Synthesis and Vibrational Spectroscopic Study of Compounds containing the $I(SCN)_2^-$, $I_2(SCN)^-$, and $I(SeCN)_2^-$ Ions †

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The salt $[N(PPh_3)_2][I(SCN)_2]$ has been prepared by addition of thiocyanogen to $[N(PPh_3)_2]I$. Bands due to the ν(CN) and ν(IS) vibrations of the $I(SCN)_2^-$ ion have been assigned in the i.r. and Raman spectra of this compound, and the results indicate a structure in which the S atoms of the SCN groups are bound to the iodine atom to give a linear or almost linear S–I–S arrangement. The stretching and interaction force constants for the S–I–S group are similar to those for the trihalide ions IX_2^- (X = Cl, Br, or I). The salt $[N(PPh_3)_2][I_2(SCN)]$ could not be obtained as a pure compound, but has been obtained as a mixture with the I_3^- and $I(SCN)_2^-$ salts in several synthetic experiments. Bands due to the $I_2(SCN)^-$ ion could be identified in the low-frequency vibrational spectra of these mixtures, and these indicate that this ion has an unsymmetrical structure with an I–I–S arrangement. The salt $[N(PPh_3)_2][I(SeCN)_2]$ has been prepared by addition of selenocyanogen to $[N(PPh_3)_2]I$. The vibrational spectra of this compound do not allow definite conclusions to be drawn about the structure of the $I(SeCN)_2^-$ ion.

IODINE reacts fairly rapidly with thiocyanate in aqueous solution under normal conditions according to equation (1). However, evidence for the existence of the intermediate species $I_2(SCN)^-$ has been obtained from distribution studies.[1] Lewis and Skoog [2] have presented spectrophotometric evidence for this species, which they suggest is stabilized at high acidity, high ionic strength, and temperatures below 10 °C. In this and other studies the molar absorption coefficient and the formation constant for the $I_2(SCN)^-$ ion have been determined and the values obtained in the different studies are in reasonable agreement.[3,4] Other workers [5] have shown that the stability increases in the series of ions $I_2Cl^- < I_2(SCN)^- < I_3^-$. No salts containing the free $I_2(SCN)^-$ ion have yet been reported, although the complexes $[M(py)_4(NCS)_2(I_2)_2]$ (M = Co or Ni, py = pyridine) have been prepared,[6,7] and the crystal structure of the cobalt complex shows that each iodine molecule is bound to the S atom of a thiocyanate group which is in turn co-ordinated to the metal atom *via* its N atom. This complex can thus be regarded as containing co-ordinated $I_2(SCN)^-$ ions.[8]

$$4I_2 + SCN^- + 4H_2O \longrightarrow 7I^- + 8H^+ + I(CN) + SO_4^{2-} \quad (1)$$

Long and Skoog [9] have shown that $I_2(SCN)^-$ can be oxidized by O_2, H_2O_2, or $K[IO_3]$ in the presence of an excess of SCN^-. The proposed reaction is (2). Similar results were obtained when iodide was used instead of iodine [equation (3)]. In both cases, the presence of the $I(SCN)_2^-$ ion in solution was inferred from the stoicheiometry of the reaction, which was monitored by following the absorbance at 302 nm. Like the $I_2(SCN)^-$ ion, $I(SCN)_2^-$ is unstable in aqueous solution, but its stability is enhanced in solutions of high acidity, high ionic strength, and low temperature. Evidence for the dissociation of $I(SCN)_2^-$ according to equation (4) was also presented.[9]

$$I_2(SCN)^- + 3SCN^- \longrightarrow 2I(SCN)_2^- + 2e \quad (2)$$

$$I^- + 2SCN^- \longrightarrow I(SCN)_2^- + 2e \quad (3)$$

$$I(SCN)_2^- \longrightarrow I^- + (SCN)_2 \quad (4)$$

In studies of the oxidative-addition reactions of thiocyanogen, $(SCN)_2$, with various organometallic complexes, Kuhnhen [10,11] prepared several compounds which appear to contain free or co-ordinated $I(SCN)_2^-$ ions. The compounds, prepared by treating the appropriate organometallic iodide with thiocyanogen, were $[RuI(CO)_3(PPh_3)_2][I(SCN)_2]$, $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\text{-}I(SCN)_2]$, and $[Fe(\eta\text{-}C_5H_5)(CO)_2(PPh_3)][I(SCN)_2]$.

