Spectrochemistry of Solutions. Part 19.[1] Complexation of Gold(I) by Cyanide in Liquid Ammonia: an Infrared and Raman Spectroscopic Study

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Complexation of Au$^{\mathrm{I}}$ by CN$^-$ in liquid ammonia is different from Ag$^{\mathrm{I}}$ with which a large number of complexes and ion pairs occur. Like the aqueous system, ligation passes through AuCN and stops at the linear species $[\mathrm{Au(CN)_2}]^-$. Frequencies in the i.r. and Raman spectra of these species in ammonia solution have been assigned. Raman spectra of the solution with $[\mathrm{CN^-}]/[\mathrm{Au^I}] = 1$ between 220 and 300 K indicate that both the free energy and entropy changes of the second complexation step are low, pointing to the existence of AuCN in ammonia as linear $(\mathrm{H_3N})\mathrm{Au(CN)}$.

We have previously reported on the complexation of silver(I) by cyanide in liquid ammonia by both Raman spectroscopy[2] and by complexometric titrations.[3] The Ag$^{\mathrm{I}}$–CN$^-$ system in ammonia is interesting because of the many complexes and ion pairs which occur in its equilibria (at least 12), and because of the difference from its aqueous counterpart.[4,5] This report on the ligation of gold(I) by cyanide, part of the continuing study of complexation of cations in liquid ammonia,[2,3,6,7] illustrates distinct differences between the Au$^{\mathrm{I}}$–CN$^-$ and the Ag$^{\mathrm{I}}$–CN$^-$ systems. Both systems can be studied in ammonia through all their complexation steps because of the solubility of the 1:1 complexes. Unlike water and other protonic solvents AgCN and AuCN are soluble in ammonia because of the higher enthalpies of ammoniation of their cations.

In this work we have used experimental techniques recently established to obtain i.r. spectra of electrolytes dissolved in ammonia to advantage.[1] All our previous work on ammonia solutions relied entirely on the Raman method as the source of vibrational spectroscopic data. Now the complementary use of i.r. spectra provides greater confidence in interpretation.

Experimental

Raman spectra of solutions in round glass tubes (internal diameter 3 mm) were obtained, by multiple scanning and coaddition on our modified Coderg PHO Raman spectrometer,[8] using settings to maximise signal/noise ratios. The techniques for obtaining i.r. spectra of solutes at ambient temperatures in liquid ammonia with high photometric accuracy and high signal/noise ratios are presented elsewhere.[1] Curve resolutions and derivative spectra were obtained from the digitised data as previously described[9–11] for Raman spectra.

Solutions were prepared by condensing pure ammonia onto weighed mixtures of AuCN–NaCN and AuCN–NaCN–$\mathrm{NaClO_4}$. Sodium cyanide, recrystallised from liquid ammonia to remove hydroxide, carbonate, and cyanate, was used as the source of CN$^-$ because it is more soluble than KCN. Cation/ligand ratios and solution concentrations are expressed as $S = [\mathrm{CN^-}]/[\mathrm{Au^I}]$, and R = (moles $\mathrm{NH_3}$)/(moles Au).

As ammonia was condensed onto AuCN the colour of the solid changed from yellow to white as the Au cations became co-ordinated by $\mathrm{NH_3}$ molecules in the solid phase. At first this solid appeared to be insoluble in ammonia, but it is the rate of solution which is slow. When a solution of R = 300 has been established it can be cycled between 300 and 200 K without crystallisation.

Infrared spectra were obtained of yellow, solid anhydrous unammoniated AuCN, solid $\mathrm{Au(CN)(NH_3)}$ obtained by recrystallisation of AuCN from ammonia, and solid $\mathrm{Na[Au(CN)_2]}$ after recrystallisation from ammonia (Found: C, 5.00; H, 1.20; N, 12.1. $\mathrm{Au(CN)(NH_3)}$ requires C, 5.00; H, 1.25; N, 11.7%. Found: C, 5.35; N, 6.50. AuCN requires C, 5.40; N, 6.30%).

Results and Discussion

The Figure illustrates the i.r. and Raman spectra of solutions at $S = 1$ and $S = 2$, and details of the spectra obtained for solutions and solids are given in the Table.

