

Infrared and Raman Spectra of Some Systems Containing Thiocyanate Groups

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Infrared spectra have been taken of solid silver thiocyanate and ammonium silver thiocyanate in the region $400-2\,200\text{ cm}^{-1}$. These spectra indicate that the latter compound is composed of silver thiocyanate and thiocyanate ions in agreement with X-ray data. The assignment of the fundamentals has not been possible because one of the fundamentals has evaded detection. A probable correspondence between the lines in the spectra of the thiocyanate ion, the silver thiocyanate and the ammonium silver thiocyanate has been given.

Raman spectra from solutions containing silver thiocyanate dissolved in ammonium and sodium thiocyanate have shown that these solutions do not contain spectroscopically detectable units having strong bonds between SCN groups and silver ions. The silver ion influences the CN stretching frequency. There is an increase in this frequency when going from the solutions to the solid compounds.

In the present paper some results from a study of systems containing silver and thiocyanate groups will be reported. The systems have been investigated by means of molecular spectroscopic methods. The principal aim of the work has been to compare the vibrational behaviour of the thiocyanate group in different environments. Therefore systems having a known crystal structure have been chosen, namely silver thiocyanate investigated by Lindqvist¹ and ammonium silver dithiocyanate studied by Lindqvist and Strandberg². Furthermore, water solutions of sodium and silver thiocyanates (Leden and Nilsson³) and ammonium and silver thiocyanates (Nilsson⁴) were examined in order to elucidate possible differences between thiocyanate groups in a solid phase and in its corresponding mother liquid.

The vibrational behaviour of the thiocyanate ion, SCN^- , is characterized by three fundamental modes (*cf.* Herzberg⁵) either it is regarded as linear (point group $C_{\infty v}$) or bent (point group C_s). There has been some discussion about its proper structure (Saraf⁶), but for the sake of simplicity it will *pro tempore* be regarded as linear. Then the first of the normal vibrations, ν_1 , corresponds to a stretching of the CN-bond. Being a triple bond it is strong

and, consequently, the vibrational frequency high, about $2\,065\text{ cm}^{-1}$. The second vibration, ν_2 , is a bending of the molecule with a frequency of about 480 cm^{-1} . It is a doubly degenerate mode. The third vibration, ν_3 , can essentially be looked upon as a stretching of the S—C-bond with a frequency of about 750 cm^{-1} . In the crystalline phase the vibrational state of the SCN^- ion corresponds in its main features to that in solution (Jones⁷). The degenerate mode, ν_2 , is split.]

In some previous works the change in the ν_1 mode frequency has been studied in order to elucidate the structure of various thiocyanate complexes. Thus Chatt *et al.*^{8,9} have found a change in the infrared absorption in the region $2\,100\text{--}2\,170\text{ cm}^{-1}$ with the position of thiocyanate groups in platinum and palladium complexes containing tri-*n*-propyl phosphine or -arsine groups. They distinguish between terminal SCN groups having absorption in the range $2\,100\text{--}2\,120\text{ cm}^{-1}$ and bridging SCN groups giving rise to frequencies in the region $2\,150\text{--}2\,185\text{ cm}^{-1}$. The difference has been attributed to increased bond order of the CN bond with increasing positive charge on the sulphur atom as a consequence of coordination to two metal atoms. However, the type of bridging is at present not definitely settled (*cf.* Ref.⁹).

Fujita, Nakamoto and Kobayashi¹⁰ have explained the higher ν_1 -stretching frequency in Cr^{3+} and Co^{3+} complexes as due to *sp* hybridization of the nitrogen atom compared to *sp*² hybridization in thioisocyanic acid. The frequencies are $2\,000\text{--}2\,180\text{ cm}^{-1}$ and $1\,963\text{ cm}^{-1}$, respectively. The interaction between the sulphur atom and outer ions such as Hg^{2+} and Ag^+ shifts the CN stretching vibration to higher frequencies.

The crystal symmetry of the silver thiocyanate is according to Lindqvist's investigation¹ monoclinic with the space group $C2/c$ (C_{2h}^6). The unit cell contains eight silver thiocyanate molecules. The structure can best be described as built up by endless chains, with the composition $(\text{AgSCN})_n$ formed by a covalent bond from a silver atom to the end sulphur of one thiocyanate group and a bond to the end nitrogen of another thiocyanate group. (The latter bond is not necessarily covalent.) The chains have a zig-zag shape and progress almost perpendicularly to the *bc* plane. There is a silver-sulphur interaction between different chains: the Ag-S distances are $2.997 \pm 0.011\text{ \AA}$ and $2.886 \pm 0.012\text{ \AA}$ compared to the Ag-S bond distance of $2.428 \pm 0.001\text{ \AA}$ and the Ag^+ -S distance of $2.9\text{--}3.1\text{ \AA}$. No significant deviation from linearity in the SCN group has been found.

The symmetry of the ammonium silver dithiocyanate is monoclinic², belonging to space group $P2_1/n$ (C_{2h}^5). The unit cell contains four molecules. The crystal is built up by AgSCN molecules, NH_4^+ ions and SCN^- ions. The silver atom coordinates four sulphur atoms in a very distorted tetrahedron. The Ag-S distances are: $2.474 \pm 0.020\text{ \AA}$ within the AgSCN molecule, $2.654 \pm 0.019\text{ \AA}$, $2.630 \pm 0.027\text{ \AA}$ and $2.742 \pm 0.029\text{ \AA}$ from one AgSCN molecule to the three surrounding SCN^- ions.

The state of the thiocyanate group in water solution at high contents of thiocyanate is, according to solubility and potentiometric data³, characterized by a series of complexes of the type $\text{Ag}_m(\text{SCN})_{2m+2}^{(m+2)-}$. The complex having $m = 1$ is the most abundant in solutions containing sodium thiocyanate.

