Spectrochemistry of Solutions. Part 16.[1] A Raman Spectroscopic Study of the Complexation of Mercury(II) by Cyanide Ligands in Liquid Ammonia at 293 K

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The pattern of complexation of $Hg(CN)_2$ by CN^- ligands in liquid ammonia has been examined. Steps involve straightforward replacements of NH_3 by CN^- on the $Hg(CN)_2(NH_3)_2$ species through $[Hg(CN)_3(NH_3)]^-$ to $[Hg(CN)_4]^{2-}$ with no change in the tetrahedral geometry around the Hg^{II} centre. No higher complexes are found. The geometry of complexation differs from that observed in both water and methanol solutions where addition of CN^- converts linear $Hg(CN)_2$ to tetrahedral $[Hg(CN)_4]^{2-}$. Band assignments of the symmetric and antisymmetric ν(CN) stretching vibrations have been made for the complexes as follows: $Hg(CN)_2(NH_3)_2$, 2 164 (sym), 2 161 (antisym); $[Hg(CN)_3(NH_3)]^-$, 2 148 (sym), 2 145 (antisym); $[Hg(CN)_4]^{2-}$, 2 139 (sym), 2 134 cm^{-1} (antisym).

The Raman and i.r. spectra of mercury dicyanide, in the solid state and in solution, have been extensively studied. It is now well established that the three Raman-active bands due to the linear $Hg(CN)_2$ appear at *ca.* 2 190 cm^{-1} (p) for the totally symmetric ν_1(C–N) stretching vibration, *ca.* 410 cm^{-1} (p) for the symmetric ν_2(Hg–C) stretching vibration, and *ca.* 274 cm^{-1} (dp) for the ν_5(C–N) vibration,[2–5] a doubly degenerate bend of π_g symmetry. From dilute aqueous[3,4,6] solutions [a concentration of *ca.* 0.4 mol dm^{-3} in $Hg(CN)_2$ is reported[2] to be attainable] Raman spectra have been recorded with bands at 2 196 (p), 414 (p), and 274 cm^{-1} (dp). The spectra of 1.2 mol dm^{-3} solutions in methanol[2,7] contain three bands with the same polarisation properties at, or near, the same frequencies.

The above band attributions are consistent with the existence of a simple linear NC–Hg–CN species in both aqueous and methanolic solutions. The absence of features in the region 2 050—2 080 cm^{-1} of the spectrum, where a band due to the ν(C–N) vibration of a free CN^- ligand would appear, indicates that $Hg(CN)_2$ is an undissociated molecule in both water and methanol.

Woodward and Owen[2] observed three bands in the Raman spectrum of an aqueous solution containing the tetrahedral $[Hg(CN)_4]^{2-}$ ion, at 2 148 (p), 342 (p), and 200 cm^{-1} (dp). Poulet and Mathieu[3] reported that the spectra of both solid $K_2[Hg(CN)_4]$ and the $[Hg(CN)_4]^{2-}$ complex in aqueous solution contain four bands which coincide at 2 148, 332, 280, and 235 cm^{-1}; additional bands at 118, 86, and 34 cm^{-1} occur in the spectrum of the solid compound. These data illustrate the significant difference between the spectra of the linear $Hg(CN)_2$ and the tetrahedral $[Hg(CN)_4]^{2-}$ species.

More recently the Raman spectra of $Hg(CN)_2$ and $Hg(SCN)_2$ dissolved in liquid ammonia have been studied.[8] $Hg(CN)_2$ is extremely soluble in ammonia. Thus by application of the laser Raman technique to very concentrated solutions (*ca.* 10 mol dm^{-3}), markedly better spectra were obtained for ammonia solutions than had previously been obtained for solutions in other solvents. Again the complete absence of bands in the region 2 050—2 080 cm^{-1} provided firm evidence that the $Hg(CN)_2$ species is also undissociated in liquid ammonia solutions. Additional bands at 3 170, 1 166, and 342 cm^{-1}, not observed in the spectrum of the solvent ammonia, were interpreted as indication of direct co-ordination by NH_3 molecules to the Hg^{II} centre. Thus there is good reason to conclude that $Hg(CN)_2(NH_3)_2$ exists in liquid ammonia as an undissociated C_{2v} tetrahedral molecular species. This should give six Raman-active bands. Five of these were identified by a comparison of the spectra of solutions in NH_3 and ND_3 and assignments were made as follows: symmetric C–N stretch at 2 169 cm^{-1} (p), antisymmetric C–N stretch at 2 152 dm^{-1} (dp), antisymmetric Hg–N stretch at 518 cm^{-1} (dp), symmetric Hg–C stretch at 374 cm^{-1} (p), and symmetric Hg–N stretch at 342 cm^{-1} (p). It was suggested that the sixth absent Raman-active band, the antisymmetric Hg–C stretch, may be such a weak feature that it is masked by the stronger symmetric Hg–C stretch at 374 cm^{-1}.

