Spectrochemistry of Solutions. Part 25.[1] Cyano-complexation of Nickel(II), Palladium(II) and Platinum(II) in Liquid Ammonia

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A vibrational spectroscopic study of cyano-ligation of Ni^{II}, Pd^{II} and Pt^{II} in liquid NH_3 has been performed. Only $[Ni(CN)_4]^{2-}$ and $[Ni(NH_3)_6]^{2+}$ are observed in the Ni^{II}–CN^-–NH_3 system. In the Pt^{II}–CN^-–NH_3 system $[Pt(CN)_4]^{2-}$, *trans*-$[Pt(NH_3)_2(CN)_2]$ and $[Pt(NH_3)_6]^{2+}$ exist in equilibrium. In contrast, the Pd^{II}–CN^-–NH_3 system slowly equilibrates (1–3 d) to mixtures containing $[Pd(NH_3)_6]^{2+}$, $[Pd(NH_3)_3(CN)]^+$, *cis*-$[Pd(NH_3)_2(CN)_2]$, $[Pd(NH_3)(CN)_3]^-$ and $[Pd(CN)_4]^{2-}$, but not *trans*-$[Pd(NH_3)_2(CN)_2]$. Infrared and Raman frequencies have been recorded. In all three systems ion pairs, in which the alkali-metal co-cation M interacts with square-planar $[M'(CN)_4]^{2-}$ through one of its CN^- ligands, have been identified as stable species: $[M^+\cdots{}^-NC{\cdot}M'(CN)_3]^-$. In liquid NH_3, cyano-complexes of Pd^{IV} and Pt^{IV} are immediately reduced to Pd^{II} and Pt^{II}.

It is well established that nickel, palladium and platinum exist in several different oxidation states in their cyano-complexes. Compounds in which Pt appears in mixed oxidation states are also known and cyclovoltammetric and X-ray spectrographic evidence[2] presented by one of us illustrated the existence of a compound in liquid NH_3 containing both Pt^{II} and Pt^{IV}. However, the most stable cyano-complexes of all three metals are undoubtedly the square-planar ones with the metal centre in its +2 oxidation state and there is no exception to this when liquid NH_3 is the solvent.

The high donor number of 49 for NH_3[3] leads to high solvation energies for most transition-metal cations generally enhancing the solubilities of lower complexes in the solvent. Accordingly it is possible to examine the partially ligated 1:1, 2:1 and 3:1 cyano-complexes of Ni^{II}, Pd^{II} and Pt^{II} in liquid NH_3, whereas in water and most other common solvents their insolubilities inhibit such study. The results in this paper add to, and amplify, our preliminary work on the Pd^{II}–CN^- system in liquid NH_3,[4] and also provide vibrational spectroscopic data for the Ni^{II}–CN^- and Pt^{II}–CN^- systems enabling a behavioural comparison of the three systems in liquid NH_3 to be made.

Experimental

Our techniques for handling liquid ammonia solutions quantitatively, and recording and analysing their vibrational spectra, are already described in the literature. Raman spectra of solutions in round sealed glass tubes were digitally recorded on a modified Coderg RS100 PHO spectrometer.[5–7] Infrared spectra were recorded at ambient temperature either on a Philips Analytical SP3-300 or on a HP9545 ratio recording spectrometer using a specially designed pressure cell and a medium band-pass filter, transparent through the C–N stretching region, to minimise heating effects by reducing radiation absorption by the sample.[8] The curve-resolution program VIPER and the derivative-convolution program TREAT were used to analyse the data.[9–11] Unless otherwise stated wavenumbers are to ±1 cm^{-1}.

Before use all salts were first dried and then recrystallised (usually twice) from liquid NH_3 using techniques previously described.[4,12]

Cyanoamminenickel(II) *complexes*.—Only two isolable complexes involving Ni^{II} and CN^- have previously been identified in the ammonia system, an ammine of $Ni(CN)_2$ of variable composition and soluble $[Ni(CN)_4]^{2-}$.[13–16] Pale blue hydrated $Ni(CN)_2$ is insoluble in NH_3 but reacts with the solvent to give purple $Ni(CN)_2{\cdot}4NH_3$, stable only under ammonia gas. Outside its ammonia atmosphere this tetraammine loses 3 NH_3 to become the stable light purple $Ni(CN)_2{\cdot}NH_3$ the solid-state infrared spectrum of which contains ν(N–H) 3380 and 3324, ν(C–N) 2170 and 2135; $\delta_d(NH_3)$ 1635; $\delta_s(NH_3)$ 1236 and 1193; $\rho_r(NH_3)$ 674, ν(Ni–N) 441 and ν(Ni–C) 420 cm^{-1}. When 2 equivalents of KCN were added to $Ni(NO_3)_2{\cdot}6H_2O$ in aqueous NH_3 light purple $Ni(CN)_2{\cdot}NH_3{\cdot}0.2H_2O$ precipitated on warming (Found: C, 18.2; H, 2.70; N, 31.8. Calc.: C, 18.3; H, 2.60; N, 32.00%). In the presence of excess of 'free' CN^- the dicyanoamminenickel(II) complexes all dissolve in both aqueous and liquid ammonia solutions to give $[Ni(CN)_4]^{2-}$

