Raman Spectroscopic Evidence for the Existence of Cyanide Linkage Isomers; Equlibria of Silver Complexes in Liquid Ammonia†

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Summary The Raman spectra of liquid ammonia solutions of the silver(I) ion in the presence of varying amounts of cyanide ion show two polarised bands for each of the species 'AgCN,' $[Ag(CN)_2]^-$, and $[Ag(CN)_3]^{2-}$; this is interpreted as evidence for the presence of cyanide linkage isomers, and from temperature variation studies it is proposed that 'AgCN' is constituted as $[Ag(NH_3)_y(CN)]$, where $y = 2$ or 3.

OUR previous work[1,2] has shown that the silver(I) ion in liquid ammonia exhibits a co-ordination number greater than two. Because of this, and the effect of the medium, the co-ordination chemistry of silver(I) in ammonia is expected to be significantly different from that observed in aqueous solutions.

We have studied the complex equilibria between silver(I) and the cyanide ion and have found extensive solvent effects which we interpret as being due both to changed cation acceptor power and to changed anion donor power. The Raman spectra in liquid ammonia of mixtures in which the (potassium) cyanide to silver concentration ratio, *R*, ranges from 0·4 to 10·0 have been obtained. The temperature range was 200—293 K and various silver ion concentrations were used. From a study of the variation over all the spectra, of the resolved band intensities relative to the nitrate ν_1 band as internal standard, we are led to conclude that each of the species 'AgCN', $[Ag(CN)_2]^-$, and $[Ag(CN)_3]^{2-}$ gives rise to two, polarised, Raman-active stretching vibrations. Representative spectra and their resolved features are shown in the Figure.

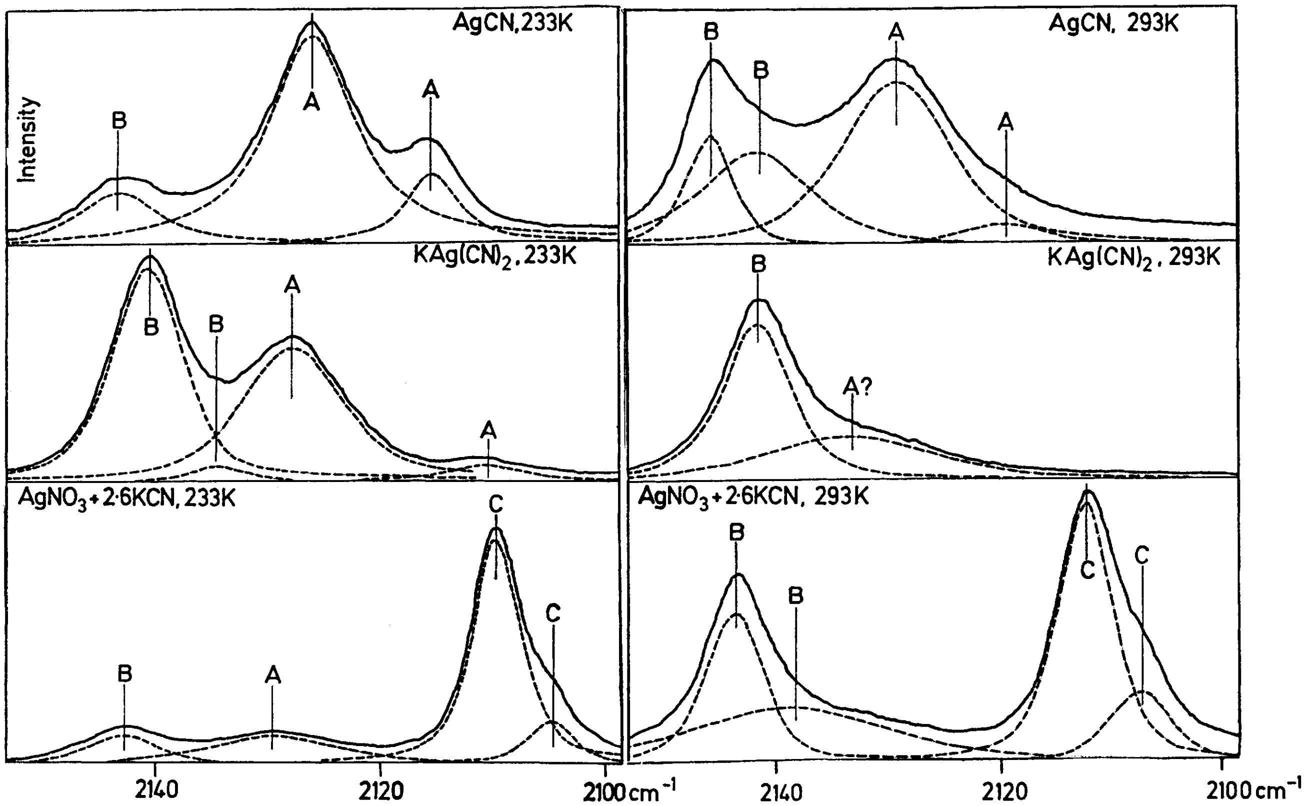

FIGURE. Raman spectra of silver(I) cyano-complexes at $R = 1$, 2, and 2·6. Intensities are on an arbitrary scale. Observed spectra are solid lines; dotted lines are computer-resolved components.

