 complex like CuNCS, or between an alkali halide dimer and a binuclear complex but alkali ion complexes (ion pairs or aggregates) are very labile and the bonding to counterions and to solvent molecules is typically ionic.

Electrochemistry does not give any valuable information on multimers of ion pairs also called aggregates. Our knowledge of these species has been obtained by non electrochemical methods : thermodynamic measurements, dielectric properties, spectroscopy, NMR and EXAFS. Infrared and Raman spectroscopies have given the most important results on the conditions of formation, the structure, the solvation and the thermodynamic properties of aggregates. The investigation of ionic association by spectroscopic methods in various experimental conditions (solutions in various solvents including liquid ammonia, rare gas matrices, molten salts) has been the subject of several reviews (Ref. 3-9).

This paper will mainly be devoted to alkali halide and pseudo halide association in non aqueous solutions although results on connected topics will also be examined. For instance aggregation in solution and in the gas state are closely related phenomena and consequently a short account of experimental results on gaseous aggregates will give a basis for a better understanding of results in solution.

[‡] *The symbol MSCN either refers to a pure thiocyanate or to the corresponding thiocyanate ion pair while MNCS refers to the isothiocyanate ion pair only.*

AGGREGATES IN THE GAS STATE

The first clear evidence of ionic aggregates has been obtained in alkali halide vapours. The lattice energy of ionic crystals is large and consequently their vapour pressure is negligible at ordinary temperature. For instance the vapour pressure of alkali halide crystals M^+X^- becomes equal to 10^{-2} torr at temperatures ranging from 800 to 1200 K. The vapours are made up of monomers MX (or ion pairs), dimers M_2X_2 (or quadrupoles) and in some cases of trimers. Miller and Kusch (Ref. 10) identified these species in 1953 by measuring the molecular velocity distribution in the vapours. It was then shown by electron diffraction (Ref 11, 12) and by IR in rare gas matrices (Ref. 13, 14) that the dimers have a rhombic structure. Consequently they behave like pure quadrupoles without any dipole moment. This result explains why no other absorption bands than those arising from ion pairs can be found in the microwave spectra of alkali halide vapours (Ref 15). In the case of lithium halides small amounts of tetramer were found by mass spectrometry (Ref. 16). The structure and the binding energy of oligomers have been calculated by different ionic models which were compared by Berkowitz et al. (Ref. 17). Ab initio calculations have been performed on oligomers of LiF up to the hexamer (Ref. 18).

Copper I (Ref. 19), silver I (Ref. 20) and thallium I (Ref 21) halide vapours are made up of monomers, dimers and sometimes higher aggregates. It has been shown by photoelectron spectroscopy (Ref. 22) that the structure of Tl_2F_2 is linear and not rhombic as in alkali halide dimers. The vapours of KCN are mostly dimerized above 700 K with small amounts of trimers (Ref. 23). Dimers of oxyanion (NO_3^-, ClO_3^-, ClO_4^-) alkali salts have been identified in argon matrices (Ref. 6). Finally large ionic clusters have been prepared by ion bombardment of alkali halides (see for instance Ref. 24) but they are not in thermodynamic equilibrium with the environment.

AGGREGATES IN SOLUTION: THE ORIGINS

From the discovery of the electrical properties of aqueous ionic solutions by Volta in 1800 their structure has constantly been a subject of debate. The first hypothesis of undissociated electrolytes by Grotthuss was superseded by Arrhenius assumption of incomplete dissociation (1887) even in strong electrolytes solutions. This hypothesis was ruled out in Debye and Hückel theory of complete dissociation (1923). This last theory and its extensions has been the keystone of most subsequent interpretations in both aqueous and non aqueous solutions. Free ions at infinite distances represent an ideal state of reference. Deviations from the ideal behaviour are explained by interionic forces.

Most 1-1 salts are completely dissociated in water while in non aqueous solutions ion pairing becomes more and more extensive when the solvent polarity is decreased. In low dielectric constant solvents ($\varepsilon < 10$) the amount of free ions may even be negligible. In such solvents molecular ionogens like HCl, HNO_3 or HCOOH behave like other protic molecules. On the contrary 1-1 salts are ionic ionogens and intermediate stages of aggregation may be found between ion pairs M^+X^- and the crystal which is an infinite aggregate $(M^+X^-)_\infty$.

At the beginning of the century colligative properties were extensively used for the determination of molecular masses. Within the ideal dilute solution model these measurements give molecular masses M_s in solution. The results are expressed as aggregation numbers $\bar{n} = M_s/M$ where M is the formal molecular mass. It was shown in 1915 by cryoscopy (Ref. 25) that LiI, $LiNO_3$ and NaI are in part dimerized in acetic acid. The first systematic investigation of aggregates was undertaken in 1934 by Kraus and his group (Ref 26-28). They especially studied trialkyl and tetraalkyl ammonium salts in non polar solvents (benzene and dioxane). They measured the dipole moments of their ion pairs and of $AgClO_4$. They showed that in some cases the aggregation number does not go far beyond 2 while in other cases it increases steadily with concentration up to large values (c.a. 30). Similar results on alkylammonium salts in benzene were later obtained by Kertes et al. (Ref 29). In 1953 Ekelin and Sillen (Ref. 30) investigated $LiClO_4-Et_2O$ solutions by vapor pressure measurements and other techniques. They concluded that probably a large series of ether-$LiClO_4$ complexes are formed and that the ratio ether/$LiClO_4$ in them is between 1 and 2. During the following ten years there was no interest for the problem of aggregates in solution and even their existence seemed dubious to many scientists involved in solution chemistry.

THE IDENTIFICATION OF ION PAIRS AND AGGREGATES IN SOLUTION

In 1963 we investigated LiBr–ZnBr$_2$ complexes in Et$_2$O by measuring the static dielectric constant ε of solutions (Ref. 31). These measurements were possible at low frequency because concentrations of free ions were extremely small. As expected ZnBr$_2$, LiZnBr$_3$ and Li$_2$ZnBr$_4$ were found to be very polar (~5–10 D) while LiBr was non polar. Consequently LiBr could not exist as ion pairs in Et$_2$O but as non polar aggregates only. Its apparent degree of aggregation as measured by VPO was found equal to 4 at all concentrations between 0.1 and 1 M (Ref. 32). At the same time Talalaeva and Rodionov (Ref. 33) obtained lower values (2–2.4) by ebullioscopy. The ebullioscopic results from Gorin et al. (Ref. 34) have confirmed the validity of our results. We assumed that the structure of Li$_4$Br$_4$ was the same as for a gaseous aggregate. An electrostatic calculation showed that a cubane like structure was the most stable for an unsolvated tetramer but the value of the binding energy calculated from that model was too large compared to the value estimated in the gas state. By solvating the gaseous tetramer with four ether molecules it was possible to find a correct value of its energy in solution. Different ideas were developped by Pettit and Bruckenstein who tried to make a theory of progressive aggregation, but their hypothesis of a trimer (Ref. 35) has been ruled out by our experimental results.

