Vibrational Study of Ionic Association in Aprotic Solvents. Part 12. Isothiocyanate M(NCS) Complexes of Non-transition-metal Ions†

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Isothiocyanate complexes M(NCS) (ion pairs) formed between SCN^- and non-transition-metal cations M^{z+} (Li^+, Na^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^+, Pb^{2+}, or Bi^{3+}) have been investigated in polar aprotic solvents (dimethyl sulphoxide or dimethylformamide). The effects of ion pairing on the CN and CS vibrations of SCN were studied by i.r. and Raman spectroscopy. The ν(CS) frequency is well correlated to the polarizing power P of M^{z+} while ν(CN) also depends on its polarizability α. As these two factors act on ν(CN) in opposite directions, the frequency shift in M(NCS) relative to SCN^- is negative when α is large. The ν(CS) frequency shift is interpreted by the mesomeric effect while other factors also contribute to the ν(CN) frequency shift: stabilization of σ orbitals of SCN^- by M^{z+}, transfer of π electrons to M^{z+}, and back donation of electrons from M^{z+} to π^* antibonding orbitals of the CN group. The i.r. intensity of the CN vibration is also correlated to P and α and in that case both factors act in the same direction. An electrostatic model of the ion pair gives results in agreement with the observed intensity enhancements. It is shown that these interpretations are also useful in the case of transition-metal complexes.

The co-ordination of the SCN^- ligand with metal ions has been reviewed in several books.[1–3] However the authors do not consider the co-ordination of alkali-metal ions although it is really a part of co-ordination chemistry. This field was reviewed by Gill[4] who was mainly concerned with solutions in liquid ammonia. In the case of mononuclear complexes $M(NCS)_p$ the SCN^- ligand can be bonded either *via* nitrogen [M(NCS), isothiocyanates] or sulphur [M(SCN), thiocyanates]. The M(NCS) bonding is by far the most usual, while M(SCN) bonding is encountered with the softest cations (*e.g.* Ag^+ and Hg^{2+}). The M(NCS)—M(SCN) isomerism is found with cations of intermediate softness (*e.g.* Cd^{2+}) although in this case M(NCS) bonding is the most common. Consequently it is not possible to investigate a large series of M(SCN) compounds.

The frequencies of the longitudinal vibrations of SCN^- are ν(CN) ≈ 2 058 cm^{-1} and ν(CS) ≈ 735 cm^{-1}. Frequency shifts and intensity variations are useful criteria for the determination of the M(SCN)—M(NCS) isomerism. For instance, the frequency shift Δν(CN) relative to SCN^- is always positive in M(NCS) and negative in M(SCN). This criterion would be commonly used if the ν(CS) vibration were not so weak in the i.r. spectrum and often blurred by other absorption brands. On the contrary, the ν(CN) band is strong, but Δν(CN) in M(NCS) can be positive, small, or even negative. Fortunately the intensity of this band in the i.r. region provides a reliable criterion of isomerism.[5]

In previous papers[6] we investigated the co-ordination of alkali-metal ions by SCN^- which give M(NCS) ion pairs and $[M(NCS)]_p$ aggregates. Now we extend the investigation of ion pairs to a large number of cations which cover a wide range of polarizing ability and softness. The relations that will be observed must give a structural explanation of the completely different behaviours of ν(CN) and ν(CS).

We focus our attention on non-transition-metal ions because the interpretation of frequency shifts for transition-metal ions is complicated by p_π–d_π interactions. The experimental conditions with different M^{z+} ions were as similar as possible. We investigate ion pairs only because in $M(NCS)_p$ complexes ($p > 1$) complications arise from coupling between NCS groups. Frequency shifts due to medium effects (site effects in the solid state, dielectric and hydrogen-bonding effects in solution) are eliminated by working in similar aprotic solvents.

