

## On the Infrared Spectra of Thiocyanic Acid and some Thiocyanato Complexes of Iron(III)

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The infrared spectra in the C—N absorption region have been recorded for (iso)thiocyanic acid extracted into various solvents. The variations in frequency and integrated absorption are related to possible solute-solvent interactions and the use of simple valence-bond models in describing this variation is discussed.

Thiocyanato complexes of iron(III) have also been examined both in the solid state and in solution. There is some evidence from the infrared data that solid octahedral complexes change configuration when dissolved in low-polar solvents. It is suggested that in such solvents they adopt the tetrahedral configuration just as iron(III) thiocyanato complexes extracted from aqueous into organic solutions.

The coordination chemistry of the ambidentate thiocyanate ion has long been a subject of interest. One way to differentiate between the bonding types is offered by infrared spectroscopy. Thus, both frequency shifts and the change of the integrated absorption of the IR-bands of the thiocyanate ion could be used (See Refs. 1–4 and references therein). Fronæus and Larsson<sup>1</sup> have shown that most of the behavior of the C—N stretching vibration upon coordination could be explained qualitatively by a changed distribution between the resonance structures of the thiocyanate ion suggested by Jones.<sup>5</sup> However, the frequency shift of the C—N stretching vibration did not follow the rules. Thus, for the complexes of the first row transition metals in aqueous solution it was obvious from the intensity measurements that no appreciable electron exchange was taking place between ligand and metal. This means that the attraction would be mainly electrostatic and that the distribution between the resonance

structures, and consequently the vibrational frequencies of the thiocyanate ion, would be unchanged upon coordination. Nevertheless, a large positive frequency shift was found in these cases, which was ascribed to mechanical squeezing of the C—N group in these complexes. Later Porai-Koshits *et al.*<sup>6</sup> showed theoretically that in complexes of this kind the frequency shift would be positive and an almost linear function of the force constant of the M—N bond.

For more covalent metal ligand bonds (M—NCS bonds) the resonance structure model would predict a negative frequency shift, but a positive one is still found although smaller than before. This may be the result when this “covalent effect” is overbalanced by the “electrostatic effect” described above.

The (iso)thiocyanato complexes of iron(III) are especially interesting in this respect. Among all the transition metal complexes in aqueous solution investigated by Fronæus and Larsson<sup>1</sup> those of iron(III) were the only ones giving a negative frequency shift of the C—N stretching vibration as compared to the free thiocyanate ion (2045 cm<sup>-1</sup> to 2066 cm<sup>-1</sup>). Furthermore, the large value of the integrated absorption reported indicates that there is a considerable electron exchange between ligand and metal in these complexes. The analysis of the spectra of the iron(III) system in aqueous solution was, however, complicated by the existence of polynuclear complexes (*cf.* also Ref. 7), resulting in broad and diffuse absorption bands.

There are exceptionally few other reports in the literature on the IR-spectra of the thiocyanato complexes of iron(III). These are usually studies on solid octahedral complexes of the

type  $(R_4N)_3Fe(NCS)_6$ .<sup>8-12</sup> The C–N stretching frequency is frequently split in these solid-state spectra and varies widely from one compound to another, but is usually found between 2070 and 2050  $cm^{-1}$ . No integrated absorptions have been reported for the vibrations.  $(Et_4N)_3Fe(NCS)_6$  has also been studied in solution (acetone).<sup>13</sup> The values of the C–N stretching frequency and the integrated absorption per SCN-group are here 2062  $cm^{-1}$  and  $15.2 \times 10^4 M^{-1} cm^{-2}$ , respectively.

Complex anions formed with pseudohalide ions, such as thiocyanate, can often be extracted from aqueous phases into organic ones. There are also some papers on iron(III) thiocyanate extraction, but the data are conflicting even for a given solvent with a specific aqueous phase. For example, some authors<sup>14</sup> have reported that diethyl ether extracts the neutral molecules  $Fe(NCS)_3$  from aqueous solutions, others<sup>15,16</sup> that the extractable species would be  $Fe(NCS)_4^-$ . Bock<sup>17</sup> has found that both kinds of species are extractable depending on the composition of the aqueous phase. However, the configuration of the species is not settled once the stoichiometric ratio Fe/SCN is determined. Maddock and Medeiros<sup>18</sup> have shown that for an extraction from water into nitrobenzene the extracted species must be the six-coordinated  $Fe(NCS)_4S_2^-$ , where *S* represents a molecule of solvent, in this case water rather than nitrobenzene. As there are some indications of a higher covalency in the metal-ligand bond of complexes with tetrahedral configuration than in those with octahedral,<sup>5,1</sup> one would expect a more pronounced negative frequency shift of the C–N stretching frequency upon tetrahedral coordination and perhaps also a larger integrated absorption.

