Spectrochemistry of Solutions. Part 14.[1] Raman and Infrared Spectra of Thiocyanatosilver(I) Complexes in Some Non-aqueous Solutions

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Infrared and Raman spectra have shown that, when Ag^+ is complexed by SCN^-, the species present and the equilibrium steps involved are solvent specific. In pyridine, complexation of Ag^+ by SCN^- passes through $[Ag_2(SCN)]^+$ and AgSCN to $[Ag(SCN)_2]^-$. Only AgSCN and $[Ag(SCN)_2]^-$ have been identified in tetrahydrofuran, dimethyl sulphoxide, and acetone, and only $[Ag(SCN)_2]^-$ was found in propylene carbonate. Solutions in dimethylformamide and dimethylacetamide at high $[SCN^-]/[Ag^+]$ ratios contain a small proportion of the SCN^- in the bridged complex $[Ag_2(SCN)_3]^-$, but in trimethyl phosphate the SCN^- is approximately equally distributed between $[Ag_2(SCN)_3]^-$ and $[Ag(SCN)_2]^-$. The spectra of thiocyanatosilver(I) complexes in hexamethylphosphoramide differ from those of all the other solutions; no linear $[Ag(SCN)_2]^-$ complex is found and two feasible explanations of the spectra are offered. No complex higher than $[Ag(SCN)_2]^-$ occurs in any of these solutions.

OUR work on thiocyanato-complexes of silver(I) in liquid ammonia solutions [2] drew to our attention a surprising degree of disagreement concerning the number, nature, and range of stability of these complexes in other solvents.

Most of the supporting evidence for the existence of specific complexes derives from stability-constant data obtained from either potentiometric or solubility product measurements. In all such cases the identification of a complex essentially relies on agreement of experimentally determined quantities with those calculated from a defined model system. In this way the complex $[Ag(SCN)_2]^-$ has been claimed to be the one with the highest ligand to silver ion ratio, in a wide range of solvents; † acetone,[3] dmf,[4,5] dma,[5] hmpa,[4] tetrahydrothiophen 1,1-dioxide,[6] nitromethane,[7] and dmso.[4,8,9] The existence of $[Ag(SCN)_3]^{2-}$ in pc,[10] and in acetamide at 371 K,[11] has been proposed but the only other claims for the tris complex have been for pyridine,[12] aqueous solutions,[13] and mixtures of alcohols, acetone,[14] and dioxane [15] in water. The complex $[Ag(SCN)_4]^{3-}$ has been invoked in some cases to explain the data obtained from aqueous solutions.[13]

Evidence for bridged thiocyanato-complexes in solution is contradictory. Leden and Nilsson [16] have claimed that a series of complexes with general formula $[Ag_m(SCN)_{2m+2}]^{(m+2)-}$, where $m > 2$, occurs in aqueous solution when $[SCN^-]_T > [Ag^+]_T$. They even suggested that bridged species were present as minor constituents of the mixture at high concentrations of SCN^-. Although this postulate has gained some support, *e.g.* the proposal of a species of stoicheiometry $[Ag_2(SCN)_6]^{4-}$ by Gryunner and Yahkhind,[17] it is in marked contrast to the suggestion by Larsson and Miezis [18,19] that bridged species occur in pyridine solutions only when $[SCN^-]_T < [Ag^+]_T$. The existence of bridged species in dmso solutions has also been postulated.

Because species in solution have characteristic and unique vibrational frequencies their presence in a system, and the conditions under which they exist, can often be established from the Raman and/or the i.r. spectra of their solutions. To this end we now report the results of a Raman and i.r. spectroscopic survey of solutions at various $[SCN^-]_T/[Ag^+]_T = S$ ratios in pyridine, dmf, dmso, dma, acetone, pc, tmp, thf, and hmpa.

EXPERIMENTAL

Solutions were prepared in one of five ways as indicated in the concentration columns of the Tables: (I) dissolution of AgSCN in a solution of $[NH_4][SCN]$; (II) mixing of solutions of $Ag[ClO_4]$ and $[NH_4][SCN]$; (III) dissolution of either AgSCN or $[NH_4][Ag(SCN)_2]$ *in* the solvent; (IV) mixing of solutions of $[NH_4][Ag(SCN)_2]$ and $Ag[ClO_4]$; and (V) mixing of solutions of $[NH_4][Ag(SCN)_2]$ and $[NH_4][SCN]$.