The IR and Raman spectra of alkali halide solutions does not give precise information on the aggregates because the only available vibrations are those of the monoatomic ions usually called cage vibrations (Ref. 5,8). They give broad low frequency bands which are seen in IR only and frequency shifts are difficult to interpret. On the contrary internal vibrations of polyatomic anions usually give narrow bands which are sensitive to ionic association. Pseudo halides, especially thiocyanates, are the best candidates for the investigation of aggregates by vibrational spectroscopy. Firstly their physico chemical properties are very close to those of halides. Secondly pseudo halides have an intense vibration in the 2000–2200 cm-1 region where most solvents have a good transparency.

The solubility of cyanides, cyanates and azides in organic solvents is generally low, their anions are ambidentate and their two coordinating sites are similar or equivalent. Thiocyanate also is ambidentate but in many cases the nitrogen site is preferred to the sulphur site. For instance lithium thiocyanate is closely similar to lithium bromide and it is highly soluble in many aprotic donor solvents.

As a whole our results on LiSCN have confirmed that the association equilibria are very simple and that in all aprotic solvents predominant species belong to four categories : free ions (i), contact ion pair (p), dimer (d) and tetramer (t). The thiocyanate species have been identified by characteristic IR or Raman frequencies. In a given solvent only one of the three following equilibria has been observed (Ref 36)

$$Li^+ + SCN^- = LiNCS \qquad (i-p)$$
$$2\ LiNCS = (LiNCS)_2 \qquad (p-d)$$
$$2\ (LiNCS)_2 = (LiNCS)_4 \qquad (d-t)$$
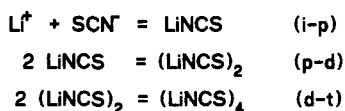
Moreover in certain solvents one species is strongly predominant within the concentration range 0.01–1 M, for instance in DMSO‡ (i), in acetone (p) and in Et$_2$O (d). This circumstance is highly favourable for studying the properties of each species. By using LiSCN as a probe we proposed (Ref. 37, Fig. 1) to separate solvents into two broad classes : ionizing (i-p) and associating (p-d) or (d-t). This classification gives a rough idea of the behaviour of solvents towards salts especially when they are not too different from LiSCN (lithium salts and other alkali halides and pseudo halides). The borderline between both classes depends upon two properties of the solvent : its Gutmann donicity DN and its dielectric constant ε. The first parameter was interpreted as measuring the specific solvation of Li$^+$ and the second the non specific solvation of both ions. Its is striking to see that MeNO$_2$, which has a high dielectric constant (ε = 36) but a low donicity number (DN = 2.7), is a (p-d) solvent relative to LiNCS.

The ν(CN) frequency of each species is slightly dependent on the solvent. In most cases we have observed that it is related to the solvent dielectric constant (Ref. 38). An even better relation to the Gutman Acceptor number AN was then given by Bacelon et al. (Ref. 39). In that region the associated species are better characterized by their frequency shifts $\Delta\nu$(CN) = ν(associated) - ν(SCN$^-$) relative to SCN$^-$ than by their absolute frequencies. In some solvents other species have been observed but always in minor proportions (<10 %). This problem will be examined in the last paragraph.

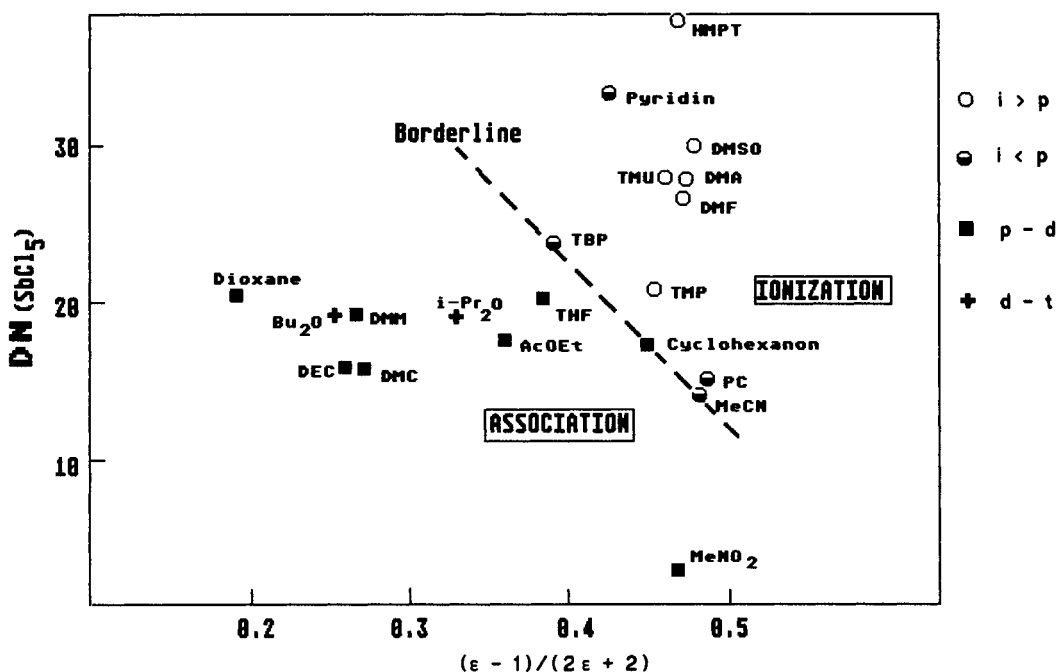$\ddagger$ *Abbreviations are listed at the end of the paper.*

Fig. 1. Associating behaviour of various solvents[±] towards LiSCN at 0.1 M (ε is the solvent dielectric constant, i > p means that predominant species are free ions)

Not only lithium salts but most lithium compounds are aggregated in non polar or slightly polar solvents. For instance a (d-t) equilibrium was found for LiAlH$_4$ in Et$_2$O (Ref 34). Lithium and sodium alkoxides are strongly associated in aprotic solvents (Ref. 40). Their aggregation is closely similar to that of alkyllithium compounds. The most common aggregation number is 4 in polar solvents (THF, pyridine) and 6 in non polar solvents (cyclohexane, benzene). The aggregation of lithium enolates has recently been the subject of an extensive review (Ref. 41). All these compounds are generally considered within the field of organolithium compounds although the border between salts and organolithium compounds is conventional. The aggregation of alkyl and aryl lithiums has also been reviewed several times (Ref. 42, 43).

In a given solvent we have found that the aggregation of lithium salts follows the reverse order of their solubility. For instance in Et$_2$O LiBr is less soluble and more aggregated than LiSCN. This is explained by the relation between solubility and lattice energy : the greater the lattice energy the smaller the solubility. Within ionic models the energy of aggregates is also in close relation with the lattice energy of the crystal. That also explains why the aggregation number $\bar{n}$ of lithium salts follows the reverse order of the anion size : LiClO$_4$< LiBr < LiCl.

