

Complexation of noble transition metals in liquid ammonia

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Abstract. Complexation of the cations, Ag^+ , Au^+ , Hg^{2+} , Cu^+ , Pt^{2+} , Pd^{2+} , Ni^{2+} , Ru^{3+} , Rh^{3+} , and Ir^{3+} , with CN^- and SCN^- in liquid ammonia is described. Vibrational spectroscopy of solutions is the main technique used.

In the $[\text{CN}^-]/[\text{Ag(I)}]$ system at least 11 species, including linkage isomers of the 1:1 and 2:1 complexes, ion pairs, and higher ion aggregates, have been identified; the 1:1 complexes are tetrahedral, and the 2:1 ones are linear. In $[\text{CN}^-]/[\text{Au(I)}]$ complexation does not proceed beyond 2:1; both the 1:1 and 2:1 complexes are linear and Au..C bonded. Successive complexation steps in $[\text{CN}^-]/[\text{Hg(II)}]$ mixtures are by simple exchange of NH_3 with CN^- at a tetrahedral Hg nucleus. Cu(I) is only stable as 3:1 and 4:1 cyano-complexes; at lower $[\text{CN}^-]/[\text{Cu}]_{\text{T}}$ ratios the metal is rapidly oxidised to Cu(II) . Only the very stable $[\text{Ni}(\text{CN})_4]^{2-}$ complex occurs with Ni(II) . All 11 $\nu(\text{CN})$ frequencies of all possible C-bonded cyano-Pd(II) complexes have been assigned; an unexpected conversion of *trans*- $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$ into its *cis*-isomer can be followed in the infrared ($t_{1/2} \sim 6\text{h}$). Only $[\text{Pt}(\text{CN})_4]^{2-}$ and *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$ occur in NH_3 solution, but if *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$ is dissolved it remains unchanged. CN^- cannot displace NH_3 from the coordination spheres of hexaammines of Ru^{3+} , Rh^{3+} , and Ir^{3+} , but it exchanges with the halide of the corresponding halopentaammines.

SCN^- complexes Ag^+ to the 1:1 stage, and with great difficulty to the 2:1 stage. With Pt^{2+} , Pd^{2+} , Ni^{2+} , Ru^{3+} , Rh^{3+} , and Ir^{3+} it does not replace NH_3 in the inner coordination shell of the cation, but bands in the $\nu(\text{CN})$ region of the infrared spectra close to that due to 'free' solvated SCN^- (2060cm^{-1}) indicate stable outer-sphere complexation between the metal amines and SCN^- .

INTRODUCTION

Complexation properties can differ markedly between solvents. No accounts appear of equilibrium relationships between simple anions/ligands and transition metal cations in liquid ammonia. This paper reviews investigations of interactions in this solvent between noble metal cations and simple cyanide and thiocyanate anions.

We have reported previously (refs. 1,2) how ammonia is an excellent solvent for vibrational spectroscopic examination of solutes. Nearly the whole range of the solvent's Raman spectrum is available above a long and flat baseline. The infrared spectrum has absorption 'windows' within which the vibrational bands of many singly charged multiatomic anions/ligands conveniently appear, including CN^- and SCN^- .

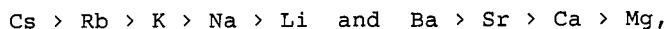
Ammonia is commonly accepted as the most powerful single-bonding donor molecule. Its solvent donicity, 59, (ref. 3) is the highest recorded. Because the solvent is present in vast excess compared with the ligand the NH_3 molecule always competes for a site on a transition metal cation on extremely favourable terms, and powerful ligands like CN^- and SCN^- are required for the formation of stable complexes. Monodentate σ -bonding ligands generally have little tendency to coordinate in an ammonia medium, though complexes with π -bonding can sometimes be generated if the translational entropic contribution to the energy of formation is increased e.g., by multidentate complexation. It is by coordination between π -bonding ligands such as CN^- and SCN^- , and metals which favour this type of bonding, that monodentate complex formation can be encouraged.

The work described here follows from our vibrational spectroscopic studies of ion associates in ammonia; reviewed at 18.ICSC.(ref. 2) Although normally considered as electrostatic interactions ion associates are just another form of complexation. The earlier review was concerned with electrostatic interactions between simple anions (or ligands) with alkali and alkaline earth metal cations. Among the types of ion association interaction which we have identified contact ion pairs and solvent-shared ion pairs are specifically identified as two of the most important. In the coordination chemist's vocabulary these species are inner-sphere and outer-sphere complexes respectively. Both of these types have been identified in the transition metal solutions we have studied.

Ion associates in equilibrium in solution are identified by analysing their spectral envelopes into components. We have used Raman and infrared spectra in a complementary manner. Parameters of component bands due to the species in solution are established using the programs VIPER and TREAT(refs. 4,5,6) to obtain computer-assisted curve resolutions and derivative spectra. Figs.1 and 2 exemplify the way anionic spectra vary with cation. Fig.1 highlights the changes which occur with cation size in the $\nu(\text{CN})$ stretching region for simple CN^- salts. The differences of ion association properties between ammonia and water are marked. In aqueous media salts of uni-charged cations must be at high concentration before there is any spectroscopic evidence of ion pairing, *i.e.*, bands other than those due to the 'free' anion are detected. For instance, solutions at 6 mol dm^{-3} were required to produce data for $\text{NaNO}_3(\text{aq.})$; $K_{\text{ass}} \sim 5 \times 10^{-2} \text{ mol}^{-1}\text{dm}^3$.(refs. 7,8) Irish *et al.*, (refs. 9,10) have shown that ion association is exhibited better in aqueous solutions when the charge of one or both of the ions is raised.

The dielectric constant of ammonia is highly temperature-sensitive; $\epsilon = 22$ at 230K, and $\epsilon = 13$ at 330K.(refs. 2,11) Because this property changes from a medium to a low value over a relatively small temperature range equilibrium distributions of ion associates are easily studied by selection of appropriate temperatures and concentrations.

