Spectrochemistry of Solutions. Part 22.[1] A Study of the Complexation of Zinc(II), Cadmium(II) and Mercury(II) by Cyanide in Liquid Ammonia by Vibrational Spectroscopy

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The stepwise ligation patterns for the complexation by CN^- of Zn^{2+}, Cd^{2+} and Hg^{2+} in liquid ammonia solutions have been established from analyses of the infrared and Raman spectra of M^{II}/CN^- mixtures between 295 and 213 K. All the cyano-complexes are soluble and complexation, complete at the 4:1 stage for all three metal cations, proceeds by direct replacement of the solvating NH_3 by CN^- on tetrahedrally co-ordinated Zn^{2+} and Hg^{2+}. Cyano-ligation of Cd^{2+} is quite different with octahedral 1:1 and 2:1 complexes, followed by a change to tetrahedral 3:1 and 4:1 complexes. There is no evidence for multinuclear complex formation, and mononuclear complexation is strong for all three metals; no uncomplexed CN^- is present until the solution composition exceeds $[CN^-]/[M^{II}] = 4.0:1$. Stable outer-sphere complexes (or ion associates) form between the 4:1 complexes and the Na^+ cocation, *viz.* $[Na^+ \cdots {}^-NC\text{-}M(CN)_3]$, and there is some evidence for similar association of the 3:1 complex of Hg^{2+}, *i.e.* $[Na^+ \cdots {}^-NC\text{-}M(CN)_2(NH_3)]$. Assignments of the $\nu_{sym}(CN)$, $\nu_{asym}(CN)$ and $\nu(M\text{-}N)$ stretching frequencies of the complexes are presented.

We are currently involved in a vibrational spectroscopic survey of the cyano- and thiocyanato-complexes of a wide range of cations in liquid ammonia. The complicated ligation pattern for CN^- on Ag^I has already been reported;[2,3] at least 11 species, including all the linkage isomers of the 1:1 and 2:1 complexes, as well as several multinuclear complexes and ion pairs coexist in the equilibria. Stepwise formation of the mononuclear complexes of Ag^I is complete at the 3:1 stage in liquid ammonia but there is a change of geometry with each step: $[Ag(CN)(NH_3)_3]$, tetrahedral; $[Ag(CN)_2]^-$, linear; and $[Ag(CN)_3]^{2-}$, trigonal. In marked contrast to this system, ligation of Au^I by CN^- produces only the linear Au–C bonded $[Au(CN)(NH_3)]$ and $[Au(CN)_2]^-$ species.[4]

No previous spectroscopic study of cyano-complexation of Zn^{II} and Cd^{II} in liquid ammonia has been reported, but earlier in this series we reported a preliminary Raman spectroscopic study of Hg^{II}/CN^- mixtures at 293 K.[5] Straughan and co-workers[6,7] have also reported the Raman spectra of mercury(II) dicyanide solutions in both NH_3 and ND_3.

In water $Hg(CN)_2$ is highly insoluble, and $Zn(CN)_2$ and $Cd(CN)_2$ are only sparingly soluble:[8] $Zn(CN)_2$ precipitates when the solution composition is $[CN^-]/[Zn^{2+}] < 4.0$, and solid $Cd(CN)_2$ appears when $[CN^-]/[Cd^{2+}] < 3.5:1$.[9,10] Thus spectroscopic study of aqueous solutions of cyano-complexes of Zn^{II}, Cd^{II} and Hg^{II} has been severely restricted. Only the tetrahedral $[M(CN)_4]^{2-}$ complexes have been examined in detail in the solution[10–12] and solid phases.[9–15] In their infrared study of aqueous solutions Penneman and Jones[10] assigned a weak band at *ca.* 2161 cm^{-1} to the $\nu_{asym}(CN)$ antisymmetric C–N stretching vibration of $[Hg(CN)_3]^-$, and bands at 2149.1 (Raman) and 2145.8 cm^{-1} (infrared) to the $\nu_{sym}(CN)$ and $\nu_{asym}(CN)$ stretching vibrations of $[Hg(CN)_4]^{2-}$. They also assigned an infrared band at *ca.* 2146.4 cm^{-1} to the $\nu_{asym}(CN)$ vibration of $[Cd(CN)_4]^{2-}$ and, by subtracting this from the total spectrum of a solution of composition $[CN^-]/[Cd^{2+}] = 3.5:1$, proposed a band at *ca.* 2148 cm^{-1} due to $[Cd(CN)_3]^-$; the $\nu_{sym}(CN)$ vibration of $[Cd(CN)_4]^{2-}$ was found at 2146.3 cm^{-1}. No comparable feature could be found for the 3:1 complex of the Zn^{II}/CN^- system.

In marked contrast to the problems encountered with aqueous solutions, high solubilities pertain in liquid ammonia for all the mononuclear complexes of Zn^{II}, Cd^{II} and Hg^{II} at all solution compositions. This is due to the high cation solvation energies generated between these cations and NH_3; liquid ammonia has a very high donor number, DN = 59.[16] Thus it is an excellent medium in which the stepwise formation of all the complexes can be followed spectroscopically.

From early work[17] on the Zn^{II}/CN^- system in dilute water solutions it might have been construed that there is little evidence for $[Zn(CN)]^+$ though, if his model is correct, Persson's potentiometric stability constant determinations[18] established regular energy gaps between the formation of $[Zn(CN)]^+$, $Zn(CN)_2$, $[Zn(CN)_3]^-$ and $[Zn(CN)_4]^{2-}$, *viz.* $\log \beta_1 = 5.34$, $\log \beta_2 = 11.03$, $\log \beta_3 = 16{,}68$ and $\log \beta_4 = 21.57$. His corresponding data for the Cd^{II}/CN^- system were in accord with the earlier data of the Rossottis;[19] $\log \beta_1 = 5.62$, $\log \beta_2 = 10.84$, $\log \beta_3 = 15.72$ and $\log \beta_4 = 19.20$.[18] For all three metals in aqueous solutions the vibrational spectra indicate the expected tetrahedral[20] geometry for $[M(CN)_4]^{2-}$.[12] The regular energy gaps then suggest that successive ligations must occur by direct replacement of solvating molecules by CN^- on a tetrahedral metal cation centre.