Gardiner *et al.*[8] did not investigate and report on the effect of addition of further CN^- ligands to $Hg(CN)_2$ in liquid ammonia. This is surprising because the spectra indicate clearly that the dicyanomercury(II) complex in ammonia exists in a different geometrical arrangement from that found in aqueous and methanol solutions. Accordingly we present the analysis of our observations of the Raman spectra obtained from the addition of CN^- ligands to $Hg(CN)_2$.

Experimental

The chemical and spectroscopic techniques were similar to those we have used previously.[9,10]

All salts were thoroughly dried *in vacuo* over P_4O_{10} before at least two recrystallisations from pure water-free liquid ammonia. Before use, $Hg(CN)_2$ was kept *in vacuo* over P_4O_{10} for 24 h at 373 K. KCN and $Hg(NO_3)_2$ were kept *in vacuo* over P_4O_{10} for 24 h at 293 K. The ammonia used had been previously distilled from a supply of 'pure anhydrous ammonia' into a reservoir cylinder containing $NaNH_2$ to remove the last traces of water.

Solutions were prepared in sealed sample tubes (9-mm outside, 6-mm inside diameter). Each tube (150-mm long, with a constriction 100-mm above the bottom to facilitate sealing) was fitted with a B10 cone and stopper to prevent ingress of H_2O and CO_2 during weighing, and to enable attachment to a vacuum line through which ammonia gas distilled from the reservoir cylinder was supplied. The appropriate quantities of KCN and $Hg(CN)_2$ were placed in the tube to obtain the required ligand:cation ratio. This operation was carried out in a glove-bag under a flow of dried oxygen-free N_2 gas. The sample tube was then evacuated on the gas-line, cooled to 200 K in a methanol–solid CO_2 bath, and ammonia gas condensed until a solvent:cation ratio (*R*) of *ca.* 125:1 was obtained.

The sample tube, isolated by a nearby tap in the main gas-line and cooled in liquid N_2, was then carefully sealed at its constriction and slowly allowed to attain room temperature.

Table 1. Resolved component band parameters for the ν(CN) region of the Raman spectra of solution mixtures of $Hg(CN)_2$ and KCN in liquid ammonia at 293 K ($R \sim 125$); the composite band A* consists of $A_s + A_a$

	Band frequency (cm^{-1})					Half-width (cm^{-1})					Relative band area (%)				
S	A*	B_s	B_a	C_s	C_a	A*	B_s	B_a	C_s	C_a	A*	B_s	B_a	C_s	C_a
2.0	2 163.6	2 148.6	—	—	—	6.0	3.8	—	—	—	99.0	1.0	—	—	—
2.55	2 164.4	2 148.3	2 145.9	—	—	6.5	4.8	8.5	—	—	35.9	39.9	24.2	—	—
2.76	2 164.6	2 149.3	2 145.1	2 138.8	—	6.5	5.6	7.0	8.0	—	18.1	48.2	28.0	5.6	—
3.0	2 163.4	2 148.1	2 144.2	2 139.3	—	8.1	5.2	3.1	11.7	—	11.0	58.9	9.0	21.0	—
3.2	2 164.7	2 148.9	2 145.2	2 139.7	2 134.1	6.2	5.1	5.2	7.0	7.3	2.2	53.9	5.7	32.6	5.5
3.46	—	2 149.4	2 146.3	2 139.9	2 133.9	—	5.2	3.7	7.0	5.8	—	37.5	2.0	53.5	7.0
4.0	—	2 147.7	—	2 139.8	2 134.8	—	8.9	—	5.9	7.4	—	5.8	—	66.3	27.8
6.1	—	—	—	2 139.5	2 134.4	—	—	—	6.2	7.6	—	—	—	69.9	30.1

Weighings made between each addition of salt and liquid ammonia determined the composition of the solution accurately.