Salts.—AnalaR $[NH_4][SCN]$ and $Ag[ClO_4]$ were dried and stored *in vacuo* over P_4O_{10}. A filtered 0.05 mol dm^{-3} solution containing K[SCN] (4.5 g) was slowly added to a filtered 0.05 mol dm^{-3} solution containing $Ag[NO_3]$ (8.5 g). The white precipitate of AgSCN was collected, washed with water, ethanol, and dry diethyl ether. The dry product was recrystallised from its liquid ammonia solution and stored *in vacuo* over P_4O_{10} in the dark. The compound AgSCN (5.1 g) was dissolved in $[NH_4][SCN]$ (4.9 g) in water (5.1 cm^3) to give a clear solution. After evaporation of a little water the crystals of $[NH_4][Ag(SCN)_2]$ were collected and stored *in vacuo* over P_4O_{10}. All operations were carried out in the dark. Infrared spectra showed all salts to be free from H_2O, NO_3^-, and NH_3.

Infrared spectra of all solutions except hmpa were recorded at × 10 wavenumber scale expansion on a Perkin-Elmer 457 spectrometer in a cell with CaF_2 windows. Cell pathlengths varied from 50 to 200 μm depending on solution concentration. All solutions were injected into the cell through a Millipore filter. Solvent compensation was achieved with an RIIC V10 variable pathlength cell containing pure solvent in the reference beam. Its pathlength was adjusted to obtain spectrum baselines which were flat for at least 200 cm^{-1} on both sides of the ν(CN) stretching region. Good compensation was achieved for all solvents except thf and hmpa.

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† Abbreviations used are as follows: dmf, dimethylformamide; dma, dimethylacetamide; hmpa, hexamethylphosphoramide; dmso, dimethyl sulphoxide; pc, propylene carbonate; thf, tetrahydrofuran; tmp, trimethyl phosphate.

Raman spectra were obtained on a Coderg RS 100 spectrometer using the 488.0 nm line of a Coherent Radiation Ar^+ ion laser. Solutions were irradiated in a fluorimeter cell (5×10 mm) and signal enhancement was achieved by multiple light passes.

Spectra were obtained from solutions over the widest possible range of S. In some cases, however, the solubility of the species was a serious limitation; in acetone, tmp, and thf completely clear solutions were only achieved when $S > 6$, and in dmf when $S > 3.5$.

Analysis of Spectra.—Except for the spectra of hmpa solutions, all spectra were traced on to transparent graph paper and good symmetrical bands were fitted under the profiles by hand measurement. Estimated band positions, intensities (Raman) and absorbances (i.r.) and widths at half-height, $w_{\frac{1}{2}}$, are shown in the Tables.

The spectra of the hmpa solutions, obtained on a Unicam SP3 300 spectrometer, were hand digitised, converted to the absorbance scale, and analysed by our VIPER program [20] on a Hewlett–Packard 9845S minicomputer.

RESULTS AND DISCUSSION

To account for the spectra reported in Table 1 we propose the formation of thiocyanatosilver(I) complexes according to the following equilibria [the state of solvation of the silver(I) centre has not been accounted for].

$$2Ag^+ + SCN^- \rightleftharpoons [Ag{-}SCN{-}Ag]^+ \quad \beta_{1,2} \quad (1)$$

$$Ag^+ + SCN^- \rightleftharpoons AgSCN \quad \beta_1 \quad (2)$$

$$2AgSCN \rightleftharpoons [Ag{-}SCN{-}Ag{-}SCN] \quad \beta_{2,2} \quad (3)$$

$$[Ag{-}SCN{-}Ag{-}SCN] + SCN^- \rightleftharpoons [NCS{-}Ag{-}SCN{-}Ag{-}SCN]^- \quad \beta_{3,2} \quad (4)$$