The aim of the present work was to prepare compounds containing the $I_2(SCN)^-$ and $I(SCN)_2^-$ ions with various organic counter ions, and to use these compounds to study the structure and bonding in the anions by means of i.r. and Raman spectroscopy. In addition, the study of the corresponding selenocyanate compounds was undertaken. The ions $X_2(SeCN)^-$ (X = Cl or Br) have previously been reported,[12] but pseudopolyhalides involving selenocyanate and iodine have apparently not been studied in detail, although the possibility of the existence of $I_2(SeCN)^-$ and $I(SeCN)_2^-$ in non-aqueous solutions has been suggested.[13]

The present work complements other recently reported studies of pseudopolyhalides such as $XI(N_3)^-$ (X = F, Cl, Br, I, N_3, OCN, or CN) [14,15] and $I(CN)_2^-$.[16]

EXPERIMENTAL

Preparation of Compounds.—Bis(triphenylphosphine)-iminium chloride, $[N(PPh_3)_2]Cl$, was prepared by a literature method.[17] The corresponding iodide (m.p. 250—252 °C) and thiocyanate (m.p. 191—194 °C) were prepared by adding aqueous solutions containing an excess of KI or K[SCN] to an aqueous solution of the chloride. The products were collected, washed with cold water, and recrystallized from ethanol–water.

Solutions of thiocyanogen in CH_2Cl_2 were prepared using silver thiocyanate and bromine.[18] Solutions of selenocyanogen in CH_2Cl_2 were prepared by an analogous pro-

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† Dithiocyanato-, iodothiocyanato-, and diselenocyanatoiodate(I) respectively.

cedure, using silver selenocyanate and bromine. Iodine thiocyanate solutions were prepared by adding the stoicheiometric amount of iodine to a CH_2Cl_2 solution of thiocyanogen.

Bis(triphenylphosphine)iminium tri-iodide, $[N(PPh_3)_2][I_3]$. Potassium iodide (0.19 g, 1.34 mmol) and iodine (0.12 g, 1.34 mmol) were dissolved in water (5 cm^3) and absolute ethanol (20 cm^3). To the resulting solution was added a solution of $[N(PPh_3)_2]Cl$ (0.19 g, 0.67 mmol) in absolute ethanol (15 cm^3). The dark brown precipitate which formed was filtered off and dried in a vacuum desiccator over silica gel. Yield 0.23 g, m.p. 204—207 °C.

Bis(triphenylphosphine)iminium dichloroiodate, $[N(PPh_3)_2][ICl_2]$. Iodine monochloride (0.11 g, 0.70 mmol) was dissolved in absolute ethanol (10 cm^3) and chilled in ice. To this was added a chilled solution of $[N(PPh_3)_2]Cl$ (0.40 g, 0.70 mmol) in absolute ethanol (5 cm^3). The yellow precipitate which formed was filtered off and recrystallized from absolute ethanol–acetonitrile. Yield 0.35 g, m.p. 216—221 °C.

Bis(triphenylphosphine)iminium bis(thiocyanato)iodate, $[N(PPh_3)_2][I(SCN)_2]$. The salt $[N(PPh_3)_2]I$ (0.30 g, 0.45 mmol) was dissolved in dry dichloromethane (20 cm^3) and the solution was chilled in an ice-bath. To this solution was added, under nitrogen, a freshly prepared solution of thiocyanogen (0.44 mmol) in dry dichloromethane (30 cm^3). The orange solution which formed was stirred, at 0 °C under nitrogen, for 5 min. Benzene (20 cm^3) was added and the volume was reduced to *ca.* 10 cm^3 whereupon an orange oil formed. n-Hexane (15 cm^3) was added to the mixture and stirring was continued for 30 min. The yellow powder which formed was filtered off and dried in a vacuum desiccator, m.p. 101—103 °C (Found: C, 57.9; H, 3.9; I, 16.1; N, 4.7. Calc. for $C_{38}H_{30}IN_3P_2S_2$: C, 58.2; H, 4.1; I, 16.2; N, 5.4%).