In water $[Hg(CN)_4]^{2-}$ is the most stable tetracyano-complex though the stability constant order is irregular; values of $\log \beta_4$ for $[M(CN)_4]^{2-}$ (at 298 K and $I = 0$) are 19.6 for M = Zn, 17.9 for Cd and 39.0 for Hg. The increase in stability between the complexes of Cd^{II} and Hg^{II} appears to correlate with the increase in force constant of the M–C stretching vibration; 128, 122 and 145 N m^{-1} for Zn, Cd and Hg respectively.[14] Thus, even in aqueous solutions, there is a distinct behavioural irregularity on passing from Zn through Cd to Hg.

This paper illustrates how we have used the vibrational spectra of the monocyano-complexes of Zn^{II}, Cd^{II} and Hg^{II} to establish the geometries which apply around the central metal cation as successive cyano-ligation occurs in liquid ammonia. Unfortunately however, although solubilities are good for the Hg^{II}/CN^- system, experimentation with solution compositions at $[CN^-]/[Hg^{II}] < 2.0$ would have been unwise. If the components are mixed to produce a composition in this range there is a vigorous reaction (virtually explosive!) even at −70 °C, and it is extremely difficult to prevent the temperature

from rising rapidly out of control. An internal oxidation-reduction must be involved in which CN^- is oxidised (probably to cyanogen) with concurrent reduction of the Hg^{II} to $[Hg_2]^{2+}$.

The geometrical interpretations made in this paper stem principally from a study of the ν(CN) stretching vibration regions of both the Raman and infrared spectra of solutions over a range of $[CN^-]/[M^{II}]$ compositions. Information from the region between 300 and 450 cm^{-1} has also been diagnostically useful. The Raman spectra have all been recorded between 200 and 300 K; in previous work[5] on Hg^{II}/CN^- solutions the Raman spectra were only measured at 293 K. The infrared spectra of these solution mixtures are presented here for the first time.

Experimental

Zinc, Cadmium and Sodium Cyanides.—The salts were dried at 293 K for 24 h *in vacuo* over P_4O_{10} before, and after, two recrystallisations from liquid ammonia [Found: C, 20.5; N, 24.0. Calc. for $Zn(CN)_2$: C, 20.5; N, 23.9. Found: C, 14.5; N, 16.9. Calc. for $Cd(CN)_2$: C, 14.6; N, 17.0%].

Mercury Cyanide.—The dry salt was twice recrystallised from liquid ammonia and dried *in vacuo* at 373 K. All salts were stored over P_4O_{10} *in vacuo*.

Zinc and Cadmium Nitrates.—The hydrated salts were dried *in vacuo* at 300 K over P_4O_{10} for 2 weeks before three recrystallisations from liquid ammonia. During recrystallisation a small amount of dry NH_4NO_3 was added to the solutions to repress ammonolysis and the formation of amino-solvated cation complexes.

Preparation of Solutions.—The apparatus and methods used to prepare solutions in liquid ammonia have previously been described in detail.[4,5,21,22] Concentrations (within ±1%) were obtained as mass of solid per unit volume of liquid ammonia for the infrared spectra, and as mass of solid per unit mass of solution for the Raman spectra. The compositions of solutions are expressed as ratios of concentrations; $[CN^-]/[M^{II}] = S$, and [moles NH_3]/[moles M^{II}] = R (M^{II} = Zn^{II}, Cd^{II} or Hg^{II}).

Spectra.—The infrared spectra were all recorded at 293 K on a Philips HP9545 ratio recording spectrometer, using optimum spectrometer conditions to minimise distortion of the spectrum. At least nine, more usually 16, consecutive spectra were collected and coadded at slow scan rates on a BBC Master Microcomputer; signal/noise ratios of *ca.* 500:1 were aimed at for good-quality curve analyses. The spectra of solutes, in absorption units, were obtained by subtraction of the spectrum of a sample of pure liquid ammonia from that of the spectrum of the solution. Raman spectra were recorded on the Coderg PHO instrument, now updated to provide digital data and spectrum coaddition.[4,22] Data were recorded at the slowest scan rate available (1 cm^{-1} min^{-1}), with spectrometer settings chosen to minimise spectrum distortion, at 0.125 cm^{-1} intervals; four or nine coadditions were made to achieve good signal/noise ratios. Because the baseline of the spectrum of pure liquid ammonia is flat between 2000 and 2200 cm^{-1} the spectral profiles of the ν(CN) stretching regions of the solutions obtained can be taken to be those of the solutes under examination.

Curve Analyses.—Spectra were resolved into their component bands using our interactive program VIPER.[23,24] As an additional aid to resolution, and for better definition of underlying band positions, the derivative and smoothing program TREAT was applied; normally the second, but sometimes the fourth, derivative was used.[25] (To reduce the calculation time, VIPER and TREAT are now run on an Archimedes 440 computer; resolution of a six-component spectrum containing 256 data points is now complete in *ca.* 5 min, whilst a three-component spectrum takes just a few seconds.)