The important features in the spectra are as follows. Bands B and C of the CN^- series (Fig. 1) are due to linkage isomers of contact ion pairs (inner-sphere complexes); $\text{M}^+.\text{CN}^-$ and $\text{M}^+.\text{NC}^-$ respectively. In the thiocyanate solutions of the alkaline earth metals (Fig. 2) bands A are due to N-bonded contact ion pairs. Species concentrations (estimated from band areas) suggest association constants for contact ion pairs between 1 and $25 \text{ mol}^{-1}\text{dm}^3$. Their stability orders,



are opposite to that predicted electrostatically. This is due to the

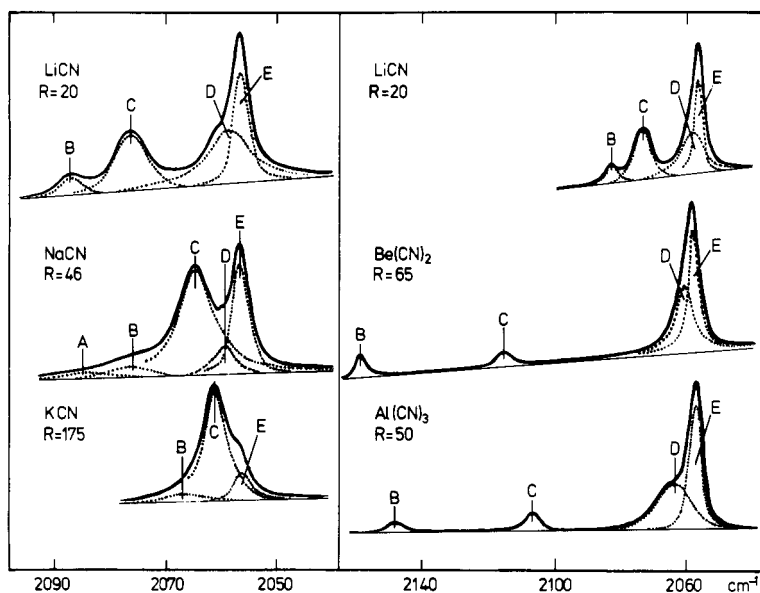


Fig.1. $\nu(\text{CN})$ stretching regions of the Raman spectra of CN^- salt solutions in liquid NH_3 at 293K. $R = [\text{NH}_3]/[\text{M}]$.

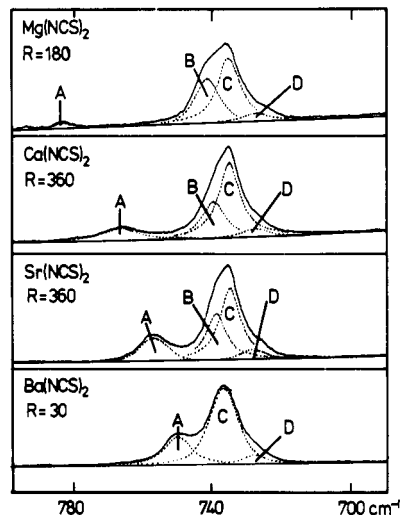
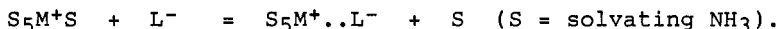


Fig. 2. $\nu(\text{CS})$ region of the Raman spectra of SCN^- solutions in liquid NH_3 at 293K.

numerical proximity of the free energies of solvation and ligation of these cations in ammonia, and the resulting small free energy change for,



As we confirm experimentally it is to be expected that an association process so finely thermodynamically balanced as this should have a marked temperature dependence. Accordingly two effects of temperature variation must always be taken into account: (i) changes in the values of the thermodynamic functions for association/complexation, and (ii) changes in the solution characteristics due to the variation of dielectric constant.

Bands B in Fig. 2, and D in Fig. 1, are due to solvent-shared ion pairs (outer-sphere complexes). These bands can be discerned in the profiles without computer assistance in the spectra of LiCN , $\text{Be}(\text{CN})_2$ and $\text{Al}(\text{CN})_3$; for NaCN solutions the existence of solvent-shared ion pairs was verified by 2nd derivatives of the spectra. (ref. 12) Assuming an equilibrium between the 'free' SCN^- and an outer-sphere complex spectrum simulations (fitted by least squares) to the observed spectra for the band centred near the frequency due to the 'free' SCN^- anion lead to the expected order for the formation constants of outer-sphere complexation; $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$.

With its high donor strength the NH_3 molecule plays a major role by solvating transition metal cations strongly. The resultant high cation solvation energies lead to a large number of soluble transition metal salts; unusual for a solvent of relatively low dielectric constant. Among the 'unexpectedly' soluble salts are HgI_2 , $\text{Hg}(\text{CN})_2$, AgSCN , AgCl , AgI , $\text{Pd}(\text{CN})_2$, $\text{Pt}(\text{CN})_2$, AuCN etc.; even CuSO_4 is soluble! (It is interesting to note that, at 293K, a solution of AgI at 8 mol dm^{-3} can be obtained.) Thus, in contrast with aqueous chemistry, where insolubility often impairs progress, the first complexation steps of many transition metal cations can be usefully followed in liquid ammonia.

COMPLEXATION BY THE CN⁻ LIGAND

Silver(I)

Ag(I) can be coordinated by CN⁻ to the 3:1 stage in ammonia (ref. 13) compared with 4:1 in water.(ref. 14) In the Raman spectra bands associated with 1:1, 2:1 and 3:1 coordination occur at *ca.* 2119cm⁻¹, 2139cm⁻¹ and 2102cm⁻¹ respectively.(ref. 13) All three regions are sensitive to both temperature and concentration, but changes in the profiles indicate that greater complexity exists. Through careful spectroscopic titration of AgNO₃ with CN⁻ (>150 spectra) at least 11 different species have been identified as outlined below. Changes in the spectra were followed as the stoichiometric ratios [CN⁻]/[Ag⁺] and [NH₃]/[Ag⁺] were varied for different temperatures. LiCN, NaCN and KCN were all used as titrants.