In this work the infrared spectra of the thiocyanato complexes of iron(III) extracted into some different organic solvents are reported, as well as the spectra of tributylammonium- and triphenylmethylarsonium-hexathiocyanato ferrate(III), both in the solid state and in various solutions.

Even if the iron(III) complexes (either octahedral or tetrahedral) in some cases show unusually low C–N stretching frequencies of the thiocyanato group, the M–NCS bond cannot be extremely covalent. As a matter of fact, high covalency would scarcely exist in any transition metal-isothiocyanato complexes. But also in

established covalent compounds such as organic isothiocyanates the C–N frequency often is higher than that of the thiocyanate ion.<sup>19,20</sup> Extremely low frequencies, however, are reported for  $P(NCS)_3$ ,  $OP(NCS)_3$ <sup>21</sup> and for tetraalkyl distannoxanes  $(SCN)_2R_2SnO_2SnR_2(NCS)_2$ ,<sup>22</sup> but at least for the last compound the lowering of the C–N stretching frequency may be interpreted as being caused by the bridging of the thiocyanate nitrogen to another tin atom. The simplest covalent compound that a thiocyanate group can form is HNCS and in gaseous HNCS the pseudoantisymmetric stretching of the NCS part (approximately  $\nu_{CN}$ ) is found at 1963  $cm^{-1}$ .<sup>23</sup> Thiocyanic acid extracts also very well into organic solvents,<sup>24</sup> and may then be investigated by IR-spectroscopy. The frequency and the integrated absorption of the C–N stretching vibration of HNCS as compared to that of  $NCS^-$  have been measured to see if more information can be obtained about the usefulness of the simple valence bond model<sup>1,5</sup> when discussing a thiocyanate group involved in covalent compounds.

## EXPERIMENTAL

*Extraction of thiocyanic acid.* Thiocyanic acid was obtained by extraction from aqueous solutions of sodium thiocyanate and perchloric acid into carbon tetrachloride, benzene, nitrobenzene, diethyl ether, and chloroform. The concentration of the thiocyanic acid in the separated organic phase was determined in the following way: A portion of the phase was added to a known volume of dilute sodium hydroxide in water and the acid was reextracted to the aqueous phase. The excess of sodium hydroxide was then titrated with standard acid, using methyl red as indicator. The thiocyanate concentration was determined gravimetrically as  $AgSCN$ . The ratio of hydrogen ions to thiocyanate ions was found to be 1:1, whence it may be concluded that only thiocyanic acid was extracted in these experiments. The same results were also obtained by analysing the aqueous phase and using the known total concentrations of acid and thiocyanate ions.

*Extraction of iron(III) thiocyanato complexes.* Iron(III) thiocyanato complexes were extracted into diethyl ether from aqueous solutions of iron(III) perchlorate and sodium thiocyanate. Because thiocyanic acid itself extracts very well into this solvent the extraction was made from very slightly acid aqueous solutions, *i.e.* at a pH just below that at which the metal ion hydrolysis begins. The iron(III) concentration in the aqueous phase was determined by titra-

tion with a mercurous nitrate solution (see Ref. 25, p. 399) and the thiocyanate concentration gravimetrically as AgSCN. Knowing the original concentrations those in the organic phase could be obtained.

**Extraction with trilaurylamine (TLA).** A 35 mM trilaurylamine (tridodecylamine) solution in benzene was pre-equilibrated with an equal volume of 35 mM nitric acid. Sodium thiocyanate and iron(III) nitrate were used in the aqueous phase to form the extractable species. Both the iron and the total thiocyanate concentrations in the aqueous phase were determined as described above, and those in the organic phase were obtained using the values in the aqueous phase and in the original solution.