Results and Discussion

The ν(CN) stretching regions of the Raman and infrared spectra of the Zn^{2+}/CN^-, Cd^{2+}/CN^- and Hg^{2+}/CN^- solutions were carefully surveyed from 2000 to 2300 cm^{-1}. Vibrational bands were found only in the narrow range between 2110 and 2150 cm^{-1}. No bands were observed between 2200 and 2300 cm^{-1} where Penneman and Jones[10] had previously assigned frequencies to multinuclear cyanomercury(II) complexes in aqueous solutions. We therefore conclude that there is no evidence for multinuclear complexes and that, in liquid ammonia, ligation of Zn^{II}, Cd^{II} and Hg^{II} by CN^- only occurs at mononuclear cation centres.

The existence of uncomplexed CN^- in solution was indicated by the characteristic and complicated spectrum of a solution of NaCN in liquid ammonia[26] between 2050 and 2090 cm^{-1}. This appeared immediately $S > 4.0$ in the Hg^{2+}/CN^- and Zn^{2+}/CN^- systems, and at $S = 3.8$ in the Cd^{2+}/CN^- system.

Hg^{II}/CN^- *Solutions.*—The analyses of the ν(CN) stretching region of the infrared spectra of a series of solutions at $R = 125$ in the composition range $2.0 < S < 4.0$ are given in Table 1. All the profiles resolve into a simple three-band system. From the variation of the relative intensities (band areas) *versus* S the three bands at *ca.* 2161, *ca.* 2144 and *ca.* 2134 cm^{-1} are assigned to the antisymmetric $\nu_{asym}(CN)$ stretching modes of $[Hg(CN)_2(NH_3)_2]$, $[Hg(CN)_3(NH_3)]^-$ and $[Hg(CN)_4]^{2-}$ respectively.

In previous work[5] five Raman bands had been positively identified with the 2:1, 3:1 and 4:1 complexes. Bands at 2164.1 (p), 2148.6 (p) and 2139.5 (p) cm^{-1} were confidently assigned to the symmetric $\nu_{sym}(CN)$ stretching vibrations of the 2:1, 3:1 and 4:1 complexes, but the two weaker features at 2145.3 (dp) and 2134.3 (dp) cm^{-1} were only tentatively assigned to the antisymmetric $\nu_{asym}(CN)$ stretching vibrations of the 3:1 and 4:1 complexes.

The infrared bands which correspond to the 3:1 and 4:1 complexes are essentially identical in frequency with the depolarised Raman bands at 2145.3 and 2134.3 cm^{-1}. Hence assignments of these bands to the antisymmetric $\nu_{asym}(CN)$ stretching modes of these two complexes is no longer in any doubt whatsoever. Positive identification of a very weak depolarised component with the $\nu_{asym}(CN)$ vibration mode of the 2:1 complex had previously been a little dubious, though careful polarisation measurements had pointed to the likelihood that a weak depolarised feature exists at *ca.* 2161 cm^{-1}. From the new infrared work it is now clear that the feature in the Raman spectra at *ca.* 2164 cm^{-1} is comprised of bands due to both the symmetric $\nu_{sym}(CN)$ and the antisymmetric $\nu_{asym}(CN)$ stretching modes of $[Hg(CN)_2(NH_3)_2]$ at *ca.* 2164 (p) and *ca.* 2161 (dp) cm^{-1} respectively; the latter has a very low intensity in the Raman. Thus the new infrared data confirm both the assignments previously made by us for the Hg^{II}/CN^- system, and that the ligands, including the solvating NH_3 groups, in each successive complex are tetrahedrally disposed around the Hg^{II} in a liquid ammonia medium.

It will be pointed out later that with the Zn^{II}/CN^- and Cd^{II}/CN^- systems addition of excess of CN^- ligand, to create a solution composition in which $S > 4.0$, causes an additional band to appear *ca.* 7 cm^{-1} higher in frequency than the maximum of the band due to the 4:1 complex. Whilst such a band is not immediately obvious from the original spectra the analysed data show it to be a component of the spectra. Close inspection of the infrared data in Table 1 indicates an irregular trend in the relative intensities of the bands at *ca.* 2144 and 2134 cm^{-1}, as S is increased; they pass through a minimum and a maximum respectively. If only the normal stepwise ligation processes were involved a steady fall in one, and a steady

Table 1 Resolved component band parameters of the C–N stretching region of the infrared spectra of Hg^{II}/CN^- mixtures in liquid ammonia at 295 K; $R = 125$

	Wavenumber/cm^{-1}			f.w.h.h./cm^{-1}			Gaussian fraction			Relative band area (%)		
S												
1.0	2161.1	—	—	10.0	—	—	0.1	—	—	100.0	—	—
2.0	2161.4	—	—	10.4	—	—	0.2	—	—	100.0	—	—
2.5	2160.5	2144.5	2132.7	13.3	8.9	6.6	0.4	0.4	—	27.4	69.4	3.2
2.75	2157.5	2144.4	2133.8	23.8	9.1	7.8	0.3	0.7	—	27.2	53.3	19.6
3.25	—	2143.4	2133.9	—	14.8	8.3	—	0.8	1.0	—	43.1	59.9
3.68	—	2142.8	2134.0	—	14.5	8.4	—	1.0	0.9	—	25.5	74.6
3.86	—	2143.0	2134.0	—	16.1	8.3	—	1.4	1.0	—	29.6	70.4
4.2	—	2142.5	2134.0	—	15.7	8.2	—	1.2	0.9	—	28.2	71.8
6.13	—	2140.6	2134.0	—	18.1	8.1	—	0.7	0.8	—	37.2	62.8

f.w.h.h. = Full width at half height.

increase in the other, would occur. Clearly another underlying band must lie close to 2144 cm^{-1} because there is a steady shift in the maximum of the profile from *ca.* 2144 at $S = 3$ to 2140.6 cm^{-1} at $S = 6.13$. Formation of the highest complex, $[Hg(CN)_4]^{2-}$, is a thermodynamically favourable process and no higher complexes form in the system. We therefore attribute the band at *ca.* 2141 cm^{-1} to an ion associate formed between $[Hg(CN)_4]^{2-}$ and the Na^+ cocation: $[Na^+ \cdots {}^-NC\text{–}Hg(CN)_3]^-$. This new information accounts for our earlier difficulty in explaining why a band still remains at *ca.* 2144 cm^{-1} in the Raman spectra of Hg^{II}/CN^- solutions,[5] the position associated with the 3:1 complex, when the solution composition is $S > 4$ and complete formation of $[Hg(CN)_4]^{2-}$ has occurred.