The dimerization of alkali salts is not limited to lithium salts but experimental results on other alkali salts are not numerous and systematic trends are difficult to establish. Within a series of alkali salts MX with a common anion X the solubility of LiX in a given solvent is usually the highest. For that reason it is difficult to find good solvents of MX (M ≠ Li) in which MX is aggregated beyond the ion pair. However NaNCS and KNCS are slightly soluble in THF and dioxolane and more dimerized than LiNCS (Ref. 44) in agreement with their lower solubility. According to Olander and Day (Ref. 45) the aggregation number of NaAlBu$_4$ in cyclohexane shows a regular increase from 1 at 0.01 M to ~ 6 at 2 M.

As a whole the state of aggregation of a given salt MX depends on the ability of the solvent to disssociate the ionic crystal (MX)$_\infty$ into smaller and smaller units in the following order

Crystal (MX)$_\infty$	?	Tetramer (MX)$_4$	Dimer (MX)$_2$	Ion Pair MX	Free ions M$^+$, X$^-$

‡ *Abbreviations are listed at the end of the paper.*

THE STRUCTURE OF ION PAIRS AND AGGREGATES

In non polar or slightly polar solvents the ionic conductivity of solutions may be extremely low and in this case precise determinations of dipole moments of ion pairs MX are feasible at low frequencies. In practice suitable solvents must have a low dielectric constant and exhibit a (p-d) behaviour. The best choice depends on the salt. Non polar solvents especially benzene (Ref. 46-48) are adapted to a limited number of cases ($AgClO_4$ and some alkylammonium salts). We used DMC ($\varepsilon = 3.1$) for LiNCS, LiBr, $LiClO_4$ and $AgClO_4$ (Ref. 49) while Ting Po I and Grunwald (Ref. 50) used octanoic acid ($\varepsilon = 2.5$) for LiCl. Dielectric increments must be extrapolated to zero concentration in order to suppress the contribution of quadrupoles.

Table I. Dipole moments of some inorganic ion pairs in solution.

Ion Pair	LiCl	LiBr	LiNCS	$AgClO_4$	$LiClO_4$
Solvent	$C_7H_{15}COOH^1$	DMC [2]			
Dipole Moment (D)	6.8^3	8.1^3	10.5	10.9^4	10.6

[1] Ref. 50   [2] Ref. 49   [3] In the gas phase (Ref 51): LiCl 7.1 D ; LiBr 7.3 D
[4] 10.7 D in benzene (Ref. 46)

The results (Table I) are close to the values which can be expected for contact ion pairs. Moreover the dipoles moments of LiCl and LiBr are in excellent agreement with the results obtained in the gas phase (Ref. 51) and consequently the ionic character of the bonding is essentially the same in both cases. However there must be some "freezing" of solvent dipoles around lithium but either solvent dipole moments were low (DMC) or "free" solvent molecules are actually engaged in non-polar dimers (octanoic acid). Such effects are small relative to large dipole moments of ion pairs but they become important in non polar aggregates.

Dipole moment values obtained from microwave properties of electrolytes seem to be less reliable. For instance the dipole moment value of $NaClO_4$ in DME is 15.8 D according to Farber and Petrucci (Ref. 52) and 12.2 D according to Badiali et al. (Ref. 53). In this case the second value seems to be more realistic.

Infrared spectra give more information on the structure of LiNCS and other MNCS ion pairs. The $\Delta\nu(CN)$ frequency shifts are nearly the same in $M^+ \cdots NCS^-$, $M^+ \cdots CN^-$ (Ref. 54) and $M^+ \cdots NCMe$ (Ref. 55) which indicates a close similarity in bonding. No splitting has been observed in the $\delta(NCS)$ frequency of LiNCS. This is in agreement with a linear structure of isothiocyanate ion pairs which is the rule in mononuclear isothiocyanate complexes. In the ion pairs between a non transition cation M^{z+} and SCN^- we observed that the $\nu(CS)$ frequency shift is proportional to the polarizing power $P = z/(rS_{eff})$ of M^{z+} (Ref. 56, Fig. 2a). On the contrary $\Delta\nu(CN)$ also depends on the polarizability α of M^{z+} (Fig. 2b). This explains why $\Delta\nu(CN)$ values may be either positive (e.g. Li^+, Al^{3+}) or negative (e.g. Tl^+, Pb^{2+}).

$$\nu(CS) = 735 + 21._7 \, P$$
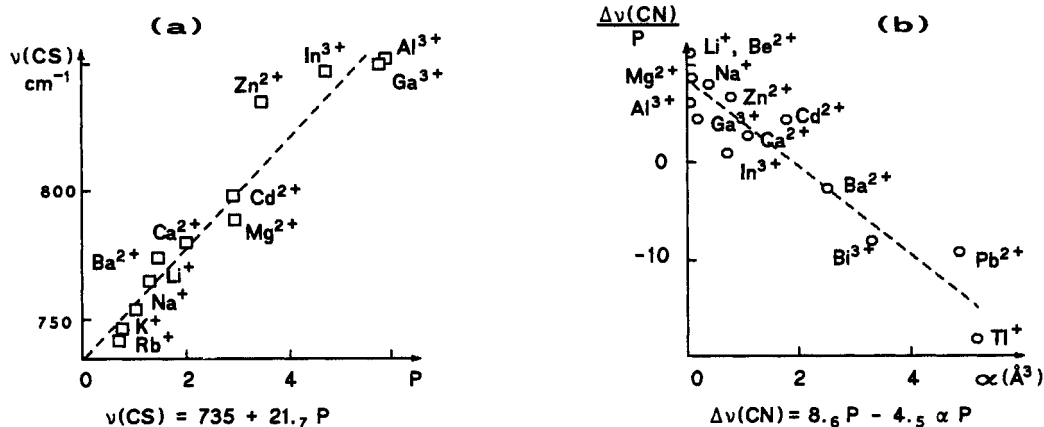
$$\Delta\nu(CN) = 8._6 \, P - 4._5 \, \alpha \, P$$

Fig. 2. (a) One parameter variation of $\nu(CS)$ and (b) two parameter variation of $\Delta\nu(CN)$ in MNCS.

We have demonstrated by ^{15}N NMR (Ref. 57) that $(LiNCS)_2$ also is nitrogen bonded (Fig. 3) i.e. has an isothiocyanate structure in agreement with IR results. The same result has been shown by IR for ion pairs and dimers of NaSCN and KSCN (Ref. 44) and for ion pairs of SCN$^-$ with most cations. However the typically soft Ag$^+$ ion gives a thiocyanate ion pair AgSCN in DMTF (Ref. 58) and in liquid ammonia (Ref. 59). In slightly polar solvents (THT-CS$_2$ mixtures) CuNCS probably dimerizes into a cyclic dimer where the SCN group is in a bridging position between both copper ions (Ref. 60).