From electron distribution functions⁴ in ammonium silver thiocyanate systems it has been found that a model based on the $\text{Ag}_m(\text{SCN})_{2m+2}^{(m+2)-}$ complexes gives one Ag-S distance, which does not correspond to a maximum of the distribution function. An idealized layer structure based upon the crystal structure of ammonium silver dithiocyanate gives Ag-S and Ag-Ag distances in agreement with the distribution curve.

EXPERIMENTAL

Material. The potassium, sodium and ammonium thiocyanates used in the present investigation were of analytical grade. The ammonium salt was recrystallized because it was slightly reddish, probably due to some iron impurities. All the solutions were prepared from distilled water and were carefully filtered. Silver thiocyanate was precipitated from silver nitrate and potassium thiocyanate solutions. It was always used just after preparation. Ammonium silver dithiocyanate was crystallized from mother liquid M I prepared from 100.0 g AgSCN , 98.8 g NH_4SCN and 102.5 g H_2O . The composition corresponds to a point in the phase diagram of $\text{AgSCN}-\text{NH}_4\text{SCN}-\text{H}_2\text{O}$ situated in the liquid area but quite near to the phase limit of $\text{NH}_4\text{Ag}(\text{SCN})_2(\text{s})$ (cf. Occleshaw¹¹). The molarities of the different ions are approximately $M_{\text{SCN}^-} = 9.5$, $M_{\text{Ag}^+} = 3.0$ and $M_{\text{NH}_4^+} = 6.5$. (M means here total concentration.) After about 30 g of $\text{NH}_4\text{Ag}(\text{SCN})_2$ had crystallized, the supernatant liquid was separated from the crystals as mother liquid M II, having the approximate composition $M_{\text{SCN}^-} = 9$, $M_{\text{Ag}^+} = 2.5$ and $M_{\text{NH}_4^+} = 6$. Mother liquid M III was prepared from 11.5 g of AgSCN , 48.5 g of NaSCN and 40 g of H_2O in order to get a saturated solution without solid phase (Occleshaw¹¹). The approximate composition is $M_{\text{SCN}^-} = 10$, $M_{\text{Ag}^+} = 1$ and $M_{\text{Na}^+} = 9$.

Infrared measurements. Infrared spectra were taken from the solid compounds using either the technique with paraffin oil mulls or with potassium bromide pellets. Spectra were run both in a Perkin-Elmer model 21 spectrophotometer equipped with NaCl, KBr and CsBr prisms and in a Beckman spectrophotometer IR-2 in the NaCl region. Difficulties arose with the KBr pellets, for even when very high pressures were used, the prisms were slightly opaque. The reason for this is believed to be the difference in compressibilities of the crystals. The softer thiocyanate material cannot be sintered with the harder potassium bromide. Nevertheless quite good spectra could be obtained in all regions of interest for the present investigation. The accuracy in the wave number determination is $\pm 2-3 \text{ cm}^{-1}$.

Jones⁷ has reported the appearance of anomalous absorption bands from potassium thiocyanate in potassium chloride and bromide disks. The type of anomaly is not stated. Furthermore, Jones¹² has observed foreign peaks from disks containing potassium silver dicyanide. As pointed out by Jones and Chamberlain¹³, this can depend upon an exchange of ions or ion complexes between the different lattices. Such an exchange between K^+ and NH_4^+ has been observed by Pliskin and Eischens¹⁴. In the present case the differences between spectra from mulls and pellets generally are small.

Raman measurements. The raman spectra of the soluble salts and of the mother liquids were obtained using a raman spectrograph arranged for both photographic and photoelectric recording (Kinell¹⁵). The sample volume was about 20 ml. A saturated sodium nitrite solution was used to filter away the 4 046 and 4 077 Å lines. The temperature in the raman tube was kept at 20°C. Depolarization measurements were made using the polaroid sheet technique. The accuracy in the wave number determinations varied with the shape of the lines and also with their intensity. Some of the lines obtained were fairly broad. The accuracy is $\pm 2-3 \text{ cm}^{-1}$, and the spectral band width used was 5–60 cm^{-1} . Under the influence of the exciting light, the solution of ammonium thiocyanate and the mother liquids M I and M II slowly became coloured reddish-brown. This was probably due to the presence of minute amounts of ferric ions and could be remedied by adding traces of a reducing agent (ascorbic acid) to the solutions. All the solutions were filtered through a Jena G4 sintered disk filter which had been thoroughly washed

Table 1. Infrared absorption frequencies (in cm^{-1}) of the thiocyanate ion in solid systems, observed with different prisms and in various preparations (vs = very strong, m = medium).

Assignments Jones ⁷	KSCN				NH ₄ SCN					Values given by Jones ⁷	In- ten- sity
	NaCl			KBr	NaCl		KBr		CsBr		
	Mull	Disk	Acetone soln	Disk	Mull	Disk	Mull	Disk	Mull		
ν_1	2 041	2 053	2 062	—	—	2 053	—	—	—	2 053	vs
$2\nu_{2a}$	967	969	—	—	935	970	970	—	—	968	m
$2\nu_{2b}$	946	948	—	—	930	951	—	—	—	951	m
ν_3	747	748	745	746	752	749	750	747	—	749	m
ν_{2a}	—	—	—	485.5	—	—	476	486	475	484	m
ν_{2b}	—	—	—	471	—	—	466	472	465	470	m

with distilled water. The solid ammonium thiocyanate and ammonium silver dithiocyanate were also run, but only the strong ν_1 vibration could be observed due to excessive scattering of mercury light. Also impurities in the mercury spectrum caused disturbances. In photographic recording, Ilford Zenith plates were used. They were processed in Kodak D-76 fine grain developer. For intensity comparisons the carbon tetrachloride line 459 cm^{-1} was used. The ratio of the heights of the actual line to the reference line was taken as a measure of the intensity (*cf.* Kinell¹⁵).