Another fact which must be explained is that the maximum of the band assigned to the 2:1 complex appears to shift to lower frequency as the temperature is reduced, whereas the positions of the bands due to the 3:1 and 4:1 complexes both remain unchanged; the band centred at 2162.8 cm^{-1} at 293 K shifts to 2159.9 cm^{-1} at 226 K (Table 2). This shift is likely to be the result of a contribution from an underlying feature attributable to another ion associate which involves the 3:1 complex, namely $[Na^+ \cdots {}^-NC\text{–}Hg(CN)_2(NH_3)]$. The concentration of such a species, and hence the band intensity in this region, would vary because of the substantial change in the relative permittivity of the solvent over this temperature range:[27] at 293 K, $\varepsilon = 17.4$; at 226 K, $\varepsilon = 23.0$.

Zn^{II}/CN^- *Solutions.*—The analyses of the ν(CN) stretching region of the infrared spectra of solutions containing mixtures of Zn^{II} and CN^- at $R = 60$ and 293 K in Table 3 were produced with the assistance of the second derivative from a knowledge of the better resolved Raman spectra. These infrared spectra were difficult to resolve at first because they all appear as single asymmetric features each of which contains more than one underlying component; each band maximum appears to shift steadily from *ca.* 2150 at $S \approx 0.5$ to *ca.* 2140 cm^{-1} at $S = 4.0$. When $S > 4.0$ the band maximum remains fixed at 2140 cm^{-1} but another feature of lower intensity emerges at *ca.* 2147 cm^{-1} as S is increased.

Four underlying features due to the four complexes of the system are much more clearly visible in the original Raman spectra; analyses of these are in Table 4. Each of these polarised bands appears at a progressively lower frequency as the solution composition is changed from $S = 0.5$ to 4.0. The bands are assigned to the symmetric ν_{sym}(CN) stretching vibrations of the cyanozinc complexes as follows: *ca.* 2150 (p), $[Zn(CN)(NH_3)_3]^+$; *ca.* 2147 (p), $[Zn(CN)_2(NH_3)_2]$; *ca.* 2145 (p), $[Zn(CN)_3(NH_3)]^-$ and *ca* 2140 (p) cm^{-1}, $[Zn(CN)_4]^{2-}$. The ν_{sym}(CN) bands are too closely spaced to allow resolution of the antisymmetric ν_{asym}(CN) stretching frequencies but their presence at low intensities is clear from the polarisation data; the polarisation ratios at these frequencies are all near to, but slightly above, *zero, i.e.* between $\alpha = 0.05$ and 0.10 {for tetrahedral $[Zn(CN)_4]^{2-}$ α should be *zero*}. The four frequencies observed for the ν_{asym}(CN) modes in the infrared, and the ν_{sym}(CN) modes in the Raman, are almost exactly coincident; previous assignments of ν_{sym}(CN) and ν_{asym}(CN) in crystalline $K_2[Zn(CN)_4]$ showed these vibration modes to be separated by substantially less than 2 cm^{-1}.[11,13]

No uncomplexed CN^- is observed in the spectrum until the solution composition is $S > 4.0$. A new feature then emerges at 2147.4 cm^{-1} in the tail of the band due to $[Zn(CN)_4]^{2-}$. The spectra of solutions of $Na_2[Zn(CN)_4]$ and $K_2[Zn(CN)_4]$ in liquid ammonia both have their maxima at *ca.* 2140 cm^{-1}, but each of these spectra contains another higher-frequency feature; 2147.4 cm^{-1} for the sodium salt, and 2145.5 cm^{-1} for the potassium salt. This new band represents 25% of the total band area at 293 K in the case of K, and an even larger proportion of the area in the case of Na.

A change in the temperature has relatively little effect on the relative intensities in the Raman spectra. When the solution composition is $S = 2.0$, lowering of the temperature from 293 to 275 K seems to favour slightly the formation of the 3:1 over the 2:1 complex (Table 5), but through the range from 275 to 213 K virtually no change is detectable in the position of the equilibrium (1). As may also be the situation with the

$$[Zn(CN)_2(NH_3)_2] + CN^- \rightleftharpoons [Zn(CN)_3(NH_3)]^- + NH_3 \quad (1)$$

corresponding step of the Hg^{2+}/CN^- system, this ligation process appears to be *entropically* and not *enthalpically* driven.