Attempted preparation of $[N(PPh_3)_2][I(SCN)_2]$ *by oxidation of iodide in the presence of an excess of thiocyanate.* Potassium iodide (0.17 g, 1.03 mmol) and sodium thiocyanate (1.65 g, 20.4 mmol) were dissolved in distilled water (15 cm^3) and absolute ethanol (10 cm^3) and the solution was chilled to 0 °C. To this was added a chilled solution of potassium iodate (0.11 g, 0.51 mmol) and concentrated sulphuric acid (0.6 cm^3, 11.3 mmol) in distilled water (15 cm^3) and absolute ethanol (10 cm^3). Half of the resulting red solution was added to a chilled solution of $[N(PPh_3)_2]Cl$ (0.20 g, 0.35 mmol) in absolute ethanol (15 cm^3). The orange precipitate which formed immediately was filtered off, washed with absolute ethanol (25 cm^3), and dried over silica gel. Yield 0.16 g. When examined under the microscope the product was found to consist of a mixture of light and dark brown microcrystalline plates. The light brown plates melted at 106—109 °C and the dark brown plates at 127—130 and 190 °C. Comparison of these melting points with those for $[N(PPh_3)_2][I_3]$ and $[N(PPh_3)_2][I(SCN)_2]$ (see above) suggests that the light brown plates are the latter while the dark brown plates melting at 190 °C are the former. The dark brown plates melting at 127—130 °C are thus likely to be $[N(PPh_3)_2][I_2(SCN)]$. There is evidence for the presence of these three compounds from the i.r. and Raman spectra of this product (see Discussion). The elemental analysis of this product is consistent with the composition proposed above {Found: C, 53.1; H, 3.8; I, 23.5; S, 2.1. Calc. for $[N(PPh_3)_2][I_2(SCN)]$: C, 52.1; H, 3.8; I, 29.8; S, 3.8. Calc. for $[N(PPh_3)_2][I_3]$: C, 46.9; H, 3.5; I, 41.3%}.

Bis(triphenylphosphine)iminium bis(selenocyanato)iodate, $[N(PPh_3)_2][I(SeCN)_2]$. A solution of selenocyanogen (0.16 g, 0.75 mmol) in dichloromethane (10 cm^3) was added at 0 °C under nitrogen to a solution of $[N(PPh_3)_2]I$ (0.39 g, 0.58 mmol) in dichloromethane (10 cm^3). To the resulting red solution was added diethyl ether (10 cm^3) and n-pentane (25 cm^3). A red oil formed. Stirring was continued for 2 h, during which the oil changed to a brown semicrystalline powder. This was filtered off and dried in a vacuum. Yield 0.24 g, m.p. 104—106 °C (Found: C, 51.8; H, 3.5; I, 15.1; N, 4.5. Calc. for $C_{38}H_{30}IP_2N_3Se_2$: C, 52.1; H, 3.5; I, 14.5; N, 4.8%).

Microanalyses and Spectroscopy.—Microanalyses were carried out by Professor A. D. Campbell at the University of Otago, Dunedin.

Infrared spectra in the range 400—4 000 cm^{-1} were obtained on a Perkin-Elmer 397 spectrometer for Nujol mulls between KBr plates, and were calibrated by using the spectrum of polystyrene. The far-i.r. spectra (50—400 cm^{-1}) were obtained on a Grubb-Parsons Cube Mk II interferometer fitted with a 6.25-μm Mylar-film beam splitter. They were run on petroleum-jelly mulls between Polythene plates, and calibrated by using the spectrum of water vapour. Far-i.r. spectra were also run at *ca.* 125 K in a Grubb-Parsons GRM 01 low-temperature cell cooled with liquid nitrogen.

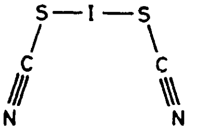
Raman spectra were obtained by Dr. M. Debeau, Departement de Recherches Physiques, Universite Paris Six, on a Coderg T800 spectrometer, and were excited by the 647.1-nm line of a krypton-ion laser. The spectra were run on polycrystalline solids in glass capillary tubes.

