Spectrochemistry of Solutions. Part 12.[1] Cyano-complexes of Silver(I) in Solution in Liquid Ammonia

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Raman spectra of cyano-complexes of silver(I) in liquid ammonia solution have been interpreted to show the existence, in equilibrium, of the following species: AgCN, AgNC, $[Ag(CN)_2]^-$, $[Ag(CN)(NC)]^-$, $[Ag(NC)_2]^-$, $[Ag(CN)_3]^{2-}$, $[Ag_2(CN)]^+$, $[Ag_2(CN)_2]$, $[Ag_2(CN)_3]^-$, $[MAg_2(CN)_5]^{2-}$ (M = Na^+ or K^+), and $[MAg(CN)_3]^-$ (M = Li^+, Na^+, or K^+). The factors affecting the linkage isomerism, ion aggregation, ion pairing, and silver complexation are discussed.

IN a preliminary report[2] we have suggested that the silver ion in liquid ammonia forms the cyano-complexes AgCN, $[Ag(CN)_2]^-$, and $[Ag(CN)_3]^{2-}$. Two polarised Raman-active CN stretching frequencies were observed for each complex, and these were attributed to C- and N-bonded linkage isomers. We now report the results of a detailed and more extensive study of the Raman spectra of silver cyano-complexes in liquid ammonia.

EXPERIMENTAL

The chemical and spectroscopic techniques used in this work were similar to those we have used previously.[3] Each series of Raman spectra were obtained from five sets of solutions at three temperatures; details of the composition of the five sets of solutions are given in the Table. The composition of each solution is described by the molar ratios of the components: *S* is the ratio of CN^- to Ag^+; *R* is the ratio of NH_3 to Ag^+; and *Q* is the ratio of alkali-metal cation to Ag^+. The spectra of series A and B were obtained from mixtures of $Ag[NO_3]$ and K[CN] in liquid ammonia at 293 and 233 K respectively. The spectra of series F, G, and H were obtained from solutions of AgCN or $K[Ag(CN)_2]$ or an equimolar mixture of AgCN and $K[Ag(CN)_2]$ in liquid ammonia at 293, 233, and 203 K. Thus, in solutions corresponding to spectra F—H, 1—12 there is no nitrate or perchlorate ion. By comparing these spectra with spectra from other series we find no evidence for the existence of nitrate or perchlorate complexes. In series A to E the total silver concentration was kept approximately constant at *R ca.* 100. All Raman bands were found to be polarised unless otherwise stated. The spectra were calibrated by reference to neon emission lines.

Composition of samples used to obtain Raman spectra of silver cyano-complexes in liquid ammonia

	$Ag[NO_3]$ + K[CN]	$Ag[NO_3]$ + Na[CN]	$Ag[NO_3]$ + Li[CN]	$Ag[NO_3]$ + Na[CN] + $Na[ClO_4]$		Ag[CN] + $K[Ag(CN)_2]$	
Spectrum no.	Series A,[a] B[b]	Series C[a]	Series D[a]	Series E[a]		Series F,[a] G,[b] H[c]	
	S[d]	*S*	*S*	*S*	*Q*[d]	*R*[d]	*S*
1	0.42	0.20	0.2	0.98	7.9	18	1
2	0.92	0.29	0.9	1.65	8.5	44	1
3	1.29	0.45	2.2	2.0	9.0	52	1
4	1.87	1.00	2.9	2.3	9.3	74	1
5	2.0	1.25	3.1	6.7	13.6	99	1
6	2.23	1.62				33	1.5
7	2.32	1.99				40	1.5
8	2.56	2.07				200	1.5
9	2.96	2.17				12	2
10	3.57	2.26				15	2
11	4.14	3.21				30	2
12	5.18	4.14				82	2
13	7.98	6.64					
14	10.4	14.1					

[a] At 293 K. [b] At 233 K. [c] At 203 K. [d] *S* = Moles CN^-/moles Ag^+; *R* = moles NH_3/moles Ag^+. *Q* = Moles alkali-metal cation/moles Ag^+. In series A, B, C, and D, *Q* = *S* and $R \approx 100$. In series E, $R \approx 100$. In series F, G, and H, $Q = S - 1$.

Most of the spectra were digitised semi-automatically on an intensity scale 0—128 at 1 024 points over a 60 cm^{-1} range. Curve resolution wa sperformed with the programs FITS[4] and VIPER.[5] Some spectra were smoothed and condensed to 128 points by fitting a parabola to groups of eight data points, and these spectra were stored on a Hewlett-Packard 9845S minicomputer. New programs were written for this computer in extended BASIC. These include a program analogous to VIPER, and programs to simulate the spectra and their second derivatives.

Both the 1 024 and 128-point data sets were subjected to numerical differentiation for the purpose of resolution enhancement. We have examined the second derivative of most of the spectra, and the fourth derivative of some spectra. The numerical differentiation was carried out by a variety of techniques including a new technique, details of which will be given elsewhere,[1,6] that we have developed for this chemical problem: the spectra were fitted using a linear least-squares method by a polynomial spline function based on fixed knots. The derivatives were obtained by analytical differentiation of the spline function. Various schemes for generating the knots were explored, and for each spectrum peaks were accepted in the derivative only if, after extensive investigation involving spline functions of degree 3, 4, and 5 based on various numbers of knots and knot distribution schemes, they appeared consistently and independently of the method of differentiation used.

RESULTS AND ASSIGNMENTS

The Raman spectra of cyano-complexes of silver(I) in liquid ammonia are much more complicated than was at first thought. The reason why this complexity was not appreciated earlier is that in two regions of the spectra (*ca.* 2 120 and 2 140 cm^{-1}) there may be up to three bands at almost the same wavenumber. The spectra could not be analysed by curve resolution alone,[7] but numerical differentiation was able to reveal peaks separately that were too close to be reliably resolved by curve analysis. The species present in each solution were inferred using an approach which combines both techniques of curve resolution and differentiation with the use of chemical logic.