RESULTS

Infrared spectra. The absorption frequencies of the thiocyanate ion obtained from the potassium and ammonium salts in the solid state are collected in Table 1, together with the values of ν_1 and ν_2 from an acetone solution of the potassium salt. The assignments are those given by Jones⁷. His values

Table 2. Infrared absorption frequencies (in cm^{-1}) of silver thiocyanate in the solid state, observed with different prisms and in various preparations (vs = very strong, m = medium, w = weak). The assignments are only to be regarded as a classification.

Assignments	NaCl		KBr		CsBr	Intensity
	Mull	Disk	Mull	Disk	Mull	
ν_1	2 169	2 083	—	—	—	vs
ν_2 overtones	901	—	895	901	—	m
	861	—	855	—	—	m
ν_3	743	—	741	736	—	m
	723	715	720	717	—	w
ν_2	—	—	446.5	444.5	444.5	m
	—	—	423	421	423	m

Table 3. Infrared absorption frequencies (in cm^{-1}) of ammonium silver dithiocyanate in the solid state, observed with different prisms and in various preparations (vs = very strong, s = strong, m = medium, w = weak). The assignments are only to be regarded as a classification.

Assignments	NaCl		KBr		CsBr	Intensity
	Mull	Disk	Mull	Disk	Mull	
ν_1	2 120	2 119	—	—	—	s
	2 090	2 070	—	—	—	vs
ν_2 overtones	940	—	—	—	—	m
	909	—	—	—	—	m
	899	901	—	901	—	m
	887	—	877	—	—	w
ν_3	738	730	736	736	—	m
	722	717	720	717	—	m
ν_2	—	—	472	470.5	470	m
	—	—	454.5	454.5	454.5	m
	—	—	450.5	—	449.5	m
	—	—	443.5	442.5	442.5	m
?	—	—	420	419	420	w

are also given in the last column. The values from disks agree very well with Jones' values. The slightly changed frequencies in paraffin oil mulls of ammonium thiocyanate cannot at present be explained. The higher ν_3 value and lower ν_1 value in acetone solution correspond to similar results found for water solutions by Jones⁷ and Gordy and Williams¹⁶.

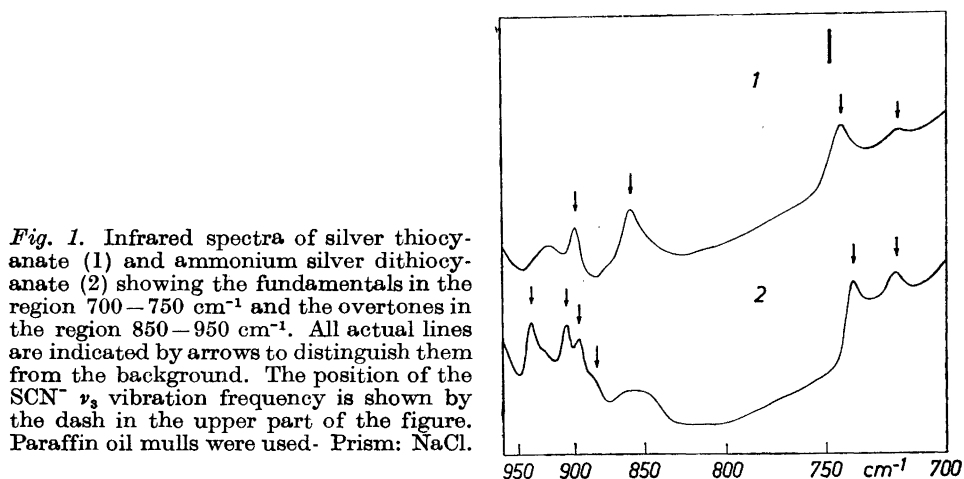


Fig. 1. Infrared spectra of silver thiocyanate (1) and ammonium silver dithiocyanate (2) showing the fundamentals in the region $700-750 \text{ cm}^{-1}$ and the overtones in the region $850-950 \text{ cm}^{-1}$. All actual lines are indicated by arrows to distinguish them from the background. The position of the $\text{SCN}^- \nu_3$ vibration frequency is shown by the dash in the upper part of the figure. Paraffin oil mulls were used. Prism: NaCl.