Ion pair LiNCS
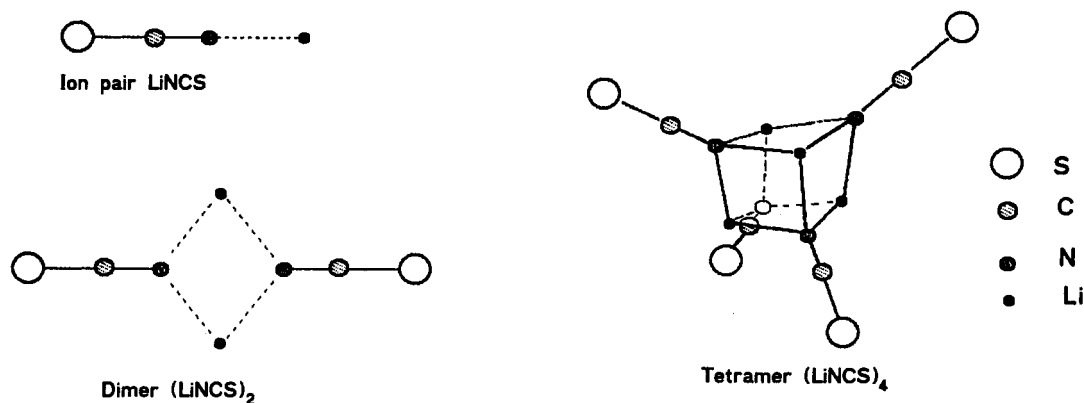
Dimer (LiNCS)$_2$

Tetramer (LiNCS)$_4$

○ S
◉ C
◍ N
● Li

Fig. 3. Structure of the LiNCS oligomers

In $(LiNCS)_2$ observed IR and Raman frequencies are slightly different (Ref. 57, 61) and consequently this aggregate is centrosymmetrical (rule of mutual exclusion). The removal of the $C_{\infty v}$ symmetry of SCN is confirmed by the splitting of the $\delta(NCS)$ frequency of $(LiNCS)_2$. The non polar structure of $(LiNCS)_2$ is in agreement with dielectric results when one takes a non ideal model of association. This problem will be considered in the paragraph on the thermodynamics association.

The vibrational spectrum of $(LiNCS)_4$ exhibits two bands at 2022 cm^{-1} (Raman pol.) and 1993 cm^{-1} (IR, Raman unpol.). Moreover the first band is completely polarized ($\rho < 0.02$). These results demonstrate the T_d symmetry of this aggregate (Ref. 62) and consequently it has a cubane like structure (Fig. 3).

The $\Delta\nu(CN)$ values in $(LiNCS)_2$ and $(LiNCS)_4$ are negative while $\Delta\nu(CN)$ values are always positive in iso-thiocyanate complexes $M(NCS)_p$ of hard non transition cations. In these complexes (for instance LiNCS) each SCN group is bonded to one cation only (nitrogen μ_1 bonding) and the MNCS group is linear. On the contrary in $(LiNCS)_2$ the SCN group is bonded to two Li$^+$ ions (nitrogen μ_2 bonding) and the LiNCS groups are non linear. In a similar manner $(LiNCS)_4$ exhibits a nitrogen μ_3 bonding. When we determined the structure of the dimer these new kinds of bonding were unknown in the solid state. The nitrogen μ_2 bonding has been afterwards identified in $(Bu_4N)_3Re_2(NCS)_{10}$ ($\Delta\nu(CN) \sim -150$ cm^{-1}) (Ref. 63) and in $Ni_3(NCS)_6L_6,2H_2O$ where L is an organic ligand ($\Delta\nu(CN) \sim -50$ cm^{-1}) (Ref. 64). The μ_3 bonding does not seem to have been identified yet in the solid state. It is interesting to see the regular variation of IR and Raman frequencies with the number of lithium atoms which are fixed on nitrogen (Fig. 4). The break observed in the $\nu(CN)$ frequency variation when the second Li$^+$ is attached correspond to the appearance of the non-linear coordination of NCS. The fact that $\Delta\nu(CN)$ is negative in μ_2 or μ_3 bonding is probably due to a transfer of bonding π electrons of CN to Li$^+$.

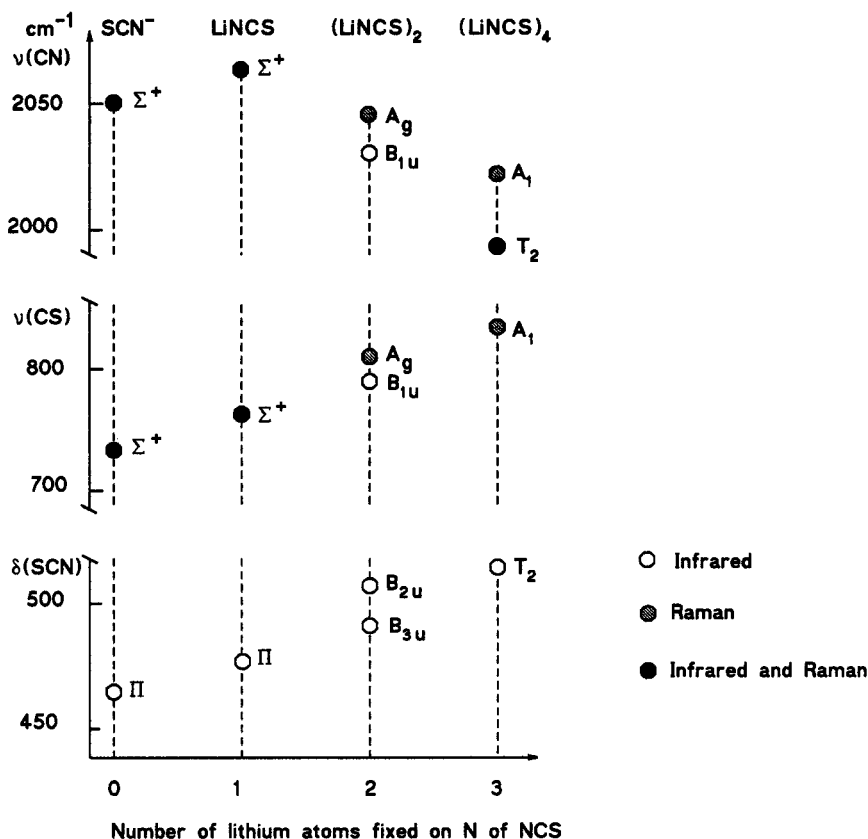**Fig. 4. The vibrational frequencies of SCN in LiNCS oligomers.**

In the EXAFS spectrum of $(LiBr)_4$ in Et_2O (Ref 65) we observed oscillations that give a Br–Br distance (3.9 Å) which is exactly the same as in solid lithium bromide. This result gives a direct evidence of a multimer of LiBr. Moreover the number of neighbours in contact with each Br is equal to 3 and that is only possible with a cubane like structure of $(LiBr)_4$.