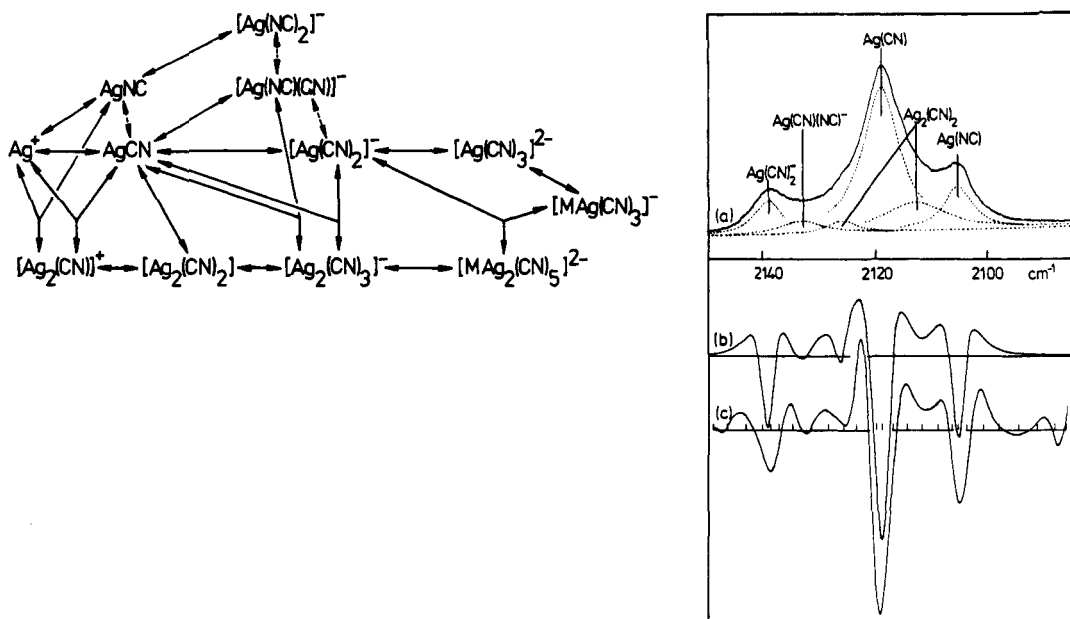


Fig. 3. (a) VIPER fitting of the observed spectrum of a mixture, [CN⁻]/[Ag⁺]=1.0 at R = 44 in liq. NH₃ (b) 2nd derivative obtained from the sum of the components, (c) 2nd derivative of the observed spectrum.

Fig. 3 illustrates how confidence in the analysis of a 6-component spectrum is achieved. Excellent fits, using VIPER (ref. 6) to fit bands with a Lorentz-Gauss sum function by a Newton-Gauss-Marquart algorithm (ref. 15), are obtained. With this process alone there can be no absolute confidence that either the correct band parameters have been obtained or, even the correct number of component bands selected - independent evidence is required! It is now our practice to complement VIPER curve-fitting with a 2nd derivative check with TREAT.(ref. 4) TREAT is a program for resolution enhancement, *i.e.*, it gives a closer estimation of the true positions of underlying bands. The check proceeds as follows. A 2nd derivative spectrum of the sum of all the component bands obtained by VIPER is first produced. If the 2nd derivative of the original spectrum produced directly by TREAT (through an alternative route) matches this the VIPER resolution of the spectrum can be accepted as in Fig.3.

The example given in Fig.3 is that of a fairly high concentration of Ag(I) at $[\text{CN}^-]/[\text{Ag}^+] = 1.00$. Bands due to the simple 1:1 and 2:1 species (C-bonded) can be seen at 2119cm^{-1} and 2139cm^{-1} , but two other bands at $\text{ca. } 2127\text{cm}^{-1}$ (bridging CN^-) and 2113cm^{-1} (terminal CN^-) are due to the dimer $(\text{AgCN})_2$. There is no doubt that these two bands derive from the same complex species because their intensities change in tandem as the solution conditions are varied.

When $[\text{CN}^-]/[\text{Ag}^+] = 2.00$ the band at 2139cm^{-1} dominates the spectrum, but at $[\text{CN}^-]/[\text{Ag}^+] = 1.00$ the band at 2119cm^{-1} is much in evidence, though even when $[\text{CN}^-]/[\text{Ag}^+] < 1.00$ the band at 2139cm^{-1} is still observed. Fig. 4 and Fig. 5 illustrate how these bands, due to the 2:1 and 1:1 complexes, vary with temperature. These spectra were obtained by subtraction of the specific components due to other species from the total spectrum to deduce a profile due to the sums of the components due specifically to species of 1:1 and 2:1 stoichiometry. The spectrum in Fig. 4 has 2 components, and that in Fig. 5 has 3. The areas of the components in both these regions are highly temperature sensitive relative to each other, indicating the existence of two different 1:1 complexes and three different 2:1 complexes; $\text{Ag}\dots\text{CN}$ and $\text{Ag}\dots\text{NC}$, and $[(\text{NC})\text{Ag}(\text{CN})]^-$, $[(\text{NC})\text{Ag}(\text{NC})]^-$ and $[(\text{CN})\text{Ag}(\text{NC})]^-$. This was the first recorded evidence for linkage isomerism in silver(I)-cyano complexes.(ref. 16)

When the relative intensity changes of bands in the 1:1 region relative to those in the 2:1 region are followed with temperature a large favourable (+ve) entropy change accompanying ligation of the 1:1 complex is noted. The frequency of the band due to the 2:1 species in NH_3 is very close to the corresponding one for the 2:1 complex in aqueous solution.(ref. 14)

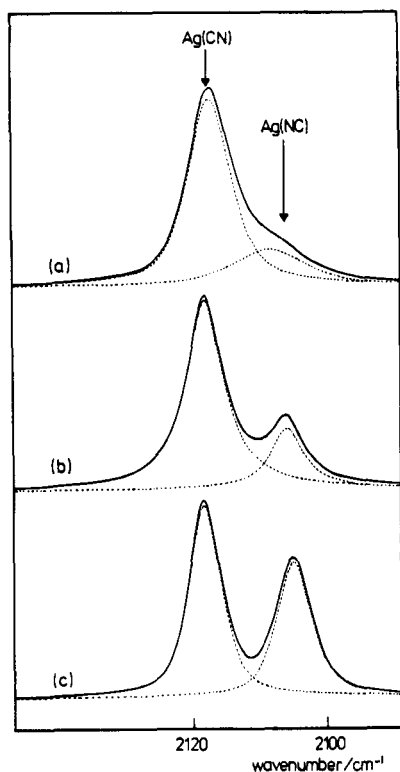


Fig. 4. Raman spectra of the $[\text{Ag}(\text{CN})_2]^-$ ions in liq. NH_3 . (a) 293K, (b) 233K, (c) 203K.