DISCUSSION

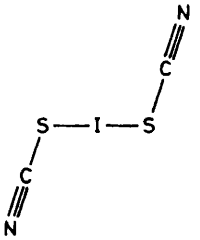
Various organic counter ions were used in attempts to obtain pure compounds containing the desired pseudopolyhalide anions. The most suitable one was found to be bis(triphenylphosphine)iminium, $N(PPh_3)_2^+$. The products obtained with tetra-alkylammonium cations such as NBu_4^+ were generally oils which could not be crystallized. Solid products could be obtained with the tetraphenylarsonium cation, but these were always less pure than the $N(PPh_3)_2^+$ salts. Since there is almost no information in the literature on the properties of polyhalides of $N(PPh_3)_2^+$, the I_3^- and ICl_2^- salts were prepared for comparison purposes. The far-i.r. spectra of these compounds showed strong bands due to the antisymmetric stretching mode of the anion at 142 (I_3^- compound) and 222 cm^{-1} (ICl_2^- compound). These frequencies agree well with the literature values for these ions in compounds with other counter ions.[19-23] Bands due to $N(PPh_3)_2^+$ in the range 50—350 cm^{-1} were very weak, so that there was no difficulty in assigning the anion bands.

The compound $[N(PPh_3)_2][I(SCN)_2]$ was prepared by the addition of $(SCN)_2$ to $[N(PPh_3)_2]I$ in an organic solvent. This method is similar to that used by Kuhnhen [10,11] to prepare various organometallic $I(SCN)_2^-$ compounds. Several structures can be considered for the $I(SCN)_2^-$ ion. One group involves bonding of the I atom to the S atom of one or both thiocyanate groups. In this connection it can be noted that i.r. evidence suggests the presence of I–S bonding in I(SCN).[24] In $I(SCN)_2^-$

the S and I atoms are expected to be bound in an approximately linear arrangement, as are the halogen atoms in trihalide ions. Two different structures are possible, depending on whether this arrangement of atoms is symmetrical (S–I–S) or unsymmetrical (I–S–S). In trihalide ions of the type XY_2^- a symmetrical arrangement (Y–X–Y) is found when Y is more electronegative than X (*e.g.* IBr_2^-) while an unsymmetrical arrangement is found when Y is less electronegative than X (*e.g.* I_2Br^-).[20] Since the SCN group is believed to be more electronegative than iodine,[13] the symmetrical S–I–S arrangement would seem to be the more likely one in $I(SCN)_2^-$. Since the bond formed with the S atom of thiocyanate is generally not collinear with the SCN group, a number of different point-group symmetries are possible, depending on the relative dispositions of the two SCN groups. The planar structures (I) and (II), of



(I)



(II)

symmetry C_{2v} and C_{2h} respectively, are two possibilities. A non-planar structure of C_2 symmetry, as found for $I(N_3)_2^-$,[15] is also possible.

The low-frequency i.r. and Raman spectra of $[N(PPh_3)_2][I(SCN)_2]$ are shown in Figures 1 and 2, and the wavenumbers and assignments of the anion bands are given in Table 1. Two closely spaced ν(CN) bands are observed in the i.r. and Raman spectra at about 2 110 and 2 120 cm^{-1}. This compares with the single i.r. bands previously reported for $[RuI(CO)_3(PPh_3)_2][I(SCN)_2]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2(PPh_3)][I(SCN)_2]$ at *ca.* 2 110 cm^{-1}.[10,11]

TABLE 1

Observed i.r. and Raman bands (cm^{-1}) of $I(SCN)_2^-$, $I_2(SCN)^-$, and $I(SeCN)_2^-$ in their $N(PPh_3)_2^+$ salts

$I(SCN)_2^-$		$I_2(SCN)^-$		$I(SeCN)_2^-$		Assignment
i.r.	Raman	i.r.	Raman	i.r.	Raman	(X = S or Se)
2 120ms	2 121vw			2 125s	2 124m	ν(CN)
2 110ms	2 107vw			2 114s	2 112m	ν(CN)
	703vw		710w		{537w	ν(CX)
					532 (sh)	ν(CX)
{188s	237vs	192vs	193s	{152vs	157vs	ν(IX) *
180s				146 (sh)	150s	ν(IX) *
		136 (sh)	132s			ν(II)

* Assignment uncertain in the case of $I(SeCN)_2^-$ (see text).