THERMODYNAMICS OF AGGREGATION

The succesive steps of the LiNCS association are (i–p), (p–d) and (d–t). We have obtained the thermodynamic parameters of these reactions by studying the equilibria at different temperatures in some typical aprotic solvents (Ref. 66). All three steps are entropy driven reactions. This is an aspect of the competition of anion and solvent molecules in the first solvation shell of Li^+ according to the scheme

$$Li^+, 4S + X^- = LiX, 3\,S + S = \tfrac{1}{2}(LiX, 2S)_2 + 2S = \tfrac{1}{4}(LiX, S)_4 + 3S$$
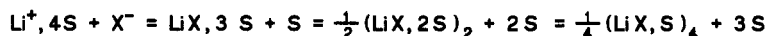
$\Delta S =$	4 R	2.5 R	4.5 R

These values can be compared to the entropies of melting of solvents, about 4 – 6 R, for instance 5.2 R for DMC (Ref. 67). One of the solvent molecules which are frozen in the first solvation shell of the aggregate is released in each step. This description gives the right order of magnitude although many effects are ignored : symmetry, non specific solvation, degrees of freedom in the aggregates.

The (p–d) equilibrium in DEC and in other slightly polar solvents is strongly non ideal at least down to 0.01 M (Ref. 68). The thermodynamic dimerization constant K is then obtained from the extrapolation of the apparent constant $K_{app} = c_d/c_p^2$ at zero concentration. It is reasonable to assume that deviations from ideality are mainly due to ion-pairs as suggested by Friedman (Ref. 69) while non polar dimers behave in an ideal manner. Consequently the activity coefficient γ_p of the ion pair at each concentration c is deduced

from the ratio K_{app}/K. It has been found that $\ln(\gamma_p)$ depends linearly upon the concentration c_p in ion pairs (Fig. 5a). In Fig. 5b the real behaviour of NaSCN in THF is compared to the behaviour which should be observed if the solution was ideal.
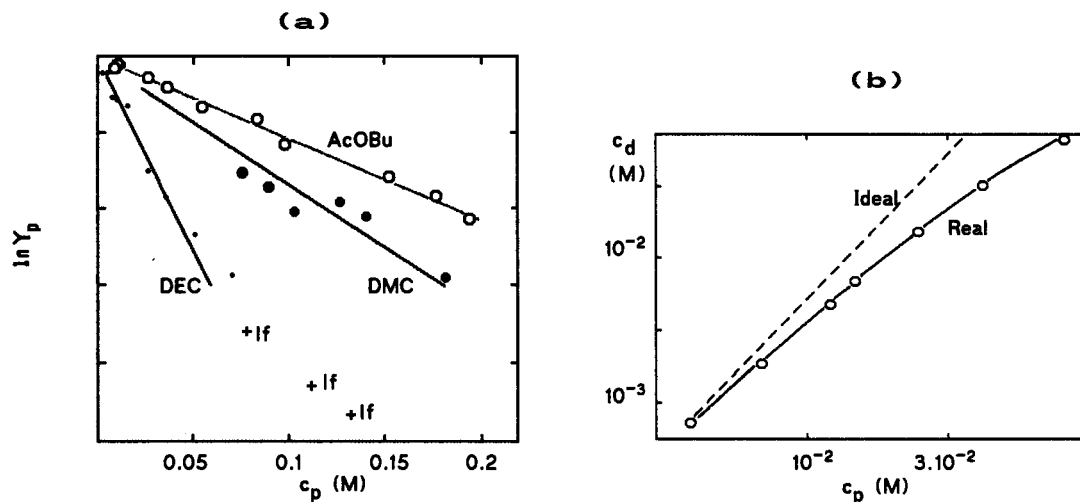

Fig. 5. **(a) System LiSCN- donor solvent** : $\ln(\gamma_p)$ of LiNCS as a function of c_p (lf = liquid film)
          (b) System NaSCN - THF (logarithmic scales): ideal (dotted line) and observed (full line)

These results can be interpreted either by dipole dipole interactions between ion pairs or by the formation of a loose dimer which cannot be distinguished by spectroscopy from the ion pair. Both models are nearly equivalent and give a correct description of non specific interactions between ion pairs. The non ideality of ion pair solutions is similar to that of ion solutions which is interpreted by the Debye and Huckel theory. However ion pair-ion pair interactions decrease faster with concentration than ion-ion interactions Consequently the variation of $\ln\gamma_p$ is linear in c_p while for ions the variation in $\ln\gamma_i$ is linear in $\sqrt{c_i}$. In a similar manner a strong decrease of K_{app} with concentration has been recently observed by Inoue et al. for the dimerization of $LiAsF_6$ in MeTHF (Ref. 70).

It must be noticed that activity coefficients of ion pairs are necessary for giving a complete interpretation of dielectric measurements. Such an interpretation can be made by assuming either an ideal behaviour of the dimerization equilibrium (Ref. 48, 49) or a zero dipole moment of the quadrupole (Ref. 47). Both asumptions give a correct fit of experimental measurements and the same value of the ion pair dipole moment but the values of dimerization constants and of the dimer dipole moment are completely different. The case of LiNCS provides a good example of a non polar quadrupole as shown by spectroscopy. We have shown that when activity coefficients are introduced the dielectric measurements are correctly interpreted (Ref. 68). Delsignore et al. (Ref. 71) reached the same conclusions while ignoring Ref. 68.

SOLVATION OF AGGREGATES

The first evidence of aggregation has been given by thermodynamics (colligative properties) and confirmed by spectroscopy. In a similar way solvation of aggregates has been confirmed by spectroscopy. In alkali salt solutions it is often possible by IR to differentiate the free solvent molecules from those which are bonded in the first solvation shell of the cation. To do that one or more solvent vibrations which are sensitive to cation-solvent interactions must be found. As for cation anion interactions the best sensitivity is achieved with lithium salts. In dilute solutions the IR band due to bonded molecules is blurred by that due to free molecules which are in considerable excess. On the other hand in concentrated solutions the results are not representative of dilute aggregates. The trick is to replace most of the free solvent by a cosolvent which must be transparent in the zone and sufficiently inert to exert a negligible competition for solvation. However if the cosolvent is completely inert (e.g. alkanes) ionic solutions usually separate into two phases of very different compositions. This demixing is due to dipole dipole interactions between ion pairs (Ref. 69). Nitromethane (Ref. 72) or even benzene may be used as weakly polar or non polar cosolvents.