Experimental

Dimethylformamide (dmf) of spectroscopic grade was dried on 3-Å molecular sieves. Anhydrous dimethyl sulphoxide (dmso) (Merck, maximum 0.03% water), thiocyanates M(SCN) (M = K, NBu_4, or Tl), and anhydrous $Mg(ClO_4)_2$ of the best commercial grade were used without further purification. Lithium thiocyanate was prepared by using the method of Lee.[7] The preparation of $M(ClO_4)_z$·6dmso (M^{z+} = Al^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, or Cd^{2+}) has been given in previous papers.[8] The dmso that they contain was not removed. Other perchlorates (M^{z+} = Ca^{2+}, Ba^{2+}, Pb^{2+}, or Mn^{2+}) were not dehydrated before being dissolved. The ion pairs of Bi^{3+} were prepared from $Bi(NO_3)_3·5H_2O$ and those of Be^{2+} from $BeSO_4·4H_2O$. When solutions were prepared from hydrated salts they were dried on 3-Å molecular sieves which removed water completely except in the case of beryllium salts. Residual water was analysed by i.r. spectroscopy in the 3 400—3 600 cm^{-1} region.

Infrared spectra were recorded on a Bruker IFS45 FTIR spectrometer. In the 2 000—4 000 cm^{-1} region CaF_2 cells were used. The spectra were fitted by a non-linear least-squares program. Each band was considered as the sum of Gauss and Lorentz contributions having the same band width. This procedure allows a direct analytical calculation of integrated intensities. Raman spectra were recorded on a Coderg T 800 spectrometer equipped with a Spectra Physics argon-ion laser (λ = 4 880 Å). A resolution of 2 cm^{-1} was used in both i.r. and Raman spectra.

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

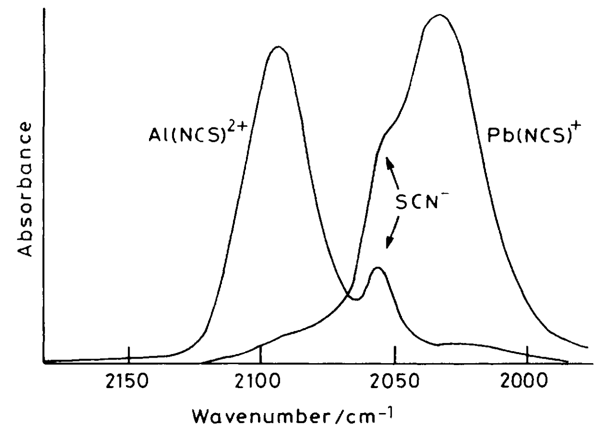

Figure 1. Infrared spectra of stoicheiometric mixtures of $M(ClO_4)_z$ – NBu_4SCN in dmf (M^{z+} = Al^{3+} and Pb^{2+}, $c \approx 0.1$ mol dm^{-3})

Table. Vibrational wavenumbers (cm^{-1}) and integrated intensities (dark, 1 dark = 1 mol^{-1} dm^3 cm^{-2}) of MNCS in dmso or dmf solutions (P = polarizing power, α = polarizability in Å^3; unstarred values are in dmso, starred values in dmf)

M^{z+}	P	α	ν(CN)	ν(CS)	B(CN)
Li^+	1.2_5	0.03	2 071*	765*	45*
Na^+	1.0_1	0.41	2 065*	754*	
K^+	0.7_5		≈2 058*	747*	
Rb^+	0.7		≈2 058*	742*	
Be^{2+}	5.1	0.01	2 112		
Mg^{2+}	2.9_3	0.1	2 080 2 083*	789*	48*
Ca^{2+}	1.9_7	1.1	2 060 2 063*	780*	43*
Ba^{2+}	1.4_2	2.5	2 047^a	≈774^a	≈60^a
Zn^{2+}	3.4_5	0.8	2 079^b 2 079*	835^b	64*
Cd^{2+}	2.8_8	1.8	2 069 2 067*	798	68*
Al^{3+}	5.8_1	0.05	2 089 2 093*	≈852	61*
Ga^{3+}	5.8	0.2	2 080	851	82
In^{3+}	4.6_9	0.7	2 058 2 059*	847	90
Tl^+	1.0	5.2	2 039*		≈44*
Pb^{2+}	2.3	4.9	2 035*		85*
Bi^{3+}	3.7_6	3.3	2 027*		115*

[a] In thf (98%)–dmf (2%), free SCN$^-$ at 2 051 cm^{-1}. [b] $Zn(NCS)_p$, p = 3 or 4.