Firstly, the condition of mass balance imposes constraints on the species that may be present in equilibrium, as instanced by equations (1) and (2). These constraints apply

$$2\mathrm{AgCN} \rightleftharpoons [\mathrm{Ag(CN)}_{1-x}]^{x+} + [\mathrm{Ag(CN)}_{1+x}]^{x-} \quad (1)$$

$$2[\mathrm{Ag(CN)}_2]^- \rightleftharpoons [\mathrm{Ag(CN)}_{2-x}]^{(1-x)+} + [\mathrm{Ag(CN)}_{2+x}]^{(1+x)-} \quad (2)$$

directly to mixtures at $S = 1$ or 2 and indirectly to other mixtures. Secondly, the heights of the peaks corresponding to each species must vary as a function of the molar ratios Q, R, and S in a manner consistent with shifts in chemical equilibria. Thirdly, the number of bands given by a stoicheiometric species must be independent of temperature, although the relative intensity of each band may vary if the variation is consistent with the existence of a temperature-dependent equilibrium between compounds of the same stoicheiometry. Fourthly, agreement was sought between the second derivative of the spectrum and of the resolved bands. Where a unique resolution was not possible due to bands being too close together agreement was sought with the second derivative of a simulation of the spectrum.

Using these principles, we have arrived at a self-consistent interpretation of the 90 or so observed spectra without making any arbitrary assumptions, and now present the spectra deduced for each chemical species, along with the reasoning upon which the assignation was made.

$[\mathrm{Ag(CN)}_2]^-$.—Concentrated solutions at $S = 2$ {made, for example, by dissolution of $\mathrm{K[Ag(CN)}_2]$} contain predominantly the ion $[\mathrm{Ag(CN)}_2]^-$, and their spectra show the presence of a small amount of $[\mathrm{Ag(CN)}_3]^{2-}$ species as a band at *ca.* 2 104 cm^{-1}. As the total concentration decreases, this band also decreases until in ' dilute ' solution the only species remaining is $[\mathrm{Ag(CN)}_2]^-$. These changes are consistent with equation (2), $x = 1$. The spectra F12, G12, H12 {solution composition $\mathrm{K[Ag(CN)}_2]$ 1 mol: NH_3 80 mol} are therefore close to the spectra of the $[\mathrm{Ag(CN)}_2]^-$ ion. These spectra and their resolved components are shown in Figure 1.

The three components shown in Figure 1 are assigned to the linkage isomers $[\mathrm{Ag(CN)}_2]^-$, $[\mathrm{Ag(CN)(NC)}]^-$, and $[\mathrm{Ag(NC)}_2]^-$. The central band at 2 131 cm^{-1} belongs to the mixed isomer, as its intensity is a maximum at the temperature that the intensities of the other two bands are approximately equal, and also because its frequency is midway between the frequencies of the other two bands. The variation of relative intensity of the three bands with temperature is nicely illustrated in Figure 1. At constant temperature, the relative intensities are approximately constant in the range $2 < S < 3$ as is to be expected for isomers in equilibrium. Recalibration of the spectra has led us to locate the other main bands at 2 139 cm^{-1} and 2 124 cm^{-1}, and not 2 142 cm^{-1} and 2 127 cm^{-1} as before.[2]

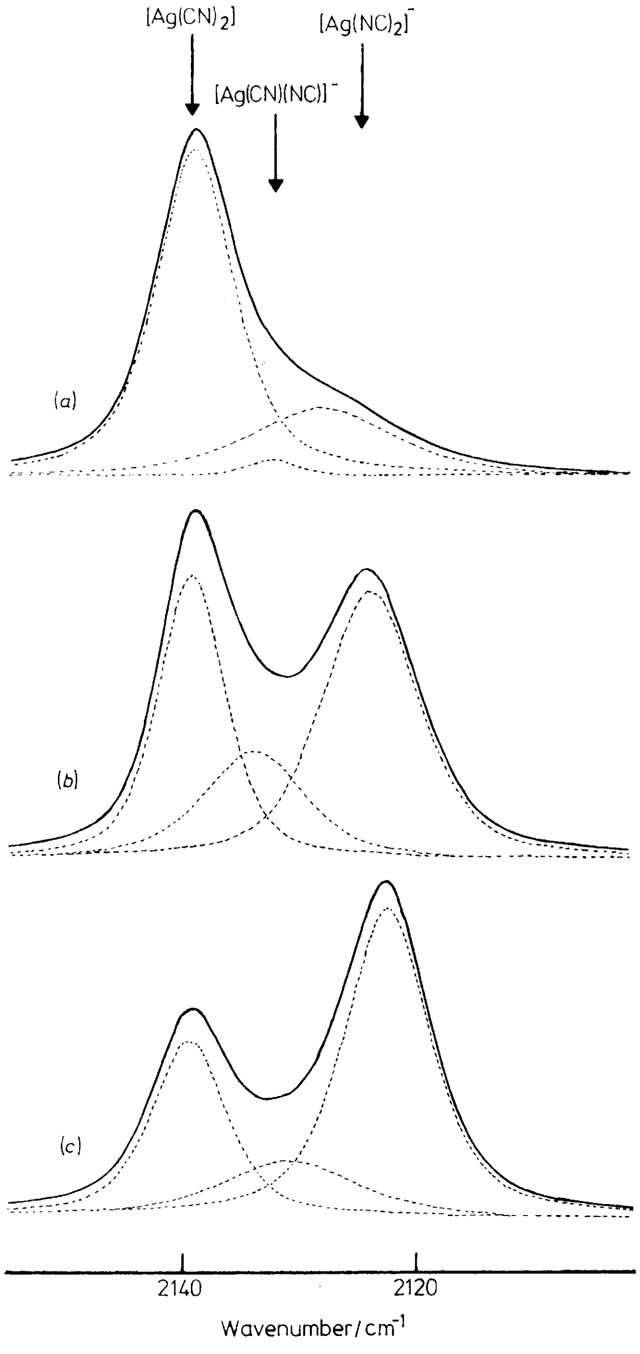


FIGURE 1 Raman spectra of the ions $[\mathrm{Ag(CN)}_2]^-$ in liquid ammonia. (*a*) At 293, (*b*) 233, (*c*) 203 K