Pure benzene does not dissolve lithium salts but when a donor solvent is added either a cosolubility of LiNCS with the solvent is observed or a demixing (Ref. 73). In the first case the Solvent/Lithium ratio gives an upper limit of the solvation number of Li^+. A more precise evaluation of that number is obtained by substracting the free solvent concentration which is measured by its specific IR band (Fig. 6 b). The fact that benzene is predominant in the mixture causes an important increase in the aggregation relative to the solution in the pure solvent. The new state of aggregation is obtained by the analysis of the IR spectrum in the $\nu(CN)$ region (Fig. 6a). The coordination number of Li^+ is the number of anions plus the number of bonded solvent molecules. It has been found to be significantly lower than 4 (3.5 - 4). This result might be due to a slight competition of benzene with the polar solvent in the first solvation shell of Li^+.
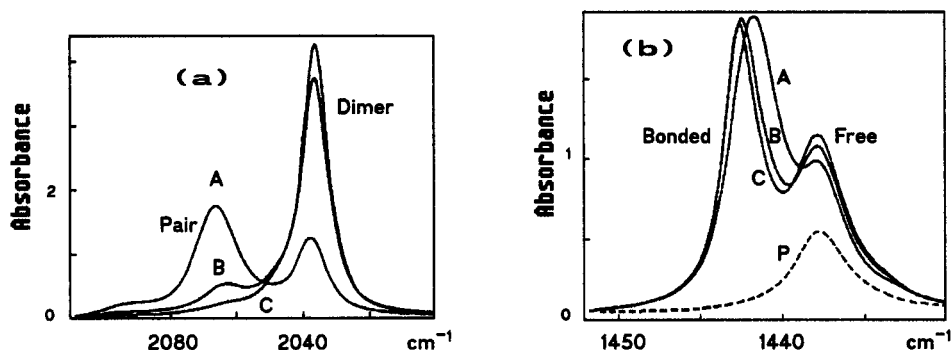

Fig. 6. Infrared spectra of LiSCN-pyridine-benzene solutions (a) in the $\nu(CN)$ region of SCN and (b) in the $\nu(CNC)$ region of pyridine. Solution A : LiSCN = 0.8M ; Pyridine = 3M ; Solutions B and C = A diluted 4 and 16 times in benzene ; solution P : pyridine (0.25 M) in benzene.

In pure solvents the steric hindrance of the solvent in the vicinity of the donor atom seems to be the main factor which governs the dimer-tetramer equilibrium (Ref. 62). This factor has been put into evidence by studying the (d-t) equilibrium in ethers ROR' with p = 0, 1 or 2 branched aliphatic chains (R or R') containing two carbon atoms or more. The following results have been obtained (c $\sim$ 0.01 M)

p = 0 (Et_2O, Bu_2O)	p = 1 (i-PrOPr, sec-BuOEt)	p = 2 (i-Pr_2O)
pure dimer	d - t equilibrium	pure tetramer

If the solvent is not bulky (Et_2O) the salt is dimerized because Li^+ can accomodate two solvent molecules in its first solvation shell which contains four ligands. In a bulky solvent (i-Pr_2O) Li^+ can accomodate one solvent molecule only. The second is replaced by a SCN ligand and the association is shifted towards the tetramer. Intermediate cases have been obtained in solvents like isopropyl propyl ether. On the other hand association does not go beyond the dimer in ROMe. Even in *tert*-BuOMe the dimer only is observed because the large steric hindrance of *tert*-Bu is compensated by that of the small methyl group. In a similar manner LiNCS is only dimerized in N-methyl piperidine while tetramerization is complete in triethylamine.

MIXED AGGREGATES BETWEEN LITHIUM SALTS AND ORGANOLITHIUM COMPOUNDS

Mixed aggregates are aggregates which contain at least two different ions of the same sign (anions or cations). The aggregate $LiNa(NCS)_2$ has been identified in THF (Ref. 44). The investigation of mixed aggregates $Li_n(NCS)_pX_{n-p}$ is easier and has been made in several solvents (Ref. 74). In the above formula X is a halide ion and n = 2 or 4. These species give indirect spectroscopic evidence of pure aggregates Li_nX_n of lithium halides especially LiCl. The NCS group is introduced as a spectroscopic probe in these species. The stability of a mixed aggregate is intermediate between that of aggregates from pure salts.

Waack et al. (Ref. 75) identified mixed LiBr - organolithium tetramers in THF. At low temperatures the Li exchange in these species is slow enough to give separate ^{7}Li NMR signals. We have investigated mixed LiSCN - RLi tetramers $Li_4R_{4-p}(NCS)_p$ in Bu_2O (Ref. 76) by IR (R = Me, Bu, *tert*-Bu). Our conclusions are in agreement with those of Waack et al. The thiocyanate group acts as a μ_3 nitrogen bonded ligand and the cubane structure of pure aggregates Li_4R_4 and $Li_4(NCS)_4$ is preserved in these species. Although LiNCS is mostly dimerized in Bu_2O the tetrameric structure of Li_4R_4 prevails in those mixed aggregates.

SOLVATED AGGREGATES IN SOLIDS

In solid solvates of salts the ions may be found in the same coordination states as in solutions (free ions, ion pairs, aggregates) and also as one, two or three dimensional infinite polymers. Unfortunately only a limited number of structures which contain aggregates have been determined in the solid state. Li_2Cl_2 was found in LiCl, dioxane (Ref. 77, angle ClLiCl = 113°). This state of aggregation is usual in dioxane solutions where LiSCN is dimerized. In the solid solvate LiCl, dioxane, H_2O the dimer no longer exists and LiCl ion pairs are formed (Ref. 78). Here the effect is the same as in solutions : the addition of polar solvents causes a disruption of the aggregates. Li_4Cl_4 was found in LiCl, HMPT (Ref. 79). The tetrameric structure is imposed by the large volume of the HMPT molecule. In the solvate LiBr, 2 Acetone the dimer Li_2Br_2 was identified by Amstutz and al. (Ref 80).

In solvates with crown ethers MNCS (M = Li, K, Rb, Cs) may be found as ion pairs or dimers wherein NCS acts as a bridging anion (Ref. 81, 82). Such polydentate ligands show a preorganization of their donor sites which induces distorsions in the structure of ionic aggregates relative to the more simple geometries which are found in solutions. An example is given by Li_2Br_2 in its pentamethyldiethylenetriamine solvate (Ref. 83).