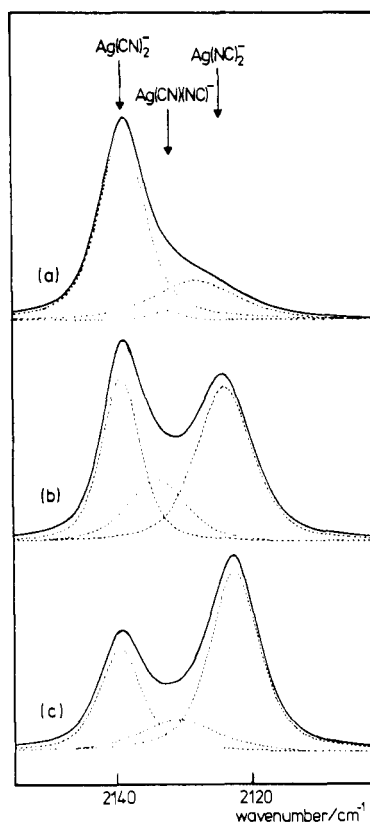


Fig. 5. Raman spectra of the $[\text{AgCN}]$ in liq. NH_3 ; (a) 293K, (b) 233K, (c) 203K.

Accordingly we must conclude that it is linear. The position of the band for the 1:1 species is unknown for aqueous solution. The $\nu(\text{Ag-N})$ stretching frequency at 269cm^{-1} for the solvated cation leads to the view that the Ag^+ cation is tetrahedrally solvated. We conclude that the first ligation step by CN^- is a simple replacement of one tetrahedrally solvated NH_3 molecule by CN^- ;



The second step,



undergoes a geometry change (tetrahedral to linear) as manifested by the large favourable change in translational entropy. The non-sequential progression of frequencies due to successive complexes (2:1 > 1:1 > 3:1) supports this.

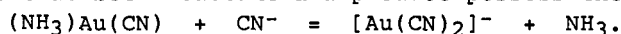
Potentiometric stepwise stability constant determinations at 233K support the conclusion that the second step is thermodynamically more favourable than the first, because $\log K_1 = 7.0$, $\log K_2 = 9.0$, and $\log K_3 = 1.5$. (ref. 17)

When the charge on the complex anion is 2- ion pairs between $[\text{Ag}(\text{CN})_3]^{2-}$ and Li^+ , Na^+ , or K^+ appear; bands at $2115\text{cm}^{-1}(\text{Li}^+)$, $2108\text{cm}^{-1}(\text{Na}^+)$ and $2104\text{cm}^{-1}(\text{K}^+)$, all on the high frequency side of the band due to the 3:1 complex anion at 2102cm^{-1} . The intensities of each of these bands can be increased by addition of the common cation as perchlorate.

Gold (I)

Complexation of gold(I) by CN^- in ammonia (ref.18) contrasts with that of silver(I). As with aqueous solutions (ref. 19,20) only 1:1 and 2:1 complexes form. There is no evidence for linkage isomerism, and the low frequency spectra indicate that the bonding is Au-CN. Band assignments are obvious from mutual exclusion between infrared and Raman (Fig. 6): for $(\text{NH}_3)\text{Au}(\text{CN})$ $\nu(\text{CN})$ appears in both the ir and Raman(dp) at 2152cm^{-1} ; for $[\text{Au}(\text{CN})_2]^-$ $\nu_1(\text{CN})$ appears in the Raman(p) at 2158cm^{-1} , with $\nu_3(\text{CN})$ in the ir at 2142cm^{-1} .

The spectra of the solutions, $2.0 > [\text{CN}^-]/[\text{Au}^+] > 1.0$, remain unchanged in the temperature interval 200K to 300K. This is unlike the Ag(I) system where there is a marked change in the equilibrium distribution of species with temperature. The near zero change in the free energy for the 1:1/2:1 step with temperature, and more important, the small translational entropy change suggests that both reactant and product possess the same geometry - linear:



The low frequency Raman spectra of these solutions support this. (ref. 18)

Copper(I) and Copper(II)

Cu(I) is unstable when its simple salts are dissolved in liquid ammonia. The solutions are always partially oxidised to give a mixture containing both Cu(I) and Cu(II). Cu(I) can be stabilised by complexation with CN^- , as $[\text{Cu}(\text{CN})_4]^{3-}$, but when the stoichiometric ratio falls so that $[\text{CN}^-]/[\text{Cu}]_T < 3.0$ the characteristic blue of Cu(II) reappears. This behaviour is characterised in the vibrational spectra of the solutions: $[\text{Cu}(\text{CN})_4]^{3-}$, ν_{S} , $2097\text{cm}^{-1}(\text{R(p)})$; ν_{AS} , $2087\text{cm}^{-1}(\text{R(dp),ir})$; $[\text{Cu}(\text{CN})_3]^{2-}$, $2094\text{cm}^{-1}(\text{ir})$, ca. $2100\text{cm}^{-1}(\text{R(p)})$.

If Cu(I) is introduced so that $[\text{CN}^-]/[\text{Cu}]_T < 3.0$, fast ammoniation (solvation) occurs at the Cu nucleus and some, but not all, of the Cu is immediately oxidised. In mixtures containing Cu(II) with CN^- , at $[\text{CN}^-]/[\text{Cu}]_T < 4$, reduction of Cu(II) can occur to give a mixture containing the ammine of Cu(II) and cyano-complexed Cu(I). An exchange of CN^- occurs between $[\text{Cu}(\text{CN})_4]^{3-}$ species and hexaammine-Cu(II) to produce an ammoniated Cu(II) cyano-complex (1:1, or 2:1, or 3:1) which exhibits a symmetrical band in the infrared spectrum at 2130cm^{-1} , and the Cu(I) complex $[\text{Cu}(\text{CN})_3]^{2-}$ with its band at 2094cm^{-1} .