The complex $[Ag(CN)_2]^-$ and its isomers are the major species present in solutions in the range $0.5 < S < 3.5$ at 293 K and $1 < S < 3$ at 233 K. Qualitatively they are the strongest cyano-complexes formed by silver(I) in liquid ammonia.

$[Ag(CN)_3]^{2-}$ *and* $[MAg(CN)_3]^-$ (M = Li, Na, *or* K).—Bands due to these species appear in the spectra of all solutions with $S > 2$ but the appearance of the spectra is dependent upon the nature and concentration of the alkali-metal cations and the assignment is different for each cation. With Li^+ the band at 2 115.5 cm^{-1} is assigned to the ion pair $[LiAg(CN)_3]^-$ and the bands at 2 102 and 2 099 cm^{-1} (depolarised) to the symmetric and antisymmetric vibrations of the free ion $[Ag(CN)_3]^{2-}$. With Na^+ the free $[Ag(CN)_3]^{2-}$ was found at 2 102 cm^{-1}, but the ion pair gave a band at 2 108 cm^{-1}. The dependence of the intensity of the ion-pair band on the concentration of excess of Na^+ is illustrated in Figure 2. Throughout the range of Q values investigated both $[NaAg(CN)_3]^-$ and $[Ag(CN)_3]^{2-}$ could be seen in equilibrium together. With K^+ two polarized bands are observed at 2 104 and 2 102 cm^{-1}. There is little variation in the overall band envelope when S is varied in the range $3 < S < 10.4$ at both 293 and 233 K. This suggests that for $S > 3$ the two bands originate from the same chemical species, namely $[KAg(CN)_3]^-$, in which the symmetry is low. It follows that ion pairing between K^+ and $[Ag(CN)_3]^{2-}$ is essentially complete at $S > 3$. Note that in solutions of series A and B, the mol ratio Q is equal to S. When the mol ratios S and Q lie in the range 2—3 there is some variation in the overall band envelope which indicates that some Raman intensity at 2 102 cm^{-1} is due to the free ion $[Ag(CN)_3]^{2-}$.

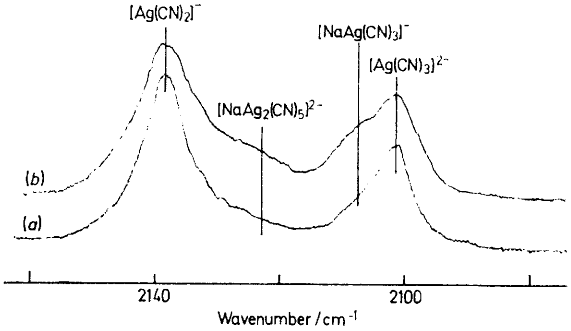


FIGURE 2 Spectra to illustrate the effect of added cation on ion pairing. The composition of the solutions was (*a*) Na[CN] 2.3 mol : $Ag[NO_3]$ 1 mol : NH_3 100 mol, (*b*) Na[CN] 2.3 mol : $Ag[NO_3]$ 1 mol : $Na[ClO_4]$ 9.3 mol : NH_3 100 mol

AgCN.—The complex AgCN is a weak complex which ionises under the experimental conditions used according to equation (1), to Ag^+ and $[Ag(CN)_2]^-$ ($x = 1$), and $[Ag_2(CN)]^+$ and $[Ag_2(CN)_3]^-$ ($x = 0.5$). In concentrated solutions it also dimerises to $[Ag_2(CN)_2]$. Because of extensive band overlap the spectra obtained at $S \approx 1$ and 293 K could not be analysed completely. The spectra of AgCN deduced from data are shown in Figure 3. The two bands observed at 2 119 and 2 106.5 cm^{-1} are assigned as before to the linkage isomers AgCN and AgNC. We note that with both AgCN and $[Ag(CN)_2]^-$ the linkage isomer whose band is at lower frequency decreases in relative concentration as the temperature increases.

It is very difficult to estimate the concentration of AgCN in a solution because the peak at 2 119 cm^{-1} is heavily overlapped by peaks due to $[Ag(CN)_2]^-$ (2 124 cm^{-1}) and $[Ag_2(CN)_3]^{2-}$ (2 122 cm^{-1}). We conclude that AgCN is present in the range $0.5 < S < 2$ but that its concentration is not large in the range $1.5 < S < 2$. The equilibrium (1) is favourable to $[Ag(CN)_2]^-$ at 293 K, but only a small proportion of $[Ag(CN)_2]^-$ is formed at 233 and 203 K.