Results and Discussion

Nickel(II).—The infrared spectra of $[Ni(CN)_4]^{2-}$ in solutions of both K^+ and Na^+ in liquid NH_3 exhibit a single asymmetric band at *ca.* 2117 cm^{-1}. The asymmetry indicates an underlying feature at *ca.* 2120 cm^{-1} the relative intensity of which always increases if a common co-cation is added either as KCN or NaCN, or as KNO_3 or $NaNO_3$. In the case of $K_2[Ni(CN)_4]$ this 'ion pair' band at 2120 cm^{-1} is much too close to the 'free' CN^- anion band, and of too low intensity, to permit VIPER resolution, but the second derivative shows it to be an integral component of the spectrum. The single sharp symmetric band at 2115 cm^{-1} [full width at half height (FWHH) 5.8 cm^{-1}] observed with a solution containing $Ni(CN)_2$ and $[NEt_4]CN$ defines the C–N E_u stretching vibrational mode of unassociated $[Ni(CN)_4]^{2-}$. (Since no spectroscopic evidence for ion association between fully substituted quaternary ammonium cations and their co-anions has yet been found we use these salts to define the frequencies due to 'free' unassociated anionic species.[17]) The analyses in Table 1 illustrate the good spectroscopic evidence for the equilibrium existence of discrete ion associates which result from direct electrostatic interaction of the alkali-metal co-cations with $[Ni(CN)_4]^{2-}$. We believe that in these associates the alkali-metal cation is situated in an outer co-ordination sphere with respect to the nickel(II) cation with the CN^- ligand situated between the two cation centres, *viz.* $[Na^+\cdots{}^-NC{\cdot}Ni(CN)_3]^-$.

This type of ion association between alkali-metal cations and

Table 1 VIPER resolutions of the ν(C–N) stretching region of the infrared spectra of Ni^{II}–CN^- mixtures in liquid NH_3

System	$[CN^-]$/ $[Ni^{II}]$	Position/ cm^{-1}	FWHH/ cm^{-1}	Gaussian fraction	%Band area
$Ni(CN)_2$ + $[NEt_4]CN$	13.1	2115.0	5.8	0.57	100
$K_2[Ni(CN)_4]$	4.0	2117.1	6.5	0.41	100
$Na_2[Ni(CN)_4]$	4.0	2116.5	6.0	0.60	79
		2119.5	8.3	0.60	21
$Na_2[Ni(CN)_4]$ + $NaNO_3$ at $[Na^+]/[Ni^{II}]$ = 11.0	4.0	2117.0	5.5	0.60	61
		2120.5	8.1	0.60	39

complex cyano-anions (inner–outer sphere complexation) appears to be common in liquid NH_3. In addition to its appearance with $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ we have noted the same property with $[Ag(CN)_3]^{2-}$,[17] $[Hg(CN)_4]^{2-}$,[12] and $[Cu(CN)_4]^{3-}$.[18,19] It is probably the formation of the ion pair in liquid NH_3 between the complex anion and its co-cation which prevents the further ligation to $[Ni(CN)_5]^{3-}$ observed in water.[20–24] Complexation of Ni^{II} by CN^- in liquid NH_3 does not proceed beyond the 4:1 stage. As soon as the solution composition reaches $[CN^-]/[Ni^{II}] = 4.05$ either the characteristic multicomponent profile of an NaCN solution[17] between 2060 and 2090 cm^{-1} or the sharp symmetric band at 2060 cm^{-1} due to 'free' CN^- in $[NEt_4]CN$ solution is observed. No further bands appear in the region expected for C–N stretching in Ni^{II}/CN^- complexes, *ca.* 2120 cm^{-1}, even if CN^- is in high excess, *e.g.* $[CN^-]/[Ni^{II}] > 40$. A competition can be assumed between (*i*) ion association of $[Ni(CN)_4]^-$ and the alkali-metal co-cation and (*ii*) further ligation of $[Ni(CN)_4]^-$ by a fifth CN^- ligand. In liquid NH_3 the stepwise stability constant, K_5, for formation of $[Ni(CN)_5]^{3-}$ should be less than it is in water, *i.e.* $\log K_5 = 2.5$.[25] It is to be expected therefore that K_5 in liquid NH_3 will be lower than the association constant $K_{ass} = [Na^+ \cdots {}^-NC{\cdot}Ni(CN)_3{}^-]/[Na^+][Ni(CN)_4{}^{2-}]$. In liquid NH_3 the value of K_{ass} should be substantial because it relates to an electrostatic interaction in a medium of low to moderate relative permittivity involving ions carrying +1 and +2 charges where ΔG_{ass} should be approximately twice that of a uni-unicharged ion–ion interaction.

It is impracticable to use $Ni(NO_3)_2$ and $Ni(BF_4)_2$ to follow complexation in the Ni^{II}–CN^- system because their solubilities rise with falling temperature (inverse solubility *vs.* temperature relationships are common among the transition-metal salts in liquid NH_3). When we prepared solutions at $[CN^-]/[Ni^{II}] < 4$ using NH_3-soluble $Ni(NCS)_2$ as the source of Ni^{II} the spectrum consisted of a single band due to $[Ni(CN)_4]^{2-}$ at 2117 cm^{-1}. No bands due to SCN^- directly complexed to Ni^{II} were observed above 2060 cm^{-1}, the band attributed to the C–N stretching vibration of 'free' SCN^-. Accordingly we conclude that, whatever the stoichiometry of the solution, $[Ni(CN)_4]^{2-}$ is the only complex formed at spectroscopically measurable levels. {It should be noted that, whilst the spectra indicate the absence of inner-sphere complexation between SCN^- and Ni^{II} in liquid NH_3, the second derivatives of the ν(C–N) profiles *ca.* 2060 cm^{-1} clearly indicate the presence in equilibrium of discrete thermodynamically stable outer-sphere complexes between $[SCN]^-$ and $[Ni(NH_3)_6]^{2+}$.}