The regular steps in the frequencies of the bands due to successively higher complexes are indicative that no change in the tetrahedral geometry of Zn^{II} occurs during successive ligations. Supporting evidence for this comes from the low-frequency region of the Raman spectra. In the spectrum of a $Zn(CN)_2$ solution the following features are found: 420 (p), ν(Zn–N); 340 (p), ν(Zn–C); 318 (dp), δ(Zn–C–N) and 278 (dp) cm^{-1}, δ(Zn–N–H). In the solvated $[Zn(NH_3)_4]^{2+}$ cation in liquid ammonia the inner-sphere ammines are tetrahedrally situated around Zn^{II}; in NO_3^- and BF_4^- solutions this gives rise to a polarised Raman band at *ca.* 435 cm^{-1} due to the tetrahedral ν(Zn–N) symmetric stretching frequency.[28] Nakomoto's attribution[29] of the frequencies at 432.0 and 432.5 cm^{-1} to the tetrahedral ν_{sym}(Zn–N) stretching vibrations on ^{64}Zn and ^{68}Zn in solid $[Zn(NH_3)_4]I_2$ confirms this. A shift in the ν_{sym}(Zn–N) stretching frequency is to be expected when $[Zn(NH_3)_4]^{2+}$ cation is successively ligated by CN^- because of weakening of the Zn–N bonds, and a progressive frequency shift of the ν_{sym}(Zn–N) vibration from *ca.* 435 to *ca.* 420 cm^{-1} is observed. The position of the ν_{sym}(Zn–C) stretching frequency for $[Zn(CN)_4]^{2-}$ in ammonia solution at 340 cm^{-1} agrees well with that recorded for it in solid $K_2[Zn(CN)_4]$; 340.5[11] and 344 cm^{-1}.[13]

Cd^{II}/CN^- *Solutions.*—The frequency patterns observed in

Table 2 Variation with temperature of the resolved component band parameters of the C–N stretching region of the Raman spectra of an Hg^{II}/CN^- mixture in liquid ammonia; $R = 125$, $S = 2.55$

	Wavenumber/cm^{-1}			f.w.h.h./cm^{-1}			Gaussian fraction		Relative band area (%)		
T/K											
293	2162.8	2147.5	2144.6	6.5	5.3	6.5	0.6	0.2	35.3	57.5	7.3
264	2161.5	2147.4	2145.5	6.5	4.9	8.9	0.4	0.2	36.2	45.0	18.9
241	2160.0	2147.4	2145.0	6.4	4.7	7.9	0.3	0.3	37.0	44.6	18.4
226	2159.9	2147.4	2145.0	6.5	5.2	7.2	0.4	0.3	37.0	55.0	8.0

Table 3 Resolved component band parameters of the C–N stretching region of the infrared spectra of Zn^{II}/CN^- mixtures in liquid ammonia at 295 K; $R = 60$

	Wavenumber/cm^{-1}			f.w.h.h./cm^{-1}			Gaussian fraction		Relative band area (%)		
S											
2.0	2147.6	2144.0	—	2.9	4.1	—	0.3	0.6	72.0	28.0	—
3.0	2147.5	2143.5	2139.8	11.6	7.1	5.6	—	—	32.0	47.1	20.9
4.0	—	2145.9	2140.1	—	7.5	13.2	1.0	0.1	—	50.0	50.0
5.0	—	2145.7	2140.1	—	6.9	14.9	1.0	—	—	39.6	60.4

Table 4 Resolved component band parameters of the C–N stretching region of the Raman spectra of Zn^{II}/CN^- mixtures in liquid ammonia at 295 K; $R = 90.0$

	Wavenumber/cm^{-1}				f.w.h.h./cm^{-1}				Gaussian fraction				Relative band area (%)			
S																
0.5	2150.4	2147.7	—	—	5.4	4.3	—	—	0.6	0.2	—	—	80.4	19.7	—	—
1.0	2152.0	2148.6	—	—	4.3	5.4	—	—	1.0	0.2	—	—	12.5	87.5	—	—
1.5	—	2147.8	2144.5	—	—	4.2	3.0	—	—	0.2	0.4	—	—	84.8	15.2	—
2.0	—	2149.2	2145.3	—	—	5.0	3.8	—	—	0.3	0.1	—	—	89.4	10.6	—
2.25	—	2148.0	2144.9	—	—	3.3	3.6	—	—	0.1	0.1	—	—	51.2	48.9	—
2.5	—	2147.9	2144.8	2140.0	—	3.1	3.7	3.3	—	0.02	—	—	—	23.3	72.6	4.1
2.75	—	2148.6	2145.5	2141.7	—	2.9	3.8	4.3	—	—	0.2	0.1	—	6.8	78.2	15.0
3.0	—	—	2144.5	2140.8	—	—	3.9	4.5	—	—	0.3	0.3	—	—	63.3	36.7
3.25	—	—	2144.0	2140.3	—	—	4.1	4.6	—	—	0.4	0.4	—	—	46.5	53.5
3.5	—	—	2144.0	2140.3	—	—	4.4	4.6	—	—	0.6	0.4	—	—	30.7	69.3
3.75	—	—	2144.5	2140.5	—	—	6.3	4.6	—	—	0.4	0.3	—	—	23.0	77.1
4.0	—	—	2145.3	2141.0	—	—	8.4	4.6	—	—	0.4	0.3	—	—	22.5	77.5
6.0	—	2147.4	—	2141.3	—	10.1	—	4.7	—	0.3	—	0.2	—	17.9	—	82.1

Table 5 Variation with temperature of the resolved component band parameters of the C–N stretching region of the Raman spectra of a $Zn(CN)_2$ solution in liquid ammonia at 295 K; $R = 90.1$, $S = 2.0$

	Wavenumber/ cm^{-1}		f.w.h.h./cm^{-1}		Gaussian fraction		Relative band area (%)	
T/K								
295	2149.2	2145.3	5.0	3.8	0.3	0.1	89.4	10.6
275	2148.8	2145.7	3.2	3.2	0.02	0.3	78.4	21.6
237	2148.3	2145.7	3.4	3.3	0.3	0.03	78.9	21.2
213	2148.1	2145.8	3.6	3.7	0.3	0.1	79.3	20.7

the spectra of Cd^{II}/CN^- solutions in liquid ammonia differ markedly from those described above for the Hg^{II}/CN^- and Zn^{II}/CN^- systems.