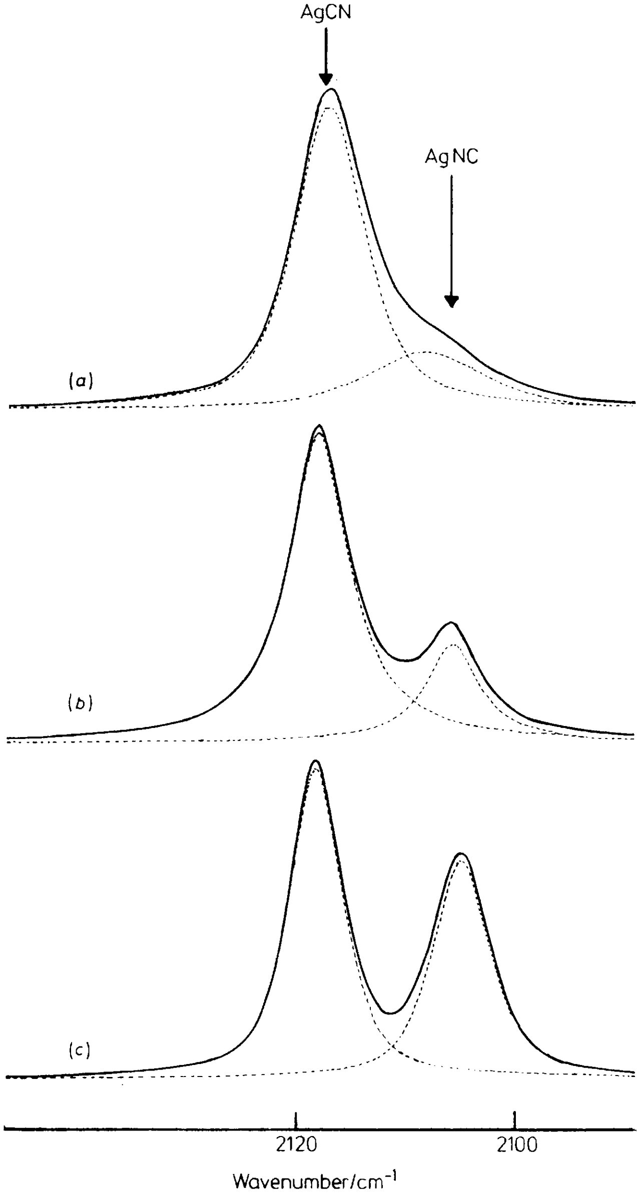


FIGURE 3 Raman spectra of the species AgCN in liquid ammonia. (*a*) At 293, (*b*) 233, (*c*) 203 K

To illustrate the complexity of the spectra obtained at $S \approx 1$ we show in Figure 4 the spectrum B2 (solution composition $Ag[NO_3]$ 1 mol : K[CN] 0.92 mol : NH_3 100 mol) together with its second derivative. Previously the spectrum was fitted with three bands, but even the six bands used in Figure 4 cannot represent the structure of the spectrum adequately as the low-frequency band belonging to $[Ag(CN)_2]^-$ is not properly represented. However, the close similarity of the second derivative of the resolved spectrum and of the fitting spline function, which extends to other spectra obtained from solutions with $S \approx 1$, is evidence that the spectra contain at least six bands at the resolution afforded by the second-derivative spectra.

$[Ag_2(CN)]^+$.—This ion gives a peak at 2 132 cm^{-1}. The band is most easily observed at $S \approx 0.5$ and 293 K, but the complex is weak since the complexes AgCN and $[Ag(CN)_2]^-$ are the major species present under these conditions. The band is not present in spectrum B1 ($S = 0.42$, 233 K), but the second derivatives of spectra taken at 233 K with $S \approx 1$ consistently show a peak which can be assigned to $[Ag_2(CN)]^+$. Unfortunately this band is almost coincident with the middle band due to $[Ag(CN)_2]^-$ and has a similar half-width to that band so that it is difficult to estimate the concentration of $[Ag_2(CN)]^+$.

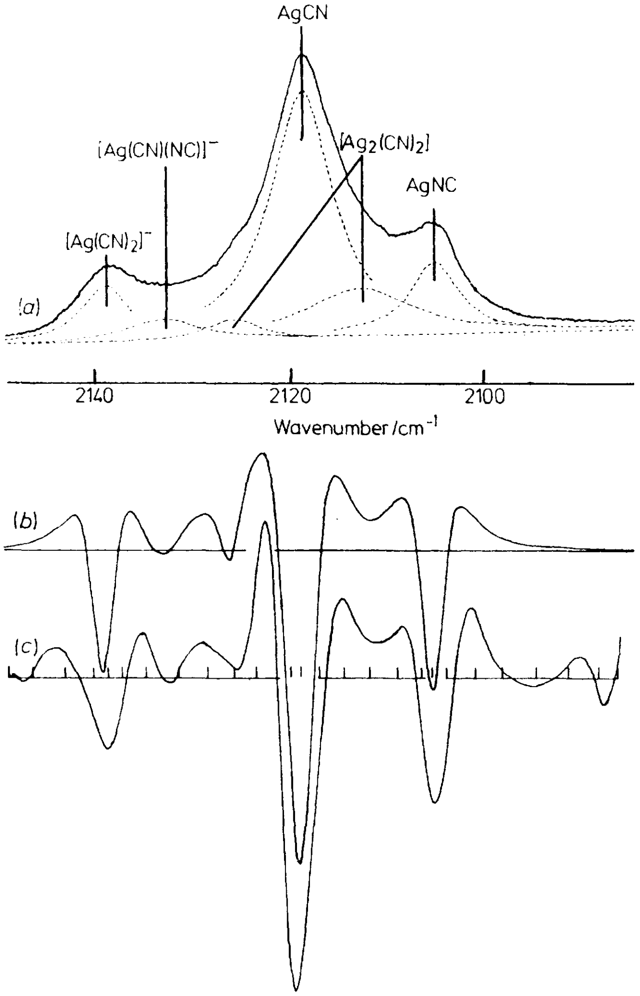


Figure 4 Raman spectrum of a mixture of composition AgCN 1 mol : NH_3 44 mol at 233 K. (*a*) Observed spectrum and decomposition into component bands. (*b*) Second derivative of the spectrum calculated by adding together the component bands. (*c*) Second derivative of the observed spectrum obtained by the spline function method