Results

Among the usual aprotic solvents of salts, dimethyl sulphoxide (dmso) generally is the most efficient. However, in some cases, it dissociates too much to allow the formation of a large proportion of ion pairs especially in dilute solutions. Below *ca.* 770 cm^{-1} it is not transparent enough in the i.r. and Raman spectra for the identification of ν(CS) frequencies. Dimethylformamide (dmf) is somewhat less polar and significantly less ionizing than dmso, and it is transparent below *ca.* 820 cm^{-1}. Finally both dmso and dmf are needed for a complete investigation of ion pairs. In dmf, ν(CS) of free SCN$^-$ was found to be at 735 cm^{-1}.[9] The value which is given in most papers is slightly higher (745 cm^{-1}) because it has been measured either on solid K(SCN) or on SCN$^-$ in water. In both cases we will see that these conditions cause a small rise in frequency due either to the bonding of SCN$^-$ with K$^+$ or to hydrogen bonding.

It can be seen in typical spectra in the ν(CN) region (Figure 1) that the ν(CN) frequency of M(NCS) can be either higher or lower than that of free SCN$^-$. When this frequency is observed in both dmso and dmf the difference between the two values is scarcely larger than 2 cm^{-1} (Table). The ν(CN) of free SCN$^-$ measured in NBu_4SCN solutions occurs at 2 055 (dmso) and 2 $057._5$ cm^{-1} (dmf). Concerning Tl(SCN), the proportion of ion pairs in dmf is low at ordinary temperature but becomes fairly large at 50 °C. In pure dmf the ion pairs of Ba^{2+} cannot be observed at all. On the other hand, ion pairing between Ba^{2+} and SCN$^-$ is complete in tetrahydrofuran–2% dmf which is much less polar than pure dmf. In the i.r. spectrum it is difficult to observe the ν(CS) band of ion pairs (700—900 cm^{-1}) because it is very weak and more or less blurred by solvent bands. For that reason, ν(CS) of M(NCS) has been measured from the Raman spectra ($c \approx$ 0.1—1 mol dm^{-3}). The values of ν(CN) and ν(CS) and of i.r. integrated intensities B(CN) are reported in the Table. The polarizability α and the polarizing power P of M^{z+} are also reported. The parameter P has been correlated by several authors to the frequency variations of NO_3^- induced by M^{z+}.[10,11] The definition of P was given by Cartledge[12] as $P = z/(rS_{\text{eff.}})$ with $S_{\text{eff.}} = 5z^{1.27}/Ir^{\frac{1}{2}}$). The values of P were evaluated from ionization potentials I(eV) and from ionic radii r(Å) tabulated by Shannon and Prewitt.[13] Polarizabilities were deduced from cation refraction values given by Batsanov.[14]

Uncharged M(NCS) ion pairs (z = 1) were obtained in solutions of the pure M(NCS) salt. Charged M(NCS) ion pairs ($z > 1$) were generally the major species in stoicheiometric mixtures of MY_z and NBu_4SCN where Y = ClO_4, except for Bi (Y = NO_3) and Be (Y = SO_4) (see Experimental section). In most cases the formation constant of M(NCS) is much higher than that of higher species and M(NCS) is the only complex present up to the stoicheiometry 1:1.[8,15] The only known exception seems to be Zn^{2+} [15] where ion pairs are less stable than the 1:3 and 1:4 complexes. For that reason, in Zn^{2+}–SCN$^-$ solutions, we have always found a second ν(CN) band in the Raman due to the coupling between vibrations in $Zn(NCS)_p$ (p = 3 or 4). The problem of the exact stoicheiometry of the complexes is not of the greatest importance here because we have checked that the ν(CN) frequencies are nearly the same for different $M(NCS)_p$ complexes, especially in the case of heavy cations. For instance, all $Ga(NCS)_p$ complexes have the same ν(CN) frequencies within ±2 cm^{-1}. In the case of Be(NCS)$^+$ we could not remove water completely. Infrared and Raman spectra of these solutions in dmso exhibit two new bands at 2 112 and 2 096 cm^{-1}. The intensity of the second band decreases after drying on 3-Å molecular sieves but it does not disappear completely and was therefore attributed to a hydrated species. A small band was observed on the high-frequency side of SCN$^-$ in the case of Pb^{2+} (2 093 cm^{-1}) and Tl^+ (2 077 cm^{-1}), while the main band due to M(NCS) was found on the low-frequency side. It is attributed to the thiocyanate isomer M(SCN) of the ion pair.

