

INFRARED AND RAMAN SPECTROSCOPIC STUDY OF ION PAIRING OF STRONTIUM(II) AND BARIUM(II) BY THIOCYANATES IN LIQUID AMMONIA

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ABSTRACT. Infrared and Raman spectroscopy techniques have been used to study the ionic interactions of strontium(II) and barium(II) with thiocyanate ion in liquid ammonia. A number of bands were observed in both $\nu(\text{CN})$ and $\nu(\text{CS})$ regions of infrared and Raman spectra and these were assigned to 1:1 contact ion pair, $[\text{M}^{2+} \cdots \text{NCS}]^+$; band (B) to a triple-ion, $\text{SCN}^- \cdots \text{M}^{2+} \cdots \text{NCS}$; band (C) to solvent-shared ion pair, $(\text{NH}_3)_x \text{M}^{2+} \leftarrow \text{NH}_3 \cdots \text{NCS}^+$; band (D) to a "free" thiocyanate anion SCN^- and band (E) to an upper stage transition arising from the excitation of a linear species already in a vibrational level above the ground state.

KEY WORDS: Ion pairing of strontium(II) with thiocyanate, Ion pairing of barium(II) with thiocyanate, Ion pairing in liquid ammonia, Infrared and Raman studies of ion pairing

INTRODUCTION

In earlier studies of ion interactions [1, 2] it was asserted that the best way of investigating the constitution of the equilibria between specific ion associates was by measurement and analysis of the vibration spectra of the solute ions of that solution. The use of vibrational spectroscopy can assist in probing the specific structural types of ion associate, and it is sometimes possible to establish the parameters which define the individual equilibria relating to their formation from the "free" solvated ions or other ion associates [3].

Complexation of the first row transition metals [4] and a range of different metal ions [5] by thiocyanate ion have been extensively studied in aqueous solutions, but less extensively studied in non-aqueous media. In liquid ammonia solutions the heavier transition metals appear to favour interaction with the thiocyanate ligand to form solvent-shared ion pair (outer-sphere complexes) [6].

The alkali metal thiocyanates have been studied in some detail in aqueous media [7, 8] in dimethylacetamide [9], dimethyl formamide (DMF) [10-12] and liquid ammonia [13, 14] and a variety of structurally different ion associates have been identified. In several non-aqueous solutions the species participating in the equilibria are 1:1 contact ion pairs, outer-sphere ion pairs and "free" SCN^- anion.

The infrared spectra of alkaline-earth metal thiocyanate solutions are complicated. Band perturbation depends heavily on the solvent. In recent infrared studies of the $\nu(\text{CN})$ region of the spectra of alkaline-earth thiocyanates in DMF [15] it was proposed that the two bands observed could be assigned to a 1:1 contact ion pair and "free" SCN^- anion. However, temperature variation studies revealed the existence of a band to slightly lower frequency due to an upper stage transition [16]. In acetonitrile it was proposed that the dominant species in solution is a 2:1 complex of SCN^- and Mg^{2+} , but there was no evidence for the 1:1 contact ion pair. This species as observed for magnesium and calcium [17, 18] may exist in lower concentrations in the Sr and

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Ba thiocyanate solutions, together with a dimer species which gives rise to a band on the lower wavelength side of the spectral profile.

In previous papers [19-21] it has been shown that bands due to both stretching and bending vibrations of anions can be attributed to specific ion paired forms. The assignments have been established by the application of a number of criteria as follows:

- (1) When a cation is complexed by a cryptand (like C222) to form inclusion complex all bands due to ion pairs disappear from the spectrum leaving only those bands due to "free" solvated anion [22].
- (2) As either the salt concentration and/or the temperature is raised the relative intensities of bands due to ion pair increase relative to that of the free anion band [20].
- (3) An increase in the concentration of a common ion causes the relative intensity of the bands due to ion pairs to increase [13].
- (4) Bands due to 1:1 contact ion pairs exhibit a simple linear relationship between the reciprocal of the cation crystallographic radius and the shift in wavenumber of the ion pair band from the free anion band [23]. The same criterion was used in the assignment of bands in this study.

In this paper a detailed investigation of strontium and barium thiocyanates in liquid ammonia is presented. The work initiated by Towning [17] some years ago proposed the existence of only four species in the solutions of alkaline-earth thiocyanates. This paper presents the infrared spectra of the solutions for the first time. The use of the co-addition facility now available on the Raman spectrometer [23-26], together with temperature-variation studies [16] have revealed the existence of yet another band in the spectral profiles of the solutions of strontium and barium studied. Thus a much more complete picture of the species and the equilibria involved in these thiocyanate solutions can now be established.