$[Ag_2(CN)_2]$.—The spectra shown in Figure 5 were deduced for species $[Ag_2(CN)_2]$ by analysis of spectra obtained at 233 and 203 K. The band at 2 127 cm^{-1} is assigned to the bridging cyanide vibration and the band at 2 113 cm^{-1} is assigned to the terminal cyanide vibration. The spectra shown in Figure 5 are, within experimental error, independent of temperature. A peak at *ca.* 2 127 cm^{-1} was found in the second derivatives of spectra obtained at 293 K and $S \approx 1$, but these spectra could not be analysed fully, so that we infer that some dimer is present in mixtures at 293 K with $S \approx 1$, but cannot quantify this inference. The concentration of dimer fell rapidly as the total silver concentration decreased. While the concentration of $[Ag_2(CN)_2]$ is a maximum at $S = 1$, it seems clear that the proportion of dimer present in a solution increases as the temperature is lowered, though this is in part a natural consequence of the shift in equilibrium (1) in favour of AgCN that also occurs.

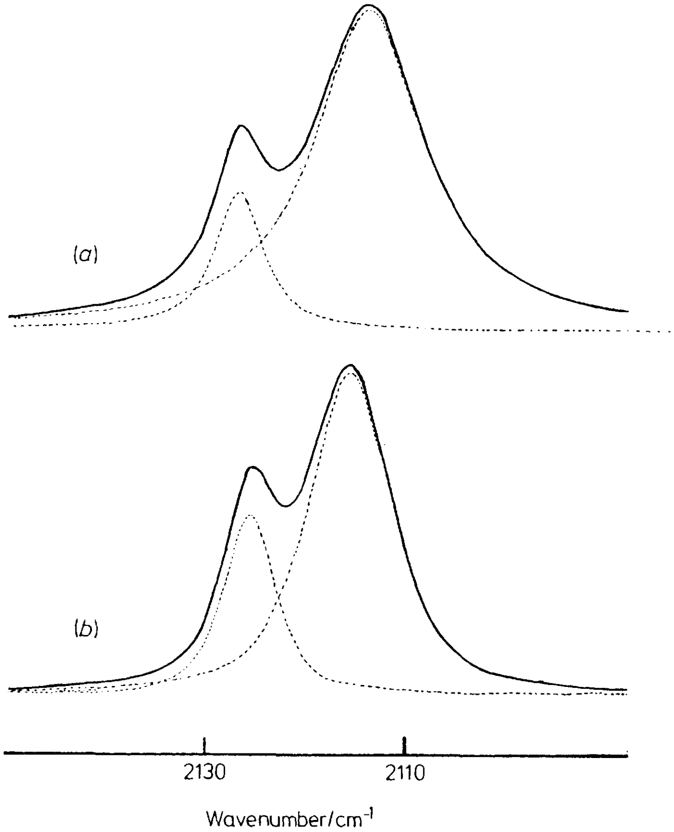


Figure 5 Raman spectra deduced for the species $[Ag_2(CN)_2]$, (*a*) At 233, (*b*) 203 K

$[Ag_2(CN)_3]^-$.—The principal evidence for this species is illustrated in Figure 6 which shows the spectra G6—G8 ($S = 1.5$, 233 K) together with the second derivatives obtained by the spline function method. The derivatives show that, at $S = 1.5$ and 233 K, there is a band at 2 125 cm^{-1} which decreases in intensity as the total solute concentration decreases. Careful study of these and other derivative spectra have led us to conclude that $[Ag_2(CN)_3]^-$ has another band at virtually the same wavenumber as that of the main $[Ag(CN)_2]^-$ band (2 139 cm^{-1}). We could assign that band to the bridging cyanide vibration, and the 2 125 cm^{-1} band to terminal cyanide vibrations. Both bands assigned to $[Ag_2(CN)_3]^-$ are very close to bands due to other species, so that the spectra cannot be analysed by curve resolution. Evidence from the heights of peaks in the