The integrated intensity B(CN) of free SCN$^-$ was measured in 13 aprotic solvents of different polarities [*e.g.* CCl_4, tetrahydrofuran (thf), acetone, pyridine, dimethyl, diethyl, and propylene carbonates, CH_3CN, and CH_3NO_2]. It is nearly the same (between 32 and 37 kdarks) in all aprotic solvents. In dmso and in dmf it is equal to $33._5$ kdarks. This value is between those measured by Kinnell and Stranberg[16] (44 kdarks) for butanone solutions of SCN$^-$ and by Hart and Hollenberg[17] (24.6 kdarks) for KSCN in KBr pellets. It seems likely that the differences arise essentially from the methods of measurement and estimation of intensities. In protic solvents the integrated intensity of SCN$^-$ is higher than in aprotic solvents (39 in CH_2Cl_2 and propanol, $42._5$ in $CHCl_3$, and 49 kdarks in ethanol). This effect, which is due to the solvation of SCN$^-$ by hydrogen bonding, is similar to that of ion pairing.

The integrated intensities of M(NCS) ion pairs are reported in the Table. They are always higher in M(NCS) than in SCN$^-$.

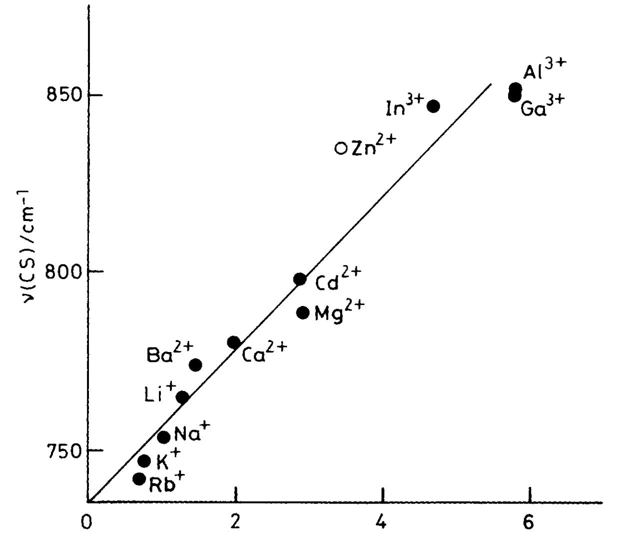

Figure 2. ν(CS) of M(NCS) as a function of the polarizing power P of M^{z+}. In the case of Zn^{2+}, complexes higher than M(NCS) are present

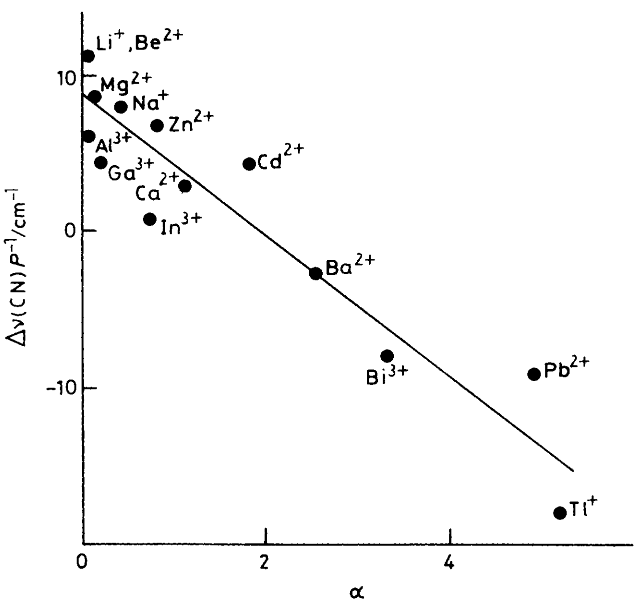

Figure 3. Δν(CN)/P of M(NCS) as a function of the polarizability α of M^{z+}

This result confirms the validity of the intensity criterion which is known as the best criterion for the determination of linkage isomerism in thiocyanate complexes.[5]

Discussion

ν(CS) *Frequency*.—The values of ν(CS) of M(NCS) ion pairs are plotted against the polarizing power of M^{z+} in Figure 2. An excellent linear relation is observed while the range of polarizing power ($1 < P < 6$) is the largest that has been explored in a given correlation. This linear relation is expressed by equation (1) [correlation coefficient 0.97, standard deviation of

$$\nu(\mathrm{CS}) = 735 + 21._7P \qquad (1)$$

ν(CS) 10 cm^{-1} and of the slope 0.9]. Such a simple relation is interpreted by the mesomeric effect due to the electrostatic interaction between M^{z+} and the SCN^- group according to the usual scheme $^-S{-}C{\equiv}N \longrightarrow S{=}C{=}N^-$.