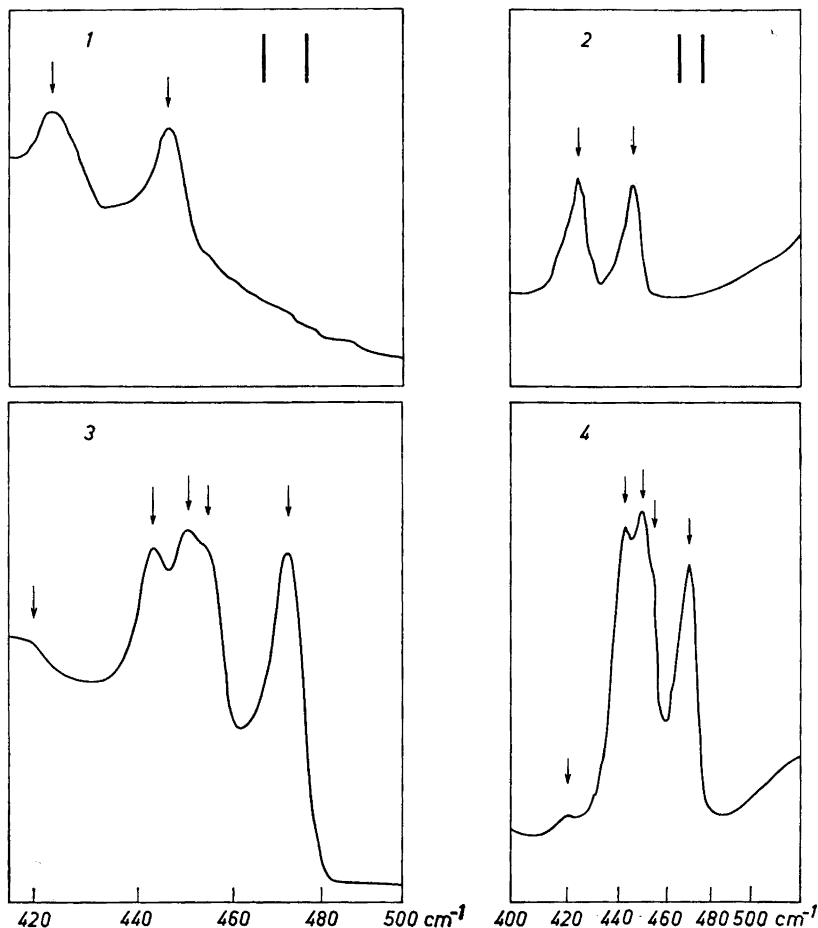


Fig. 2. Infrared spectra of thiocyanates: 1) AgSCN, KBr prism; 2) AgSCN, CsBr prism; 3) $\text{NH}_4\text{Ag}(\text{SCN})_2$, KBr prism; 4) $\text{NH}_4\text{Ag}(\text{SCN})_2$, CsBr prism. The actual lines are indicated by arrows. The positions of the ν_2 vibration frequencies of the SCN^- ion are shown by the dashes in the upper part of the figure. Paraffin oil mulls were used.

The absorption frequencies of solid silver thiocyanate are collected in Table 2. There are some disagreements between paraffin mull and potassium bromide disk values. The high frequency 2160 cm^{-1} corresponds very well to the value 2149 cm^{-1} reported by Chatt⁹. In potassium bromide disks a line at 455 cm^{-1} has been observed. It has a tendency to decrease with the age of the disks. As it does not appear in any of the other spectra, it has been discarded. No indications of any lines which could be associated with silver thiocyanate were found in the region $400\text{--}250\text{ cm}^{-1}$.

Finally the absorption frequencies of solid ammonium silver dithiocyanate are given in Table 3. The ν_2 values at 450 and 455 cm^{-1} are from bands which

Table 4. Raman lines of the thiocyanate ion (in cm^{-1}) in water solutions of potassium and ammonium thiocyanate. The figures within parentheses under the wave numbers are the intensities of the lines compared to the 459 cm^{-1} carbon tetrachloride line as a reference.

Assignments	KSCN				NH_4SCN	
	Photo-electric	Photographic			Photo-electric	Photo-graphic
		Light unpol.	Light pol.	Light pol. \perp		
ν_1	2 065 (170)	2 063	2 064	2 064	2 066 (120)	2 062
$2\nu_2$	—	940	—	—	—	—
ν_3	745 (20)	746	—	—	752 (15)	—
$\nu_2 ?$	481 (2)	488	—	—	485 (2)	—

are not completely resolved. Not even in this case could any vibrations be found in the low frequency region $400\text{--}250 \text{ cm}^{-1}$.

The assignments in Tables 2 and 3 are to be regarded as a classification only.

The intensities given in the tables are estimations of the relative heights of the absorption bands. In Fig. 1 parts of the spectra from silver thiocyanate and ammonium silver dithiocyanate obtained in single beam runs (Beckman IR-2) are shown. The actual absorption maxima are indicated by arrows. The 450 cm^{-1} bands of the same compounds recorded in the double beam instrument (Perkin-Elmer model 21) using KBr and CsBr prisms respectively

Table 5. Raman lines of mother liquids M I, M II, M III. For explanation cf. Table 4.

Assignments	M I	M II	M I'	M II'	M III		
	Photoelectric	Photographic	Photographic	Photographic	Photographic		
					Light unpol.	Light pol.	Light pol. \perp
ν_1	2 093 (105)	2 089 (140)	2 086	2 082	2 075	2 073	2 074
$2\nu_2$	—	—	921	924	931	—	—
ν_3	771 ? 737 (10)	771 ? 735 (10)	732	735	746	—	—
ν_2	465 (6)	455 (4)	461	463	466	—	—