Spectra were recorded on a Coderg PHO Raman spectrometer using concave mirrors at 180 and 270° to the direction of the laser beam to improve the signal by collection of some of the light dispersed in the opposite direction to the instrument's collector lens. The 488 nm line of a Coherent Radiation model 52 argon-ion laser was used at a rating of 1 W. Care was taken to obtain optimum conditions of spectrometer detector and recorder responses, scan rate, and monochromator slit width, to achieve maximum signal:noise ratios with minimum spectral distortion. Scan rates were 1 cm^{-1} min^{-1}. Depending on solution concentrations, slit widths were either 0.5 or 1.0 cm^{-1}, *i.e.* always less than 0.25 of the bandwidth at half-height, $w_{\frac{1}{2}}$.

The recorder output was digitised semi-automatically over 1 024 points in a range of 60 cm^{-1} starting from 2 195, 2 180, or 2 170 cm^{-1}. Curve resolutions used the programs FITS[11] and VIPER.[12] Observed vibrational frequencies were calibrated against a mercury-emission line from the room lights at 2 178.7 cm^{-1}.

Throughout we use the following terms to express solution concentrations and ligand:cation ratios: R = (moles of NH_3)/(moles of Hg) and $S = [CN^-]/[Hg^{II}]$.

Results and Discussion

The changes in the Raman spectrum caused by the addition of CN^- ligand to $Hg(CN)_2$ in liquid ammonia solutions are illustrated in Figure 1. The band-resolution data obtained from our computer-assisted resolution procedure are listed in Table 1. Relative band positions can be identified to ±0.5 cm^{-1}. Thus we have identified the following bands (frequencies are relative to the mercury emission line at 2 178.7 cm^{-1}): A_s, 2 164.1 (p); A_a, 2 161 (dp); B_s, 2 148.6 (p); B_a, 2 145.3 (dp); C_s, 2 139.5 (p); and C_a, 2 134.3 cm^{-1} (dp).

In the low-frequency region of the spectra of $Hg(CN)_2$ solutions, our results mainly confirm the data previously reported.[8] We found four bands in a spectrum of a solution of R = 8.5, which agree with the assignments already made, listed as follows: 368 cm^{-1} (p), strong, symmetric Hg–C stretching mode; 342 cm^{-1} (p), medium, symmetric Hg–N stretching mode; 260 cm^{-1} (dp), weak, Hg–C bending mode; and 245 cm^{-1} (dp), weak shoulder, Hg–N bending mode. The assignment made by Gardiner *et al.*[8] for the band at 518 cm^{-1} (probably dp) to the Hg–C antisymmetric stretching mode must now come into doubt because we find that this very weak band is polarised. We also agree with the argument that the band due to the symmetric Hg–N stretching mode of the tetrahedrally solvated $[Hg(NH_3)_4]^{2+}$ cation [414 (ref. 9), 401 cm^{-1} (ref. 13)] shifts to lower frequency (342 cm^{-1})[8] when two NH_3 groups are replaced by CN^-. The observation of an intermediate Hg–N stretching frequency of 352 cm^{-1} for the $[Hg(NH_3)_3I]^+$ species[13] is consistent with these assignments.

Table 2. Resolved component band parameters for the ν(CN) region of the spectra of solutions of $Hg(CN)_2(NH_3)_2$ in liquid ammonia at 293 K

	Band frequency (cm^{-1})		Half-width (cm^{-1})	
R	A_s	B_s	A_s	B_s
8.5	2 164.6	2 148.2	9.6	10.4
19.4	2 164.2	2 149.3	7.7	8.1
44.7	2 164.0	2 148.3	6.9	6.8
138.8	2 163.6	2 148.6	6.0	3.8
931	2 163.9	—	5.8	—

We also have observed that additional bands, not seen in the spectrum of the pure solvent ammonia, but attributable to stretching and bending modes of NH_3 co-ordinated to an $Hg(CN)_2$ species appear at 3 170 and 1 166 cm^{-1}.