The relation (1) can also be used for interpretation of ν(CS) values in the literature. Taking into account an uncertainty of about 10 cm^{-1} equation (1) gives the following ν(CS) ranges for M(NCS) according to the categories of M^{z+} ions: M^+ ($P < 2$), 740—780 cm^{-1}; M^{2+} and lanthanide M^{3+} ($P \approx 2.5$—4), 780—830 cm^{-1}; other M^{3+} ions ($P \approx 4.5$—6), 820—870 cm^{-1}; M^{4+} ($P \approx 5.5$—7), 840—900 cm^{-1}.

These results are generally in good agreement with the ν(CS) values observed for $M(NCS)_p$ complexes, even in the solid state, in spite of various medium and mechanical coupling effects. For instance, the following values have been observed for M^{4+} complexes: $M(NCS)_4{\cdot}2HMPT$ (HMPT = hexamethylphosphoramide),[18] 858 (M = Ti) and 852 cm^{-1} (M = Zr); $[M(NCS)_6]^{2-}$,[19,20] 879 (M = Zr or Sn) and 876 cm^{-1} (M = Hf). In water, $Eu(NCS)^{2+}$ [21] ($P = 3.3$) exhibits a Raman ν(CS) frequency at 787 cm^{-1} (calc. 804 cm^{-1} from $P = 3.3$). The ion pair Cu(NCS) has been observed at 780 cm^{-1} in dimethylthioformamide,[22] while the estimated value ($P = 1.6$) is 769 cm^{-1}. Hester and Krishnan[23] investigated $M(NCS)_2$ (M = Mg, Ca, Zn, Cd, or Pb) diluted in molten K(SCN). Their frequencies are close to the values which are given here except for Ca^{2+} where ν(CS) (819 cm^{-1}) is higher than expected. Their value for Pb^{2+} (793 cm^{-1}) is also in good agreement with the expected value for $Pb(NCS)^+$ (785 cm^{-1}).

For transition-metal ions equation (1) also gives a first estimation of ν(CS). For instance, from $P = 2.9$, we obtain ν(CS) 796 cm^{-1} for $Mn(NCS)^+$, while our measured value in dmf is 792 cm^{-1}. As expected the ν(CS) frequency of cobalt(III) complexes is found in the range 830—840 cm^{-1}.[24] On the other hand ν(CS) frequencies of square-planar complexes of Ni^{2+}, Pd^{2+}, and Pt^{2+} [25] are significantly higher (830—860 cm^{-1}) than estimated. The estimated frequency of $Fe(NCS)^+$ (800 cm^{-1}) is close to that (809 cm^{-1}) observed for $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline).[26] In that case, if the attributions are correct, ν(CS) is the same for high-spin and low-spin complexes while the ν(CN) values are quite different (2 063 and 2 108 cm^{-1}).

ν(CN) *Frequency*.—The ν(CN) and ν(CS) frequencies behave in a similar manner when SCN^- is co-ordinated to hard cations. Both frequency shifts are positive and they increase with P. However ν(CN) is less sensitive than ν(CS) and its frequency shift is smaller than expected and even negative with soft cations. However we did not observe a quantitative relation between Δν(CN) and the softness parameter as defined by Pearson.[27] The most negative shifts were observed for the highly polarizable cations Tl^+, Pb^{2+}, and Bi^{3+}. An acceptable empirical relation between Δν(CN), P, and α must give Δν(CN) = 0 when $P = 0$. The simplest form of such a two-parameter relation is (2).