In the visible spectrum of $[Ni(NH_3)_6]^{2+}$ in liquid NH_3 the ${}^3T_{1g} \longrightarrow {}^3A_{2g}$ transition occurs at $\lambda_{max} = 565$ nm. This is always observed with solutions at $[CN^-]/[Ni^{II}] = 2.0$ containing $Ni(NCS)_2$–NaCN mixtures; the absorbance of this band approaches zero as $[CN^-]/[Ni^{II}]$ approaches 4.0. No precipitation occurs from any mixtures of either $Ni(NCS)_2$ and NaCN, or $Ni(NCS)_2$ and $[Ni(CN)_4]^{2-}$. Thus, unlike their Pd^{II}–CN^- and Pt^{II}–CN^- counterparts, Ni^{II}–CN^- solutions always consist of simple equilibrium mixtures of $[Ni(NH_3)_6]^{2+}$ and $[Ni(CN)_4]^{2-}$.

The Raman spectrum of $[Ni(CN)_4]^{2-}$ in liquid NH_3 exhibits features at 397p and 298dp cm^{-1} attributable respectively to the Ni–C stretching (A_{1g}) and C–Ni–C bending (E_g) modes. Careful examination of the perpendicularly polarised spectrum of the highly polarised band at 397 cm^{-1} indicates an underlying depolarised low-intensity feature at 400 ± 2 cm^{-1} assignable to the Ni–C stretching (B_{1g}) mode.

Platinum(II).—The infrared spectrum of a solution of $K_2[Pt(CN)_4]$ in liquid NH_3 contains a band due to the C–N stretching vibration at 2123 cm^{-1}. Like the Ni^{II}–CN^- system, excess of CN^- does not complex Pt^{II} beyond $[Pt(CN)_4]^{2-}$: the spectrum of NaCN in liquid NH_3 is already evident at $[CN^-]/[Pt^{II}] = 4.05$. The absence of features above 2130 cm^{-1} indicates that multinuclear complexation involving more than one platinum centre does not occur in the system.

Solutions of *cis*-$[Pt(NH_3)_2(CN)_2]$, which can only be produced if solid *cis*-$Pt(CN)_2$ is dissolved directly in liquid NH_3, exhibit bands in the infrared spectrum at 2142 and 2127 cm^{-1}. The addition of 1 equivalent of NaCN to a solution of the *cis* isomer produces a spectrum containing two bands at 2141 and 2124 cm^{-1}, the latter being the more intense. Here the feature at 2127 cm^{-1}, due to residual *cis*-$[Pt(NH_3)_2(CN)_2]$, is masked by the band at 2124 cm^{-1} due to $[Pt(CN)_4]^{2-}$. Solutions containing *trans*-$[Pt(NH_3)_2(CN)_2]$ give rise to a single infrared band at 2116 cm^{-1}. These spectra do not change with time.

Immediately after its preparation the infrared spectrum of a solution containing a NaCN–$[Pt(NH_3)_4][ClO_4]_2$ mixture at $[CN^-]/[Pt^{II}] = 4.0$ exhibits bands due to $[Pt(CN)_4]^{2-}$ and *trans*-$[Pt(NH_3)_2(CN)_2]$ at 2124 and 2116 cm^{-1} (Fig. 1). The band of lower intensity at 2116 cm^{-1} disappears slowly; after 2 h it appears only as an inflexion in the 'tail' of the main band at 2124 cm^{-1} and after 5 h it has disappeared completely. Thereafter the remaining spectrum consists of the single feature at 2124 cm^{-1}. If $[CN^-]/[Pt^{II}] < 4.0$ the band at 2116 cm^{-1} remains in the spectrum.

Thus solutions prepared by mixing NaCN and uncomplexed $[Pt(NH_3)_4]^+$ contain only *trans*-$[Pt(NH_3)_2(CN)_2]$ and $[Pt(CN)_4]^{2-}$ and, in contrast with the Pd^{II}–CN^- system, there is no spectroscopic evidence at all for the three other square-planar complexes, $[Pt(NH_3)_3(CN)]^+$, *cis*-$[Pt(NH_3)_2(CN)_2]$ and $[Pt(NH_3)(CN)_3]^-$. It would not be reasonable to suppose that $[Pt(NH_3)_3(CN)]^+$ and $[Pt(NH_3)(CN)_3]^-$ are non-participants in the complexation steps to $[Pt(CN)_4]^{2-}$ and the absence from the spectra of features due to them must have a kinetic explanation. The rate of CN^- addition to the 1:1 and 3:1 complexes in forming the *trans*-2:1 and -4:1 complexes respectively must be so rapid that neither the 1:1 nor the 3:1 complex can be detected spectroscopically. The processes of ligation of $[Pt(NH_3)_4]^{2+}$ and *trans*-$[Pt(NH_3)_2(CN)_2]$ by CN^- must be comparatively slow because the intensities of the two bands associated with *trans*-$[Pt(NH_3)_2(CN)_2]$ change in intensity over several hours before the final equilibrium position, corresponding to unchanging concentrations of the more kinetically stable *trans*-2:1 and -4:1 complexes, is reached. Slow addition of CN^- at the third step is the reason for the observation of *trans*-$[Pt(NH_3)_2(CN)_2]$ in the spectra when $[CN^-]/[Pt^{II}] > 2.0$. The ammine situated in the position *trans* to CN^- in $[Pt(NH_3)_3(CN)]^+$ is clearly much more labile than the ammines of its *cis*-2:1 isomer. Addition of a third CN^- to *trans*-$[Pt(NH_3)_2(CN)_2]$ is also slow because of the relatively low *cis* effect of the two CN^- ligands *trans* to each other; statistically there are fewer sites available for incoming CN^- ligands.