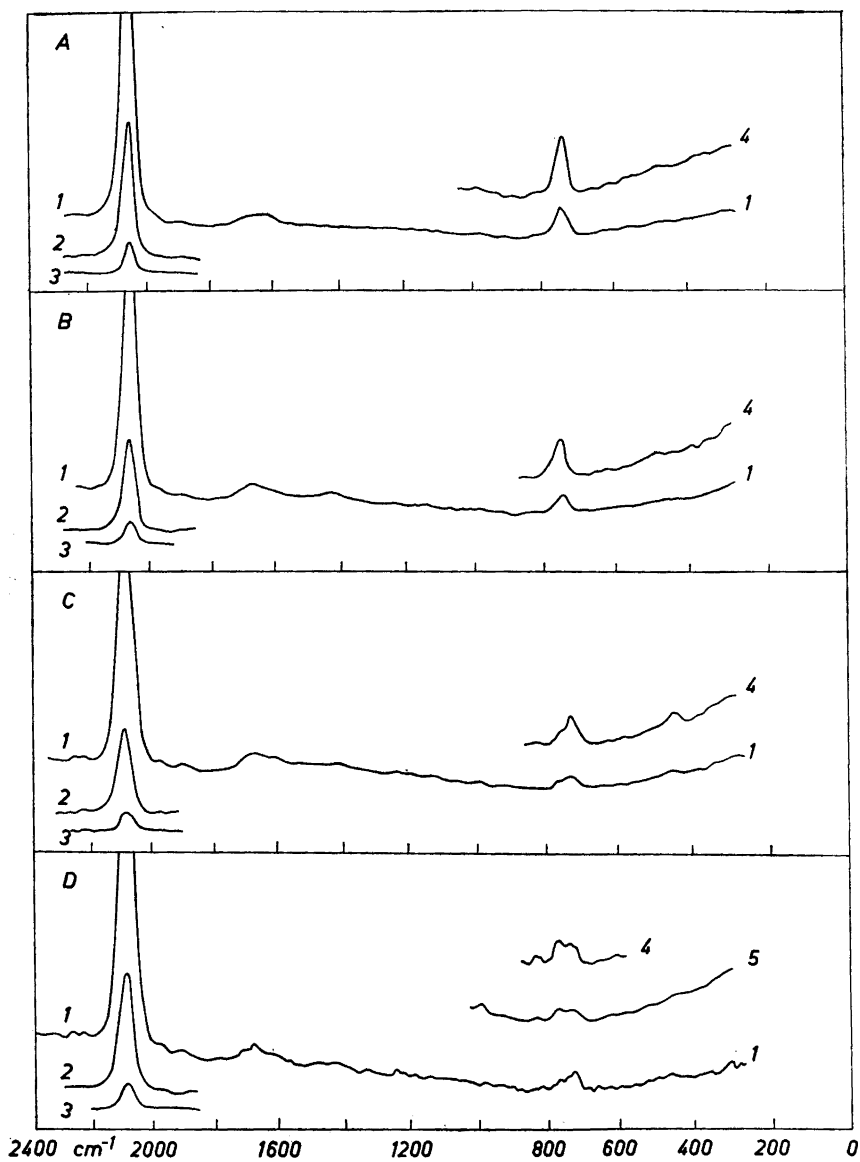


Fig. 3. Photoelectrically recorded Raman spectra of A) water solution of KSCN; B) water solution of NH_4SCN ; C) mother liquid M I and D) mother liquid M II. Spectra marked with the same figure are directly comparable.

are given in Fig. 2. In both figures the position of the corresponding bands of ammonium thiocyanate has been indicated.

For the present purpose the absorption bands due to the ammonium ion were not studied.

Raman spectra. The frequencies of the raman displacements observed in water solutions of the thiocyanate ion and in the mother liquids are given in Tables 4 and 5. A dash indicates that the line was observed but its frequency not estimated. The existence of the line 485 cm^{-1} as a fundamental mode excited from the Hg line $4\,358\text{ \AA}$ is dubious. The value is in agreement with the ν_1 mode excited by $4\,077\text{ \AA}$. However, existence of a ν_2 mode is evident from the first harmonic at 940 cm^{-1} . Then the ν_2 frequency would be 470 cm^{-1} . This is in good agreement with the infrared data and with the value in water solution observed in the infrared by Jones⁷. The value given by Saraf⁶, 499 cm^{-1} , seems too high. The corresponding line from the mother liquids is easily observed. The ν_1 mode excited from $4\,077\text{ \AA}$ would appear at about 500 cm^{-1} . In some of the spectra of the mother liquids a splitting of the ν_3 line was observed. In test runs (M I', M II') it could not be reproduced. No indications of a splitting of the other lines have been found in runs made and photographs taken at different slit widths. The ν_1 line is slightly skew towards shorter wave lengths.

The general appearance of the spectra is shown in Fig. 3. All the spectra No. 1 have been recorded under the same conditions. The bands between $1\,400\text{--}1\,800\text{ cm}^{-1}$ are due to the water molecules and to the ammonium ions. From spectra Nos. C:3 and D:3 the skewness of the ν_1 line can be seen. The results of the runs made on solid ammonium thiocyanate and ammonium silver dithiocyanate are given in Fig. 4. In the first case the existence of a line at about $2\,065\text{ cm}^{-1}$ is quite clear from a comparison of the background spectrum (4) with the actual spectrum (5). In the last case both the background (1) and the actual curve (2) are reproducible in all essential details. The curve (3) representing the difference between (2) and (1) has two maxima indicating absorption at $2\,085\text{--}2\,090\text{ cm}^{-1}$ and at about $2\,120\text{ cm}^{-1}$. In Fig. 5 the ν_1 vibration of potassium thiocyanate is recorded at four different concentrations. No significant change in the position of the line can be found.

In order to find any possible differences between the state of polarization of the raman lines of the thiocyanate group in pure water solution and in the mother liquid, spectra with the incident light polarized in directions parallel and perpendicular to the direction of observation were taken. From these, the depolarization factors were found to be 0.58 and 0.65 for the ν_1 line in potassium thiocyanate solution and in mother liquid M III, respectively. The value 0.58 corresponds with the figure 0.55 given by Saraf⁶. Both of the values obtained here show that the ν_1 mode is polarized. There are no significant shifts in the position of the lines (*cf.* Tables 4 and 5), and thus it is not probable that the higher depolarization factor from M III should indicate the presence of a depolarized line quite near to a polarized one. The other lines were not measured, but the photographically obtained spectra showed that they are polarized. This is also the case with the $2\nu_2$ mode.