The absence of bands due to free CN^- ligand in the region 2 050—2 080 cm^{-1} of the spectrum confirms the proposal that mercury(II) cyanide in liquid ammonia exists mainly as an undissociated tetrahedral C_{2v} species $Hg(CN)_2(NH_3)_2$.

We have also recorded the low-frequency region of a spectrum of a solution in ammonia at S = 3.0 and found bands at 425 (p), 368 (p), 342 (p), 252 (dp), and 233 cm^{-1} (dp).

Our study principally concerned the observation of the changes in the Raman spectrum in the ν(CN) stretching region for a range of solutions in liquid ammonia at 293 K in which the ligand:cation ratio was varied between S = 2.0 and S = 6.0. A study of the region between S = 0 and S = 2 was not possible because of the thermodynamic instability of the $[Hg(CN)]^+$ species in ammonia. All attempts to prepare solutions in this stoicheiometric range failed. When ammonia is condensed into an evacuated tube containing a mixture of $Hg(CN)_2$ and $Hg(NO_3)_2$ at $S < 2$ violent reaction occurs with evolution of gas even at *ca.* 215 K. The same result is obtained when ammonia gas is condensed on to starting mixtures of $Hg(NO_3)_2$ and KCN at $S < 2$. Thus it must be concluded that the monocyano-complex is unstable even at 215 K. Because this reaction was violent even on a milligram scale, we decided not to pursue experiments in the $0 < S < 2$ range. It is possible that it involves the formation of the Hg_2^{2+} species together with the liberation of cyanogen gas, $(CN)_2$.

All the important changes in the spectrum which relate to the stepwise complexation of Hg^{II} occur between 2 125 and 2 170 cm^{-1}. When $S < 4$ no bands due to free CN^- ligand are observed between 2 050 and 2 080 cm^{-1}. As S is increased above 4, cation-dependent bands appear in this region. When the cation is Na^+ the spectrum characteristic of the equilibria between $Na^+ \cdots CN^-$ ion pairs and 'free' solvated CN^- anions is observed. Similarly when the cation is K^+ the spectrum due to $K^+ \cdots CN^-$ ion pairing occurs.[14]