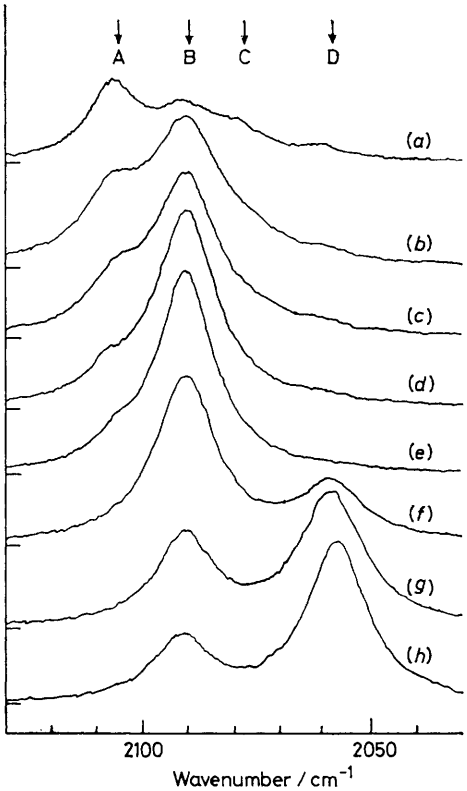
$$AgSCN + SCN^- \rightleftharpoons [Ag(SCN)_2]^- \quad \beta_2 \quad (5)$$

Previous reports on the vibrational spectra of thiocyanatosilver(I) complexes are limited to acetone,[3] pyridine,[18,19] ammonia,[2] and aqueous solution.[21] Using liquid ammonia solutions we were able firmly to assign bands at 2 078 cm^{-1} and 727 cm^{-1} to the ν(CN) and ν(CS) stretching frequencies of the *S*-bonded AgSCN complex respectively. When the SCN^- ligand was in large excess in liquid ammonia, *i.e.*, $S > 4$, the formation of a very small proportion of the bis complex, $[Ag(SCN)_2]^-$, was indicated by a Raman band of low intensity at 2 094 cm^{-1}. Using these and previous assignments as a guide we can now assign the bands observed at four positions in the ν(CN) stretching region.

A band A observed at $2\,106 \pm 2$ cm^{-1} (Raman) and $2\,104 \pm 2$ cm^{-1} (i.r.) is taken as evidence of a complex containing SCN^- as a bridging ligand. Bands B at $2\,093 \pm 4$ cm^{-1} (Raman) and $2\,086 \pm 4$ cm^{-1} (i.r.) are assigned to the symmetric and the asymmetric C–N stretching vibrations of the $[Ag(SCN)_2]^-$ complex. A band C at $2\,077 \pm 3$ cm^{-1} (Raman) and $2\,074 \pm 4$ cm^{-1} (i.r.) can be assigned either to the uncharged AgSCN complex or to the terminal –SCN group of a bridged complex. The free SCN^- ligand gives rise to a band D at $2\,057 \pm 3$ cm^{-1} (Raman) and $2\,054 \pm 4$ cm^{-1} (i.r.). An additional band at 2 116 cm^{-1} found in the i.r. spectra of hmpa solutions suggests the existence of a further complex possibly involving an alternative arrangement of bridging –SCN– ligands. Solvent shifts all appeared to be comparatively small and can be accounted for within the frequency spreads quoted above.

Because of overlap by solvent bands it was impossible, except for the Raman spectra of the dmf solution, to obtain information from the ν(CS) stretching region.

Pyridine.—The Figure shows the manner in which the Raman spectrum changes with S for pyridine solutions and illustrates that all four bands A, B, C, and D are observed at various stages of the spectroscopic titration of Ag^+ with SCN^-. The i.r. profiles follow essentially the same intensity changes. The spectra of solutions between $S = 0$ and 2 are all dominated by band B due to the $[Ag(SCN)_2]^-$ complex, the only observable band due to any complex species at $S > 1$. Its relative intensity is unexpectedly high when S is low; 50% of the total spectrum area at $S = 0.059$. The appearance of band D, due to uncomplexed SCN^- ligand, is unexpected at low S but its presence can be in no doubt because it appears as a small peak at *ca.* 2 059 cm^{-1}. At $S < 1$ band A, which appears as a well defined shoulder on the upper frequency side of B, decreases in relative intensity with increasing S and disappears completely at $S > 1$. A clearly discernible shoulder on the lower frequency side of B at $S = 0.06$ indicates band C in the Raman. As S