As the cyanide concentration of the solution is increased up to $S = 4.0$ a single asymmetric feature shifts from *ca.* 2138 to *ca.* 2133 cm^{-1}. When the solution composition is $S < 2$ a band of much lower intensity is seen at *ca.* 2115 cm^{-1}, but this disappears rapidly near $S = 2.0$; at $S = 1$ $I_{2135}:I_{2115} \approx 20:1$. Table 6 shows how the C–N stretching region of the spectrum of a solution at $S = 2.0$ analyses into three components at 2137.5, 2133.0 and *ca.* 2116 cm^{-1}. However as S is increased above 4.0 a new band appears at *ca.* 2143 cm^{-1} in the 'tail' of the high-frequency wing of the main band.

The Raman spectra follow the same pattern as the infrared spectra. Fortunately there is much better resolution and two separate components are discerned in the 2138–2133 cm^{-1} region of the original spectra. The analyses in Table 7 indicate Raman band frequencies at 2137.1, 2133.4 and 2116.0 cm^{-1} with a further band appearing at *ca.* 2143 cm^{-1} in the spectra of solutions where $S > 2.75$.

The relative intensities of the bands at *ca.* 2137 and *ca.* 2133 cm^{-1}, assigned to the ν_{sym}(C–N) stretching frequencies of the 3:1 and 4:1 complexes respectively, are dependent on the salt concentration; for a $Cd(CN)_2$ solution at $R = 55$ $I_{2137}/I_{2133} \approx 1:1$, but when $R = 180$ this ratio increases to 4:1. This four-fold increase in the relative intensity ratio points to an equilibrium shift in favour of the 3:1 complex on dilution. The only reasonable explanation of such a large concentration effect is in terms of the activities of the species. (Activity coefficients cannot be applied to the system. They are unknown for these species in liquid ammonia. Ionic behaviour in liquid ammonia solutions is highly non-ideal and the ions possess abnormal activity–concentration relationships;[30] moreover we are considering here concentrations greater than 0.2 mol dm^{-3}.)

Beyond $S > 3.8$, when uncomplexed CN^- first appears, the band which dominates the spectrum is the one at *ca.* 2133 cm^{-1} attributed to $[Cd(CN)_4]^{2-}$. As S is increased above 3.0 there is an increasing contribution to the spectrum from a band (or bands) situated between 2145 and 2141 cm^{-1}. As with the Zn^{II}/CN^- and Hg^{II}/CN^- systems this feature can be attributed to the ion associate (or outer-sphere complex) $[Na^+ \cdots {}^-NC\text{–}Cd(CN)_3]^-$. Confirmation of this assignment is in the spectrum of a solution at $S = 4.0$ containing $NaClO_4$ in the composition ratio $[Cd(CN)_4{}^{2-}]/[NaClO_4] = 3:1$ the ratio of relative intensities of the bands, I_{2142}/I_{2133}, increases three-fold in the presence of $NaClO_4$.

Table 6 Resolved component band parameters of the C–N stretching region of the infrared spectra of Cd^{II}/CN^- mixtures in liquid ammonia at 295 K; $R = 60.0$

	Wavenumber/cm^{-1}				f.w.h.h./cm^{-1}				Gaussian fraction		Relative band area (%)			
S														
1.0	—	2138.1	2133.0	2115.3	—	12.0	8.7	10.0	0.1	0.2	—	73.0	12.0	15.0
2.0	—	2137.5	2133.0	2115.2	—	12.0	8.4	9.9	0.3	0.9	—	59.0	31.0	10.0
3.0	2146.6	2139.0	2132.9	2116.4	13.2	13.0	7.9	16.4	0.1	1.0	6.3	39.4	48.6	5.6
4.0	2149.9	2138.1	2132.9	—	6.8	15.6	7.3	—	—	—	0.6	57.1	42.0	—

Table 7 Resolved component band parameters of the C–N stretching region of the Raman spectra of Cd^{II}/CN^- mixtures in liquid ammonia at 295 K; $R = 97.4$

	Wavenumber/cm^{-1}				f.w.h.h./cm^{-1}				Relative band area (%)			
S												
0.5	—	2138.1	2134.1	2116.1	—	4.8	5.8	5.1	—	58.1	32.2	9.7
1.0	—	2138.5	2134.1	2116.2	—	5.5	5.4	4.7	—	62.4	33.0	4.5
1.5	—	2138.3	2134.2	2115.5	—	5.1	5.1	2.7	—	63.3	35.1	1.6
2.0	—	2137.1	2133.4	2116.0	—	5.5	6.0	3.8	—	62.3	35.5	0.9
2.25	—	2137.7	2133.9	2116.1	—	4.5	6.2	4.1	—	52.3	47.7	0.9
2.5	—	2137.9	2133.8	2115.4	—	4.5	4.8	2.4	—	51.8	47.4	0.8
2.75	2145.0	2137.6	2133.6	—	8.1	4.3	5.5	—	3.8	45.2	51.0	—
3.25	2143.7	2137.6	2133.5	—	13.5	4.5	4.9	—	8.2	23.8	68.0	—
3.5	2144.7	2137.7	2133.7	—	17.3	4.9	4.8	—	10.6	16.4	73.0	—
3.75	2139.1	—	2133.7	—	11.5	—	4.8	—	19.3	—	80.7	—
4.0	2139.7	—	2133.5	—	9.4	—	4.8	—	14.5	—	85.5	—
6.0	2140.8	—	2133.3	—	10.5	—	4.8	—	14.5	—	85.5	—