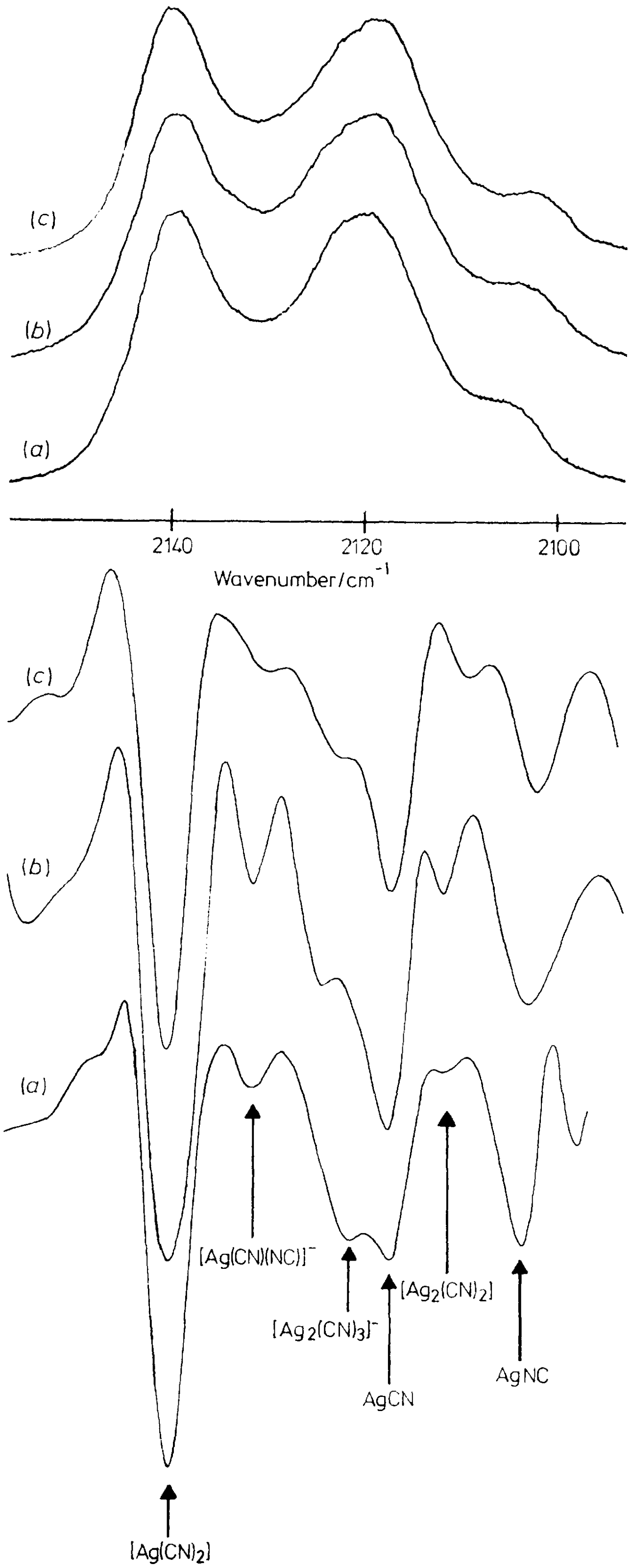


FIGURE 6 Raman spectra (upper curves) and second derivatives obtained by the spline function method (lower curves) of mixtures whose composition was AgCN : [KAg(CN)$_2$] : NH$_3$ 1 : 1 : R at 233 K. (*a*) R = 33, (*b*) R = 40, (*c*) R = 200

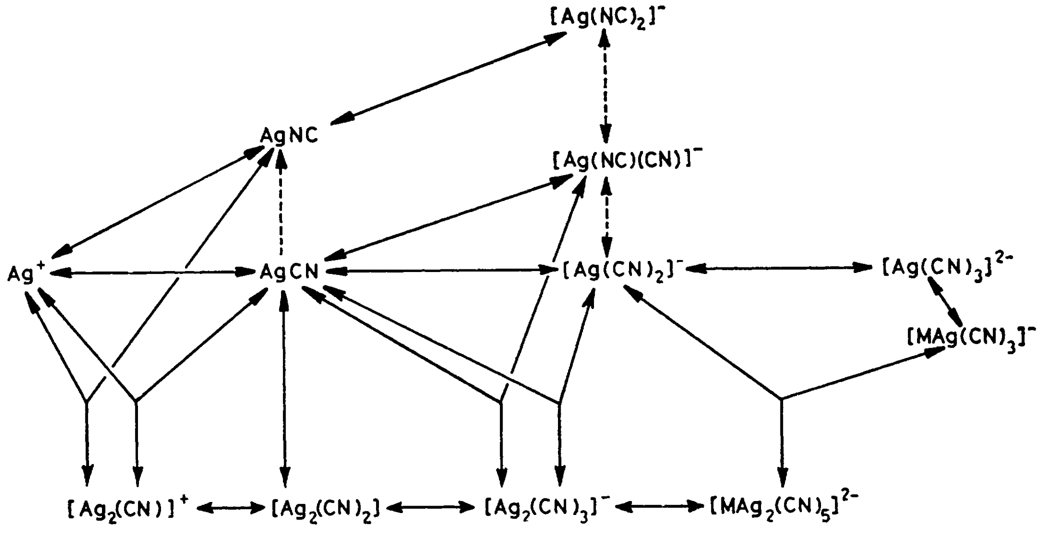
differentiated spectra suggests that [Ag$_2$(CN)$_3$]$^-$ is formed in the more concentrated solutions in the range $1 < S < 1.6$ at 233 K. There is faint but clear evidence for the presence of [Ag$_2$(CN)$_3$]$^-$ at 293 K and $S = 1.5$.

[MAg$_2$(CN)$_5$]$^{2-}$ (M = Na *or* K).—The presence of this species is not established with certainty, but it seems reasonable to assign a band at *ca.* 2 124 cm^{-1} to it. The dependence of intensity in this region at $S \approx 2.5$ upon the concentration of Na$^+$ is illustrated in Figure 2 and parallels the intensity dependence of the band associated with [NaAg(CN)$_3$]$^-$. This clearly suggests that the band at *ca.* 2 124 cm^{-1} is due to an ion-paired species. There is no evidence in other spectra for an ion-paired species M[Ag(CN)$_2$], and a species M$_2$[Ag(CN)$_3$] seems unlikely in view of the large amount of free [Ag(CN)$_3$]$^{2-}$ ion present. Hence by a process of elimination, we suggest that the species responsible for the band at 2 124 cm^{-1} may be [MAg$_2$(CN)$_5$]$^{2-}$. Although the concentration of this species is never high, it appears to be a maximum at $S = 2.5$ from the scanty evidence available.

DISCUSSION

The equilibria amongst cyano-complexes of silver(I) that have been found in liquid ammonia are summarised in the Scheme, and encompass four different phenomena. In the horizontal direction the Scheme shows a change in the ratio of cyanide to silver in both mononuclear and binuclear complexes. Compounds which lie on a vertical axis in the Scheme are linkage isomers of each other with the exception of [Ag$_2$(CN)$_2$] which is a dimer of AgCN. Compounds in the bottom row of the Scheme are binuclear complexes formed by joining together a pair of mononuclear complexes. Finally, the compound [MAg(CN)$_3$]$^-$ is a heterobinuclear complex, or ion pair, formed from [Ag(CN)$_3$]$^{2-}$ and alkali-metal cation. Each of the four phenomena will be discussed in turn, although they are necessarily inter-related.