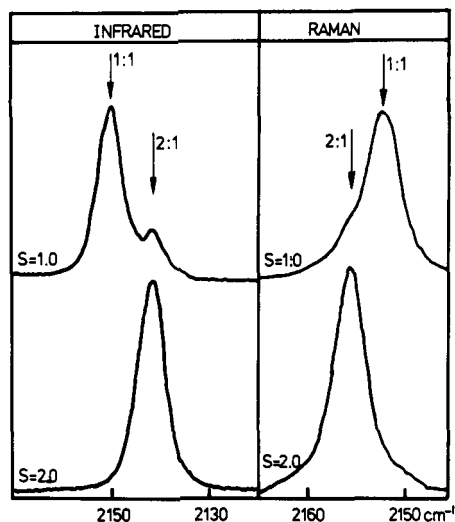


Fig. 6. $\nu(\text{CN})$ region of the Raman and infrared spectra of CN^-/Au^+ mixtures in liq. NH_3 at 293K.

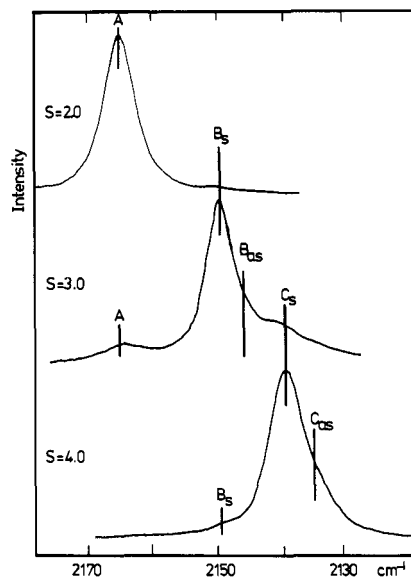


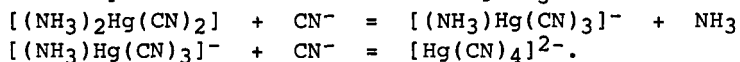
Fig. 7. $\nu(\text{CN})$ region of the Raman spectra of $\text{CN}^-/\text{Hg}^{2+}$ mixtures in liq. NH_3 at 293K.

So far the evidence suggests that ammoniation at the Cu(I) atom encourages rapid oxidation. Conversely substitution of CN^- into an ammoniated Cu(II) nucleus is a slow process. The implication is that the 3:1 complex of Cu(I), $[\text{Cu}(\text{CN})_3]^{2-}$, does not contain an NH_3 ligand, and that it is likely to contain trigonally bonded CN^- .

Mercury(II)

Only the ligation steps between the 2:1 and 4:1 complexes have been examined in ammonia. (ref. 21) Attempts to prepare the 1:1 complex, either by adding CN^- to $\text{Hg}(\text{NO}_3)_2$ or, by adding $\text{Hg}(\text{NO}_3)_2$ to a solution of $\text{Hg}(\text{CN})_2$, result in vigorous reaction in which Hg metal is precipitated. Cyanogen is thought to be liberated by oxidation of the CN^- ligand in the 1:1 complex. Alternatively a bimetallic cyano-bridged intermediate, could be involved. This redox reaction is so exothermic that it was considered unsafe to proceed with investigations of solutions at low $[\text{CN}^-]/[\text{Hg}^{2+}]$ compositions, even at 200K.

Fig. 7 shows that the steps from the 2:1 to 3:1 to 4:1 complexes are straightforward. A steady progression of descending Raman frequencies suggests simple substitutions of CN^- at the Hg(II) centre involving no geometry changes: $\nu_{\text{S}}(\text{CN})$, 2164cm^{-1} (2:1), 2148cm^{-1} (3:1), 2140cm^{-1} (4:1); $\nu_{\text{AS}}(\text{CN})$, 2164cm^{-1} (2:1) (composite with ν_{S}), 2145cm^{-1} (3:1), 2134cm^{-1} (4:1). Solvation of Hg^{2+} in ammonia has been investigated by us, (ref. 22) and by Straughan *et al.* (ref. 23) Our results concur and, using the values and sequences of observed $\nu(\text{M-N})$ frequencies (ref. 22) for the solvated alkaline earth metal and Zn^{2+} , Cd^{2+} , and Hg^{2+} cations, we conclude that Hg^{2+} is tetrahedrally solvated. Thus cyano-ligation of the 2:1 Hg(II) complex is by successive replacements of the solvating NH_3 's at a tetrahedral Hg centre;



It is interesting to note that whilst $\text{Hg}(\text{CN})_2$ is linear in the solid, like $[\text{Ag}(\text{CN})_2]^-$, Hg^{2+} adopts a tetrahedral configuration in ammonia solution, probably due to the affinity of NH_3 for the Hg^{2+} nucleus and favourable partial solvation.

Palladium(II)

At first sight the spectra of cyano-Pd(II) mixtures are extremely complicated. There are many bands between 2152cm^{-1} and 2127cm^{-1} , but ligation of Pd^{2+} is complete at the 4:1 stage. Above 4:1 stoichiometry there is always evidence of free CN^- ligand, but CN^- is absent even when $[\text{CN}^-]/[\text{Pd}^{2+}]$ is only marginally below 4.0. This is indicative of strong complexation to form the square-planar $[\text{Pd}(\text{CN})_4]^{2-}$.

All 11 $\nu(\text{CN})$ frequencies of the 5 square-planar (including the *cis*- and *trans*-2:1 isomers) have been identified. (ref. 24) Four of these are unambiguously assigned by mutual exclusion at compositions $[\text{CN}^-]/[\text{Pd}^{2+}] = 2$ and 4. The strongly polarised intense Raman bands due to the symmetric stretching vibrations of *trans*- $[(\text{NH}_3)_2\text{Pd}(\text{CN})_2]$ and $[\text{Pd}(\text{CN})_4]^{2-}$ occur at $2142\text{cm}^{-1}(\text{A}_1)$ and $2150\text{cm}^{-1}(\text{A}_{1g})$, whilst the bands at $2127\text{cm}^{-1}(\text{B}_{1u})$ and $2128\text{cm}^{-1}(\text{E}_u)$, active in the infrared only, are due to *trans*- $[(\text{NH}_3)_2\text{Pd}(\text{CN})_2]$ and $[\text{Pd}(\text{CN})_4]^{2-}$. A band in both the ir and Raman(p) at 2134cm^{-1} , which appears when $[\text{CN}^-]/[\text{Pd}^{2+}] < 1.0$, is attributable to the A_1 vibration of $[(\text{NH}_3)_3\text{Pd}(\text{CN})]^+$. The remaining band assignments (in the Table) were made using (i) the variation of band intensities with solution composition and, (ii) Raman polarisation properties.