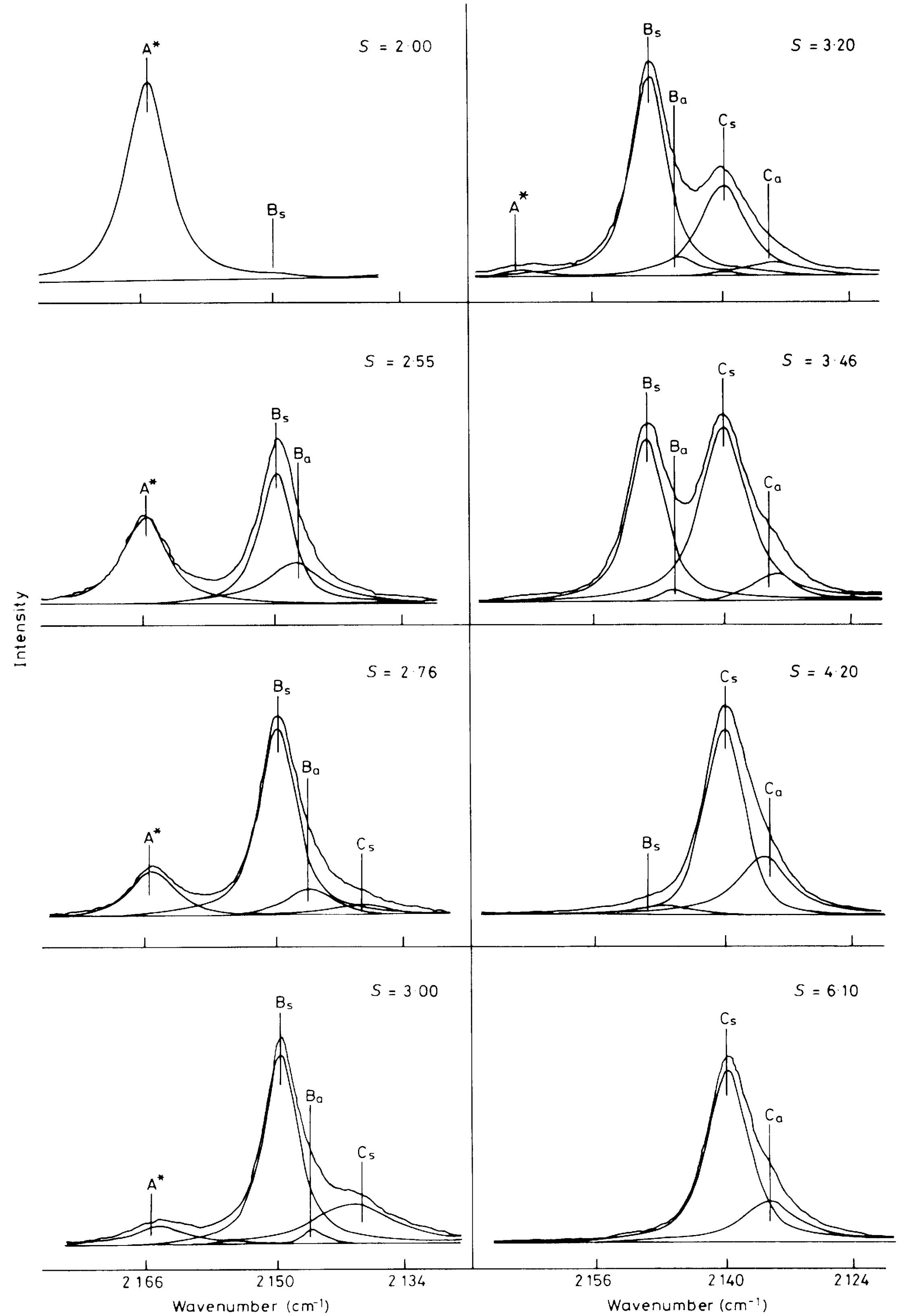

Figure 1. The effect of added CN^- ligand on the ν(CN) stretching region of the Raman spectra of $Hg(CN)_2$ in liquid ammonia at 293 K ($R \sim 125$). The band marked A* is a composite comprising the two bands $A_s + A_a$

The analysed data for the spectra of various concentrations of solutions at $S = 2$ are given in Table 2, and the spectrum of the solution at $R = 8.5$ is shown in Figure 2, which also illustrates the polarisation properties of the bands. Excellent fits of this profile to two component bands were obtained using a Lorentz–Gauss sum function with a 20% Gaussian contri-

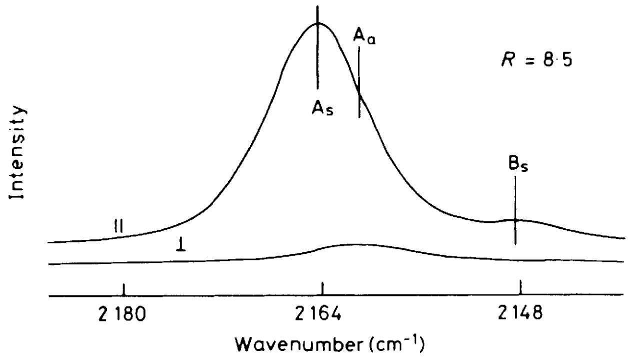

Figure 2. The ν(CN) stretching region of the Raman spectrum of a solution of $Hg(CN)_2$ in liquid ammonia at 293 K, indicating the polarisation properties