**Preparation of  $Fe(NCS)_6^{3-}$  complexes.**  $(Bu_3HN)_3Fe(NCS)_6$  was prepared from iron(III) chloride, ammonium thiocyanate and a tributylammonium acetate solution as described by Ziegler *et al.*,<sup>26</sup>  $(Ph_3MeAs)_3Fe(NCS)_6$  from ammonium thiocyanate, iron(III) ammonium sulfate, and triphenylmethylarsonium chloride according to Dwyer and Gibson.<sup>27</sup>  $Ph_3MeAsSCN$  was also obtained as an intermediate. All the compounds were soluble in several organic solvents.

The stoichiometry of the iron compounds was checked by carbon-hydrogen-nitrogen analysis at the Analytical Laboratory, Chemical Center, Lund. Calc. for  $(Bu_3HN)_3Fe(NCS)_6$ : C 52.36; H 8.79; N 13.08. Found: C 52.5; H 8.70; N 13.2. Calc. for  $(Ph_3MeAs)_3Fe(NCS)_6$ : C 55.31; H 3.98; N 6.14. Found: C 55.36; H 3.89; N 6.06.

**Chemicals.** Most of the chemicals were of *p.a.* quality and used as purchased without further purification. Only the chloroform was purified from the stabilizing ethanol (1 %) by means of molecular sieves. Trilaurylamine (tridodecylamine) was of "qualité nucléaire" from Rhône-Poulenc-Paris.

**Infrared spectra.** The infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer. The spectral slit width (reso-

lution) of the spectrophotometer was about 1.5  $cm^{-1}$ . The integrated absorptions were determined by direct graphical integration.<sup>4</sup> The solid samples were examined in KBr pellets and the solutions in  $CaF_2$  cells usually of thickness 0.1 mm. The concentration of the solid sample in a KBr pellet was obtained by accurate weighing of the sample before it was mixed up and by a determination of the volume of the pellet when it had been pressed. The accuracy of the integrated absorption was estimated to be within 10 %.

## RESULTS AND DISCUSSION

As a basis for the discussion of the binding type in thiocyanic acid and the thiocyanato complexes of iron(III), the frequencies and integrated absorptions of  $NaSCN$  and  $Ph_3MeAsSCN$  are given in Table 1. Judging from the frequencies both compounds would be regarded as ionic compounds but the integrated absorptions suggest there are some interactions between the triphenylmethylarsonium ion and the thiocyanate ion which increase the integrated absorption. This effect should be remembered when anionic thiocyanato complexes are investigated. Generally, these are prepared from non-aqueous solvents as salts of large quaternary cations, to avoid the presence of water of solvation that often occurs with the salts of alkali metal cations prepared from aqueous solution. It is then not certain that these cations could be regarded as fully inactive in their relation to the thiocyanate-containing species, and that the infrared absorption of the thiocyanate groups would not be governed only by the interaction between these groups and the central atom.

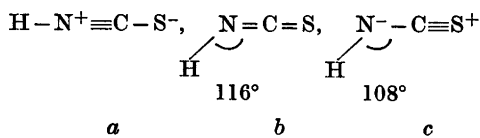
Table 1. Infrared spectral data of sodium thiocyanate and triphenylmethylarsonium thiocyanate in different solvents.

	Solvent <i>etc.</i>	$\nu_{CN}$ ( $cm^{-1}$ )	$\epsilon$ ( $M^{-1} cm^{-1}$ )	$\Delta\nu_{1/2}$ ( $cm^{-1}$ )	$\epsilon\Delta\nu_{1/2} \times 10^{-4}$ ( $M^{-1} cm^{-2}$ )	$A \times 10^{-4}$ ( $M^{-1} cm^{-2}$ )
$Na^+SCN^-$	KBr-pellets	2070	310	39	1.22	3.25
	Pyridine	2059	1020	15	1.53	4.28
	Acetonitrile	2062	700	18.5	1.30	4.29
	Dimethyl sulfoxide	2056	850	13	1.11	3.31
$Ph_3MeAs^+SCN^-$	Pyridine	2055	1270	16	2.03	6.04
	Acetonitrile	2058	1465	15	2.20	7.37
	Nitrobenzene	2056	790	21	1.66	5.37
	Dimethyl sulfoxide	2055	1390	13	1.81	5.34

Table 2. The spectral data of the C–N stretching vibration of HNCS in various solvents.