There are no $\nu(\text{CN})$ vibrations due to multinuclear cyano-bridged complexes at higher frequencies. However, the system contains an unexpected feature. The *trans*-2:1 complex appears to be converted into its *cis*-isomer. This was first realised when repeating the Raman spectrum of a solution at $[\text{CN}^-]/[\text{Pd}^{2+}] = 2.0$ which had been stored at 293K for three weeks. It is normal to prepare solutions for Raman spectra in sealed glass tubes at low temperatures (200K to 230K). The original spectrum, which had defined the A_g vibration of the *trans*-2:1 species at 2142cm^{-1} , had been obtained within 1h of the preparation of the solution. After 2 weeks the intense and strongly polarised Raman band had completely disappeared leaving a spectrum consisting of two much weaker bands due to the *cis*-2:1 isomer (2145cm^{-1}), and probably a mixture of the 1:1 and 3:1 isomers (coincident *ca.* 2134cm^{-1}). The change in species distribution with time can be followed better in the infrared spectra (Fig. 8); the process has a half-life of *ca.* 6h at 293K.

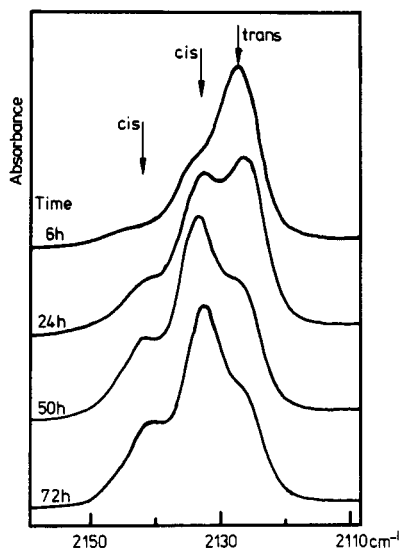


Fig. 8. Variation with time of the ir spectra of liq. NH_3 solutions with $[\text{CN}^-]/[\text{Pd}^{2+}] = 2.0$ at 293K.

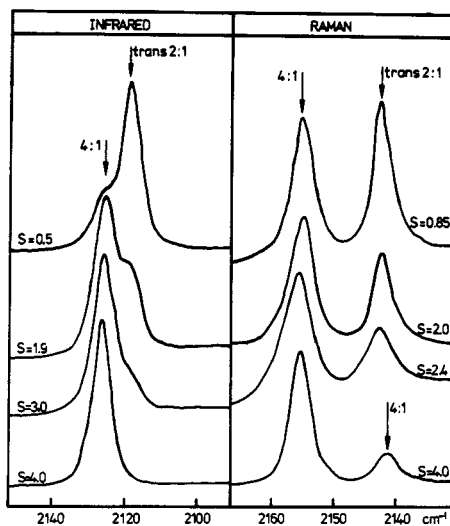


Fig. 9. $\nu(\text{CN})$ region of the Raman and ir spectra of $\text{CN}^-/\text{Pt}^{2+}$ mixtures in liq. NH_3 at 293K.

TABLE Infrared and Raman bands in the $\nu(\text{CN})$ stretching region of the spectra of mixtures of Au(I), Pd(II) and Pt(II) with CN^- in liquid NH_3

S	Frequency/ cm^{-1}	Assignment	S	Frequency/ cm^{-1}	Assignment
<u>Au(I)/CN^- mixtures</u>			<u>Pt(II)/CN^- mixtures</u>		
1	2142(ir)	$[\text{Au}(\text{CN})_2]^-$	< 4	2126(ir)	$[\text{Pt}(\text{CN})_4]^{2-}$
	2152(R,ir)	$[(\text{NH}_3)\text{Au}(\text{CN})]$		2117(ir)	<i>trans</i> - $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$
	2158(R)	$[\text{Au}(\text{CN})_2]^-$		2158(R)	$[\text{Pt}(\text{CN})_4]^{2-}$
2	2142(ir)	$[\text{Au}(\text{CN})_2]^-$	2143(R)	<i>trans</i> - $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$	
	2158(R)	$[\text{Au}(\text{CN})_2]^-$		2142(R)	$[\text{Pt}(\text{CN})_4]^{2-}$
<u>Pd(II)/CN^- mixtures</u>			> 4	2126(ir)	$[\text{Pt}(\text{CN})_4]^{2-}$
2150(R)	$[\text{Pd}(\text{CN})_4]^{2-}$	2158(R)		$[\text{Pt}(\text{CN})_4]^{2-}$	
2148(R,ir)	$[\text{Pd}(\text{NH}_3)(\text{CN})_3]^-$	2142(R)		$[\text{Pt}(\text{CN})_4]^{2-}$	
2145(R,ir)	<i>cis</i> - $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$	2142(R,ir)		<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$	
2142(R)	<i>trans</i> - $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$	2126(R,ir)		<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{CN})_2]$	
2141(R)	$[\text{Pd}(\text{NH}_3)(\text{CN})_3]$				
2138(R)	$[\text{Pd}(\text{CN})_4]^{2-}$				
2136(R,ir)	<i>cis</i> - $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$				
2134(R,ir)	$[\text{Pd}(\text{NH}_3)(\text{CN})_3]^-$				
2134(R,ir)	$[\text{Pd}(\text{NH}_3)_3(\text{CN})]^+$				
2128(ir)	$[\text{Pd}(\text{CN})_4]^{2-}$				
2127(ir)	<i>trans</i> - $[\text{Pd}(\text{NH}_3)_2(\text{CN})_2]$				

Platinum(II)

The behaviour of the $\text{CN}^-/\text{Pt(II)}$ system is markedly different from its Pd(II) analogue. Only two square-planar species are detected spectroscopically: *trans*- $[(\text{NH}_3)_2\text{Pt}(\text{CN})_2]$ and $[\text{Pt}(\text{CN})_4]^{2-}$ (Fig. 9); assignments are in the Table. They are almost identical with the corresponding Pd(II) species. As for Pd(II) solutions complexation is complete at 4:1 stoichiometry, and the system is dominated by the highly stable 4:1 complex. There is no evidence of cyano-bridged multinuclear complexation. Because there is no redistribution of species when solid $[\text{Pt}(\text{CN})_2]$ is dissolved the bands due to the *cis*-2:1 isomer can be assigned. The spectra of solutions of the *cis*-2:1 complex remain stable and consist simply of two symmetric bands at 2140cm^{-1} (R(p),ir) and 2126cm^{-1} (R(dp),ir).