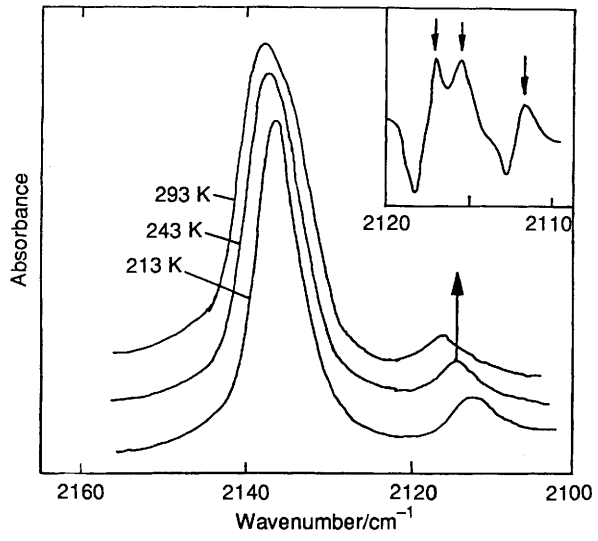

Fig. 1 Variation with temperature of the ν(CN) stretching region of the Raman spectrum of a Cd^{II}/CN^- mixture at $S = 1.0$ and $R = 60$ in liquid ammonia. The insert illustrates the fourth derivative of part of the spectrum of the solution at 243 K

The spectra of several solutions were studied with respect to changes in temperature. The analyses of the spectra of the solution at $S = 2.0$ in Table 8 indicate a shift in the equilibrium between the 3:1 and 4:1 complexes in favour of the 4:1 species as the temperature is lowered. Also the species associated with the feature at *ca.* 2116 cm^{-1}, namely the 1:1 and 2:1 complexes, are favoured at lower temperatures.

Measurements on a solution at $S = 2.75$ and $R = 95$ (Table 9) show how the band at *ca.* 2133 cm^{-1} due to $[Cd(CN)_4]^{2-}$ dominates the spectrum at 213 K (97%), whilst at 293 K the bands at 2133 and 2138 cm^{-1} due to $[Cd(CN)_4]^{2-}$ and $[Cd(CN)_3(NH_3)]^-$ have similar intensities. It is not unreasonable to consider these temperature data in terms of a two-species equilibrium, and conclude qualitatively that the 3:1/4:1 ligation step is strongly *exothermic*.

A temperature variation study of the band profiles at *ca.* 2115 cm^{-1} leads to the assignment of underlying features due to the 1:1 and 2:1 complexes. Fig. 1 illustrates how the band maximum shifts from *ca.* 2116 at 293 K to *ca.* 2113 cm^{-1} at 213 K. This band obviously consists of two or more components. The derivatives of the profiles of the spectra of a number of solutions with compositions below $S = 2.0$ at several temperatures, analysed by TREAT, identify three underlying features. The fourth-derivative spectrum of the solution at $S = 1.0$ and 243 K, shown in the insert in Fig. 1, places these at 2116.7, 2115.4 and 2113.6 cm^{-1}. Hence three different complexes with stoichiometry $[CN^-]/[Cd^{II}] < 2.0:1$ exist in the composition region $S < 2$. These bands are to be associated with the 1:1 and 2:1 complexes. They are at lower frequencies than the bands due to the tetrahedral 3:1 and 4:1 complexes, and unlike the frequencies of the Zn^{II}/CN^- and Hg^{II}/CN^- systems they fall out of the regular sequence observed for a set of complexes all with tetrahedral geometry. It is normal for the ν(CN) stretching frequency of a complexed CN^- ligand to be lower if the co-ordination number is higher. Accordingly it is concluded that these bands are due to the six-co-ordinate octahedral species, $[Cd(CN)(NH_3)_5]^+$ and *cis*- and *trans*-$[Cd(CN)_2(NH_3)_4]$.

Good supporting evidence for the attributions to the 1:1 and 2:1 complexes comes from the low-frequency region of the Raman spectra. For solutions with composition between $S = 2.0$ and 3.0, illustrated in Fig. 2, two different polarised bands due to symmetric ν_{sym}(Cd–N) stretching occur. One of these is at *ca.* 340 cm^{-1} when $S < 2.0$. The other, which appears at *ca.* 410 cm^{-1} when $S > 2.0$, is most in evidence at $S = 3.0$. On a tetrahedrally solvated cadmium centre the polarised band due to the ν_{sym}(Cd–N) vibration would be expected at *ca.* 420–425 cm^{-1}, intermediate between the ν_{sym}(M–N) frequencies of tetrahedrally solvated $[Zn(NH_3)_4]^{2+}$ and $[Hg(NH_3)_4]^{2+}$ at 432 and 415 cm^{-1};[28] ligating CN^- groups present in this tetrahedral co-ordination sphere would reduce the ν_{sym}(M–N) frequency. Hence we assign the polarised band at 411 cm^{-1},

Table 8 Variation with temperature of the resolved component band parameters of the C–N stretching region of the Raman spectra of $Cd(CN)_2$ solution in liquid ammonia; $R = 97.4$, $S = 2.0$

	Wavenumber/cm^{-1}			f.w.h.h./cm^{-1}			Gaussian fraction		Relative band area (%)		
T/K											
295	2137.1	2133.4	2116.0	5.5	6.0	3.8	—	—	62.3	35.5	0.9
279	2136.8	2133.4	2114.5	4.5	7.1	4.8	0.3	0.7	39.7	55.6	4.7
263	2136.6	2133.1	2114.1	4.4	7.0	4.5	0.1	0.8	36.7	57.9	5.4
242	2136.4	2133.4	2113.1	5.0	6.9	3.3	0.2	0.8	37.2	58.6	4.2
228	2135.9	2133.6	2112.3	5.4	7.0	4.2	0.3	0.9	46.0	48.1	5.6
214	2136.6	2134.9	2112.0	5.2	7.8	4.3	0.4	0.7	47.1	47.5	5.4