Solvent	$\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	$\epsilon\Delta\nu_{1/2} \times 10^{-4}$ ( $\text{M}^{-1} \text{cm}^{-2}$ )	$A \times 10^{-4}$ ( $\text{M}^{-1} \text{cm}^{-2}$ )
Carbon tetrachloride	1980	1110	23	2.6	8.4
Chloroform	1987	390	46	1.8	6.1
Benzene	1992	530	45	2.4	7.0
Nitrobenzene	2021	260	60	1.6	4.2
Diethyl ether	2027	260	54	1.4	3.9

*Thiocyanic acid.* The infrared spectrum<sup>23</sup> shows that the acid has the structure HNCS and it should therefore be called isothiocyanic. From microwave studies the dimensions of HNCS have been accurately determined.<sup>28</sup> The bond lengths are: C–S 1.56 Å, C–N 1.22 Å and N–H 1.01 Å. The H–N–C bond angle is 136° and the N–C–S group is linear. Probable resonance structures are (*cf.* Pauling<sup>29</sup>)



Using the experimental lengths and Pauling's formulae relating the amount of single-, double-, and triple-bond character to observed bond lengths, one will find that there is approximately equal resonance among the three structures. Also the bond angle would then have the expected value. As mentioned above,  $\nu_{\text{CN}}$  for gaseous HNCS is 1963  $\text{cm}^{-1}$ . The deviations from this value found for HNCS in different solvents (Table 2) are too large to be explained by changes in the force fields caused by differences in the dielectric constant *e.g.* by the classical Kirkwood-Bauer-Magat relation.<sup>30</sup> They are therefore likely to depend on specific solute-solvent interactions. High C–N stretching frequencies of HNCS would imply high bond orders of the C–N bond, which means that structure *a* is growing in importance. It is known that the nitrogen in *a* (*sp*-hybridization) is more electronegative than that of *b* (*sp*<sup>2</sup>-hybridization). Therefore, one would interpret such an increase of  $\nu_{\text{CN}}$ (HNCS) as an increase of ionic character of the isothiocyanic acid. In the limit it would lead to a displacement of the electronic structure

of the NCS group in HNCS to that of the free NCS<sup>−</sup> ion.<sup>5</sup>  $\nu_{\text{CN}}$ (SCN<sup>−</sup>) is usually found at 2055–2070  $\text{cm}^{-1}$  depending on the solvent used.

It is very difficult to find any general quantitative measure of the form of solute-solvent interactions. Some successful attempts to relate observed frequency changes of a solute to the electron density at likely centers of interaction of the solvents based upon the Taft (Hammett) inductive factors have been made (see, *e.g.*, Ref. 31). Most of the solvents used in this investigation would, however, have different atoms as centers of interaction and therefore a discussion about the inductive factors of the groups bonded to them is not meaningful.

It is reasonable to suggest that the solvent-solute interactions in this case could be a hydrogen bond formation  $\text{RX}\cdots\text{HNCS}$ . Such hydrogen bonds would cause a weakening of the H–N bond, which in the valence bond treatment could be described as a decrease of the covalent character of the bond. It would also increase the bond order of the N–C bond and consequently  $\nu_{\text{CN}}$ . If the solvent-solute interaction in this way is supposed to be directed towards the hydrogen atom of HNCS, a high electron density on the interacting atom of the solvent molecule would promote it.

Carbon tetrachloride and chloroform would use a chlorine atom as the center of interaction, but as could be inferred from the Taft inductive factors of  $-\text{CCl}_3$  and  $-\text{CHCl}_2$  (+2.65 and +1.94) this atom would be more negative for chloroform. Benzene is supposed to interact by the  $\pi$  electron cloud of the aromatic ring, whereas nitrobenzene is more likely to use an oxygen of the electronegative nitro group. It is therefore probable that the interaction of nitrobenzene is larger than that of benzene. The last member of the solvents used is diethyl ether,

which apparently is more basic than nitrobenzene (cf. the  $pK_a$  values reported in Ref. 32). Although the order of the solvents suggested above according to their possibilities to interact with the isothiocyanic acid hydrogen is very approximate, it is nevertheless the same that is given by the experimentally determined  $\nu_{\text{CN}}(\text{HNCS})$  in these solvents.