Nickel(II)

Only the square-planar 4:1 complex occurs in ammonia. When Ni^{2+} is added to $[\text{Ni}(\text{CN})_4]^{2-}$ in water pale blue $[\text{Ni}(\text{CN})_2 \cdot \text{H}_2\text{O}]$ is precipitated. Although $[\text{Ni}(\text{CN})_2]$ is insoluble in ammonia ammoniation of the solid occurs to give $[\text{Ni}(\text{CN})_2 \cdot \text{NH}_3]$. The only species in solution, $[\text{Ni}(\text{CN})_4]^{2-}$, is defined by a sharp symmetric band in the ir at 2117cm^{-1} . When $[\text{CN}^-]/[\text{Ni}] < 4$, $[\text{Ni}(\text{CN})_2 \cdot \text{NH}_3]$ cannot be precipitated but the presence of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ has been established from the visible spectra of the solutions.

Ruthenium(III)

Addition of CN^- to Ru(III) solutions in ammonia produces a yellow precipitate. In recrystallisation Ru is present in both solid and filtrate; disproportionation to Ru(II) and Ru(IV) probably occurs. Such a process is not unlikely because the reduction potential between Ru(II) and Ru(III) is small. (ref. 25) Solutions with excess CN^- ($[\text{CN}^-]/[\text{Ru}^{3+}] = 9.5$), exhibit two features in their infrared spectra due to CN^- in the inner coordination sphere of the Ru cation; 2142cm^{-1} and 2126cm^{-1} . Only the latter of these appears in the spectrum when there is no excess CN^- in the solution $[\text{CN}^-]/[\text{Ru}] = 2.0$.

This can also be followed in an absorption band shift in the visible spectrum of the solution from λ_{\max} at 422nm to λ_{\max} at 443nm. Similar spectrum changes occur when CN^- is added to both halopentammine- and hexaammine-Ru(III). When CN^- is added to Ru(II), as $[\text{Ru}(\text{NH}_3)_6]^{2+}$, the hexaammine band at 430nm shifts to 451nm indicating complexation in the inner sphere, but no band appears in the infrared which we can relate to this.

Rhodium(III) and Iridium(III)

In contrast with Ru(III) addition of CN^- to hexaamines of Rh(III) and Ir(III) produces no cyano-complexes whatsoever, irrespective of coanion. However, addition of CN^- to halopentaamines of Rh(III) and Ir(III) produces solutions whose infrared spectra each contain a sharp symmetrical band in the $\nu(\text{CN})$ stretching region: 2116cm^{-1} (Rh) and 2124cm^{-1} (Ir); attributable to monocyano-complexes, $[\text{M}(\text{NH}_3)_5(\text{CN})]^{2+}$. The characteristic spectrum of NaCN in liquid ammonia (Fig. 1) is present even though the $[\text{CN}^-]/[\text{M}]$ ratio is much less than 6. There would appear to be an inner-outer sphere exchange between halide ligand and CN^- .

Visible spectra show a differentiation between Rh(III) and Ir(III). After CN^- has been added to $[\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$ the band (λ_{\max} , 352nm) due to $[\text{Ir}(\text{NH}_3)_5(\text{CN})]^{2+}$ remains constant in both intensity and position. In contrast the corresponding band at $\lambda_{\max} = 405\text{nm}$, associated with $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$, slowly shifts to 460nm with time ($t \sim 50\text{h}$) with a corresponding change of intensity. Whilst this could be due to slow replacement of CN^- in the inner coordination sphere of $[\text{Rh}(\text{NH}_3)_5(\text{CN})]^{2+}$ by NH_3 to form the kinetically "inert" and thermodynamically stable $[\text{Rh}(\text{NH}_3)_6]^{3+}$, it might also be a manifestation of the exchange of a further CN^- ligand into the inner sphere. If the corresponding process for Ir(III) is thermodynamically favourable, it is kinetically much too slow for observation.

COMPLEXATION BY THIOCYANATE

Silver(I)

SCN^- ligates Ag^+ to form an S-bonded 1:1 complex. Bands due to this species can be identified in both the $\nu(\text{CN})$ and the $\nu(\text{CS})$ regions of the Raman spectra (ref. 27) at 2078cm^{-1} and 727cm^{-1} ; bands at 2060cm^{-1} and 736cm^{-1} are due to 'free' SCN^- . A second SCN^- is added only with difficulty; the $[\text{SCN}^-]/[\text{Ag}^+]$ ratio must be raised to 20:1 before a band at 2094cm^{-1} due to $[\text{Ag}(\text{SCN})_2]$ appears as ca. 1% of the total band area. The formation constant of the 1:1 complex has been estimated both from spectra, and from potentiometric titrations, (ref. 17) of KNCS and AgNO_3 solutions; K_1 is ca. $5-7 \text{ mol}^{-1} \text{ dm}^3$

Palladium(II), Platinum(II) and Nickel(II)

Nitrate solutions of Pd(II) and Pt(II) in ammonia, to which SCN^- has been added, as KSCN exhibit no vibrational bands attributable to inner-sphere complexation between the metal cation and SCN^- . All earlier work on ion association in alkali thiocyanate solutions showed that it was the $\nu(\text{CS})$ stretching region which was more informative, (ref. 28) with the $\nu(\text{CN})$ region generally broad and difficult to resolve.