Table 9 Variation with temperature of the resolved component band parameters of the C–N stretching region of the Raman spectra of a Cd^{II}/CN^- mixture in liquid ammonia at 294 K; $R = 97.4$, $S = 2.75$

	Wavenumber/cm^{-1}			f.w.h.h./cm^{-1}			Gaussian fraction		Relative band area (%)		
T/K											
295	2145.0	2137.6	2133.6	8.1	4.3	5.5	—	—	3.8	45.2	51.0
281	—	2137.3	2133.4	—	4.2	5.4	0.2	0.5	—	41.9	58.1
266	—	2136.9	2133.1	—	3.9	5.4	0.2	0.4	—	30.6	69.4
242	—	2137.0	2133.6	—	3.5	5.3	0.4	0.4	—	15.4	84.7
225	—	2137.4	2134.1	—	2.9	5.1	0.6	0.3	—	5.4	94.6
213	—	2137.5	2134.5	—	3.5	4.9	1.1	0.3	—	2.7	97.3

Table 10 Summary of band assignments in the C–N stretching region for the cyano-complexes of Zn^{II}, Cd^{II} and Hg^{II} in liquid ammonia

	$[M(CN)(NH_3)_3]^+$	$[M(CN)_2(NH_3)_2]$		$[M(CN)_3(NH_3)]^-$		$[M(CN)_4]^{2-}$		$[Na^+ \cdots {}^-(NC)_3M(NH_3)]$	$[Na^+ \cdots {}^-(NC)_4M]^-$	
M	ν	ν_{sym}	ν_{asym}	ν_{sym}	ν_{asym}	ν_{sym}	ν_{asym}	ν	ν_{sym}	ν_{asym}
Zn	2150	2147		2145	2144	2140	2139		2147[a]	
Cd	2116[b]	←2115[b]→		2137	2137	2133	2133		2143	2143
		2114[b]								
Hg		2164	2161	2149	2144	2134	2159	2159	2141	

[a] 2145 cm^{-1} in the case of the potassium salt solution. [b] Octahedral complex.

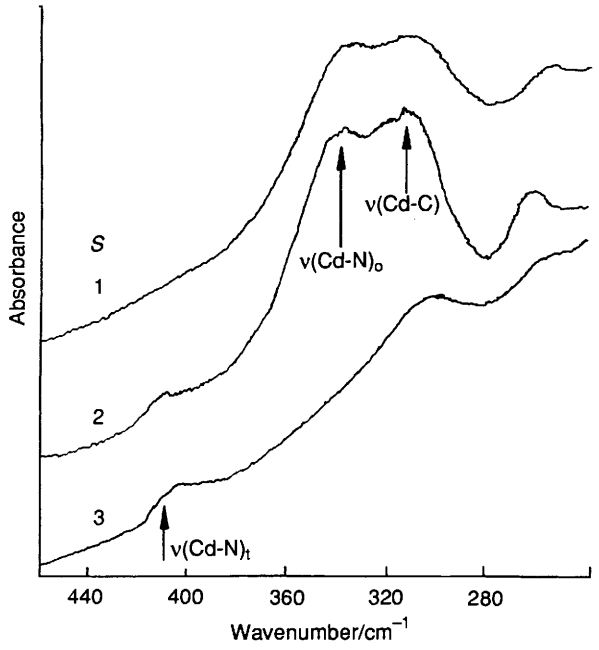

Fig. 2 The ν(Cd–N) stretching region of the Raman spectra of Cd^{II}/CN^- mixtures in liquid ammonia at 293 K

observed for a solution at $S = 3.0$, to the ν_{sym}(Cd–N) stretching frequency of tetrahedral $[Cd(CN)_3(NH_3)]^-$; corresponding frequencies for the amminecyano-zinc and -mercury complexes are at *ca.* 411 and *ca.* 401 cm^{-1}.

The band at 340 cm^{-1} observed with solutions at $S < 2.0$ must then be associated with the ν_{sym}(Cd–N) stretching frequency in an octahedral environment around the cadmium centre. The ions $[Zn(NH_3)_4]^{2+}$ and $[Hg(NH_3)_4]^{2+}$ are both tetrahedrally solvated in ammonia and, compared with these, the octahedrally solvated $[Cd(NH_3)_6]^{2+}$ is irregular.[28] The band due to the ν_{sym}(Cd–N) vibration at *ca.* 340 (p) cm^{-1} in the spectra of Cd^{II}/CN^- mixtures at $S < 2.0$ is therefore excellent evidence that the 1:1 and 2:1 amminecyanocadmium complexes possess six-co-ordinate geometry. Accordingly our assignments reflect the change in the geometry at the Cd^{II} in the 2:1 to 3:1 ligation step: $[Cd(CN)(NH_3)_5]^+$ (octahedral), 2116.7; *cis*-$[Cd(CN)_2(NH_3)_4]$ (octahedral), 2115.4; *trans*-$[Cd(CN)_2(NH_3)_4]$ (octahedral), 2113.6; $[Cd(CN)_3(NH_3)]^-$ (tetrahedral), 2138.8; $[Cd(CN)_4]^{2-}$ (tetrahedral), 2133.7 cm^{-1}.

We list in Table 10 all the ν(CN) stretching frequencies observed in the course of this work on the infrared and Raman spectra of mixtures of CN^- with Zn^{II}, Cd^{II} and Hg^{II} in liquid ammonia with their assignments.

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