It is also interesting to see in Table 2 that the integrated absorptions follow an opposite trend as to the frequency. As has been argued before,<sup>3</sup> this is a logical change when a simple fixed charge model is used. This model would suggest that the larger the integrated absorptions for the thiocyanate groups the more covalent the H—NCS bond would be. The absolute values of the integrated absorption are, however, surprisingly small. As could be seen in, e.g., Ref. 33 many N-bonded complexes would have integrated absorptions near  $20 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$  and for organic thiocyanates they are between 15 and  $20 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ .<sup>19</sup> It should, however, be remembered that the model presupposes an almost independent  $\text{SCN}^-$  group and this is apparently not the case when the group is, for the main part, covalently bound to other atoms.

*Iron(III) thiocyanato complexes.* Thiocyanato complexes of iron(III) could be extracted into diethyl ether but not in appreciable amounts in the other solvents used when thiocyanic acid was extracted. The extraction into nitrobenzene has been reported by Maddock and Medeiros<sup>18</sup> but it was an extraction of tracer iron with a total iron concentration of  $10^{-6} \text{ M}$ , which is too small to give observable IR-absorption bands of the complexes extracted. When in this work more concentrated solutions were used, there

were some species extracted that showed an intense IR-absorption at  $1996 \text{ cm}^{-1}$ . This band could hardly be the C—N stretching vibration of a ferric thiocyanato complex. The ratio Fe:SCN in the organic phase, as calculated from the total concentrations and those in the aqueous phase, would be 1:23. NaSCN cannot be extracted into nitrobenzene and therefore it must be suggested that the thiocyanate group has decomposed in some way and that the spectrum has its origin in these degradation products.

The infrared spectrum of the ether solution has an intense absorption band at  $2042 \text{ cm}^{-1}$  (Fig. 1 and Table 3). The integrated absorption of this band (calculated per SCN group) was  $15.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ . Analysis gave the stoichiometric ratio  $\text{Fe}^{3+}:\text{SCN}^- = 1:4.5$ . This suggests either that more than one ferric thiocyanate species are extracted or that some thiocyanate ions are extracted in another form. The absorption band is, however, somewhat asymmetric at the low frequency side, and as the C—N stretching frequency of HNCS is usually found at  $2027 \text{ cm}^{-1}$ , the most probable explanation would be that the ferric species is  $\text{Fe}(\text{NCS})_4^-$  and that HNCS is co-extracted in spite of the precautionary measures (see the experimental part). If this is so, the value of the integrated absorption also contains the contribution from the thiocyanate group in HNCS. Therefore, this quantity for the iron(III) thiocyanates is not known exactly but it may be supposed that it is  $> 15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ .

Also an extraction of iron(III) thiocyanato complexes with trilaurylamine or rather trilaurylammonium nitrate has been performed. There are indications<sup>7</sup> that the only iron-con-

Table 3. Infrared spectral data of the extracted iron(III) thiocyanate complexes [probably  $\text{Fe}(\text{NCS})_4^-$ ] and  $\text{TLAH}^+ \text{NCS}^-$ . The values of  $\epsilon$ ,  $\epsilon A\nu_{1/2}$  and A are calculated per SCN group.

	Solvent	$\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$\epsilon$ ( $\text{M}^{-1} \text{ cm}^{-1}$ )	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	$\epsilon A\nu_{1/2} \times 10^{-4}$ ( $\text{M}^{-1} \text{ cm}^{-2}$ )	$A \times 10^{-4}$ ( $\text{M}^{-1} \text{ cm}^{-2}$ )
$\text{Fe}(\text{NCS})_4^-$	Diethyl ether	2042	1540	35	5.4	15.1
$\text{TLAH}^+ \text{Fe}(\text{NCS})_4^-$	Benzene	2048	790	57	4.5	12
$\text{TLAH}^+ \text{NCS}^-$	Benzene	2042	630	45	2.8	8.4