'AgCN' gives rise to two bands at *ca.* 2112 and 2126 cm^{-1}, (A in the Figure), whose intensities are a maximum at $R = 1$. There is no aqueous solution analogue. The relative proportion of the low frequency band is greater at lower temperatures. The relative intensities of the two bands are almost concentration independent. This suggests that neither band belongs to a self-associated species. Also, association of the neutral 'AgCN' grouping with other ions is unlikely to produce a separately identifiable band.

These facts are consistent with an equilibrium between

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† No reprints available.

linkage isomers [equation (1)]. An alternative equilibrium

$$(NH_3)_yAg\text{-}CN \rightleftharpoons (NH_3)_yAg\text{-}NC \qquad (1)$$

[equation (2)] cannot be ruled out but is less likely. We

$$(NH_3)_yAgCN \rightleftharpoons (NH_3)_zAgCN + (y-z)NH_3 \qquad (2)$$

believe that this is the first evidence for the existence of linkage isomers of the cyanide ligand[3] though it is well known that cyanide can bond through both atoms in bridged complexes such as AgCN in the solid state.[4]

The $[Ag(CN_2)]^-$ ion gives rise to two, polarised, bands at *ca.* 2142 and 2136 cm^{-1} (B in the Figure), whose intensities are a maximum at $R = 2$. In aqueous solution ν_{sym} is observed[5] at 2139 cm^{-1}. In view of the very small frequency difference (almost the experimental uncertainty) we propose that the same linear 2-co-ordinate species $[Ag(CN)_2]^-$ exists in both solvents. A temperature-sensitive equilibrium exists between the species responsible for the two bands.

The $[Ag(CN)_3]^{2-}$ ion gives rise to two, polarised, bands at *ca.* 2108 and 2104 cm^{-1} (C in the Figure), whose intensities increase from zero at $R < 2$ to an approximately constant value at $R \geqslant 3$. In aqueous solution the corresponding band is found[5] at 2105 cm^{-1}. Again we propose that the same complex anion is present in ammonia and water, this time the ion being $[Ag(CN)_3]^{2-}$. Its second vibration (i.r.[6] 2105 cm^{-1}) would not give a polarised band and thus has not been observed.

We find no evidence for the ion $[Ag(CN)_4]^{3-}$ or for the putative complexes $[Ag_2(CN)_3]^-$ or $[(NC)Ag(NO_3)]^-$ in ammonia solutions. Linkage isomerism may be responsible for the two bands observed in both $[Ag(CN)_2]^-$ and $[Ag(CN)_3]^{2-}$, though valid alternative hypotheses can be proposed for these ions.

The step-wise equilibria involved in the reactions can be presented by equations (3)—(5).

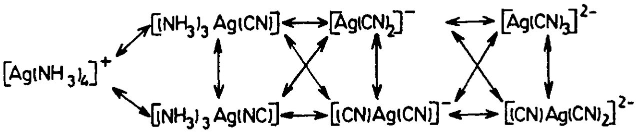
$$CN^- + [(NH_3)_xAg]^+ \rightleftharpoons (NH_3)_yAgCN + (x-y)NH_3 \quad K_1 \qquad (3)$$

$$CN^- + [(NH_3)_yAgCN] \rightleftharpoons [Ag(CN)_2]^- + yNH_3 \quad K_2 \qquad (4)$$

$$CN^- + [Ag(CN)_2]^- \rightleftharpoons [Ag(CN)_3]^{2-} \quad K_3 \qquad (5)$$

We cannot comment on K_1 since free cyanide ion is not observable at $R < 2$. As can be seen in the Figure, K_2 decreases sharply with decreasing temperature. Making the common assumption that the enthalpy change of reaction is temperature-independent, the entropy change of reaction (4) must be positive. Only if y is greater than one will there be a net increase in the number of particles and a large gain of entropy in reaction (4). Hence we propose that y is two or three, consistent with x being three or four as previously proposed.[2] K_3 increases with temperature decrease as expected on the basis of analogous arguments for reaction (5).

Thus the equilibria obtaining in liquid ammonia can be represented as in the Scheme.



Thus in comparing the aqueous and ammonia chemistry of silver-cyano complexes the following points can be made; (1) $[Ag(CN)_4]^{3-}$ is weak in water[7] ($K_4 < 1$) but not formed in ammonia. (2) In water β_2 is very large[7] (*ca.* 10^{21}) and AgCN is insoluble (K_{so} *ca.* 10^{-11}). In ammonia K_2 is not very large, as shown by the co-existence of species over wide range of R, and 'AgCN' is freely soluble. As in the case of 'AgI,'[2] the latter fact is to be associated with extra solvation of the cation, that is $y > 1$. (3) In ammonia the results can be interpreted as supporting the presence of linkage isomers, particularly with 'AgCN'. This is unexpected with silver(I) which normally behaves as a class B[8] (soft[9]) acceptor. However, the presence of two or three ammonia ligands would make $[(NH_3)_yAg]^+$ a somewhat 'harder' acceptor. We further suggest that the donor power of the ligand is affected by its being solvated by ammonia, and that this could make *N*-donation a more favourable process for the cyanide ligand.

Thus, the change of solvent from water to ammonia is accompanied not only by the expected change in acceptor power of the silver(I) cation, but also by a change in donor power of the cyanide anion.

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