EXPERIMENTAL

Strontium thiocyanate. The salt was prepared by the method described by Towning [17]. Small quantities of strontium metal were added to a solution of ammonium thiocyanate in liquid ammonia until a permanent blue colour just remained. A few more crystals of the ammonium salt were then added, to remove the blue colour of the electron solution, and to prevent amide formation. The solution was filtered and the solvent evaporated so that the salt crystallized when the solution was cooled. The $\text{Sr}(\text{SCN})_2$ was twice-recrystallized from liquid ammonia and stored in *vacuo* over P_4O_{10} at 293 K. (Calculated for $\text{Sr}(\text{SCN})_2$: S, 31.5; C, 11.8; N, 13.7%; found S, 31.2; C, 11.6; N, 13.7 %).

Barium thiocyanate. Analar barium thiocyanate salt was first dried in *vacuo* over P_4O_{10} for 48 hours. It was then dissolved in acetonitrile, filtered and vacuum-distilled on a rotary evaporator. The solvent was evaporated off to leave pure $\text{Ba}(\text{SCN})_2$ salt in the distillation flask. The pure salt was then dried in *vacuo* over P_4O_{10} for 24 hours. (Calculated for $\text{Ba}(\text{SCN})_2$: S, 23.5; C, 9.5; N, 11.1%; found S, 23.0; C, 9.5; N, 11.0 %).

Liquid ammonia solutions. Pure anhydrous liquid ammonia (EX ICI Ltd) was transferred to a cylinder containing a charge of the thiocyanate salt. Pure dry ammonia gas distilled from this into a vacuum line. Solutions in liquid ammonia were prepared by condensation of this gaseous ammonia on to the preweighed salts in a graduated tube. From this measuring tube the solutions were transferred directly to the sample cells [3]. Concentrations (within $\pm 1\%$) were obtained as mass of solid per unit volume of solvent for infrared spectra, and as mass of solid per unit mass of solution for the Raman spectra. The composition of solutions were expressed as ratios of concentration: $[\text{moles NH}_3]/[\text{moles M}^{2+}] = R$; and $(\text{M}^{2+} = \text{Sr}^{2+} \text{ and } \text{Ba}^{2+})$ [23].

Infrared and Raman spectra. The infrared spectra were recorded at preset temperatures between 273 and 333 K on a Philips HP9545 ratio recording spectrometer using optimum spectrometer conditions to minimize spectrum distortion. Normally 16 consecutive spectrum scans were collected digitally and coadded at equal slow scan rate; the resultant S/N ratios of *Ca.* 500:1 were sought. Raman spectra were recorded on an old Coderg PHO, now updated to provide digital data at 0.125 cm^{-1} intervals and spectrum coaddition [24, 26] the slowest available scan rate ($1\text{ cm}^{-1}/\text{min}$) with spectrometer settings chosen to minimize spectrum distortion; 4 to 9 coadditions were needed to achieve good S/N ratios.

Curve analysis. Spectra were resolved into their component bands using an interactive program, VIPER [27, 28]. The derivative and smoothing program TREAT [29] was used as a resolution aid; the second, and sometimes fourth, derivatives of the spectra were used to establish the position of underlying bands.

RESULTS AND DISCUSSION

Heavy overlapping of the bands in the $\nu(\text{CN})$ of both infrared and Raman spectra of the alkaline-earth metal thiocyanate solutions restricted extensive study of this region. However, improved instrument resolution facilities enabled an improvement in the determination of the spectra over those previously recorded [17] to be achieved.

M^{2+}/SCN^- solutions ($M^{2+} = \text{Sr}^{2+}$ and Ba^{2+}) in $\nu(\text{CN})$ region. The analyses of the $\nu(\text{CN})$ stretching region of the infrared spectra of the solutions containing mixtures of $\text{Sr}^{2+}/\text{SCN}^-$ at $R = 500$ and $\text{Ba}^{2+}/\text{SCN}^-$ at $R = 513$ and 295 K are given in Table 1. Both spectra consist of an asymmetric band whose resolved band parameters in Table 1, indicate underlying band at *ca.* 2061 cm^{-1} attributable to solvent-shared ion pair and the band at *ca.* 2056 cm^{-1} to “free” SCN^- anion. However, there is no measurable intensity attributable to a band assigned to a 1:1 contact ion pair. The uncertainty and problems encountered with the resolution of the bands of the $\nu(\text{CN})$ region shifted the investigation and attention to the $\nu(\text{CS})$ region of the Raman spectra. Changes in the band envelopes were studied with changes in both concentration and temperature.