Linkage Isomerism.—We have previously claimed that the cyanoargentate complexes AgCN and [Ag(CN)$_2$]$^-$ in liquid ammonia solution afforded the first example of complexes in which the cyanide ligand bonds to a metal ion through either C- or N-donor atoms.[2] This claim has now been more firmly substantiated by the identification of all three possible isomers of [Ag(CN)$_2$]$^-$. We now also know that the silver ion is not unique in forming linkage isomers with the cyanide ion; the ions Li$^+$, Na$^+$, Be^{2+}, Mg^{2+}, and Al^{3+} all form C- and N-bonded cyano-complexes in liquid ammonia.[8] In fact, of all the cyanide salts so far studied in liquid ammonia, only the mercury salts show no evidence of linkage isomerism (at 293 K).[8,9] We have suggested before that anion solvation plays an important role in determining the co-ordination mode of the cyanide ligand.[2] The C–N stretching vibration of the free cyanide ion shifts by some 20 cm^{-1} on changing the solvent from water to liquid ammonia, which indicates a large change in solvation. Probably in aqueous solution there is hydrogen bonding to the nitrogen end of CN$^-$, such as occurs extensively in liquid hydrogen cyanide,[10] as well as to the carbon end. In ammonia both interactions are decreased because ammonia is less acidic than water, and is a poorer hydrogen-bond donor. Therefore we expect that the



SCHEME

free energy of desolvation required to form both metal complexes is less in ammonia than in water.

The indirect evidence presented below suggests that in $[Ag(CN)_2]^-$ the Ag–CN forms are preferred to the Ag–NC forms at 293 K, but at 203 K, the situation is reversed; the two forms are of comparable stability in AgCN at 203 K. With the alkali-metal ions the linkage isomer with the lower C–N stretching band, which perhaps corresponds to the lower frequency band in the silver complexes, is predominant even at 293 K. Thus the silver ion is only a slightly softer accepter than the alkali-metal ions, as gauged by its tendency to form Ag–C bonds preferentially.

We have found no evidence for linkage isomerism in the $[Ag(CN)_3]^{2-}$ ion. The two bands attributable to compounds with a cyanide to silver ratio of 3 : 1 are now assigned to the species $[Ag(CN)_3]^{2-}$ and $[MAg(CN)_3]^-$ as discussed below; this is probably due to a change in the relative strengths of the Ag–C and Ag–N bonds brought about by the greater overall charge of the complex. We have also been unable to find evidence for linkage isomerism in the binuclear complexes, where the terminal cyanide groups may obviously bond in either manner, but this reflects the experimental difficulty in deducing the spectra of these species, and linkage isomerism may well be present. The assignment of linkage isomers can be tentatively based upon some indirect evidence. Firstly, the wavenumbers of the Raman bands of the ions $[Ag(CN)_2]^-$ and $[Ag(CN)_3]^{2-}$ in liquid ammonia are very close indeed to the wavenumbers of the same species in aqueous solution.[11] From this we can conclude with some certainty that the complexes have the same structure in the two solvents. Now, it is widely assumed that cyano-complexes are C-bonded in aqueous solution; force constants calculated from ^{13}C and ^{15}N substituted species of $[Ag(CN)_2]^-$ gave some support to this assumption.[12] We may conclude that the band at 2 139 cm^{-1} belongs to the ion $[Ag(CN)_2]^-$, whereas the band at 2 124 cm^{-1} belongs to the ion $[Ag(NC)_2]^-$. Secondly, in the boron linkage isomers $[BH_3(CN)]^-$ and $[BH_3(NC)]^-$ the isomer which gave the broader ^{11}B n.m.r. spectrum was assigned as N-bonded because of the quadrupolar nature of the ^{14}N nucleus, and this isomer gave an i.r. band some 110 cm^{-1} lower than the C–N stretching band due to the C-bonded isomer.[13] A similar n.m.r. based assignment for the adduct $Me_3N{\cdot}BH_2(CN)$ showed the band due to the N-bonded isomer some 60 cm^{-1} less than the band due to the C-bonded isomer.[14] Other evidence comes from trimethylsilyl cyanide.[15] The band due to the N-bonded isomer was placed 98 cm^{-1} below the band due to the C-bonded isomer, and it shifted by 39 cm^{-1} on ^{13}C substitution, whereas the band due to the C-bonded isomer shifted by 49 cm^{-1}.

In the boron and silicon cases, then, the C–N stretching band of the N-bonded isomer was also found at lower frequency than that of the C-bonded isomer. If we assign the bands in this way for the silver complexes the assignments are consistent with the species present in aqueous solution being the C-bonded isomer.

Aggregation.—We have now succeeded in characterising the aggregated species indicated in the bottom row of the Scheme. The aggregates are always minor species in ammonia solution and their concentration is highest when the concentrations of both precursors are high. This requires in all cases that the overall solute concentration be high ($R < 100$) and at 233 K that the composition of the mixture should correspond with that of the aggregate. The latter is less true at 293 K since there is extensive ionisation of AgCN to Ag^+ and $[Ag(CN)_2]^-$. Thus, at the higher temperature the complex $[Ag_2(CN)_2]$ can be formed by interaction of Ag^+ and $[Ag(CN)_2]^-$, though that is not indicated on the Scheme. The concentration of aggregated species appears to increase as the temperature of a solution is decreased, as is to be expected on the basis of the unfavourable translational entropy change on forming one complex from two precursors; the unfavourable component of the $T\Delta S$ term decreases with decreasing T.