$$\Delta\nu(\mathrm{CN}) = AP + B\alpha P \qquad (2)$$

The quality of this relation can be tested by plotting Δν(CN)/P against α (Figure 3). The parameters estimated are $A = 8._6$ and $B = -4._5$ with a correlation coefficient of 0.94 and a standard deviation of Δν(CN) of 3 cm^{-1}. It is interesting to test the application of equation (2) to mercury isothiocyanate bonding. In solutions Hg^{2+} always gives thiocyanate complexes $Hg(SCN)_p$. Fortunately, Hg(NCS) bonding is known in one solid compound: the 4:1 adduct of $Hg(NCS)_2$ with hexamethylenetetramine (3,6-diazaoctane-1,8-diamine)[28] where ν(CN) 2 055 cm^{-1}. Mercury(II) is generally considered as the softest of all the usual cations. If Δν(CN) is strictly related to softness it should be strongly negative in $Hg(NCS)^+$. From equation (2) and ν(SCN^-) 2 052 cm^{-1} in the solid state we obtain Δν(CN) = 7 cm^{-1} and ν(CN) 2 059 cm^{-1} for $Hg(NCS)^+$, which is in excellent agreement with the experimental value. The value of ν(CN) is nearly the same as that for SCN^- because the

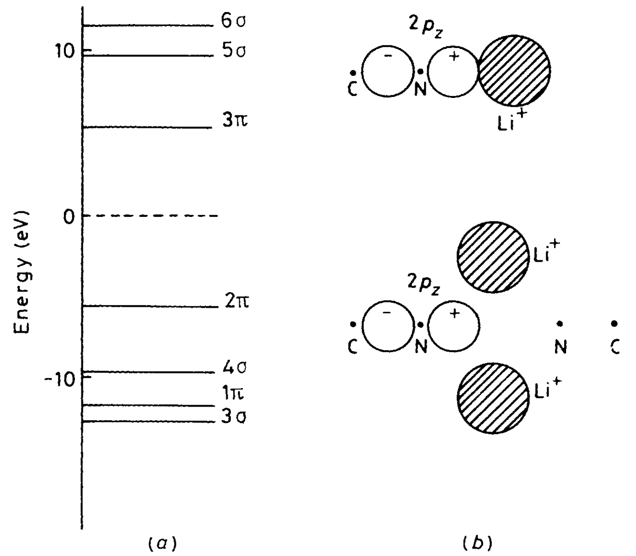

Figure 4. Highest-energy levels[31] for the thiocyanate ion (*a*) and the nitrogen $2p_z$ orbital in Li(NCS) and $[Li(NCS)]_2$ (*b*)

term arising from the polarizability of Hg^{2+} is almost the opposite of the term arising from its polarizing power. The observed ν(CS) frequency (815 cm^{-1}) is in the range of values for $M(NCS)^+$ ion pairs (790—820 cm^{-1}) although somewhat higher than estimated from equation (1) (798 cm^{-1}).

In M(NCS) ion pairs ν(CN) is almost free from mechanical coupling with ν(MN) and the coupling with ν(CS) is small. We have checked by force-constant calculations that most of the Δν(CN) shift is due to the variation in *F*(CN) force constant and consequently Δν(CN) and Δ*F*(CN) are nearly proportional.

The energy levels of SCN^- calculated by Di Sipio *et al.*[29] are represented on Figure 4. The common origin of Δν(CN) in CN^-, SCN^-, and CH_3CN has been described by several authors.[30—31] According to Nakamoto[31] 'σ donation tends to raise ν(CN) since electrons are removed from the (highest occupied) σ orbital which is weakly antibonding while π back bonding tends to decrease ν(CN) because electrons enter in the (lowest unoccupied) $p_{\pi*}$ orbital'. In the light of our results this interpretation should be slightly modified. First the term 'weakly antibonding' is not well adapted because occupied SCN^- π orbitals are more or less bonding in agreement with Lewis structures, but their energy is higher in an anion than in a neutral compound. Secondly electrostatic interactions cause a stabilization of 3σ and 4σ orbitals by lowering the Coulomb integrals, especially those arising from nitrogen $2p_z$ orbitals which are located close to M^+ and which bring an important contribution to 3σ and 4σ. The population of the nitrogen $2p_z$ orbital must be enhanced by the M^+ attraction: these effects should be strong with small cations because the outer lobe of $2p_z$ is in direct contact with M^+, but also they should decrease rapidly when the radius of M^+ is increased. In general, true σ donation should not be important because, for instance in the case of Li(NCS), the large gap between 4σ of SCN^- (−9.8 eV) and 2*s* of Li^+ (−5.4 eV) must prevent a significant σ donation.