Table 1. The resolved component band parameters for the $\nu(\text{CN})$ region of the infrared spectra of strontium and barium thiocyanate solutions in liquid ammonia at 295 K .

Salt	Band frequency (cm^{-1})		F. W. H. H. (cm^{-1})		Relative intensity (%)	
	B	C	B	C	B	C
$\text{Sr}(\text{SCN})_2$	2061.6	2056.9	10.6	12.5	38.3	61.7
$\text{Ba}(\text{SCN})_2$	2060.4	2055.7	11.6	12.6	34.3	65.7

F.W.H.H. = full width at half height.

$\text{Sr}^{2+}/\text{SCN}^-$ solutions in $\nu(\text{CS})$ region. The analyses of the $\nu(\text{CS})$ stretching region of the Raman spectra of solutions containing mixtures of Sr^{2+} and SCN^- at concentrations between $R = 45$ and 363 and 295 K are given in Table 2. The spectral profile resolved into four underlying bands at *ca.* 757 cm^{-1} (A), *ca.* 740 cm^{-1} (C), *ca.* 737 cm^{-1} (D) and *ca.* 730 cm^{-1} (E). A change in solution concentration causes change in the band profile. Band A moves to higher wave number, by *ca.* 2 cm^{-1} , whilst the remaining bands remain unchanged in position. As the concentration is decreased bands A and D both increase whilst bands C and E decrease in relative intensity.

Table 2. The resolved component band parameters of $\nu(\text{CS})$ region of Raman spectra of strontium thiocyanate solutions in liquid ammonia at 295 K.

R	Band frequency (cm^{-1})				F. W. H. H. (cm^{-1})				Relative intensity (%)			
	A	C	D	E	A	C	D	E	A	C	D	E
45.0	756.8	741.0	737.9	731.4	11.3	10.6	7.9	6.2	15.0	43.4	37.3	4.4
57.0	757.2	739.9	736.5	729.8	7.2	7.2	7.1	5.9	12.3	40.3	42.0	5.5
90.0	757.6	739.7	736.4	729.6	8.9	8.6	7.6	6.0	15.7	41.3	39.1	4.0
100.7	758.1	740.1	736.6	729.6	9.5	7.5	7.4	7.0	18.8	32.8	43.3	5.1
194.0	758.3	739.8	736.2	729.7	8.9	7.0	7.3	5.8	19.9	30.0	47.1	3.0
363.0	758.3	740.2	736.3	729.2	8.5	6.4	7.6	6.4	20.6	19.4	56.4	3.6

$R = [\text{moles of } \text{NH}_3]/[\text{moles of } \text{Sr}^{2+}]$ and F.W.H.H. = full width at half height.

The analyses of the spectra of the $\nu(\text{CS})$ stretching region of the Raman spectra from temperature variation studies between 295 and 203 K are given in Table 3. On analysis the spectra profile is seen to resolve into four bands at *ca.* 758 cm^{-1} (A) which shifts to higher wavenumber by *ca.* 3 cm^{-1} on lowering temperature, *ca.* 740 cm^{-1} (C), *ca.* 737 cm^{-1} (D) and *ca.* 730 cm^{-1} (E). The shift in frequency observed for band A with both concentration and temperature is a clear indication that this band consists of more than one feature. As described above in curve analysis spectra, the combination of an interactive programme, VIPER [27, 28] and the derivative and smoothing programme TREAT [29] has been used before to resolve the position of underlying bands in a spectra which may not be easily seen as previously demonstrated [16, 18, 30]. The second derivative as shown in (Figure 1a), has also been used to resolve the spectra into two bands at *ca.* 759 cm^{-1} and *ca.* 756 cm^{-1} , labeled A and B, respectively.

Table 3. The resolved component band parameters for the $\nu(\text{CS})$ region of the Raman spectrum of strontium thiocyanate solution in liquid ammonia at $R = 90$.