Although the *cis*-2:1 isomer is not observed when CN^- is added directly to $[Pt(NH_3)_4]^{2+}$ it remains as the stable entity in the solution when solid *cis*-$[Pt(NH_3)_2(CN)_2]$ is dissolved directly into liquid NH_3. The spectrum of a solution at $[CN^-]/[Pt^{II}] = 3.0$, prepared from *cis*-$[Pt(NH_3)_2(CN)_2]$ and NaCN,

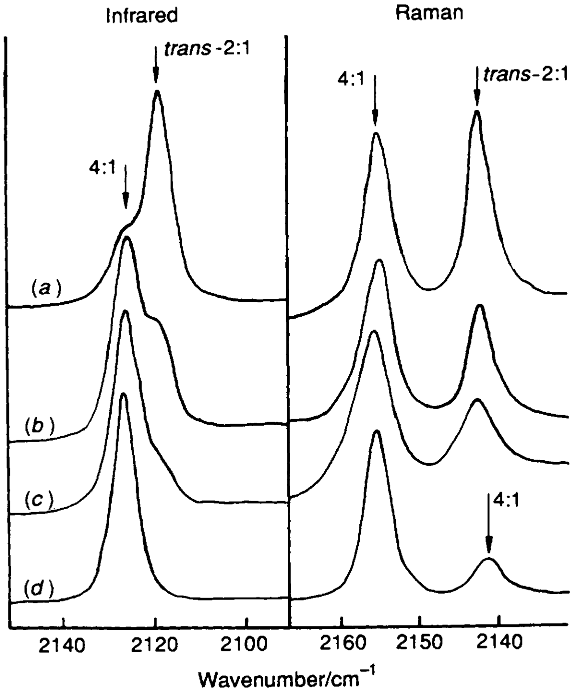

Fig. 1 The ν(C–N) stretching regions of the infrared and Raman spectra of Pt^{II}–CN$^-$ mixtures in liquid NH$_3$ at 293 K at [CN$^-$]/[Pt^{II}] = 0.5 (*a*), 1.9 (*b*), 3.0 (*c*) and 4.0 (*d*)

Table 2 Observed band positions and assignments for the cyano-complexes of Ni^{II}, Pd^{II} and Pt^{II} in liquid NH$_3$

Complex	Band position/cm^{-1}	Assignment
$[NEt_4]_2[Ni(CN)_4]$	2115	ν(C–N), E$_u$, IR
$K_2[Ni(CN)_4]$	2134p	ν(C–N), A$_{1g}$, R
	2127dp	ν(C–N), B$_{1g}$, R
	2117	ν(C–N), E$_u$, IR
	400dp	ν(Ni–C), B$_{1g}$, R
	397p	ν(Ni–C), A$_{1g}$, R
	298dp	δ(CNiC), E$_g$, R
$K_2[Pt(CN)_4]$	2158p	ν(C–N), A$_{1g}$, R
	2142dp	ν(C–N), B$_{1g}$, R
	2123	ν(C–N), E$_u$, IR
	461p	ν(Pt–C), A$_{1g}$, R
	461 ± 3dp	ν(Pt–C), B$_{1g}$, R
	321dp	δ(CPtC), E$_g$, R
trans-$[Pt(NH_3)_2(CN)_2]$	2143p	ν(C–N), A$_g$, R
	2116	ν(C–N), B$_{1u}$, IR
cis-$[Pt(NH_3)_2(CN)_2]$	2142p	ν(C–N), A$_1$, R, IR
	2127dp	ν(C–N), B$_1$, R, IR
$K_2[Pd(CN)_4]$	2150p	ν(C–N), A$_{1g}$, R
	2139dp	ν(C–N), B$_{1g}$, R
	2128	ν(C–N), E$_u$, IR
	416p	ν(Pd–C), A$_{1g}$, R
	414 ± 3dp	ν(Pd–C), B$_{1g}$, R
	296dp	δ(CPdC), E$_g$, R
$[Pd(NH_3)(CN)_3]^-$	2147p	ν(C–N), A$_1$, R, IR
cis-$[Pd(NH_3)_2(CN)_2]$	2142p	ν(C–N), A$_1$, R, IR
	2135dp	ν(C–N), B$_1$, R, IR
$[Pd(NH_3)_3(CN)]^+$	2135p	ν(C–N), A$_1$, R, IR
trans-$[Pd(NH_3)_2(CN)_2]$	2142p	ν(C–N), A$_{1g}$, R

exhibits bands due only to *cis*-[Pt(NH$_3$)$_2$(CN)$_2$] and [Pt(CN)$_4$]$^{2-}$. Unfortunately the band at 2127 cm^{-1} due to the C–N B$_1$ stretching mode of the *cis*-2:1 isomer is too close to the higher-intensity band at 2124 cm^{-1} due to the 4:1 complex for VIPER resolution. The band attributable to the C–N A$_1$ stretching mode of *cis*-[Pt(NH$_3$)$_2$(CN)$_2$] is at 2142 cm^{-1}.