The ν(C–N) stretching region of the Raman spectra of pyridine solutions containing various mixtures of Ag^+ and SCN^- ions. (*a*) $S = 0.06$, (*b*) 0.10, (*c*) 0.22, (*d*) 0.50, (*e*) 1.00, (*f*) 2.00, (*g*) 3.57, (*h*) 6.14

TABLE 1

Band analyses of the ν(CN) stretching regions of the i.r. and Raman spectra (cm^{-1}) of thiocyanatosilver(I) complexes in a number of non-aqueous solutions *

S	[Ag$^+$]/mol dm^{-3}		A	B	C	D
(*a*) Pyridine						
0.06	0.494 (II)	Raman	[32] 2 106 (13)	[53] 2 090 (17)	[10] 2 078 (?)	[5] 2 060 (12)
0.10	0.978 (II)	Raman	[28] 2 106 (15)	[61] 2 090 (18)	[8] 2 078 (?)	[3] 2 060 (12)
		i.r.	[9] 2 104 (16)	[88] 2 085 (20)	?	[3] 2 060 (15)
0.22	0.448 (II)	Raman	[21] 2 105 (14)	[71] 2 090 (16)	[5] 2 074 (?)	[3] 2 060 (8)
		i.r.	[10] 2 106 (12)	[84] 2 085 (18)	?	[6] 2 060 (18)
0.50	0.199 (II)	Raman	[11] 2 107 (10)	[89] 2 090 (16)		?
		i.r.	[7] 2 106 (10)	[89] 2 086 (18)		[4] 2 059 (17)
0.95	0.102 (II)	Raman	[9] 2 105 (10)	[91] 2 090 (15)		
		i.r.	[3] 2 104 (10)	[89] 2 085 (20)		[8] 2 058 (20)
1.00	0.050 (III)	Raman	[9] 2 105 (10)	[91] 2 089 (15)		
		i.r.	[3] 2 104 (11)	[91] 2 085 (20)		[6] 2 057 (20)
1.98	0.050 (II)	Raman		[87] 2 090 (16)		[13] 2 058 (15)
		i.r.		[60] 2 085 (25)		[40] 2 053 (20)
2.00	0.028 (III)	Raman		[75] 2 090 (16)		[25] 2 058 (16)
		i.r.		[60] 2 085 (26)		[40] 2 053 (22)
3.57	0.028 (II)	Raman		[40] 2 090 (15)		[60] 2 058 (17)
		i.r.		[21] 2 082 (25)		[76] 2 053 (28)
6.14	0.014 (II)	Raman		[28] 2 090 (15)		[72] 2 056 (16)
		i.r.		[15] 2 082 (26)		[85] 2 052 (30)
(*b*) Dmso						
2.0	0.017 (II)	Raman		[79] 2 095 (21)	[11] 2 078 (16)	[10] 2 056 (18)
		i.r.		[68] 2 087 (24)	[13] 2 070 (20)	[19] 2 052 (16)
3.0	0.050 (I)	Raman		[75] 2 095 (20)	[5] 2 074 (10)	[20] 2 056 (13)
		i.r.		[52] 2 085 (30)	[4] 2 070 (10)	[44] 2 055 (24)
4.1	0.048 (I)	Raman		[63] 2 095 (17)	[2] 2 075 (14)	[35] 2 056 (15)
		i.r.		[52] 2 085 (32)	[2] 2 070 (15)	[46] 2 054 (25)
6.0	0.050 (I)	Raman		[48] 2 094 (15)		[52] 2 056 (14)
		i.r.		[43] 2 084 (33)	[3] 2 070 (18?)	[57] 2 052 (30)
(*c*) Dma						
2.5	0.047 (I)	Raman				
		i.r.	[25] 2 105 (17)	[14] 2 088 (20)	[14] 2 077	[47] 2 057 (20)
3.2	0.047 (I)	Raman	[6] 2 108 (12)	[68] 2 095 (16)	[6] 2 077 (12)	[20] 2 058 (12)
		i.r.	[13] 2 104 (18)	[35] 2 087 (20)	[5] 2 078	[43] 2 055 (23)
5.4	0.008 (I)	Raman	[5] 2 107 (10)	[25] 2 094 (16)		[70] 2 058 (12)
		i.r.	[11] 2 104 (14)	[30] 2 087 (18)		[59] 2 056 (16)
(*d*) Pc						
2.1	0.015 (II)	i.r.		[43] 2 088 (26)		[57] 2 054 (15)
2.5	0.013 (II)	Raman		[59] 2 096 (18)		[41] 2 057 (16)
3.2	0.011 (II)	i.r.		[33] 2 088 (24)		[67] 2 053 (26)
4.1	0.049 (I)	i.r.		[36] 2 087 (27)		[64] 2 053 (35)
5.9	0.054 (I)	Raman		[53] 2 096 (20)		[47] 2 055 (18)
		i.r.		[42] 2 087 (30)		[58] 2 052 (45)
(*e*) Dmf						
3.8	0.054 (I)	Raman	[5] 2 109 (9)	[70] 2 094 (14)		[25] 2 058 (10)
		i.r.	[7] 2 102 (15)	[45] 2 086 (25)		[48] 2 052 (22)
(*f*) Tmp						
6.1	0.007 (II)	Raman	[26] 2 105 (16)	[26] 2 094 (16)	[5] 2 078 (10)	[43] 2 060 (16)
		i.r.	[25] 2 102 (15)	[25] 2 087 (20)	[5] 2 075	[45] 2 052 (14)
(*g*) Thf						
6.1	0.049 (I)	Raman		[47] 2 097 (20)	[29] 2 075 (20)	[24] 2 050 (20)
(*h*) Acetone						
6.7	0.030 (I)	Raman		[46] 2 098 (11)	[3] 2 080 (10)	[51] 2 060 (10)
		i.r.		[47] 2 087 (28)	[2] 2 075	[51] 2 052 (35)