The far-i.r. and Raman spectra show strong bands which can be assigned to ν(IS) modes (Table 1). The wavenumbers of these bands would be expected to be similar to those for the ν(IX) modes in IX_2^- (X = Cl or Br). In fact they lie between those for the corresponding ICl_2^- and IBr_2^- modes.[20] Moreover, the wavenumber of the i.r.-active ν(IS) mode is close to that (192 cm^{-1}) previously assigned by Kuhnhen[11] for $[Fe(\eta\text{-}C_5H_5)(CO)_2(PPh_3)][I(SCN)_2]$. There appears to be mutual exclusion of the ν(SI) bands between the i.r. and Raman spectra (although there is a possible weak band in the i.r. spectrum corresponding to the strong Raman band at 237 cm^{-1}). This result supports the postulated S–I–S atomic arrangement in $I(SCN)_2^-$, the i.r. and Raman bands corresponding respectively to the antisymmetric (average ν_{asym} at 184 cm^{-1}) and symmetric (ν_{sym} at 237 cm^{-1}) vibrations of the S–I–S group.

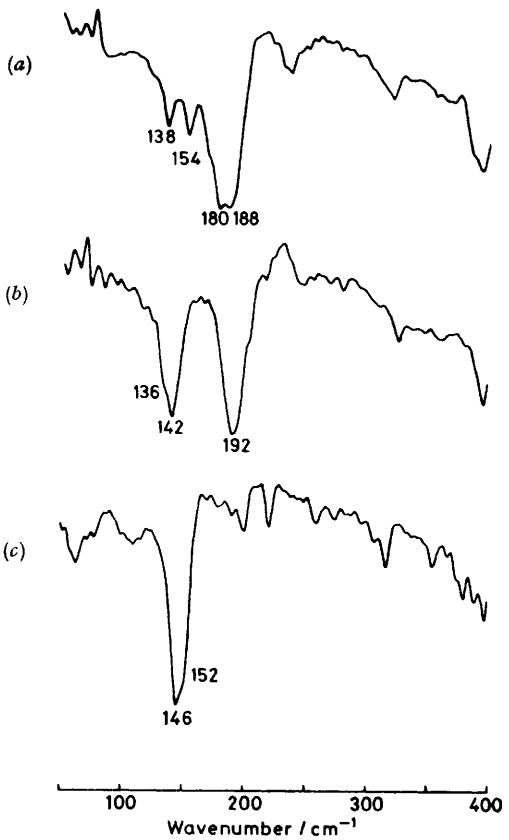


FIGURE 1 Far-i.r. spectra (at *ca.* 125 K) of (*a*) $[N(PPh_3)_2][I(SCN)_2]$, (*b*) mixture of $[N(PPh_3)_2][I(SCN)_2]$, $[N(PPh_3)_2][I_2(SCN)]$, and $[N(PPh_3)_2][I_3]$, and (*c*) $[N(PPh_3)_2][I(SeCN)_2]$

The question of the exact symmetry of the $I(SCN)_2^-$ ion in this compound is less easy to decide. The C_{2v} and C_2 structures should show two ν(CN) and ν(SI) bands in both the i.r. and Raman spectra, whereas the centrosymmetric C_{2h} structure should show single bands for these vibrations, with mutual exclusion between the i.r. and Raman spectra. The observation of two ν(CN) bands in the i.r. and Raman and the possible weak i.r. activity of the symmetric ν(SI) mode perhaps argue in favour of the lower-symmetry structures, but this conclusion is by no means certain since the spectra were obtained on solid samples and complications could be caused by factor- or site-group effects.