The Raman spectra of [Pt(NH$_3$)$_4$]$^{2+}$–NaCN solutions in the range 0.5 < [CN$^-$]/[Pt^{II}] < 3.0 exhibit two bands due to [Pt(CN)$_4$]$^{2-}$, a polarised band at 2158p cm^{-1} (A$_{1g}$) and an apparently depolarised feature at 2142 cm^{-1} (B$_{1g}$) (Fig. 1). Evidence of a coincident underlying weaker polarised feature due to *cis*-[Pt(NH$_3$)$_2$(CN)$_2$], at *ca.* 2142p cm^{-1} (A$_1$), comes from the perpendicularly polarised spectrum; mutual exclusion aids assignment. Although these Raman spectra do not change with time the overlap of the bands is a severe handicap to curve resolution. Theoretically it ought to be possible to hold constant the parameters for the band due to [Pt(CN)$_4$]$^{2-}$ during the curve-fitting process {using the spectrum parameters of a K$_2$[Pt(CN)$_4$] solution}, but these are too sensitive to complex concentration, relative co-cation concentration, *etc.*

In the low-wavenumber region bands due to the Pt–C stretching (A$_{1g}$) and C–Pt–C bending (E$_g$) vibrational modes of [Pt(CN)$_4$]$^{2-}$ appear at 461p and 321dp cm^{-1} respectively. The polarisation properties of the band at 461 cm^{-1} lead to the assignment of a very low-intensity broad feature at 461 ± 3 cm^{-1} to its Pt–C stretching (B$_{1g}$) mode.

Excess of Na$^+$ cation added to [Pt(CN)$_4$]$^{2-}$ (either as NaCN or NaNO$_3$) causes the A$_{1g}$ band at 2158 cm^{-1} to become broader and asymmetric because of the appearance of a feature on its high-wavenumber side at 2162 cm^{-1}. As with the Ni^{II}–CN$^-$ system this feature is due to the [Na$^+$ $\cdots$ $^-$NC·Pt(CN)$_3$]$^-$ ion pair. The depolarised band at 2142 cm^{-1} also shows evidence of broadening when the excess of Na$^+$ is high, but here the main effect observed is in the increase in its intensity at 2142 cm^{-1} relative to its more intense partner at 2158 cm^{-1}.

Palladium(II).—The Pd^{II}–CN$^-$ system contrasts sharply with its Ni^{II}–CN$^-$ and Pt^{II}–CN$^-$ counterparts. Here the rates of successive CN$^-$ substitutions are slow and four of the five square-planar complexes (all except *trans*-2:1) can be readily identified in the spectra. However, band analyses are complicated by the slow changes with time of the relative concentrations of the constituent complexes (the kinetics of each substitution step depends on the specific species under consideration, and on the initial stoichiometric composition of the solution). Our experiments have shown how ligand exchange invariably leads to an equilibrium mixture when the solutions have been prepared from [Pd(NH$_3$)$_4$]$^{2+}$ and [Pd(CN)$_4$]$^{2-}$, but that no ligand exchange occurs if either one of these two palladium(II) centres is replaced by Pt^{II} or Ni^{II}. The spectra described here refer only to solutions of Pd^{II}–CN$^-$ mixtures in which ligand exchange has reached thermodynamic equilibrium. Assignments of bands are in Table 2.

Solutions of K$_2$[Pd(CN)$_4$] in NH$_3$ exhibit bands in the infrared at 2128 cm^{-1} (E$_u$) and in the Raman at 2150p (A$_{1g}$) and 2139dp cm^{-1} (B$_{1g}$). Unlike the Pt^{II}–CN$^-$ system it is the *cis*-2:1 isomer which remains in the equilibrium when Pd(CN)$_2$ is dissolved and [CN$^-$]/[Pd^{II}] < 4.0. The infrared spectrum taken immediately after preparation of a solution at [CN$^-$]/[Pd^{II}] = 2.0, obtained by dissolving *cis*-[Pd(NH$_3$)$_2$(CN)$_2$], contains bands due to *cis*-[Pd(NH$_3$)$_2$(CN)$_2$] at 2142 (A$_1$) and 2135 cm^{-1} (B$_1$). A shoulder at *ca.* 2128 cm^{-1}, attributable to the E$_u$ mode of [Pd(CN)$_4$]$^{2-}$, also appears on the profile of the band at 2135 cm^{-1} (Fig. 2). The Raman spectrum of this solution confirms the frequencies of the A$_1$ and B$_1$ stretching vibrational modes of *cis*-[Pd(NH$_3$)$_2$(CN)$_2$] at 2142p and 2135dp cm^{-1} respectively. The polarisation properties of an underlying band seen in the second-derivative spectrum, *ca.* 3 cm^{-1} lower than the A$_{1g}$ mode of [Pd(CN)$_4$]$^{2-}$, defines the A$_1$ mode of [Pd(NH$_3$)(CN)$_3$]$^-$ at 2147p cm^{-1}.