* Relative band intensities (Raman) and absorbances (i.r.) are expressed as percentages of the total for the ν(CN) region in square brackets. Band widths at half height, $w_{\frac{1}{2}}$, are given in parentheses.

increases this shoulder gives way to an inflexion at *ca.* 2 078 cm^{-1} and the band ceases to be observed around $S = 0.50$. Resolution of a band C from the i.r. spectra was extremely difficult because of its low intensity, although we consider that a small contribution from this band ought to be included in the 2 076 cm^{-1} region for $S = 0.10$ and 0.22.

At $S > 1$ only one complexed species $[Ag(SCN)_2]^-$ is present in the solution. It is surprising that about 50% of the total SCN$^-$ ligand is present in the bis complex form at $S = 0.06$ and it must therefore be inferred that this is by far the most stable complex in pyridine solutions. However at low S a small proportion of uncomplexed ligand exists in solution, and at $S = 2$, when $[Ag(SCN)_2]^-$ is the only complex present, a relatively high proportion of free SCN$^-$ still remains in equilibrium. It is thus to be inferred that the stability constant β_2 can, at best, be only moderately large, *cf.* log β_2 *ca.* 11 for aqueous solutions. If, in the absence of accurate band intensity data, equal intensity coefficients are assumed for the Raman spectra at $S = 2.0$ and 3.57 a stoicheiometric formation constant for the bis complex, β_2 *ca.* $4(\pm 2) \times 10^3$ mol^2 dm^{-6}, is obtained. This value is markedly lower than that reported for log β_2 in most other solvents, *e.g.* water, 11,[13] dmso, 8.4,[8] dmf, 12,[4] though it is of a similar order of magnitude to that obtained by Larsson and Miezis ($\beta_2 = 20 \times 10^3$ mol^2 dm^{-6}) from the potentiometric measurements [12] which followed their i.r. studies.[18,19] We are, however, in disagreement with these workers' interpretation of their spectra. They proposed that the broad feature ($w_{\frac{1}{2}}$ *ca.* 30 cm^{-1}) centred at 2 089 cm^{-1} was a composite band attributable to all three complexes AgSCN, $[Ag(SCN)_2]^-$, and $[Ag(SCN)_3]^{2-}$. The improved resolution obtained in our spectra, particularly in the Raman, allows us firmly to attribute the Raman band B at *ca.* 2 090 cm^{-1} to the symmetric C–N stretching vibration, and the i.r. band B at 2 085 cm^{-1} to the asymmetric C–N stretching vibration, of the $[Ag(SCN)_2]^-$ complex. A clear indication that $[Ag(SCN)_2]^-$ is the highest complex found in the system is provided by the well resolved Raman spectra obtained when S is raised from 2 to 6; both the band position at 2 090 cm^{-1} and its half-width $w_{\frac{1}{2}}$ *ca.* 15 cm^{-1} remain constant.