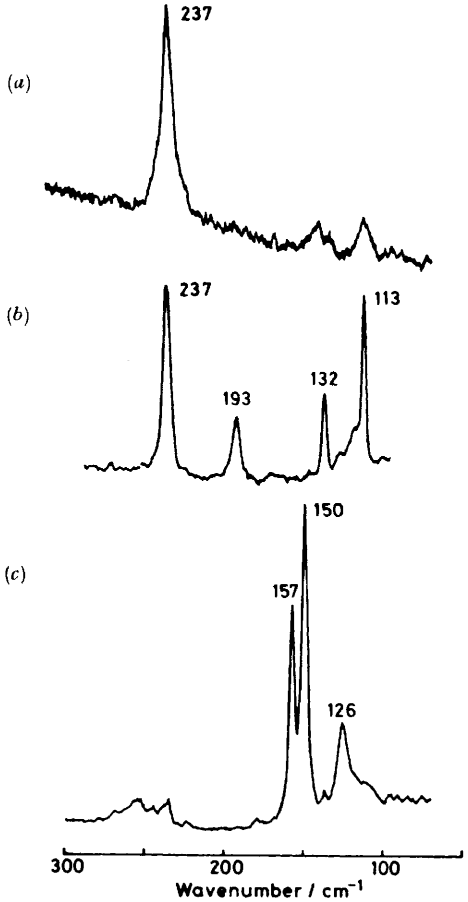


FIGURE 2 Low-frequency Raman spectra (at *ca.* 40 K). Details as in Figure 1

Another attempt to prepare $[N(PPh_3)_2][I(SCN)_2]$ was based on the work of Long and Skoog,[9] who prepared aqueous solutions of $I(SCN)_2^-$ by oxidation of iodide in the presence of an excess of thiocyanate. In the present work similar solutions were prepared and $[N(PPh_3)_2]Cl$ solution was added in an attempt to isolate the $I(SCN)_2^-$ ion as its $N(PPh_3)_2^+$ salt. These experiments resulted in the precipitation of mixtures which appear to contain the I_3^-, $I_2(SCN)^-$, and $I(SCN)_2^-$ salts of $N(PPh_3)_2^+$. The low-frequency Raman spectrum of one such preparation (see Experimental section) is shown in Figure 2. The strong band at 237 cm^{-1} is assigned to the symmetric ν(IS) stretching mode of $I(SCN)_2^-$ as it corresponds to the single low-frequency band observed for $[N(PPh_3)_2][I(SCN)_2]$. The strong band at 113 cm^{-1} is assigned to the symmetric stretching mode of I_3^- in $[N(PPh_3)_2][I_3]$. Frequencies in the range 103—114 cm^{-1} have been found for this mode in other tri-iodide compounds.[20,22] The weaker bands at 193 and 132 cm^{-1} are assigned to the $I_2(SCN)^-$ ion. The presence of two bands indicates that this ion has an unsymmetrical I–I–S structure, as found for co-ordinated $I_2(SCN)^-$ in $[Co(py)_4(NCSI_2)_2]$.[8] The higher- and lower-frequency bands have been assigned as ν(IS) and ν(II) respectively, although there will of course be some mixing of the S–I and I–I co-ordinates in these vibrations, and these designations correspond to the co-ordinate which is expected to contribute most to the potential-energy distribution of the mode concerned. The far-i.r. spectrum of the same mixture is shown in Figure 1. This contains only two strong bands as a result of accidental coincidences of some of the vibrational frequencies of the three anions present. The band at 142 cm^{-1} lies at exactly the same frequency as that of $[N(PPh_3)_2][I_3]$ (see above) and is assigned to the antisymmetric stretching mode of I_3^- in this compound. The unsymmetrical $I_2(SCN)^-$ ion would be expected to exhibit coincidence in the i.r. and Raman spectra. Thus the shoulder at 136 cm^{-1} and the band at 192 cm^{-1} in the i.r. spectrum are assigned to $I_2(SCN)^-$. The antisymmetric ν(SI) mode for $I(SCN)_2^-$ occurs in the range 180—190 cm^{-1} in $[N(PPh_3)_2][I(SCN)_2]$, and so occurs at about the same frequency as ν(SI) in $I_2(SCN)^-$. The fact that the product appeared to be inhomogeneous and showed three different melting points suggests that it consists of a mixture of the $N(PPh_3)_2^+$ salts of I_3^-, $I_2(SCN)^-$, and $I(SCN)_2^-$.

The formation of such a mixture in this experiment was unexpected. The overall stoicheiometry of the reaction used is (5). An excess of thiocyanate and acid

$$2I^- + 6SCN^- + IO_3^- + 6H^+ \longrightarrow 3I(SCN)_2^- + 3H_2O \quad (5)$$

were used, but the amounts of iodide and iodate were those calculated to give complete conversion into $I(SCN)_2^-$. According to the spectrophotometric studies of Long and Skoog [9] this reaction is complete at 0.5 mol of iodate per mol of iodide. These authors noted that further addition of iodate resulted in increased absorption at 302 nm and they attributed this to the formation of $I(SCN)_2^-$ and $(SCN)_2$ by iodate oxidation of thiocyanate. The results of the present study could be better understood if the solution obtained on addition of 0.5 mol of IO_3^- per mol of I^- consists of a mixture of I_3^-, $I_2(SCN)^-$, $I(SCN)_2^-$, and $(SCN)_2$. Addition of $[N(PPh_3)_2]Cl$ would then lead to precipitation of the $N(PPh_3)_2^+$ salts of the ionic species, as observed experimentally. The possibility that the $(SCN)_2$ present could combine with SCN^- to produce $(SCN)_3^-$ was considered, as this ion has been postulated in other studies,[25-28] and it might have been precipitated as $[N(PPh_3)_2][(SCN)_3]$ in the present study. However, attempts to prepare $[N(PPh_3)_2][(SCN)_3]$ by addition of $[N(PPh_3)_2]Cl$

to solutions containing $(SCN)_2$ and SCN^- were unsuccessful.