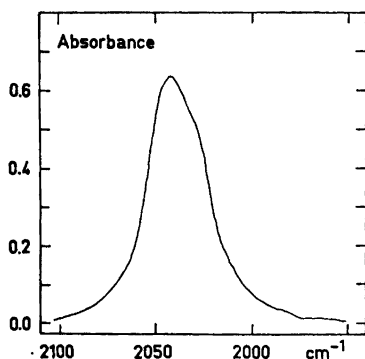
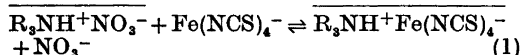


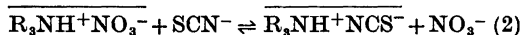
Fig. 1. The infrared spectrum in the C-N stretching range of the iron(III) thiocyanato complexes extracted into diethyl ether.  $C_{\text{Fe}^{3+}} = 9.0 \times 10^{-3}$  (M) and  $C_{\text{SCN}^-} = 40.6 \times 10^{-3}$  (M). The cell thickness is 0.10 mm.

taining anion extracted should be  $\text{Fe}(\text{NCS})_4^-$ , but of course also other anions, e.g.  $\text{NCS}^-$ , could be extracted simultaneously.

The extraction of anions or anionic complexes by high molecular weight ammonium salts may be regarded as an anion exchange reaction. If for example an aqueous phase containing  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  ion is shaken with a benzene solution of trilaurylammonium nitrate there would be exchanges in the following ways (cf. Ref. 7):



and



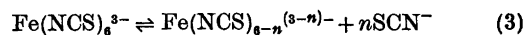
The ammonium salts, when dissolved in the common low dielectric constant organic solvents, usually exist as ion pairs, but also higher aggregations may occur in special cases. The main feature that characterizes an ion pair is the electrostatic nature of the interaction and no directed valence bonds would be involved. The infrared data of  $\text{TLAH}^+\text{NCS}^-$  (Table 3) show, however, a much lower C-N frequency and higher absorption intensity than would be expected from a thiocyanate ion with little electron exchange (cf. the values found not only for  $\text{NaSCN}$  but also for  $\text{Ph}_3\text{MeAsSCN}$ ). It may be suggested that in the actual case a hydrogen bond formation  $\text{R}_3\text{NH}^+\cdots\text{NCS}^-$  is possible, because such bonding would give the effect on the infrared spectra that has been found. This

conclusion is supported by the reported<sup>24</sup>  $\nu_{\text{CN}}$  values of  $\text{R}_4\text{N.NCS}$  and  $\text{R}_3\text{NHNCS}$  ( $\text{R} = \text{C}_{10}\text{H}_{21}$ ). For the tetradecylammonium salt, where hydrogen bonding is excluded,  $\nu_{\text{CN}} = 2050$  cm, but for tridecylammonium thiocyanate the lower value  $\nu_{\text{CN}} = 2043$  cm<sup>-1</sup> was found.

The C-N frequency of  $\text{TLAH}^+\text{NCS}^-$  is also below that of  $\text{TLAH}^+\text{Fe}(\text{NCS})_4^-$  (2042 cm<sup>-1</sup> and 2048 cm<sup>-1</sup>, respectively). But the difference is not large enough to let the two bands be fully resolved at the simultaneous extraction of both species. However, by assuming that the ratio  $\text{Fe}^{3+}:\text{SCN}^-$  is 4 the  $\text{TLAH}^+\text{SCN}^-$  concentration could be obtained from the total concentrations of iron and thiocyanate. Then a spectrum of  $\text{TLAH}^+\text{SCN}^-$  alone with the same concentration was run and the integrated absorption of the ferric complex determined graphically as the difference of the total, unresolved band and the  $\text{TLAH}^+\text{SCN}^-$  band. The method is rather rough because it cannot be excluded that there could be any interaction between the ferric species and  $\text{TLAH}^+\text{SCN}^-$  and therefore the value of the integrated absorption given in Table 3 ( $12 \times 10^4$  M<sup>-1</sup> cm<sup>-2</sup>) should be regarded as approximate. This is still well above that of the unbounded thiocyanate group.

As mentioned above the extracted ferric thiocyanato complexes would probably be four-coordinated. Also six-coordinated complexes, tributylammonium- and triphenylmethylarsonium-hexathiocyanato ferrate(III), were prepared and investigated both in the solid state and in solution, and the results are given in Table 4.