The appearance of band C due to AgSCN as a distinct feature at low S, albeit at low intensity, adds further validity to our interpretation. From the intensity data it is clear that the value of β_1 must be very low. On the other hand there is a considerable degree of formation of bridged complex ($\beta_{1,2}$) as indicated by the intensity of band A at low S and its disappearance from the spectrum at $S > 1$. Accordingly we propose that A is due to the bridged complex defined by equation (1). The dimer species defined by equation (3) is unlikely. Except for the solutions of the lowest S values, in which its formation is least likely, there is no band in the 2 078 cm^{-1} region which could be attributed to the terminal –SCN group. Thus we find ourselves partly in agreement with Larsson and Miezis [18] in that band A at *ca.* 2 106 cm^{-1} is due to the bridging –SCN– group in the binuclear complex $[Ag{-}SCN{-}Ag]^+$.

Dimethyl Sulphoxide.—Although the insoluble AgSCN was taken up into solution at $S = 1.55$, solutions between $S = 1.55$ and 2.0 were turbid and unsuitable for spectroscopic examination.

Only three bands, B, C, and D, could be identified at $S > 2$ but their intensity variation pattern with S was the same in the Raman as in the i.r. Band C is seen in the Raman at $S = 2$ and 3 as a distinct asymmetry on the low-frequency side of the predominant band B and as a distinct inflexion at *ca.* 2 078 cm^{-1} at $S = 4.12$. It appears in the i.r. as a shoulder at *ca.* 2 070 cm^{-1} at $S = 2.0$. No evidence for a feature in the band A region was obtained.

The high relative intensity of band B in the spectra of all solutions at $S > 2$ indicates that $[Ag(SCN)_2]^-$ is the principal complex formed but the appearance of band C in these spectra indicates that the AgSCN monomers may still be present up to $S = 6$. Whilst previous conductimetric, potentiometric,[8] and solubility [9] studies suggest the presence of $[Ag_2(SCN)]^+$, $[Ag_2(SCN)_3]^-$, and $[Ag_3(SCN)_4]^-$ in the system we cannot present any spectroscopic evidence either to confirm or disprove their existence. Their formation at $S = 1.5$ and below cannot be ruled out particularly in view of the high solubility of AgSCN at $S = 1.5$ to 1.6.

The complexation scheme at $S > 2$ in dmso can be best represented by the simple equilibrium steps (2) and (5).

Acetone.—The Raman spectrum at $S = 6.7$ contains two sharp well separated bands in the B and D regions. Band B is asymmetric and a small contribution, 2—3%, can be estimated for band C. Good analytical agreement is found between the Raman and the i.r. spectra.

Thus at S *ca.* 6 the equilibrium mixture consists substantially of $[Ag(SCN)_2]^-$ and free SCN$^-$ ligand but a small proportion of the monomer AgSCN is still present. The equilibrium composition appears to be similar to that in dmso.

Dimethylacetamide.—Spectra were obtained at $S > 2.5$ and bands were found in all four regions. At $S = 2.5$ the high relative intensity of band A indicates that the main constituent complex contains the –SCN– bridging group; probably the 3 : 2 complex $[Ag_2(SCN)_3]^-$ species of equilibrium step (4). With increasing S the proportion of this species decreases with the formation of $[Ag(SCN)_2]^-$.