When $S > 2$, but not when $S < 2$, the spectrum characteristic of NaCN in ammonia ($\nu_{\mathrm{max.}}$ *ca.* 2 060 cm^{-1}) appears between 2 050 and 2 090 cm^{-1}.[12] No further spectrum changes are observed when S is increased beyond $S = 2$, indicating that complexation stops at the 2:1 stage. There are no bands between 2 170 and 2 400 cm^{-1} in the spectra of any solutions, indicating the absence of species containing bridging –C–N– groups; yellow, unammoniated solid AuCN contains a band at *ca.* 2 236 cm^{-1} due to bridging –C–N–.[13]

The i.r. spectrum of the solution at $S = 1$ and $R = 340$ contains two overlapping Lorentzian bands at 2 142 and 2 152 cm^{-1} in relative intensity ratio 1:10 respectively. The Raman spectrum of the $S = 1$ solution at $R = 127$ exhibits two sharper Lorentzian bands at 2 152 (dp) and 2 158 cm^{-1} (p) in the intensity ratio 16:1. A further weak band occurs at 522 cm^{-1} ($\rho = 0.37$) in the Raman spectrum.

The spectra of the solution at $S = 2$ consist of single sharp Lorentzian bands at 2 142 (i.r.) and 2 158 cm^{-1} (p) (Raman) with a further weak band in the Raman at 291 cm^{-1} (dp). Mutual exclusion of the ν_1(CN) symmetric and the ν_3(CN) antisymmetric vibrations confirms the centrosymmetric structure of $[\mathrm{Au(CN)_2}]^-$ and makes assignment of the ν(CN) stretching frequencies obvious: $\nu_1(\mathrm{CN}) = 2\,158$, $\nu_3(\mathrm{CN}) = 2\,142$ cm^{-1}.

The band of higher intensity at 2 152 cm^{-1} in both the i.r. and Raman (dp) spectra of $S = 1$ solutions is due to the ν(CN) stretching frequency of AuCN. The bands of low relative intensities at 2 142 (i.r.) and 2 158 cm^{-1} (Raman) show that, at this stoicheiometry, the solution mixture contains $[\mathrm{Au(CN)_2}]^-$ at 5—10%.

Clearly complexation at Au$^{\mathrm{I}}$ by CN$^-$ is straightforward, involving simple two-step ligation through AuCN to $[\mathrm{Au(CN)_2}]^-$. The sharp symmetric Lorentzian bands suggest linkage isomerism to be unlikely. The fact that the band shape does not change, and no additional bands appear in the Raman spectra when excess $\mathrm{NaClO_4}$ is added with respect to $[\mathrm{Au^I}]$ up to $[\mathrm{ClO_4}^-]/[\mathrm{Au^I}] = 3.1$, confirms that ion pairing between Na$^+$ and $[\mathrm{Au(CN)_2}]^-$ is insignificant.

Complexation of Au$^{\mathrm{I}}$ by CN$^-$ in ammonia contrasts with that of Ag$^{\mathrm{I}}$ because ligation to Au$^{\mathrm{I}}$ is by a simple two-step process with no complexation beyond the 2:1 stage like that reported for the aqueous system.[4,14,15] Up to the third

Table. Spectroscopic details[a] of solutions and solids

	$\tilde{\nu}$/cm^{-1}	
	I.r.	Raman
Solutions[b]		
$S = 1.0$	2 152 (6.2) [10] 2 142 (6.1) [1]	2 152 (2.9) [16], $\rho = 0.23$ 2 158 (2.4) [1], $\rho < 0.01$ 522 (15.0), $\rho = 0.40$
$S = 2.0$	2 142 (6.5)	2 158 (3.0), $\rho < 0.01$ 291 (10.0), $\rho = 0.70$
$S = 2.80$	2 142 (6.5) 2 060[c]	2 158 (3.2), $\rho < 0.01$
$S = 4.40$	2 142 (6.5) [8] 2 060[c] [1]	
$S = 10.7$	2 142 (6.5) [1.4] 2 060[c] [1]	
Solids		
AuCN	2 236 ± 2 (12)	
$Au(CN)(NH_3)$	3 340—3 190 2 142 ± 1 (6.5) 1 323 ± 2 (25) 745 ± 3 (br) 525 ± 3 (br) 502 ± 3 (8.5) 454 ± 2 (8.0)	
$Na[Au(CN)_2]$	2 153 ± 1 (9.0) 441 ± 1 (16)	

[a] Values in parentheses are widths at half-height; values in square brackets are relative intensities; ρ = polarisation ratio. [b] $S = [CN^-]/[Ag^I]$. [c] Position of the main feature of the multicomponent spectrum characteristic of NaCN in liquid ammonia;[12] not observed when $S < 2$.