If M^+ (or M^{z+}) is a hard unpolarizable cation the stabilization of σ orbitals in M(NCS) causes an important strengthening of the CN bond. This effect is in part counterbalanced by the charge transfer from S to N due to the usual resonance effect $^-S{-}C{\equiv}N \longrightarrow S{=}C{=}N^-$, hence a small positive Δν(CN) shift. On the contrary, in the case of large cations the coulombic stabilization of σ orbitals should decrease strongly and the resonance effect should become predominant.

A second effect is related to the large polarizability of ions like Tl^+, Pb^{2+}, and Bi^{3+}. These ions have large and deformable 6*s* orbitals. Their deformation by an electric field E_z is equivalent to a transfer of a part of the charge into the empty $6p_z$ orbital. In a similar manner a part of the charge on the 1π and 2π bonding orbitals may be transferred to $6p_\pi$ orbitals of M^{z+}. Back donation from filled d_π orbitals of M^+ to the antibonding 3π orbital of SCN^- is also possible for these cations but it is excluded in cations of Groups 1A and 2A like Ba^{2+}.

The analysis[9] of the bonding in $[Li(NCS)]_2$ is in agreement with the role played by π orbitals. In that case the $2p_z$ orbital of nitrogen is not directed towards Li^+ and consequently its stabilization by coulombic interaction must be negligible [Figure 4(*b*)]. On the other hand the 2π orbital of SCN^- and the 2*s* orbitals of Li^+ ions have the same symmetry and nearly the same energy (−5.7 and −5.4 eV). Consequently there must be some charge transfer from the 2π orbital to the 2*s* orbitals of Li^+. This kind of bonding is similar to that observed in boron compounds but much less covalent. The transfer of π electrons from a bonding orbital of SCN^- to Li^+ also causes a lowering of the CN bond and force constant. The interpretation of large negative shifts found in other μ_2 and μ_3 isothiocyanates like $[Li(NCS)]_4$,[6] $[Re_2(NCS)_{10}]^{-3}$,[32] and $[Ni_3(NCS)_6]$[33] is similar. For instance ν(CN) ≈ 2 000 cm^{-1} for $[Li(NCS)]_4$ and Δν(CN) ≈ −50 cm^{-1}.

Large negative shifts [Δν(CN) ≈ −50 to −100 cm^{-1}] have also been found for some $M(NCS)_6$ compounds (M^{z+} = Zr^{4+}, Hf^{4+}, Nb^{5+}, or Ta^{5+}).[20,34] In these ions the low-lying empty *d* orbitals are available for d_π–p_π bonding. They may draw a part of the π electronic charge of CN in the same way as the 2*s* orbitals of Li. The availability of *d* orbitals for bonding is attested to by low-energy absorption bands in the 300—400 nm region which have been interpreted as electron transfers from NCS to the metal (Nb or Ta).[34]

Integrated Intensities.—The variation of integrated intensity in M(NCS) is estimated by using the electrostatic model that we described in a previous paper.[9] The only difference from that treatment is the introduction of the Lorentz–Lorentz field correction as did Hart and Hollenberg.[17] The transition moment of an i.r. band ν_i is related to its integrated intensity B_i (dark) by the relation ($c = 3 \times 10^{10}$ cm s^{-1})$\partial\mu/\partial Q_i = AB_i^{\frac{1}{2}}$ with $A = [3\,000/\pi]^{\frac{1}{2}}(10^{10}c/N_A)(3/\varepsilon_\infty + 2)$. By taking $\varepsilon_\infty \approx 2$ we obtain $A = 0.0175$. Including that correction, the transition moment μ′(CN) for SCN^- is equal to 2.11 D/Å (D ≈ 3.34 × 10^{-30} cm). A part of that moment (external moment) comes from the displacements of the charges of SCN^- relative to the counter ion.

Three terms contribute to the variation in transition moment of SCN^- with ion pairing: the change in external moment and the transition moments induced by M^{z+} on SCN^- and by SCN^- on M^{z+}. The external moment depends on the cartesian displacements of the atoms and on their charges. These displacements are calculated from the force field of SCN in M(NCS). As couplings between SCN vibrations and ν(MN) are supposed to be negligible, this is true for the cartesian displacements of M.