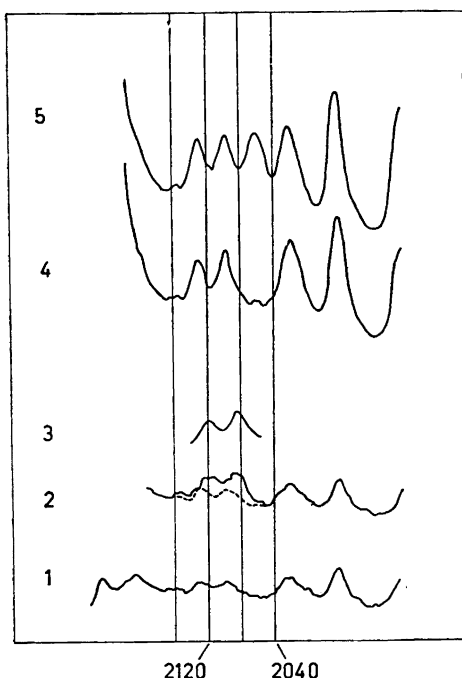


Fig. 4. Raman spectra of solid thiocyanates: 1) and 4) mercury lamp background; 2) background and superimposed spectrum of $\text{NH}_4\text{Ag}(\text{SCN})_2(\text{s})$; 3) spectrum of $\text{NH}_4\text{Ag}(\text{SCN})_2(\text{s})$; 5) background and spectrum of $\text{NH}_4\text{SCN}(\text{s})$.

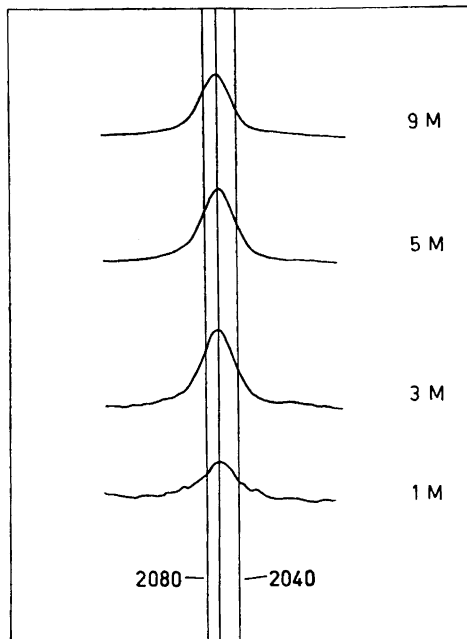


Fig. 5. The ν_1 line of SCN^- in water solutions of potassium thiocyanate of different concentrations.

DISCUSSION

Interpretation of spectra. In the following section some remarks concerning the interpretation of the spectra obtained will be made. The complete assignment of the frequencies must be postponed to a later occasion (Kinell, work in progress).

The only symmetry element of an isolated four atomic molecule of the type AgSCN is a plane of symmetry, *i.e.* the plane containing all the atoms. The number of normal modes is six. The molecule belongs to the point group C_s . This contains two species of normal vibrations; A' , symmetric with respect to the plane of symmetry and, A'' , antisymmetric with respect to this plane. Then, the representation which has the vibrational motions as its basis can be broken down into its irreducible components in the following way

$$\Gamma_{\text{vib}} = 5A' + A''.$$

All the vibrations belonging to A' must occur in the plane of symmetry and the only one of A'' , at right angle to this plane. All six vibrations are active in both raman and infrared spectra.

In a crystal the field of force, in which the molecules are located, will cause a splitting of the internal vibrational modes. Furthermore, the classification and the selection rules of the modes will change because of the different symmetry properties of the molecule and the crystal. Applying the methods (*cf.* Bhagavantam and Venkatarayudu¹⁷, Hornig¹⁸, and Winston and Halford¹⁹) worked out for analysis of the normal vibrations of molecules in crystals, one finds for the silver thiocyanate that its factor group of the space group C_{2h}^6 , having the invariant subgroup of the lattice translations as its identity element, is isomorphic to the point group C_{2h} . Then the following reduction of the representation which has the internal vibrational modes as its basis will be obtained

$$\Gamma_{\text{vib}} = 4A_{g1} + 6B_g + 6A_u + 6B_u$$

Only the species symmetric with respect to inversion will be raman active, and the species antisymmetric with respect to the same operation infrared active. Thus, the six normal modes of the isolated AgSCN molecule will in the crystal be split into twelve vibrations.

In silver thiocyanate the crystal can be regarded as built up from AgSCN chains¹, and then the line group method of Tobin²⁰ can be used for the analysis of the normal modes. The chains are regarded as isolated and infinite. Their symmetry is described by a one dimensional space group, a line group. The symmetry of the repeating unit is characterized by the elements of the factor group of the line group, which has the invariant subgroup of the chain translations as its identity element. The repeating unit consists of two AgSCN molecules and the factor group is isomorphic to the point group C_s . Then we have for the internal vibrations

$$\Gamma_{\text{vib}} = 8A' + 8A''.$$

Both of the species A' and A'' are raman and infrared active. Thus even in this case more frequencies than for the isolated molecule will appear. Taking even lattice modes under consideration, one finds that each factor group mode of the line group corresponds to one infrared active and one raman active mode under the space group. The silver thiocyanate molecules are located on general points in the unit cell and thus no classification is obtained under the site group (*cf.* Hornig¹⁸).

The above analyses indicate that the silver thiocyanate in the solid state ought to have a rather complicated spectrum in the infrared. On the contrary, the observed spectrum contains only a few lines. If the 900 cm^{-1} lines are regarded as overtones, only five fundamental frequencies have been found. The silver atom is heavy compared to all the other atoms in the silver thiocyanate molecule, and therefore any frequency involving the stretching of the Ag-S bond or bending of the Ag-S-C angle will be low and probably evade observation with the instruments used. An investigation of the isocyanic acid (Herzberg and Reid²¹) has shown that this molecule, which has the same geometrical shape as the silver thiocyanate molecule, has bending modes at 572, 670 and 797 cm^{-1} . The last value refers to the H-N-C angle. In addition, Eyster and Gillette²² have shown that the frequency of the bending deforma-

tion of the angle in hydrazoic acid and methyl azide decreases from 1 153 cm^{-1} to 259 cm^{-1} when the methyl group is substituted for the hydrogen atom. Also in methyl isocyanate and methyl isocyanide the frequencies are low, 353 cm^{-1} and 290 cm^{-1} , respectively. A more thoroughgoing analysis of possible overtones and combination lines in the spectrum of AgSCN (except those already given here) has been started. It is hoped that the new data can give information about possible low frequencies.