During the first hour after its preparation the infrared spectrum of a solution containing Pd(CN)$_2$ and NaCN at [CN$^-$]/[Pd^{II}] = 3.0 exhibits features at 2142 and 2127 cm^{-1}. For solutions at equilibrium in the concentration region [CN$^-$]/[Pd^{II}] < 2.0 the spectrum shows two bands at 2142 and 2135 cm^{-1}, but in the range 2.0 < [CN$^-$]/[Pd^{II}] < 4.0 three bands

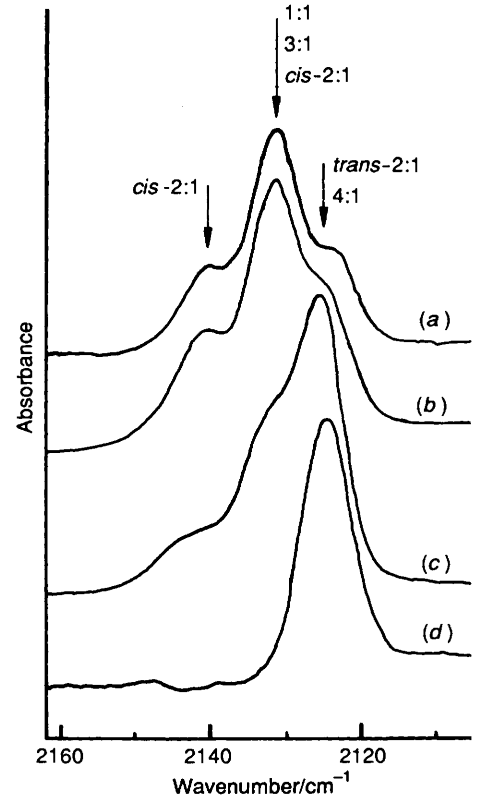

Fig. 2 The ν(C–N) stretching region of the infrared spectra of solutions of Pd^{II}–CN^- mixtures in liquid NH_3 at 293 K after equilibrium has been attained at $[CN^-]/[Pd^{II}]$ = 1.0 (*a*), 2.0 (*b*), 3.0 (*c*) and 4.0 (*d*). Positions of bands due to constituent complexes are indicated

are observed at 2142, 2135 and 2128 cm^{-1}. The intensities of the components at 2142 and 2135 cm^{-1} do not vary with solution composition, but that of the band at 2128 cm^{-1} depends on (*i*) the initial composition of the solution and (*ii*) the time elapsed since its preparation. This band, due to $[Pd(CN)_4]^{2-}$ (E_u), increases in intensity relative to the other two bands as $[CN^-]/[Pd^{II}]$ increases, dominates the spectrum in the range $3.0 < [CN^-]/[Pd^{II}] < 4.0$, and is the only feature at $[CN^-]/[Pd^{II}] = 4.0$; the band parameters are independent of time. A slight excess of CN^- to give $[CN^-]/[Pd^{II}] = 4.05$ results in the characteristic spectrum of NaCN–NH_3 between 2050 and 2090 cm^{-1} indicating that ligation of Pd^{II} stops at the 4:1 stage.

As with $[Ni(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ there is evidence of the $[M^+ \cdots {}^-NC{\cdot}Pd(CN)_3]^-$ ion pair. The low-intensity cation-dependent feature due to this species observed in the higher-frequency 'tail' of the band attributable to the ν_{asym}(C–N) stretching vibration of $[Pd(CN)_4]^{2-}$ appears at 2130 cm^{-1} for K^+ and 2131 cm^{-1} for Na^+.

At first sight the infrared spectra in Fig. 2 might suggest that there are only two complexes in the system. Three bands appear at 2128 $\{[Pd(CN)_4]^{2-}\}$, and 2142 and 2135 cm^{-1} {*cis*-$[Pd(NH_3)_2(CN)_2]$} but no isosbestic points are found if the spectra of solutions of increasing palladium(II) concentrations (adjusted to a corresponding concentration value) are plotted. The Raman spectra (Fig. 3), however, indicate four of the five possible square-planar complexes. Linkage isomerism and multinuclear complex formation can be discounted. The Raman spectrum of a $K_2[Pd(CN)_4]$ solution exhibits two bands in the ν(C–N) stretching region, 2150p and 2139dp cm^{-1}. The spectrum of a $Pd(CN)_2$ solution contains two bands, one at 2135dp and another at 2143p cm^{-1} with a well defined shoulder at 2147p cm^{-1}.

Solutions at equilibrium in the composition range $0 < [CN^-]/[Pd^{II}] < 2.0$ exhibit bands in their Raman spectra at 2142p and 2135dp cm^{-1} the relative intensities of which depend on the initial $[CN^-]/[Pd^{II}]$ ratio. The intensity of the polarised feature at *ca.* 2135 cm^{-1}, due to the ν(C–N) stretching vibration of $[Pd(NH_3)_3(CN)]^+$, increases as $[CN^-]/[Pd^{II}]$ is reduced. At $[CN^-]/[Pd^{II}] = 0.5$ it is the principal feature of the spectrum, but as $[CN^-]/[Pd^{II}]$ approaches 2.0 its intensity decreases relative to that of the band at 2142 cm^{-1} due to *cis*-$[Pd(NH_3)_2(CN)_2]$. Thus from the polarisation data and the relative intensity trends it must be concluded that the frequencies of the C–N stretching mode of $[Pd(NH_3)_3(CN)]^+$ and the C–N stretching (B_1) mode of *cis*-$[Pd(NH_3)_2(CN)_2]$ coincide at 2135 cm^{-1}.