PROSPECTS AND APPLICATIONS

The present description of ionic association has been built around the scheme of successive equilibria between ions, ion pair, dimer, tetramer (or charges, dipole, quadrupole, octupole). At least in certain solvents this scheme is oversimplified as characteristic frequencies of other species are seen by IR and Raman. In lithium thiocyanate solutions these species are always in minor proportions and great care must be exercised to avoid misinterpretations due to impurities. For instance a strong band observed at 2088 cm^{-1} in LiSCN- DMM solutions is not due to $LiSCNLi^+$ as stated by the authors (Ref. 84) but to a hydrogen bonding impurity (probably methanol). These authors (Ref. 85) found a band at 2086 cm^{-1} in LiSCN- THF solutions (c = 0.21 M) which has a similar origin. When the solvent is well purified concentrated solutions (~1 M) exhibit a band in that zone but at a slightly higher frequency (2094 cm^{-1}). A similar band was identified by Bacelon et al. (Ref. 86) and by Perelygin and Klimchuk (Ref. 87) in $MeNO_2$ at 2100 cm^{-1}. The frequency difference (6 cm^{-1}) between the values in $MeNO_2$ and in THF is due to well known dielectric effects. The usual attribution of this band to the triple cation $LiSCNLi^+$ is in agreement with the expected frequency shift value. In NaSCN-THF solutions a similar band was found at 2084 cm^{-1}. Its attribution to $NaSCNNa^+$ is in agreement with the variation of its height with concentration (Ref. 44). However by spectroscopy alone it seems difficult to make the difference between a triple cation $MSCNM^+$ and an open dimer MSCNMNCS and between a triple anion $SCNMNCS^-$ and an ion pair MNCS. The task is made even more difficult by the fact that these aggregates are in important proportions in concentrated solutions only.

When LiSCN is dissolved in unsymmetrical ethers small bands are seen in the $\nu(CN)$ region. In the first case they are due to species whose aggregation number is close to 4. One frequency is as high as 2123 cm^{-1} which indicates a μ_2 or μ_3 sulphur bonding. Unidentified aggregates of LiSCN have also been observed when a slightly polar donor solvent is diluted in benzene (Ref. 73).

Ionic aggregates are important in the field of organic synthesis although their role has often been ignored. For instance LiBr in Et_2O catalyses the decomposition of aryldiazomethanes to cis-stilbenes with a remarkable stereoselectivity (Ref. 88). The specificity of this reaction is probably due to the aggregation of LiBr to $(LiBr)_4$ although such aggregation was not taken into account by the authors. Pocker et al. have written a series of papers (Ref. 89) on the catalysis of organic reactions by ionic aggregates (especially $LiClO_4$ in Et_2O). The catalysis by Li_2Cl_2 was investigated by Corset (Ref. 90). The recent review by Seebach (Ref. 41) on structure and reactivity of ionic aggregates shows the interest which is now taken in that field.

ABBREVIATIONS

Ions and 1—1 salt oligomers : i = free ions ; p = ion pair ; d = dimer ; t = tetramer
Radicals : Me, Et, i-Pr, Bu = methyl, ethyl, isopropyl, butyl ; Ac = CH_3CO
Ethers : THF = tetrahydrofuran ; DMM = dimethoxymethane ; DME = 1, 2-dimethoxyethane
Amides and ureas : DMF = dimethylformamide ; DMA = dimethylacetamide ; TMU = tetramethylurea
Carbonates : DMC, DEC = dimethyl, diethyl carbonate ; PC = propylene carbonate
Sulphur compounds : DMSO = dimethylsulfoxide ; THT = tetrahydrothiophene ; DMTF = dimethylthioformamide
Phosphorus compounds : TMP, TBP = trimethyl, tributyl phosphate ; HMPT = hexamethylphosphotriamide

REFERENCES

1. N. Bjerrum, Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd., 7, 1, 1926
2. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 55, 2387, 1933
3. D.E. Irish, Ionic Interactions, Vol II, Chap 9, "Vibrational Spectral Studies of Electrolyte Solutions and Fused Salts ", Ed. S. Petrucci, Acad. Press N.Y. (1971)
4. D.E. Irish and M.H. Brooker, Advances in Infrared and Raman Spectroscopy, Vol 2, Chap. 6, "Raman and Infrared Spectral Studies of Electrolytes", Ed R.J.H. Clark and R.E. Hester, Heyden, London, (1976)
5. D. J. Gardiner, Advances in Infrared and Raman Spectroscopy, Vol 3, Chap. 5, "Vibrational Spectra of Non-Aqueous Solutions", Ed R.J.H. Clark and R.E. Hester, Heyden, London, (1977)
6. J.P. Devlin, Advances in Infrared and Raman Spectroscopy, Vol 2, Chap. 5, "The Vibrational Spectra of Ionic Vapours, Liquids and Glasses" ", Ed R.J.H. Clark and R.E. Hester, Heyden, London, (1976)
7. The Chemical Physics of Solvation, Part B Spectroscopy of Solvation, Ed. R.R. Dogonadze et al., Elsevier, Amsterdam, 1986.
8. A.I. Popov, Pure and Appl. Chem., 41, 275, 1975
9. J.B. Gill, Pure and Appl. Chem, 59, 1127, 1987
10. R.C. Miller and P. Kusch, J. Chem. Phys. 21, 1424, 1953; ibidem, 25, 860, 1956
11. P.A. Akishin and N.G. Rambidi, Z. Phys. Chem., 213, 111, 1960
12. S.H. Bauer, T. Ino and R.F. Porter, J. Chem. Phys., 33, 685, 1960
13. S. Schlick and O. Schnepp, J. Chem. Phys., 41, 463, 1964
14. A. Snelson, J. Chem. Phys., 46, 3652, 1967
15. A. Honig, M. Mandel, M.L. Stitch and C. H. Townes, Phys. Rev., 96, 629, 1954
16. J. Berkowitz and W.A. Chupka, J. Chem. Phys., 29, 653, 1958
17. J. Berkowitz, C.H. Batson and G.L. Goodman, J. Chim. Phys. Phys.-Chim. Biol., 77, 631, 1980
18. K. Raghavachari, A.M. Sapse and D.C. Jain, Inorg. Chem., 26, 2585, 1987
19. T. E. Joyce and E. J. Rolinski, J. Phys. Chem., 76, 2310, 1972
20. T.P. Martin and H. Schaber, J. Chem. Phys., 73, 3541, 1980
21. F.J. Kenesha and D. Cubiccioti, J. Phys. Chem., 71, 1958, 1967
22. J.J. Dehmer, J. Berkowitz and L. C. Cusachs, J. Chem. Phys., 58, 5681, 1973
23. L.L. Simmons, L.F. Lowden and T.C. Ehlert, J. Phys. Chem., 81, 709, 1977
24. T.P. Martin, Angew. Chem. Int. Ed. Engl., 25, 197, 1986
25. W.E.S. Turner and C.C. Bissett, J. Chem. Soc. 105, 1777, 1915
26. C.A. Kraus and R.A. Vingee, J. Am. Chem. Soc., 56, 511 and 2017, 1934
27. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., 57, 1, 1935
28. D.T. Copenhafer and C.A. Kraus, J. Am. Chem. Soc., 73, 4557, 1951
29. A.S. Kertes, O.Levy and G.Markowitz, J. Phys. Chem., 74, 3568, 1970
30. K. Ekelin and L.G. Sillen, Acta Chem. Scand., 7, 987, 1953
31. P. Bonnet and M. Chabanel, C. R. Acad. Sc. Paris, 257, 1280, 1963
32. M. Chabanel, J. Chim. Phys. Phys.-Chim. Biol., 62, 678, 1965 ; ibidem, 63, 1147, 1966
33. T.V. Talalaeva and A.N. Rodionov, Doklady Akad. Nauk SSSR, 154, 174, 1954
34. P. Gorin, J.-C. Marchon, J. Tranchant, S. Kovacevic and J.-P. Marsault, Bull. Soc. Chim. France, 3790, 1970
35. L. D. Pettit and S. Bruckenstein, J. Am. Chem. Soc., 88, 4783, 1966
36. M. Chabanel, C. Ménard and G. Guilhéneuf, C. R. Acad. Sc. Paris série C, 272, 253, 1971
37. C. Ménard, B. Wojtkowiak and M. Chabanel, C. R. Acad. Sc. Paris série C, 278, 553, 1974
38. C. Ménard, B. Wojtkowiak and M. Chabanel, Bull. Soc. Chim. Belges, 81, 241, 1972
39. P. Bacelon, J. Corset, and C. de Lozé, J. Solution Chem., 12, 23, 1983
40. V. Halaska, L. Lochmann and D. Lim, Collection Cczechoslov. Commun., 33, 3245, 1968
41. D. Seebach, Angew. Chem. Int. Ed. Engl., 27, 1624, 1988
42. B.J. Wakefield, The Chemistry of Organolithium Compounds, Chap. 1, Pergamon Press, Oxford, 1976
43. R.B. Bates and C.A. Ogle, Carbanion Chemistry, Vol. 17, Springer Verlag, Berlin, p. 3-12, 1984
44. M. Chabanel and Z. Wang, J. Phys. Chem., 88, 1441, 1984
45. J.A. Olander and M.C. Day, J. Am. Chem. Soc., 93, 3584, 1971
46. G.S. Hooper and C.A. Kraus, J. Am. Chem. Soc., 56, 2265, 1934
47. E.A.Richardson and K.H. Stern, J. Am. Chem. Soc., 82, 1296, 1960
48. K. Bauge and J.W. Smith, J. Chem. Soc., 4244, 1964
49. D. Ménard and M. Chabanel, J. Phys. Chem., 79, 1081, 1975
50. Ting-Po I and E. Grunwald, J. Am. Chem. Soc., 96, 2387, 1974
51. A.J. Hebert, F.W. Breivogel and K. Street, J. Chem. Phys. 41, 2368, 1964 ; ibidem, 48, 2824, 1968
52. H. Farber and S. Petrucci, J. Phys. Chem., 85, 2987, 1981