The spectrum of the ammonium silver dithiocyanate is also fairly simple. In the case of completely free AgSCN and SCN^- units it should consist of nine fundamental frequencies, all of which are allowed in both the raman and infrared spectrum. The factor group analysis (the space group C_{2h}^5 of the crystal has a factor group having the invariant subgroup of the lattice translations as its identity element, which is isomorphic to the point group C_{2h}) gives for the internal vibrational modes

$$\Gamma_{\text{vib}} = 9A_g + 9B_g + 9A_u + 9B_u.$$

The gerade species are raman active, the ungerade infrared active. The observed spectrum may contain nine lines (the 900 cm^{-1} bands are tentatively regar-

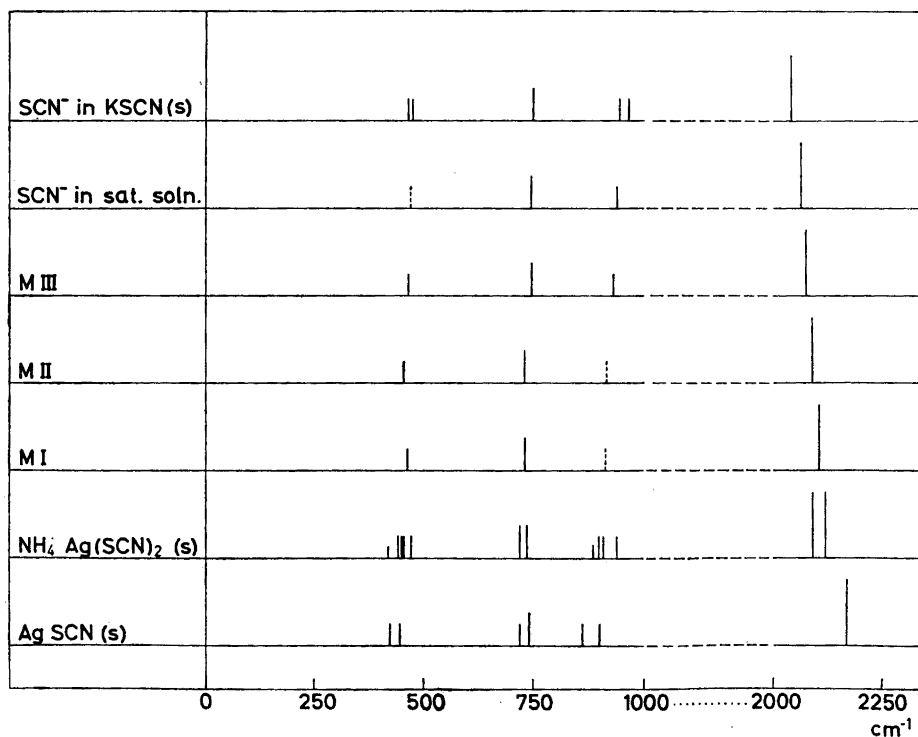


Fig. 6. Schematic raman and infrared spectra of systems containing thiocyanate groups. The intensities are only approximate.

ded as overtones), but only a more thorough study of possible overtones and combination bands in other regions will give a definite answer.

From Fig. 6, where all the spectra have been collected in a schematic diagram, it follows that the spectrum of ammonium silver dithiocyanate seems to be a superposition of the spectra of the SCN^- ion and the AgSCN molecule. This is in agreement with the structure given by Lindqvist and Strandberg². If the lines $2\,090\text{ cm}^{-1}$, 738 cm^{-1} , 472 cm^{-1} and 454.5 cm^{-1} (Table 3) are assumed to belong to the thiocyanate ion, then the remaining lines $2\,120\text{ cm}^{-1}$, 722 cm^{-1} , 450.5 cm^{-1} , 443.5 cm^{-1} and 420 cm^{-1} should correspond to the silver thiocyanate lines (Table 2) except for one missing ν_3 line and one extra ν_2 line. The ν_3 line may not be resolved from the SCN^- line. The interpretation of the 420 cm^{-1} line as a fundamental may be somewhat doubtful because of its very low intensity. It could be an overtone of a low frequency vibration at about 200 cm^{-1} , which would evade detection by the equipment used. The 423 cm^{-1} of silver thiocyanate is most probably a fundamental. Then the following coordination between the spectral lines can be done on the basis of the present data:

	SCN^-		$\text{NH}_4\text{Ag}(\text{SCN})_2$		AgSCN
Fundamentals	2 053	—————	2 120	—————	2 169
			2 090		
Overtones	}	—————	940		
		—————	909		
			899	—————	901
			887	—————	861
Fundamentals	}	—————	738	—————	743
			722	—————	723
		—————	472		
		—————	454.5		
			450.5	—————	446.5
			443.5	—————	423
Overtone?	{		420	?

The raman spectra of the mother liquids are very similar to the spectrum of the SCN^- ion in water solution. Therefore it seems quite reasonable to make the same assignments of the lines in both cases. Due to the weakness of the 460 cm^{-1} band, no detailed study of its structure can be made. The broadening of the energy levels on account of the strong interaction in the solution may have smoothed out a possible splitting. On the other hand, bending modes are not very sensitive to changes in the symmetry of the local field (Bauer and Magat²³). This has clearly been demonstrated in the case of the nitrate ion in water solutions, where at higher concentrations only one of the two doubly degenerate vibrations is split, the other one is not because it should approach a pure bending of the ion (Mathieu and Lounsbury²⁴).