bution. We believe that the principal feature, a polarised band A_s, at 2 164 cm^{-1} is the band which Gardiner *et al.*[8] observed in their spectrum at 2 169 cm^{-1}, and which they correctly assigned to the symmetric C–N stretching mode of $Hg(CN)_2(NH_3)_2$. However they incorrectly assigned the band they observed at 2 152 cm^{-1} as due to the antisymmetric C–N stretching mode. This must be the polarised band B_s we observe at 2 148 cm^{-1}, a very weak feature which disappears from the spectrum as the concentration of $Hg(CN)_2(NH_3)_2$ falls to $R > 140$, and which increases rapidly in relative intensity as S is increased from 2 to 3. Careful polarisation measurements indicate that a weak depolarised band (A_a) occurs at 2 161 cm^{-1} ($\rho \sim 0.75$) close to the symmetric C–N stretching vibration of $Hg(CN)_2(NH_3)_2$. We attribute this band (A_a) to the antisymmetric C–N stretching mode of $Hg(CN)_2(NH_3)_2$. Because A_a is very weak compared with A_s and both of these bands are due to the same species, it is allowable to combine them into one composite band. This aids the band-resolution process for the spectra of the solutions between $S = 2$ and $S = 6$, first, by reducing the number of component bands to be fitted and, second, by eliminating resolution problems which may arise from high degrees of correlation of band parameters between this closely spaced pair of bands.[15]

It is interesting to note that B_s which contributes to 3.7% of the total spectrum at $R = 8.5$ reduces to zero at $R > 140$ (Table 2). This relative band intensity change of B_s with concentration cannot, in this case, be attributed to some form of ion pairing.[14] Any ion-paired species, formed through an ion-dipole interaction, would have to be solvent-shared $CN^- \cdots H_3N{\cdot}Hg(CN)_2(NH_3)$, or a solvent-separated species. The perturbation of the C–N stretching frequency from 2 164 cm^{-1} could not be as great as 16 cm^{-1}: our observations on solvent-shared ion pairs[1] have indicated very small shifts of the order of 1 cm^{-1}. Thus we attribute the polarised band B_s at 2 148 cm^{-1} to the symmetric C–N stretching mode of the small concentration of the 3:1 complex $[Hg(CN)_3(NH_3)]^-$ present in equilibrium with the 2:1 complex $Hg(CN)_2(NH_3)_2$ in a solution of $S = 2$.

The band B_s only manifests itself at $R < 140$, *i.e.* when the solution concentration exceeds 0.4 mol dm^{-3}. If $[Hg(CN)_3]^-$ forms in the solution, mass-balance considerations demand that the stoicheiometry must be compensated by the presence of a species with stoicheiometry $S < 2$. Two likely possibilities arise: equations (1) and (2). Our failure to prepare solutions at $S = 1$

$$2\,Hg(CN)_2 \rightleftharpoons [Hg(CN)]^+ + [Hg(CN)_3]^- \qquad (1)$$

$$3\,Hg(CN)_2 \rightleftharpoons Hg^{2+} + 2\,[Hg(CN)_3]^- \qquad (2)$$

because of the apparent thermodynamic instability of the $[Hg(CN)]^+$ moiety lead us to conclude that in concentrated solutions, where $R < 20$ and $S = 2$, $Hg(CN)_2(NH_3)_2$ is dominant, but the solution must also contain Hg^{2+} and $[Hg(CN)_3(NH_3)]^-$ at low concentrations which are limited by a dissociation constant for equation (2) of $K_{diss} = [Hg^{2+}][Hg(CN)_3^-]^2/[Hg(CN)_2]^3 < 10^{-4}$.

A plot of the relative band areas (directly representing the relative concentrations of each component species in solution) against the stoicheiometric S value of the solution makes the attribution of bands to species facile. As S increases above 2 the relative band areas of ($A_s + A_a$) fall rapidly to less than 10% of the total spectrum at $S = 3$. In this region bands B_s and B_a increase to a maximum as S increases and passes through 3. Accordingly we attribute the polarised band B_s at 2 148 cm^{-1} to the symmetric C–N stretching mode, and the much weaker depolarised band B_a at 2 145 cm^{-1} to the antisymmetric stretching mode of $[Hg(CN)_3(NH_3)]^-$. The polarised band at 342 cm^{-1}, observed in a solution of $S = 3$, due to the Hg–N stretching vibration is indicative that an NH_3 molecule remains co-ordinated to the Hg^{II} metal centre. Bands C_s and C_a first appear at *ca.* $S = 2.75$. Their relative intensities increase to become *ca.* 95% of the spectrum at $S = 4$. At higher S, up to $S = 6$, no further change in the spectrum occurs beyond $S = 4.2$. Here the spectrum is a simple two-band system composed of the strong polarised band C_s at 2 139 cm^{-1} and the weaker depolarised band C_a at 2 134 cm^{-1}. At $S = 4.2$ the last trace of B_s disappears and addition of further CN^- ligand causes no change in the spectrum. Thus the band C_s can be attributed to the symmetric CN stretching mode, and the band C_a to the antisymmetric stretching mode, of the 4:1 $[Hg(CN)_4]^{2-}$ complex ion.