The $\nu(\text{CS})$ stretching regions of the Raman spectra of $\text{M}(\text{SCN})_2/\text{KSCN}$ mixtures ($\text{M} = \text{Pd}$ or Pt) are identical with those of KSCN solutions, suggesting that little inner-sphere complexation occurs between the transition metal cation and SCN^- . On the other hand it is clear that solutions of $\text{trans-}[\text{Pt}(\text{SCN})_2]$ and $\text{Ni}(\text{SCN})_2$, not containing counter cations such as K^+ , exhibit more than one feature in their $\nu(\text{CN})$ stretching regions as in Fig. 10.

For $\text{Ni}(\text{SCN})_2$ solutions the frequencies of two underlying components are rather close, 2055cm^{-1} and 2063cm^{-1} , but neither of these can be associated with free SCN^- (2060cm^{-1}). Moreover, they cannot be associated with inner-sphere complexation because the frequency shifts from 2060cm^{-1} are too small; in the solids $\text{Ni}(\text{SCN})_2$ and $[\text{Ni}(\text{NH}_3)_4(\text{SCN})_2]$ $\nu(\text{CN})$ is at 2175cm^{-1} and 2095cm^{-1} respectively. The band due to *trans*- $[\text{Pt}(\text{SCN})_2]$ in a freshly prepared ammonia solution occurs at 2116cm^{-1} (*o.f.*, *ca.* 2107cm^{-1} , solid). This band disappears completely from the solution spectrum in 1 to 2h leaving the spectrum seen in Fig. 10 and which indicates outer-sphere complexation.

Identification, from the derivatives, of the features due to outer-sphere coordination is best in the case of Ni(II) where the absorption maximum of the $\nu(\text{CN})$ profile is shifted to a lower frequency than 2060cm^{-1} . There is also evidence for outer-sphere coordination in the Pt(II) solutions in the $\nu(\text{CN})$ region, and particularly in the $\nu(\text{CS})$ region where a feature at 746cm^{-1} appears as a shoulder of the 'free' SCN^- band at 736cm^{-1} . The corresponding Pd(SCN)₂ solutions give rise to a slightly asymmetric band at 2060cm^{-1} . The 2nd derivatives suggest that a small band due to outer-sphere complexation should be incorporated on the lower frequency side of the main band, *ca.* 2052cm^{-1} .

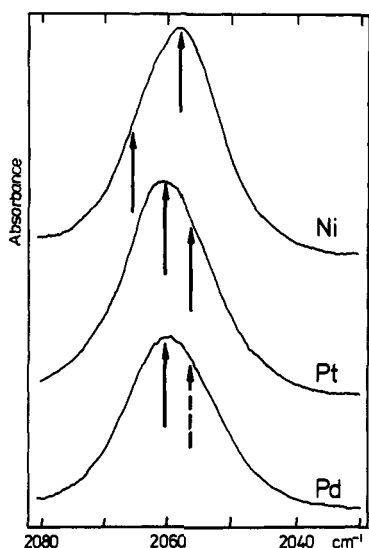


Fig.10. $\nu(\text{CN})$ region of the ir spectra of Ni(II), Pt(II), Pd(II) thiocyanates in liq. NH_3 at 293K. The arrows mark the positions of underlying bands.

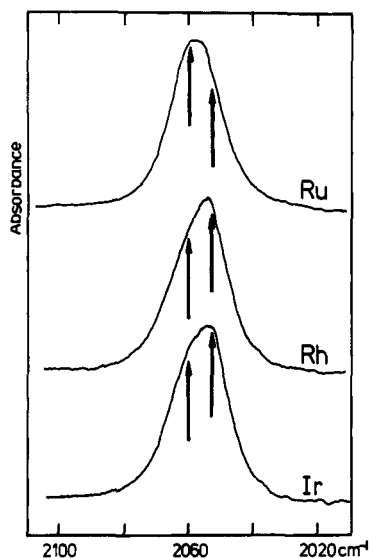


Fig. 11. $\nu(\text{CN})$ region of the ir spectra of Ru(III), Rh(III), Ir(II) thiocyanates in liq. NH_3 at 293K. The arrows mark the positions of underlying bands.

The only reasonable assignment of these bands is to outer-sphere interactions. It is tempting to attribute the two bands resolved from the spectra of the $\text{Ni}(\text{SCN})_2$ solutions to two different outer-sphere species, perhaps to 1:1 and 2:1 outer-sphere complexes respectively. A less likely explanation is that different orientations of the SCN^- ligand exist so that either the N- or the S- of the SCN^- ligand can lie nearest to the hexaamminenickel(II) cation.

Structurally a thiocyanato- outer-sphere complex of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ must be different from that of $[\text{Ni}(\text{NH}_3)_6]^{2+}$. For Pt(II) solutions the main feature close to 2060cm^{-1} indicates that free SCN^- is the principal species in solution. Outer-sphere complexation is weaker still in Pd(SCN)₂ solutions, and the stability order, Ni(II) > Pt(II) > Pd(II) is established. These interactions must be very weak because, with the introduction of K^+ ions, the spectrum invariably reverts to that of a simple ion-paired KNCS solution. Qualitatively the stability constants for outer-sphere complexation of these 3 transition metal cations are so low that $\text{K}^+ \cdot \text{NCS}^-$ ion pairing is favoured.

Ruthenium(III), Rhodium(III) and Iridium(III)

SCN⁻ does not enter the inner-spheres of the stable hexaamines of Ru(III), Rh(III) and Ir(III), but bands in the infrared, to both the high and low frequency sides of 2060cm⁻¹ ('free' SCN⁻), indicate the existence of more than one species involving SCN⁻; Fig. 11. We propose that outer-sphere complexation occurs with all 3 metal ions. Although the band separations are about twice as large as those for Ni(II), Pd(II) and Pt(II) thiocyanates, the shifts in frequency of the components from 2060cm⁻¹ are much too small to be attributed to inner-sphere coordination. Because the hexaamines of Ru³⁺, Rh³⁺ and Ir³⁺ are well known as extremely stable inner-sphere complexes. The larger band separations for the Ru(III), Rh(III) and Ir(III) cations, compared with Ni(II), Pd(II) and Pt(II), must simply reflect the greater perturbation of the $\nu(\text{CN})$ stretching frequencies in the outer sphere complexes by the higher cation charges.

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