Attempts to prepare pure $[N(PPh_3)_2][I_2(SCN)]$ were also unsuccessful. These preparations were based on reactions (6) and (7). Reaction (6) has been studied in

$$SCN^- + I_2 \longrightarrow I_2(SCN)^- \tag{6}$$

$$I^- + I(SCN) \longrightarrow I_2(SCN)^- \tag{7}$$

aqueous solution by Lewis and Skoog.[2] Similar solutions were prepared in the present study and $[N(PPh_3)_2]Cl$ was added in an attempt to precipitate the $I_2(SCN)^-$ ion as its $N(PPh_3)_2^+$ salt. As in the similar experiment to precipitate $I(SCN)_2^-$ from aqueous solution, the product was found to be a mixture of the $N(PPh_3)_2^+$ salts of I_3^-, $I_2(SCN)^-$, and $I(SCN)_2^-$, although with a greater proportion of I_3^- and $I_2(SCN)^-$ in this case. In attempts to prepare $[N(PPh_3)_2][I_2(SCN)]$ in non-aqueous solvents such as CH_2Cl_2, $[N(PPh_3)_2][SCN]$ or $[N(PPh_3)_2]I$ were used as sources of SCN^- or I^- in the reactions (6) and (7). The products of these preparations were also mixtures of I_3^-, $I_2(SCN)^-$, and $I(SCN)_2^-$ compounds. In the case of reaction (7) the formation of such a mixture can be understood on the basis of the previously proposed disproportionation (8) of I(SCN) in organic solvents.[24] The reaction of the three species

$$2I(SCN) \rightleftharpoons I_2 + (SCN)_2 \tag{8}$$

involved in this equilibrium with I^- would give the I_3^-, $I_2(SCN)^-$, and $I(SCN)_2^-$ ions observed in the mixed product.

The ν(IS) and ν(II) frequencies found for $I_2(SCN)^-$ (Table 1) can be compared with the frequencies (160, 150 cm^{-1}) attributed to the I–I–S group in co-ordinated $I_2(SCN)^-$ in $[M(py)_4(NCSI_2)_2]$ (M = Co or Ni).[8] This comparison indicates that the strength of the S–I bond is reduced by co-ordination of the thiocyanate group *via* its N atom to a metal atom, so that the ν(I–S) frequency is reduced from its value (193 cm^{-1}) in uncomplexed $I_2(SCN)^-$, while the ν(I–I) frequency is increased (from 132 cm^{-1}; the I–I bond strength increases as the I–S bond strength decreases).

The large difference between the frequencies of the symmetric and antisymmetric ν(I–S) stretching vibrations of the $I(SCN)_2^-$ ion (ν_{sym} at 237, ν_{asym} at 184 cm^{-1}) is also worthy of comment. For linear symmetric XY_2 species, the frequencies of these vibrations are given by equations (9) and (10) where μ_X and μ_Y are the reciprocal

$$4\pi^2c^2\nu_{sym}^2 = (k + k_{12})\mu_Y \tag{9}$$

$$4\pi^2c^2\nu_{asym}^2 = (k - k_{12})(\mu_Y + 2\mu_X) \tag{10}$$

atomic masses of X and Y, k is the force constant for stretching of the X–Y bond, and k_{12} is the interaction constant. The force constants for the IX_2^- ions (X = Cl, Br, or I) are listed in Table 2. As has been pointed out by other authors,[19-21] these ions have unusually large interaction constants. The quotient k_{12}/k, normally less than 0.1 for molecules like CO_2 and CS_2, lies in the range 0.25—0.4 for these ions. Large values of k_{12} tend to increase ν_{sym} relative to ν_{asym} [see equations (9) and (10)]. In ICl_2^- this effect, together with the small mass of Cl relative to I, results in ν_{sym} being greater than ν_{asym}.[19,20] The same order is observed for the ν(IS) vibrations in $I(SCN)_2^-$, possibly for similar reasons.