For isolated octahedral ions of the type  $\text{M}(\text{NCS})_6^{3-}$  belonging to the point group  $O_h$ , one would expect a single C-N stretching absorption band. In the solid state, however, splitting could appear owing to site symmetry and correlation effects.<sup>10</sup> This is probably the case for  $(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$  pressed in KBr pellets. The splitting observed when the compounds are dissolved in the various solvents could hardly be due to such effects, but may be caused by a decomposition of the complex. A plausible way is then a partial dissociation:



The "free" thiocyanate ion would have about

Table 4. Frequencies and integrated absorptions of the C–N vibration of  $(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$  and  $(\text{Ph}_3\text{MeAs})_3\text{Fe}(\text{NCS})_6$  in various solvents.  $A$  is the total integrated absorption over all bands cited and is calculated per SCN group.

Solvent etc.	$(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$		$(\text{Ph}_3\text{MeAs})_3\text{Fe}(\text{NCS})_6$	
	$\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$A \times 10^{-4}$ ( $\text{M}^{-1} \text{cm}^{-2}$ )	$\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$A \times 10^{-4}$ ( $\text{M}^{-1} \text{cm}^{-2}$ )
KBr	2080, 2055	5.6	2060	6.0
Diethyl ether	2040, 2070sh	<sup>a</sup>	<sup>b</sup>	<sup>b</sup>
Chloroform	2045, 2000sh	13.2	2067	<sup>a</sup>
Pyridine	2038, 2055sh	9.5	2055, 2036sh	7.8
Nitrobenzene	2033, 2060sh, 1995sh	14.4	2059, 2037	12.7
Acetonitrile	2054	13.7	2059	11.7
Dimethyl sulfoxide	2055, 2038sh	6.8	2055, 2038sh	6.8

<sup>a</sup> The solubility of the compound is too low to permit determination of the integrated absorption.

<sup>b</sup> The compound is insoluble in this solvent. sh=shoulder.

the same frequency as  $\text{Fe}(\text{NCS})_6^{3-}$  and therefore would be difficult to observe. The low frequency band (2040–2030  $\text{cm}^{-1}$ ) in the spectrum could then be assigned to the complex formed through the dissociation of  $\text{Fe}(\text{NCS})_6^{3-}$ . The large frequency shift is a strong indication of different configurations of the two complexes. Of course the infrared spectrum gives no definite evidence that the complex formed is tetrahedral, but, as has been mentioned previously, the frequency shift is that expected from a change from octahedral to tetrahedral configuration. The expected increase of the integrated absorption is more difficult to observe as the equilibrium between the forms changes from solvent to solvent and also depends on the kind of

cation present. The solvents in Table 4 are given in an order of increasing dielectric constants and from a theoretical point of view one would expect the equilibrium (3) to be further to the right for solvents of low polarity because highly charged species are disfavoured in such solvents. This seems also to be partly justified by the frequencies given in the table although the dimethyl sulfoxide solutions show an obvious dissociation of the six-coordinated complex. As expected, the cation influence on the equilibrium is also accentuated in solutions of low polarity. Generally  $(\text{Ph}_3\text{MeAs})_3\text{Fe}(\text{NCS})_6$  is less soluble than  $(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$  and it is also less disposed to dissociate. This is best illustrated by the chloroform solutions. The spectra of  $(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$  in chloroform and in nitrobenzene (Fig. 2) reveal another peculiarity, viz. traces of absorption peaks at about 2000  $\text{cm}^{-1}$ . It may be suggested that this is due to a decomposition of thiocyanate groups like that found above at the extraction of thiocyanato complexes of iron(III) into nitrobenzene.

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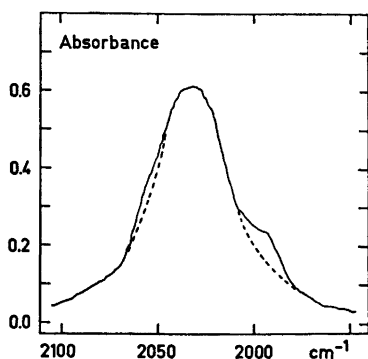


Fig. 2. The infrared spectrum in the C–N stretching range of  $(\text{Bu}_3\text{NH})_3\text{Fe}(\text{NCS})_6$  dissolved in nitrobenzene ( $8.85 \times 10^{-3}$  M). The cell thickness is 0.10 mm.

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