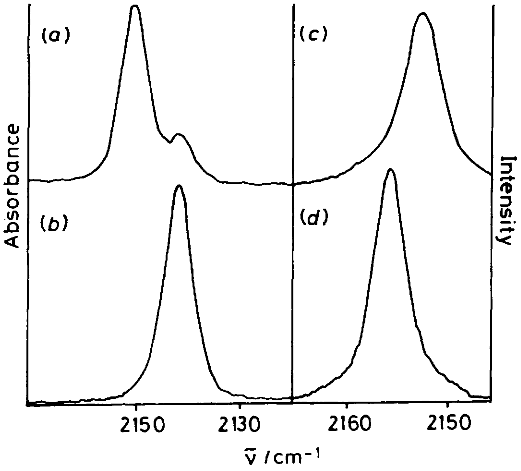

Figure. The ν(CN) frequency region of the spectra of Au^I–CN^- mixtures in liquid ammonia at 293 K: i.r. spectra of solutions at (*a*) $S = 1$ and (*b*) $S = 2$; Raman spectra of solutions at (*c*) $S = 1$ and (*d*) $S = 2$

step the Ag^I–CN^- system in ammonia can be regarded as stoicheiometrically similar to its aqueous counterpart for which 1:1, 2:1, and 3:1 species have been established and 4:1 complexes have been claimed.[16,17] However, in ammonia, there is much greater complexity. In addition to $[Ag(CN)_3]^{2-}$, all possible linkage isomers of AgCN and $[Ag(CN)_2]^-$ are found as well as the 2:2 species $Ag_2(CN)_2$ and ion pairs between the counter cation and the 3:1 complex; no 4:1 species occurs.

A further difference from the Ag^I–CN^- system concerns the solvent frequency shifts observed for the ν(CN) vibrations of $[Au(CN)_2]^-$. For $[Ag(CN)_2]^-$ there is no solvent frequency shift between ammonia and water. In water the ν(CN) stretching frequencies for $[Au(CN)_2]^-$ were reported as follows: $\nu_1(CN) = 2\,164$, $\nu_3(CN) = 2\,145$ cm^{-1}.

A low-intensity depolarised (dp) feature due to the $\nu_5(CN)$ bending vibration of $[Au(CN)_2]^-$ is found at 291 cm^{-1} in the Raman spectrum of the $S = 2$ solution. Our attribution of this concurs with that of Jones[14,15] for the depolarised band at *ca.* 300 cm^{-1} obtained from concentrated aqueous solutions of $K[Au(CN)_2]$. We also find a band of low intensity at 522 cm^{-1} ($\rho = 0.4$) in the Raman spectrum of the $S = 1$ solution which may be due to the ν(Au–N) stretching frequency of NH_3 co-ordinated to AuCN.

Recrystallisation of AuCN from liquid ammonia produces a white 'monoammoniate,' $Au(CN)(NH_3)$. Like $AuCl(NH_3)$ this is probably linear.[18] Its i.r. spectrum contains at least three overlapping bands between 3 340 and 3 190 cm^{-1} in the ν(NH) stretching region, and a band at 2 142 cm^{-1} due to its ν(CN) stretching vibration. Further bands occur at 1 323 (due to the $\delta_{sym.}$ deformation mode of co-ordinated ammonia) and 525 cm^{-1} (close in frequency to the band at 522 cm^{-1} in the Raman spectrum of the $S = 1$ solution). The similarity between the spectra of the solid ammoniate and the $S = 1$ solution points to the existence in solution of AuCN as a linear monoammoniated uncharged complex. Unassigned weak bands appear also at 502 and 454 cm^{-1} in the i.r. spectrum of this solid ammoniate.

The i.r. spectrum of solid $Na[Au(CN)_2]$, recrystallised from ammonia, contains bands at 2 153 cm^{-1} due to the $\nu_3(CN)$ stretching vibration, and 441 cm^{-1} due to the $\nu_4(Au–C)$ antisymmetric stretching vibration; Jones[4,19,20] reported frequencies in the i.r. spectra of solid $K[Au(CN)_2]$ at 2 140 and 427 cm^{-1}.

The relative intensities of the two component bands of the Raman spectra of the $S = 1$ solution remain unchanged when the temperature is changed between 293 and 220 K. Hence the free energy change, ΔG, for the complexation step (1) is nearly

$$Au(CN)(NH_3) + CN^- \longrightarrow [Au(CN)_2]^- + NH_3 \quad (1)$$

constant over this temperature interval. It is also clear from this observation that ΔH is near zero and ΔS is small. In the corresponding step for the Ag^I–CN^- system in ammonia a large positive ΔS (due mainly to translational entropy change) reflects the geometry change between tetrahedral co-ordination by three NH_3 groups and one CN^- in the 1:1 complex, and linear co-ordination by two CN^- groups in the 2:1 complex: equation (2).

$$Ag(CN)(NH_3)_3 + CN^- \longrightarrow [Ag(CN)_2]^- + 3NH_3 \quad (2)$$

Thus there is good supporting evidence that AuCN exists in ammonia as a linear 1:1:1 ammoniate because replacement of the ammonia ligand by CN^- in linear $(H_3N)Au(CN)$ to form linear $[(NC)Au(CN)]^-$ will only involve a small translational entropy change.

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