TABLE 2

Stretching and interaction force constants for some trihalide ions and for the S–I–S group in $I(SCN)_2^-$

Ion	k/N m^{-1}	k_{12}/N m^{-1}	k_{12}/k	Ref.
ICl_2^-	100	36	0.36	19
	102	33	0.32	20
IBr_2^-	91	30	0.33	20, 21
I_3^-	62—68	19—22	0.29—0.32	*a*
	69	18	0.26	23
$I(SCN)_2^-$	74—87	28—35	0.38—0.41	*b*

[a] Calculated using equations (9) and (10) from the data in ref. 22 for several $[NR_4][I_3]$ compounds. [b] This work.

In order to investigate this, approximate normal-co-ordinate analyses were carried out for this ion using the Wilson FG method. C_{2h} Structures like (II) were assumed, with ISC angles in the range 90—100°. {The value found for this angle in the co-ordinated $I_2(SCN)^-$ ion in $[Co(py)_4(NCSI_2)_2]$ is 95.2°.[8]} The values used for the internal force constants for the SCN group were those of the free SCN^- ion.[29] The CSI and SIS bending force constants were assumed to be small, and it was found that variation of the values of these constants between 0 and 10 N m^{-1} did not have a significant effect on the frequencies of the stretching modes. Values for the force constants k and k_{12} for the S–I–S group were initially approximated by means of equations (9) and (10) with the mass of Y equal to that of the SCN group. Use of these values in the normal-co-ordinate calculation produced ν(IS) frequencies which were higher than the observed ones. The values of k and k_{12} were then varied until the calculated ν(IS) frequencies agreed with the observed ones. The ranges of the resulting force constants for the geometries considered are given in Table 2. The values are quite similar to those for the trihalide ions listed in this table. Although there is considerable uncertainty in these values because of the approximations involved in the normal-co-ordinate analysis, the results indicate that the bonding in the S–I–S group in $I(SCN)_2^-$ is similar to that in the trihalide ions.

The compound $[N(PPh_3)_2][I(SeCN)_2]$ was prepared by a method analogous to that used for the corresponding thiocyanate. The low-frequency i.r. and Raman spectra of this compound are shown in Figures 1 and 2, and the wavenumbers and assignments of the anion bands are given in Table 1. There are two ν(CN) bands at *ca.* 2 120 cm^{-1} in both the i.r. and Raman spectra. The far-i.r. spectrum shows a strong band (possibly a doublet) at *ca.* 150 cm^{-1}, while the low-frequency Raman spectrum shows three medium-to-strong bands, the strongest of which coincides exactly with the i.r. band, at 150 cm^{-1}.

The same structures as those for $I(SCN)_2^-$ can be considered for I(SeCN)$_2^-$. However, it is not so easy to rule out unsymmetrical structures in this case. As discussed above, unsymmetrical XY$_2^-$ trihalides are observed when X is more electronegative than Y. Since it has been shown that the SeCN group is less electronegative than I,[13] an unsymmetrical structure with an I–Se–Se arrangement would be possible for I(SeCN)$_2^-$ on this basis. Such a structure would be similar to that found for the (SeCN)$_3^-$ ion,[30,31] with one of the terminal SeCN groups replaced by an iodine atom. For this structure, two low-frequency stretching modes for the I–Se–Se group are expected in both the i.r. and Raman spectra. This prediction seems to fit the bands observed at *ca.* 150 cm^{-1}. This frequency is less than ν(IS) in I(SCN)$_2^-$ or I$_2$(SCN)$^-$ and so is reasonable for a mode involving I–Se stretching. It lies between the frequencies of the bands assigned to the symmetric and antisymmetric stretching modes of the Se–Se–Se group in (SeCN)$_3^-$ (134 and 188 cm^{-1} respectively),[12] and so is reasonable for a mode involving Se–Se stretching. However, it is also possible that a low-symmetry (*e.g.* C_{2v} or C_2) structure involving an Se–I–Se arrangement could account for the results. The situation is not as clear as that for I(SCN)$_2^-$, where the large frequency difference between the symmetric and antisymmetric ν(IS) modes allows a more definite conclusion to be reached.

Weak ν(CS) or ν(CSe) bands were observed in the Raman spectra of the ions listed in Table 1. Several other bands are expected in the vibrational spectra of these anions, but these could not be assigned because of interference from bands due to the N(PPh$_3$)$_2^+$ cation.

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