As a summary of this discussion, one could say (*cf.* Fig. 6) that irrespective of the environmental conditions, the vibrational frequencies of the SCN^-

unit fall into four groups, which are well separated from each other. The environmental circumstances influence the position of the lines in each group. Especially the displacement of the 2 050 cm^{-1} band to higher frequencies is noticeable. There may be a fifth group of frequencies, however, this one has most certainly to do with vibrations involving the silver atom.

The state of the SCN group in solution. From the foregoing discussion it is evident that the behaviour of the SCN group in the different environments can approximately be described by the three vibrational modes of the free SCN^- ion. The dependence of the ν_2 and ν_3 vibrations on the conditions of the solution is noticeable but not very pronounced and no conclusions of general value can be drawn.

The vibration of the CN group seems to be the most sensitive to differences in the composition of the solution. The spectra taken at various slit widths show that a splitting of the line is very unlikely. The polarization measurements indicate the improbability of the presence of different symmetry types of SCN groups having very nearly equal frequencies. The existence of complexes of the type $\text{Ag}(\text{SCN})_4^{3-}$ (Leden and Nilsson ³) with a strong bond between the silver and sulphur atoms should at the concentrations and exposure times used certainly have revealed new raman lines separated from those of the thiocyanate ion. Assuming I_d symmetry of the complex ion one gets the following reduction of the normal mode representation

$$\Gamma_{\text{vib}} = 3A_1 + 3E + 2F_1 + 6F_2$$

The totally symmetric A_1 species, the doubly degenerate E species and the triply degenerate F_2 species are raman active. The last species is the only one active in infrared. Of these the three totally symmetric lines can be expected to have rather high intensities. Complexes of the type $\text{Ag}_2(\text{SCN})_6^{4-}$ have on the assumption of D_{2h} symmetry,

$$\Gamma_{\text{vib}} = 10A_g + 6B_{1g} + 5B_{2g} + 6B_{3g} + 3A_u + 9B_{1u} + 9B_{2u} + 6B_{3u}.$$

The gerade species are raman active and the ten totally symmetric modes are expected to have the highest intensity. However, Leden and Nilsson ³ have found that the concentration of this complex is much lower than that of the mononuclear complex, and therefore it is doubtful if any of its lines could have been found under the actual recording conditions.

The frequency of the CN stretching mode as a function of the molar ratio of Ag/SCN is given in Fig. 7. Evidently the displacement of the line is dependent upon the amount of silver present in the system. Furthermore, there is an increase of the frequency going from the various solutions to the solid compounds. The displacement cannot be an effect of the SCN^- concentration. This follows from the frequencies in the M I and M III solutions, which have almost the same SCN^- molarity, and also from the results given in Fig. 5 on the ν_1 frequency in potassium thiocyanate at different concentrations. It can also be concluded that the effect cannot be a first order electrostatic phenomenon because M I, M III and the KSCN solution have each the same molarity of positive ions. The differences in ionic radii of Ag^+ (1.26 Å),

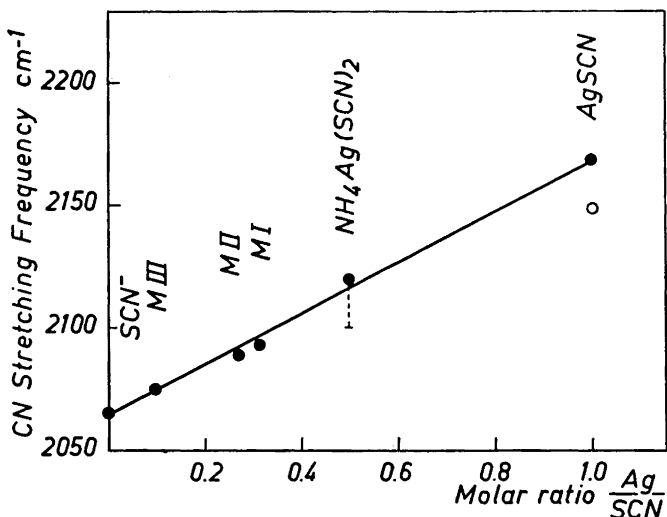


Fig. 7. The frequency of the CN stretching mode as a function of the molar ratio Ag/SCN. O at Ag/SCN = 1 is the value taken from Chatt's *et al.* work⁹. The dotted line at Ag/SCN = 0.5 corresponds to the frequencies given by Chatt *et al.*⁸ for platinum and palladium complexes having terminal SCN groups.

Na^+ (0.95 Å), K^+ (1.33 Å) and NH_4^+ (1.48 Å) indicate that sodium could approach the SCN^- ion more closely than the ammonium ion, and consequently in the case of a pure electrostatic attraction, the M III solution would expect to give a higher displacement than the M I solution.

It is of interest to note that the platinum and palladium complexes studied by Chatt *et al.*⁸, and having terminal SCN groups, fit into the pattern. The frequencies of complexes having molar ratios of Pt/SCN and Pd/SCN equal to unity and containing bridging SCN groups fall in the region 2154–2169 cm^{-1} . Thus they correspond to the behaviour of silver thiocyanate.

The possibility that the ν_1 line should consist of two unresolvable lines, one from the free SCN^- ion and the other from a SCN group bound to the silver ion, is not probable because the half intensity width of the line in M I (53 cm^{-1}) is only slightly higher than in a solution of potassium thiocyanate (47 cm^{-1}). The peak distance of such lines would be at least 50 cm^{-1} and thus the half intensity width of the sum line would be expected to be at least about twice this value.

The evidences given here indicate that the presence of the silver ions in the solutions influences all the thiocyanate groups to approximately the same amount. The displacements observed in the CN stretching vibration are directly dependent upon the amount of silver present per thiocyanate group. The binding of the sulphur atoms to the silver nucleus is not strong enough to give the complexes a character of independent units, which can be detected by spectroscopic means. The data also show that there is a difference between the structure of the solid ammonium silver thiocyanate and its mother liquid.

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