Because band C can be attributed either to the monomer AgSCN or to the terminal group of the bridged $[Ag_2(SCN)_3]^-$ it is impossible to be certain that AgSCN is absent.

The evidence suggests that the equilibria at $S > 2.5$ consist of the combination of the steps (2), (3), (4), and (5) but as S increases steps (2) and (3) cease to be observable and step (5) eventually dominates over step (4).

Dimethylformamide.—At $S = 3.8$ the Raman spectrum consists of two sharp polarised solute bands in the ν(C–S) stretching region located at *ca.* 736 cm^{-1} and *ca.* 730 cm^{-1} both of half-width $w_{\frac{1}{2}}$ *ca.* 6 cm^{-1}. These are well separated from the nearest solvent band at *ca.* 714 cm^{-1} which is of approximately equal intensity. The intensity ratio $I_{736}/I_{730} \simeq 2$. Following the assignments we made for thiocyanatosilver(I) complexed in liquid ammonia [2] we now assign the 736 cm^{-1} band to free SCN^- ligand and the 730 cm^{-1} band to an *S*-bonded complex. There was no evidence for the formation of an Ag–N bonded species in the spectra.[22]

In the ν(CN) stretching region three bands A, B, and D are observed. A small shoulder in the region of A on the high-frequency side of B indicates a small proportion of bridging $-SCN^-$ groups and the absence of band C at $S = 3.8$ indicates little or no AgSCN. Thus the equilibrium consists principally of a mixture of $[Ag(SCN)_2]^-$, free SCN^- ligand, and a small proportion of bridged complex, probably $[Ag_2(SCN)_3]^-$ indicating a close similarity with dma.

TABLE 2

Band analyses of the ν(CN) stretching region of the i.r. spectra of the thiocyanatosilver(I) complexes in hmpa *

S	$[Ag^+]$/mol dm^{-3}	Band positions/cm^{-1}			
0.20	0.025 (IV)	2 114	2 108	2 080	
0.05	0.025 (IV)	2 118	2 107	2 086	
1.00	0.025 (II)	[13] 2 119 (9)	[74] 2 108 (10)	[13] 2 085 (34)	
1.50	0.025 (IV)	[21] 2 119 (10)	[62] 2 107 (11)	[15] 2 081 (25)	[2] 2 059 (17)
2.00	0.025 (III)	[20] 2 116 (10)	[53] 2 102 (11)	[17] 2 078 (23)	[11] 2 057 (12)
2.48	0.017 (V)	[15] 2 116 (11)	[45] 2 103 (8)	[12] 2 078 (22)	[28] 2 058 (10)
2.98	0.012 (V)	[5] 2 118 (8)	[8] 2 104 (13)	[5] 2 080	[82] 2 060 (8)
4.95	0.006 (V)	2 119	2 105	2 080	2 060

* Relative absorbances are shown as the percentages of the total absorbance of the ν(CN) regions in square brackets. Band widths at half height, $w_{\frac{1}{2}}$, are given in parentheses.

Propylene Carbonate.—Though the spectra of solutions between $S = 2.1$ and 5.9 showed only the two bands, B and D, indicating $[Ag(SCN)_2]^-$ as the only complexed species in this range, the intensity data indicate that complexation is not complete until $S > 4$.

A previous potentiometric titration study led to extremely high stability constants; [10] $\log \beta_2 = 16.0$ and $\log \beta_3 = 18.7$. Although this work appears to have been carefully carried out using the normal background constant ionic strength conditions it is incompatible with the stoicheiometric stability constant for equilibrium step (5) calculated from our Raman spectral intensity data; $\log \beta_2$ *ca.* 3.8. Moreover, we find no evidence for $[Ag(SCN)_3]^{2-}$.