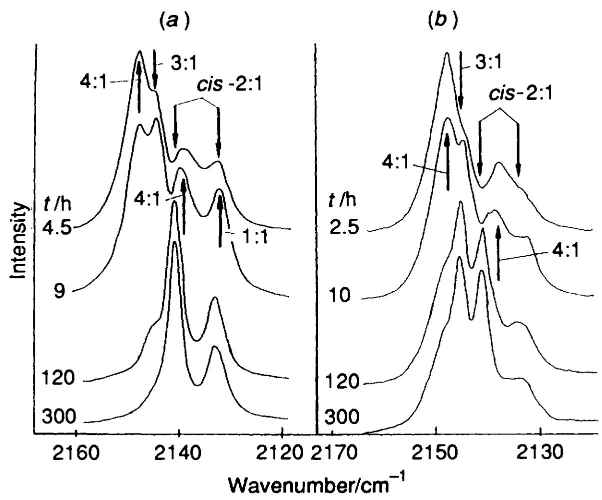

Fig. 3 The ν(C–N) stretching region of the Raman spectra of $[Pd(NH_3)_4]^{2+}$–NaCN mixtures in liquid NH_3 at 293 K illustrating the band positions and their time dependencies: $[CN^-]/[Pd^{II}]$ = 1.6 (*a*) or 2.7 (*b*)

At $[CN^-]/[Pd^{II}] = 2.0$ the composition of the solution is 'critical'. Fig. 3 shows how at $[CN^-]/[Pd^{II}] < 2.0$ the spectra differ from those of solutions where $[CN^-]/[Pd^{II}] > 2.0$. In the former case the spectra contain bands at 2142 and 2135 cm^{-1} the relative intensities of which depend on (*i*) the time after the preparation of the solution and (*ii*) the initial $[CN^-]/[Pd^{II}]$ ratio. Spectra recorded for solutions at $[CN^-]/[Pd^{II}] > 2.0$ are more complicated not only in the way they change with time but also after the solution has reached equilibrium. The Raman spectrum of a solution containing $[Pd(NH_3)_4][NO_3]_2$ and NaCN at $[CN^-]/[Pd^{II}] = 2.7$ has five distinguishable components: 2150p, 2147p, 2142p, 2139dp and 2135dp cm^{-1}. The intensities of the bands at 2150 and 2139 cm^{-1} increase relative to those at 2142 and 2135 cm^{-1} as $[CN^-]/[Pd^{II}]$ increases to 4.0, and at $[CN^-]/[Pd^{II}] = 4.0$ these are the only features remaining. Accordingly we assign them to the A_1 and B_1 stretching modes of *cis*-$[Pd(NH_3)_2(CN)_2]$. Because the remaining polarised band at 2147p cm^{-1}, observed with all solutions in the range $2.0 < [CN^-]/[Pd^{II}] < 4.0$, is at its maximum intensity near $[CN^-]/[Pd^{II}] = 3.0$ it is assigned to the ν(C–N) A_1 stretching mode of $[Pd(NH_3)(CN)_3]^-$. By following changes in relative band intensities with solution composition in the $[CN^-]/[Pd^{II}] < 2.0$ region we find that the band at 2135 cm^{-1} is a composite of two overlapping bands due to *cis*-$[Pd(NH_3)_2(CN)_2]$ and $[Pd(NH_3)_3(CN)]^+$, supporting the attributions made from the infrared spectra.

The complex *trans*-$[Pd(NH_3)_2(CN)_2]$ is the only square-planar cyanopalladium(II) complex which cannot be positively identified in the spectra of ammonia solutions at ambient temperature although bands attributable to it have been previously reported for a solution of stoichiometry $[CN^-]/[Pd^{II}] = 2.0$ at −40 °C.[4] The spectrum of this solution recorded after standing for 24 h at room temperature no longer contained the sharp intense polarised feature originally observed at 2142 cm^{-1} and attributed to the symmetric stretching mode (A_{1g}) of *trans*-$[Pd(NH_3)_2(CN)_2]$. The spectrum had become that of a solution consisting mainly of $[Pd(CN)_4]^{2-}$. The only feasible explanation is that the $[Pd(CN)_4]^{2-}$ produced undergoes further slow ligand exchange with $[Pd(NH_3)_4]^{2+}$, or $[Pd(NH_3)_3(CN)]^+$, the relative concentration of which depends on the stoichiometry of the solution. {Without suitable equipment for the measurement of the infrared spectra of ammonia solutions at sub-ambient temperatures it has not been possible to define the frequency of the antisymmetric C–N stretching mode (E_u) of *trans*-$[Pd(NH_3)_2(CN)_2]$.}

Hence, from the evidence available, it is seen that the Pd^{II}–CN^- and the Pt^{II}–CN^- systems are alike in as much as when CN^- is added to $[Pd(NH_3)_4]^{2+}$ it is the *trans*-2:1 isomer which forms first, presumably through $[Pd(NH_3)_3(CN)]^+$. However, unlike the Pt^{II}–CN^- system, which equilibrates to a mixture of *trans*-$[Pt(NH_3)_2(CN)_2]$ and $[Pt(CN)_4]^{2-}$, the Pd^{II}–CN^- system passes on to $[Pd(CN)_4]^{2-}$ through *trans*-$[Pd(NH_3)_2(CN)_2]$ and $[Pd(NH_3)(CN)_3]^-$ before further re-equilibration involving NH_3–CN^- exchange at the Pd^{II} to produce *cis*-$[Pd(NH_3)_2(CN)_2]$. At equilibrium the *cis* isomer is always the dominant species in the range $0.5 < [CN^-]/[Pd^{II}] < 3.5$. $[Pd(CN)_4]^{2-}$ is only observed when $[CN^-]/[Pd^{II}] > 2.0$ and is not detected if $[CN^-]/[Pd^{II}] \leqslant 2.0$.