We can assume that there is a bridging cyanide group in all the binuclear complexes, in which both the C and N atoms are acting as electron-pair donors, as in solid silver cyanide.[16] It is probable, therefore, that the complexes $[Ag_2(CN)]^+$, AgCN, $[Ag_2(CN)_2]$, $[Ag_2(CN)_3]^-$, and $[Ag(CN)_2]^-$ are all linear {evidence for $[Ag(CN)_2]^-$ is considered below} and that the aggregation process is one in which linear chains of silver and cyanide are built up. The same process presumably occurs in aqueous solution but there the insolubility of the infinite chain compound, solid AgCN,[16] prevents the observation of small aggregates. The fact that the cyanide ion can form linear bridges is entirely consistent with its ambidentate nature in forming linkage isomers.

There is some evidence that very concentrated solutions of the salt $K[Ag(CN)_2]$ contain a second species in addition to the main one, $[Ag(CN)_2]^-$. The spectra obtained from mixtures containing 12 moles of solvent per mol of $K[Ag(CN)_2]$, are noticeably different from the spectra obtained with more dilute solutions of the same salt. The differences are in the relative intensity and positions of the bands, and are of such a magnitude as to be unlikely to originate in the dissociation of $[Ag(CN)_2]^-$ to $[Ag(CN)_3]^{2-}$ and something else {the concentration of $[Ag(CN)_3]^{2-}$ can be monitored at *ca.* 2 104 cm^{-1}}. The second species may be the dimer of $[Ag(CN)_2]^-$, in the free or ion-paired state, or it may be the ion pair $K[Ag(CN)_2]$.

Ion Pairing.—The alkali-metal cations have been found to form ion pairs with all the cyanoargentate complexes of charge $\geqslant 2$, but by contrast evidence for the formation of ion pairs with the monovalent anion $[Ag(CN)_2]^-$ is extremely tenuous, as discussed above. We can conclude that the interaction between $[Ag(CN)_2]^-$ and M^+ in ammonia is exceedingly weak. Thus, $[Ag(CN)_2]^-$ is only the third anion for which Raman spectroscopy has given us no clear evidence of ion pairing in liquid ammonia, the others being the perchlorate and fluoroborate ions. In all three cases the anion is highly symmetrical and the negative charge can be equally distributed amongst the ligands attached to the central cation. Since the ion pairing is largely electrostatic, being a consequence of the relatively low dielectric permittivity of the solvent medium, a reduction in overall charge by sharing amongst ligands would be expected to cause a decrease in the amount of ion pairing. With complexes of overall charge of two or more the fractional charge on the cyanide ligands must be sufficient to make ion pairing energetically favourable. We note, however, that the ions $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ were found to associate with lithium cations in concentrated aqueous solution.[17]

The frequencies and intensities of the bands due to the ion pairs $[MAg(CN)_3]^-$ follow the same pattern that has been widely observed for ion pairs in liquid ammonia.[18] The frequency separation between the free ion and ion-pair bands decreases in the order Li > Na > K but the extent of ion pairing decreases in the reverse order. With Li^+ the extent of ion pairing is small (<10%) and approximately independent of S and R; other ion pairs involving the lithium cation show a similar slight dependence on concentration of excess of alkali-metal ion. With Na^+ the concentration of ion-paired species is strongly dependent on both S and Q (S and Q cannot be varied altogether independently). With K^+ the ion pairing is extensive.

Mononuclear Complexes.—The only aspect of the stepwise formation of silver cyano-complexes that we have not discussed is the non-formation of the ion $[Ag(CN)_4]^{3-}$. In aqueous solution the stepwise formation constant for this species is small,[19] $K_4 \approx 1$, so we need only postulate a slight decrease in stability in ammonia relative to water. Moreover, the conditions were not as favourable for its formation as appears at first sight, because when an excess of alkali-metal cyanide is added to a solution containing $[Ag(CN)_3]^{2-}$ ions, much of the excess is present in the form of alkali-metal ion pairs, MCN, and the excess of free cyanide ion is much smaller than the stoicheiometric excess.

Structure.—The spectra of the ion $[Ag(CN)_2]^-$ in aqueous and ammonia solution both contain a band at *ca.* 2 139 cm^{-1} and in both cases a depolarised band was observed at *ca.* 250 cm^{-1}. The latter has been assigned to the rocking mode of Π_g symmetry in the point group $D_{\infty h}$ and is highly characteristic of the linear structure.[12, 20] We conclude from these observations that the same ion is present in both solutions, and that it is linear and unsolvated. Some evidence has been presented that this ion is the C-bonded isomer.[12]

The ion $[Ag(CN)_3]^{2-}$ is also likely to have the same structure in ammonia and aqueous solutions, since the C–N stretching frequency shows a solvent shift of only 6 cm^{-1}. If the structure is the same it follows that this ion is also unsolvated. On the other hand the complex AgCN is almost certainly solvated in ammonia. It can be generally expected that the silver ion would have a minimum co-ordination number of two, but we have found that in ammonia the co-ordination number is greater than two,[3] as the band near 370 cm^{-1} which is characteristic of the ion $[(H_3N)Ag(NH_3)]^+$ in aqueous solution is not present in spectra of silver salts in ammonia.[21] The spectra of solutions in which AgCN is a major component show no Raman intensity near 370 cm^{-1}, nor any features at lower frequency which could be definitely assigned to Ag–N stretching modes. Therefore we suggest that silver cyanide has the structure $[Ag(CN)(NH_3)_2]$ or $[Ag(CN)(NH_3)_3]$ in ammonia solution. Presumably the formation of a solvate such as these is an important factor in making silver cyanide so much more soluble in ammonia than in water.

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