It is clear from the spectra that in liquid ammonia cyano–mercury(II) complexation occurs, with no change of geometry around the metal atom, by straightforward successive replacements of the co-ordinated NH_3 ligands in the tetrahedral $Hg(CN)_2(NH_3)_2$ and $[Hg(CN)_3(NH_3)]^-$ complexes by CN^- ligands. This is a distinctly different stepwise equilibrium situation from that in both water[2–4] and methanol[2,7] where both spectroscopic and stability constant data[16] indicate geometry changes between the bis- and tris-cyano-complexes, and perhaps between the tris- and tetra-cyano-complexes. The retention of tetrahedral geometry through the complexation steps is consistent with the observation that the Hg^{2+} solvated cation contains four tetrahedrally distributed NH_3 groups in its primary solvation sphere.[9,13] That the solvation energy of Hg^{2+} cation in ammonia is high is obvious from the high solubilities of HgI_2, $Hg(SCN)_2$, and $Hg(CN)_2$ in ammonia. The bonding of the co-ordinated ammonias to the Hg^{II} centre must be highly enthalpically stabilised. Another manifestation of the strong bonding between Hg^{2+} and solvating NH_3 molecules occurs in the nitrate stretching and bending regions of the Raman spectra of solutions of $Hg(NO_3)_2$ in liquid ammonia. Here there is clear indication that a lower degree of contact ion pairing exists than would normally be expected from a 2:1 charged system, and we believe that in nitrate solutions a solvent-shared ion pair $Hg^{2+} \cdots NH_3 \cdots NO_3^-$ arrangement will be favoured.[17]

The complexation of Hg^{II} by CN^- in ammonia should be compared with that of Ag^I. The spectra of the cyano–silver(I) system shows that 1:1 and 2:1 complexes form easily in ammonia when CN^- ligand is added.[10] Excess CN^- must be added to produce an appreciable concentration of the $[Ag(CN)_3]^{2-}$ complex, and there is no evidence for a 4:1 complex even after the addition of very large excesses of CN^- ligand. Complexation of the Hg^{II} centre by CN^- in the 3:1 and 4:1 steps is clearly much easier than for Ag^I and the stability contants for these steps must be significantly larger. The fact that we observe all three Hg^{II} complex species simultaneously in our spectra leads us to the qualitative conclusion that log K_3 and log K_4 will probably be in the range 1—3; K_3 ($dm^3\,mol^{-1}$) =

$[Hg(CN)_3(NH_3)^-]/[Hg(CN)_2(NH_3)_2][CN^-]$, K_4 ($dm^3\ mol^{-1}$) = $[Hg(CN)_4{}^{2-}]/[Hg(CN)(NH_3)_3{}^-][CN^-]$. The unavailability of suitable band-intensity coefficients and the errors of determination of some of the relative band areas would render the results of any calculation of these values useless. However, based on the detection limit of uncomplexed CN^- ion in our Raman method, we can place a lower limit on the stability constant of the $Hg(CN)_2(NH_3)_2$ complex of log $\beta_2 > 7$ $\{\beta_2(dm^6\ mol^{-2}) = [Hg(CN)_2(NH_3)_2]/[Hg^{2+}][CN^-]^2\}$.

The proliferation of complexed species which occurs in the cyano–silver(I) system, due principally to the presence in the equilibria of linkage isomers, *e.g.* Ag–CN and Ag–NC, has not been observed in the Hg^{II} system. Linkage isomerism among the cyano–silver(I) complexes was highlighted by the changes observed in the spectra when the temperature of the solutions was lowered. Similar changes were not apparent when the spectra of the cyano–mercury(II) complexes in ammonia at S = 2 and 3 were observed at 250 K. Thus we conclude from our spectra, together with the interpretation of the low-frequency region for $Hg(CN)_2$ solutions by Gardiner *et al.*,[8] that complexation must be entirely of the Hg–CN type.

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