Platinum(IV) *and Palladium*(IV).—Whenever CN^- is present in liquid NH_3 with compounds containing Pd^{IV} and Pt^{IV} the higher oxidation states are reduced immediately to Pd^{II} and Pt^{II}. When NaCN is added to $[NH_4]_2[Pt^{IV}Cl_6]$ so that $[CN^-]/[Pt^{IV}] = 7.7$ the ν(C–N) region of the infrared spectrum of the solution contains the single sharp band at 2123 cm^{-1} due to $[Pt^{II}(CN)_4]^{2-}$ and the characteristic multicomponent spectrum of NaCN solution between 2080 and 2050 cm^{-1}. Also indicative of reduction to $[Pt^{II}(CN)_4]^{2-}$, the Raman spectrum contains two bands at 2158p and 2142dp cm^{-1}, and two bands at 460 and 322 cm^{-1}. The spectra of solutions containing Pd^{IV}–NaCN mixtures behave similarly. A solution comprising a mixture of $[NH_4]_2[Pd^{IV}Cl_6]$ and NaCN at $[CN^-]/[Pd^{IV}] = 4.5$ exhibited a single infrared band at 2127 cm^{-1}, whilst at $[CN^-]/[Pd^{IV}] = 7.3$ its Raman spectrum contained two C–N stretching vibrations at 2151p and 2140dp cm^{-1}, and two bands at 417p and 295dp cm^{-1}.

Whenever Pd^{IV} and Pt^{IV} are treated with CN^- in liquid NH_3 a new band is observed in the spectrum at 2151 ± 3 cm^{-1}. A band at this frequency also occurs when Cu^{II} is reduced to Cu^I by CN^- in liquid NH_3.[19] No oxidation product of CN^- has been isolated but it seems reasonable to attribute this feature to such a product.

Conclusions

Table 2 summarises our spectroscopic data for the cyano-complexes of Ni^{II}, Pd^{II} and Pt^{II} in liquid NH_3. Cyano-complexation is complete at the 4:1 stage, but for all three metals addition of excess of CN^- so that $[CN^-]/[M^{II}] > 4$ results in the formation of a stable ion associate, designated as $[M^+ \cdots {}^-NC{\cdot}M'(CN)_3]^-$, where M and M′ represent alkali- and transition-metal cations respectively. For all three M′ cations the contributions of the 4:1 complexes in the equilibrium mixtures are greater than is to be expected from the $[CN^-]/[M^{II}]$ stoichiometries. This being the case there must be contributions from either the ammine complexes of M′ or the monocyano complexes.

Irrespective of the initial solution composition, $[Ni(CN)_4]^{2-}$ is the only cyano-complex present after NaCN has been added to $[Ni(NH_3)_6]^{2+}$, and $[Ni(NH_3)_6]^{2+}$ is always present if $[CN^-]/[Ni^{II}] < 4.0$. In contrast to the aqueous system, an excess of CN^- added to the ammonia solution so that $[CN^-]/[Ni^{II}] > 4.0$ does not produce $[Ni(CN)_5]^{3-}$. Ammines of $Ni(CN)_2$ can be produced only by treating solid $Ni(CN)_2$ with either gaseous or liquid NH_3 and cannot be obtained in solution from the reaction between NaCN and $[Ni(NH_3)_6]^{2+}$.

Solutions prepared from the reaction of $[Pt(NH_3)_4]^{2+}$ with NaCN produce only *trans*-$[Pt(NH_3)_2(CN)_2]$ and $[Pt(CN)_4]^{2-}$ at spectroscopically detectable levels. The platinum(II) centre is not as labile as Pd^{II} and any attempt to form the 1:1 and 3:1 complexes of Pt^{II} in the ammonia environment would be fruitless because even at $[CN^-]/[Pt^{II}] = 3.0$ the *trans*-2:1 isomer is the dominant ammine–cyano-complex in solution. A liquid ammonia solution of *cis*-$[Pt(NH_3)_2(CN)_2]$ can only be obtained by direct dissolution of solid *cis*-$[Pt(NH_3)_2(CN)_2]$ in the solvent, and this species does not revert to its *trans* isomer.

The ion $[Pd(CN)_4]^{2-}$, in detectable concentrations, rapidly forms on addition of NaCN to palladium(II) ammines through the whole composition range $0.5 < [CN^-]/[Pd^{II}] < 4.0$. When $[CN^-]/[Pd^{II}] < 4.0$ slow ligand exchange (half-lives ranging from *ca.* 1 h to several days) always leads to an equilibrium mixture containing $[Pd(NH_3)(CN)_3]^-$, *cis*-$[Pd(NH_3)_2(CN)_2]$ and $[Pd(NH_3)_3(CN)]^+$. The rate of ligand exchange and the proportion of each species in the equilibrium mixture depend on the initial $[CN^-]/[Pd^{II}]$ ratio of the solution. The complex *trans*-$[Pd(NH_3)_2(CN)_2]$ has only been detected in the liquid ammonia medium in solutions prepared and kept at *ca.* −50 °C. It rapidly disappears as the temperature rises; therefore it might be feasible to trap it out by crystallisation between −75 and −40 °C. In a background of CN^- anions in liquid NH_3 both Pd^{IV} and Pt^{IV} are immediately reduced to Pd^{II} and Pt^{II}.

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