Trimethyl Phosphate.—The analyses of the Raman and i.r. spectra of solutions at $S = 6.1$ are almost identical. Bands are found in all four positions A, B, C, and D. Bands A and B appear as a double-topped wide feature, and band C as a low intensity maximum in the Raman and as an inflexion in the i.r. Even at $S = 6.1$ the formation of $[Ag(SCN)_2]^-$ is far from complete and β_2 is low compared with other solvent systems. A considerable proportion of the SCN^- ligand still remains in a bridged complex form, presumably $[Ag_2(SCN)_3]^-$ as in step (4). Because it is spectroscopically impossible to differentiate between the $-SCN^-$ of the mono complex and the terminal group of a bridged species we cannot be sure that no AgSCN complex still remains in the equilibrium at $S = 6$.

An unidentified band of low relative intensity appears at *ca.* 2 152 cm^{-1} in the i.r. only.

Tetrahydrofuran.—Both the i.r. and the Raman spectra of thf solutions at $S = 6.1$ are complicated by a feature of the solvent spectrum at 2 024 cm^{-1} (i.r.) and 2 030 cm^{-1} (Raman). Resolution of the i.r. spectrum is impossible because the whole ν(CN) region consists of a flat-topped broad band *ca.* 100 cm^{-1} wide. The Raman spectrum is easily resolvable into three sharp bands B, C, and D with the solvent feature at 2 030 cm^{-1} as a shoulder on D. In the absence of band A there is no evidence for multinuclear complexation. A surprisingly large proportion of AgSCN persists at $S = 6$, and further complexation to $[Ag(SCN)_2]^-$ is far from complete.

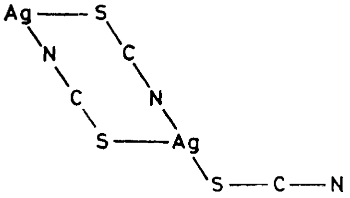
Hexamethylphosphoramide.—Raman spectroscopy of the thiocyanatosilver(I) complexes is impossible in this solvent because silver metal is deposited on the cell walls when the sample is exposed to the laser beam.

Four bands at 2 118, 2 105, 2 080, and 2 058 cm^{-1} are clearly distinguishable in the i.r. as indicated in Table 2. Inspection of the band positions and their intensity trends indicates the complexation system to be substantially different from that observed in the other solvents. This is probably due to (*a*) the powerful donor and solvating property of hmpa whereby it may compete favourably as a ligand with SCN^- for co-ordination sites on the Ag^+ ion, and (*b*) the bulky nature and shape of the hmpa molecule.

Plots of relative band intensities against S show that there is a direct correlation between the 2 118 and 2 080 cm^{-1} bands. Both appear at their highest relative intensity in the region $S = 1.5$ to $S = 2$ and accordingly we attribute both these bands to the same species. The 2 105 cm^{-1} band is the principal feature of the spectrum at $S = 0.5$, but although its relative intensity decreases with increasing S it is still in evidence in the spectrum at $S = 3$. In accord with previous attributions we therefore assign the 2 105 cm^{-1} band to the $[Ag_2(SCN)]^+$ species. The absence of a band in the 2 085—2 095 cm^{-1} region indicates the complete absence of the linear bis complex observed in all the other systems. The mono complex might be a minor component of the system because, if present, it would contribute to the band at *ca.* 2 080 cm^{-1}.

The attribution of the 2 118 cm^{-1} and 2 080 cm^{-1} bands to linkage isomeric complexes containing *N*- and *S*-bonded thiocyanate ligands (either in mono complexes or in the terminal groups of bridged complexes) is unlikely because we would expect the frequency to be lowered by *N*-bonded complexation.[22] A possible explanation lies in the attribution of these bands to the symmetric and asymmetric vibrations of a tetrahedral $[Ag(SCN)_2(hmpa)_2]^-$ species. This structure is not to be entirely unexpected because tetrahedral complexes of a number of transition-metal ions each containing two bulky hmpa ligands have been isolated.[23] Also, we have previously reported [24] that Ag^+ appears to solvate tetrahedrally in the powerful donor solvent ammonia.

A feasible alternative explanation of the spectra arises from the proposal of a multinuclear complex containing two –SCN– bridges between the Ag^+ centres (see below). This requires two frequencies (symmetric and asymmetric) due to the bridging ligands (2 118 and 2 105 cm^{-1}) and one due to the terminal ligand (2 080 cm^{-1}).



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