The main problem is the estimation of the charges on the atoms of SCN^-. Quantum mechanical calculations show that the charge on the carbon atom is nearly zero, in agreement with the usual limit formulae. From the semiempricial calculation performed by Di Sipio *et al.*[29] it has been found that the charge of SCN^- is equally distributed between sulphur and nitrogen. This is a rough approximation as shown by an *ab initio* calculation which gives a more important charge on nitrogen (−0.68 e).[35] We have assumed a linear relationship between the distance r_{cs} and the charge q_s. The second value to be put in this relation has been obtained from CS_2(r_{cs} = 1.55_4 Å) where there are two

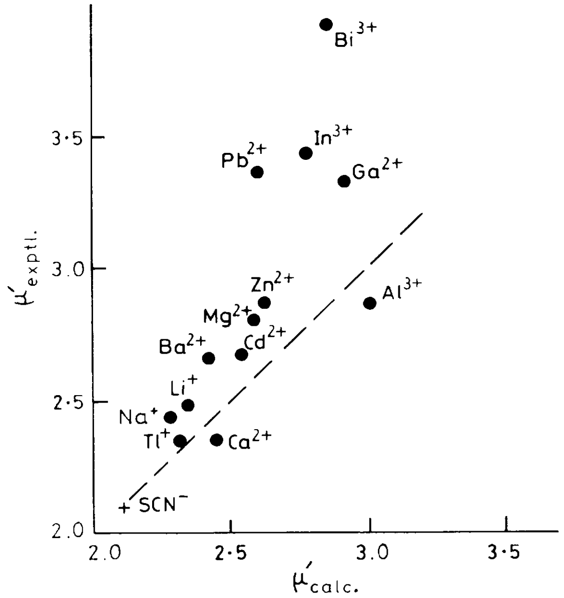

Figure 5. Experimental values of transition moments $\mu'_{\text{exptl.}} = \partial\mu(\text{CN})/\partial Q$ against the values $\mu'_{\text{calc.}}$ calculated by an electrostatic model of the ion pair

formal double bonds and therefore where q_s is taken as zero. The well known Badger–Bauer rule[36] $F_{cs} = a/r^6$ was used to deduce r_{cs} from F_{cs} where F_{cs} is the C–S force constant (Ncm^{-1}). From the compounds[37–39] OCS, CS$_2$, HNCS, K(NCS), and CH$_3$SH we obtained $a = 110 \pm 5$ N Å^6 cm^{-1}.

There is no doubt about the sign of the effect of ion pairing on B(CN) because all terms are of the same sign. It is reversed for thiocyanates M(SCN) in agreement with experimental results. Moreover the variations in B(CN) are almost always large, the reason why intensity measurements are such a good criterion for the determination of the linkage isomerism M(NCS)–M(SCN).

In Figure 5 the experimental transition moments $\mu'_{\text{exptl.}}$ are plotted against their estimated values $\mu'_{\text{calc.}}$. This calculation gives a semi-quantitative estimation of the increase in transition moment from SCN$^-$ to M(NCS). However the result is generally underestimated, especially in the case of polarizable ions. This electrostatic model does not take into account a possible back donation of electrons from M^{z+} to SCN$^-$ which would increase the negative charge on nitrogen. The fact that this back donation must give an additional increase in intensity was confirmed by the investigation of Fe(NCS)$^{2+}$ in dmso. In that complex ν(CN) was found at 2 045 cm^{-1}. This value is exceptionally low for a transition-metal complex of M^{3+}. The interpretation should be the same as that given for [Fe(phen)$_2$(NCS)$_2$],[26] *i.e.* back donation of d electrons from Fe^{3+} to SCN$^-$. The integrated intensity is quite high in that complex: 110 kdark, *i.e.* 40% higher than in Ga(NCS)$^{2+}$. Gallium has similar values of P and α as Fe^{3+}, but there is no possibility of back donation from an incomplete d subshell.

In conclusion we have investigated M–NCS bonding by covering a wide range of polarizing ability of M^{z+} from Rb$^+$ and K$^+$ to Be^{2+} and Al^{3+}. The polarizing power of P of M^{z+} has proved to be a good parameter for the prediction of ν(CS). When this frequency is much lower than expected there is a strong indication of a bridging co-ordination of NCS. On the other hand, variations in ν(CN) are more complicated. In the case of non-transition metals they are not only related to P but also to the polarizability α of M^{z+}. In transition-metal complexes ν(CN) is also sensitive to specific interactions between π orbitals of the ligand and d orbitals of the metal. The relation between Δν(CN) and α of M^{3+} is attributed mainly to some covalent bonding between SCN$^-$ and M^{z+}.

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