53. J.-P. Badiali, H. Cachet et J.-C. Lestrade, Pure and Appl. Chem., 53, 1383, 1981

54. A. Loupy and J. Corset, C. R. Acad. Sc. Paris, série C, 279, 713, 1974

55. Z. Kecki and J. Golaszewska, Rocz. Chem., 41, 1817, 1967

56. M. Chabanel, A. Bencheikh and D. Puchalska, J. Chem. Soc. Dalton Trans., in press

57. J. Vaes, M. Chabanel and M. L. Martin, J. Phys. Chem., 82, 2420, 1978

58. D. Paoli and M. Chabanel, C. R. Acad. Sc. Paris, série C, 284, 95, 1977

59. P. Gans, B. Gill and M. Griffin, J. Chem. Soc. Faraday Trans. I, 74, 532, 1978

60. J. Rannou and M. Chabanel, Inorg. Chem., 24, 2319, 1984

61. D. Paoli, M. Luçon and M. Chabanel, Spectrochim. Acta, 35A, 593, 1979

62. M. Chabanel, M. Luçon and D. Paoli, J. Phys. Chem., 85, 1058, 1981

63. F. A. Cotton, A. Davison, W. H. Isley and H. S. Trop, Inorg. Chem., 18, 2719, 1979

64. G. A. van Albada, R. A. G. De Graaff, J. G. Haasnoot and J. Reedijk, Inorg. Chem., 23, 1404, 1984

65. J. Goulon, C. Goulon-Ginet and M. Chabanel, J. Solution Chem., 10, 649, 1981

66. Y. H. Kim, D. Paoli and M. Chabanel, C. R. Acad. Sc. Paris, série C, 301, 1113, 1985

67. J.-L. Glimois, D. Paoli and M. Chabanel, C. R. Acad. Sc. Paris, série C, 277, 125, 1973

68. M. Chabanel and D. Paoli, J. Chim. Phys. Phys.-chim. Biol., 77, 912, 1980

69. H. L. Friedman, J. Phys. Chem., 66, 1595, 1962

70. N. Inoue, M. Xu and S. Petrucci, J. Phys. Chem., 91, 4628, 1987

71. M. Delsignore, H. Farber and S. Petrucci, J. Phys. Chem., 89, 4968, 1985

72. M. K. Wong, W. J. McKinney and A. I. Popov, J. Phys. Chem., 75, 56, 1971

73. M. Chabanel and Z. Wang, Can. J. Chem., 62, 2320, 1984

74. P. Goralski and M. Chabanel, Inorg. Chem., 26, 2169, 1987

75. R. Waack, M. A. Doran and E. B. Baker, J. Chem. Soc. Chem. Commun., 1967, 1291

76. P. Goralski and M. Chabanel, C. R. Acad. Sc., série II, 304, 1107, 1987

77. F. Durant, Y. Gobillon, P. Piret and M. Van Meerssche, Bull. Soc. Chim. Belges, 75, 52, 1966

78. F. Durant and M. Griffé, Bull. Soc. Chim. Belges, 77, 557, 1968

79. D. Barr, W. Clegg, R. E. Mulvey and D. S. Wright, J. Chem. Soc. Chem. Commun., 1987, 716

80. R. Amstutz, J. D. Dunitz, T. Laube W. Schweizer and D. Seebach, Chem. Ber., 119, 434, 1986

81. N. S. Poonia and A. V. Bajaj, Chem. Rev., 79, 389, 1979

82. P. Groth, Acta Chem. Scand., A36, 109, 1982

83. S. R. Hall, C. L. Raston, B. W. Skelton and A. H. White, Inorg. Chem., 22, 4070, 1983

84. D. Saar, J. Brauner, H. Farber and S. Petrucci, J. Phys. Chem., 84, 341, 1980

85. D. Saar and S. Petrucci, J. Phys. Chem., 90, 3326, 1986

86. P. Bacelon, J. Corset and C. de Lozé, J. Solution Chem., 9, 129, 1980

87. I. S. Perelygin and M. A. Klimchuk, Zh. Prikl. Spektrosk., 36, 761, 1982

88. N. Nakajima and J. P. Anselme, J. Chem. Soc. Chem. Commun., 1980, 796

89. Y. Pocker and J. C. Ciula, J. Am. Chem. Soc., 110, 2904, 1988

90. J. Corset, Pure Appl. Chem., 58, 1133, 1986