Temp. (K)	Band frequency (cm^{-1})				F. W. H. H. (cm^{-1})				Relative intensity (%)			
	A	C	D	E	A	C	D	E	A	C	D	E
295	757.6	739.7	736.4	729.6	8.9	8.6	7.6	6.0	15.7	41.3	39.1	4.0
257	757.9	740.8	737.5	730.4	6.5	7.2	7.1	4.2	6.3	34.0	57.6	2.1
233	758.1	740.4	737.3	729.6	5.2	6.6	6.3	3.2	3.7	42.1	53.0	1.2
227	759.4	741.6	738.4	730.2	4.4	6.2	6.4	4.1	3.5	30.3	64.7	1.5
203	760.6	741.9	738.6	729.8	5.0	6.1	6.5	1.9	2.5	36.1	61.0	0.4

F.W.H.H. = full width at half height.

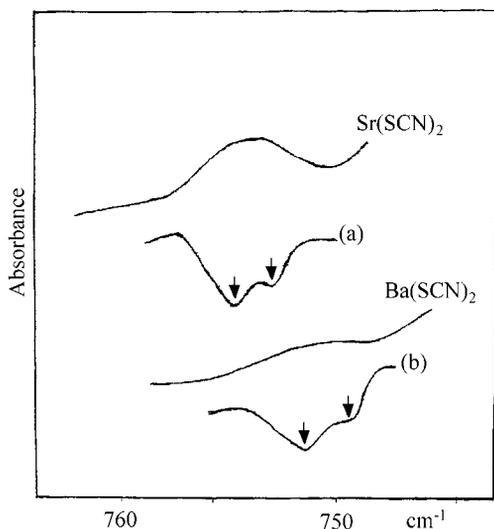


Figure 1. The second derivative of the $\nu(\text{CS})$ region of the Raman spectra of strontium thiocyanate at $R = 45$ and (b) barium thiocyanate at $R = 15.6$.

Ba²⁺/SCN⁻ solutions in $\nu(\text{CS})$ region. The analyses of the $\nu(\text{CS})$ stretching region of the Raman spectra of the solutions containing mixtures of $\text{Ba}^{2+}/\text{SCN}^-$ at concentration between $R = 15.6$ and 620 at 295 K are given in Table 4. The spectral profiles resolved into four bands at *ca.* 753 cm^{-1} (A) which also shifts to the higher wavenumber, *ca.* 2 cm^{-1} , *ca.* 740 cm^{-1} (C), *ca.* 737 cm^{-1} (D) and *ca.* 730 cm^{-1} (E). There is very little change in the FWHH's and there is no meaningful change in the relative intensities with change in concentration.

Table 4. The resolved component band parameters for the $\nu(\text{CS})$ region of the Raman spectra of barium thiocyanate solutions in liquid ammonia at 295 K.

R	Band frequency (cm^{-1})				F. W. H. H. (cm^{-1})				Relative intensity (%)			
	A	C	D	E	A	C	D	E	A	C	D	E
15.6	751.7	740.7	737.4	730.2	11.3	9.6	9.1	5.3	27.4	44.8	26.0	1.8
45.0	752.3	740.1	737.0	730.9	8.8	9.0	7.4	6.4	23.2	47.5	25.9	3.4
90.0	753.0	740.1	737.2	729.2	9.7	9.5	8.5	5.1	25.4	25.1	47.2	2.3
135.0	753.5	741.3	736.6	729.3	11.3	9.6	8.2	4.5	29.4	30.1	39.0	1.5
620.0	753.5	737.7	735.9	727.9	8.7	10.7	6.1	4.2	28.6	53.2	16.8	1.3

$R = [\text{moles of } \text{NH}_3]/[\text{moles of } \text{Ba}^{2+}]$ and F.W.H.H. = full width at half height.

The analyses of the temperature variation studies of the $\nu(\text{CS})$ stretching region of the Raman spectra of a mixtures of Ba^{2+} and SCN^- at $R = 90$ and temperatures between 295 and 203 K are given in Table 5. The spectral profile contains four bands at *ca.* 750 cm^{-1} (A), which shifts to lower wavenumber by *ca.* 3 cm^{-1} . Similarly, the second derivative (Figure 1b) of the $\text{Ba}(\text{SCN})_2/\text{NH}_3$ solution at $R = 15.6$ also shows band A consisting of two components at *ca.* 753 cm^{-1} (A) and *ca.* 749 cm^{-1} (B) if the same criterion is used. The positions of bands C, D and E do not shift with change in temperature.

Table 5. The resolved component band parameters for the $\nu(\text{CS})$ region of the Raman spectrum of barium thiocyanate solution in liquid ammonia at $R = 90$.

Temp. (K)	Band frequency (cm^{-1})				F. W. H. H. (cm^{-1})				Relative intensity (%)			
	A	C	D	E	A	C	D	E	A	C	D	E
295	753.1	740.1	737.2	729.2	9.7	9.5	8.5	5.1	25.4	25.1	47.2	2.3
259	751.5	740.9	737.8	729.0	8.5	6.3	7.7	4.0	13.1	17.7	67.9	1.3
233	749.5	739.0	736.7	728.9	9.5	7.9	5.4	4.8	6.3	71.1	20.8	1.9
227	749.7	739.9	737.4	729.7	10.5	7.3	5.8	4.8	4.3	59.2	34.5	2.1
203	-	740.7	738.0	729.2	-	6.7	6.1	3.1	-	46.4	52.7	0.9

F.W.H.H. = full width at half height.

It can be seen from Figure 2 and the curve-fitting data of the spectra of each salt solution (Tables 1-5) that the positions occupied by band A depend on both the charge and the ionic radius of the cation. Similar trends were observed in the $\nu(\text{CN})$ region above. This is in accord with values calculated for group IA set by Griffin [13] and for group IIA by Towing [17]. Similarly the position of band B is both cation- and temperature-dependent.

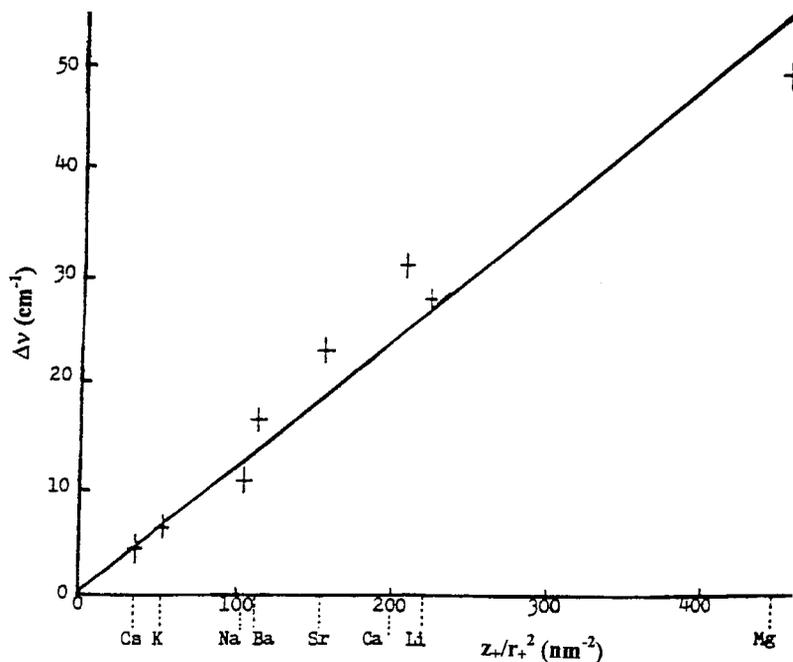


Figure 2. Plot of frequency perturbation $\Delta\nu$ (cm^{-1}) for a series of cations *versus* z_+/r_+^2 (nm^{-2}).

It is generally accepted that N-bonded thiocyanates shift the $\nu(\text{CS})$ vibration to the higher frequency side of the band associated with unperturbed "uncomplexed" SCN^- [16, 30]. The most likely assignment of bands in the $\nu(\text{CS})$ region of the Raman spectra is: band A to a 1:1 contact ion pair $[\text{M}^{2+} \cdots \text{NCS}]^+$ and band B to a 2:1 species (triple-ion) $\text{SCN}^- \cdots \text{M}^{2+} \cdots \text{NCS}$ in which both SCN^- are situated within the inner coordination sphere of the cation.

Bands C, D, and E are common in the spectra of strontium and barium thiocyanates. Bands C and D both increase slightly in intensity on dilution and decrease with temperature. Band C can therefore be assigned as solvent-shared 1:1 ion associate in which the anion experiences only a relatively small frequency perturbation effect from the cation [4] and band D since it is at or near the position observed for the band unambiguously assigned to the “free” SCN⁻ in group IA thiocyanates following the use of cryptand ligand to complex and isolate the cation [22].

The intensity of band E, the band of low intensity on the lower wavenumber side of the spectral profile, is significantly affected by the temperature. As the temperature is lowered the relative intensity of band E decreases. Similar and parallel behaviour was observed in the spectra of group IA metal thiocyanate solutions spatial interactions and group IIA metal thiocyanate solutions [31]. We can also confidently explain this band in terms of an upper stage transition arising from the excitation of a linear species already in a vibrational level above the ground state.

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