The Structures in Aqueous Solution of Pentacyanonickelate(II) and Pentacyanocobaltate(II) Ions

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The Raman spectra (2000—2200 cm^{-1}) of aqueous solutions of $[M(CN)_5]^{3-}$ (M = Ni or Co) together with complementary i.r. data suggest that both anions have a square-based pyramidal arrangement of cyanide ligands.

A RECENT crystal structure determination of the salt $[Cr(en)_3][Ni(CN)_5],1\frac{1}{2}H_2O$ showed that two different structural types of anion were present in equal proportions: the square-based pyramid (C_{4v}) and the trigonal bipyramid (D_{3h}).[1] It is of interest to establish whether this situation continues in solutions containing $[Ni(CN)_5]^{3-}$; i.r. data suggest [2] the C_{4v} structure, but the evidence was not conclusive since two of the three expected bands were obscured. Raman spectroscopy provides an excellent method for studying structures in aqueous solution, and in the cyanide stretching region (2000—2200 cm^{-1}) the bands are strong, sharp, and not subject to interference from solvent modes. Raman and i.r. spectra, used together, should be able to distinguish between the two most likely structures: for C_{4v}, square-based pyramid, we expect four CN stretches $[(2A_1 + B_1 + E)$; all Raman active with the A_1 modes polarised and the other depolarised; three i.r. bands are expected $(2A_1 + E)$ coincident with their Raman counterparts]; for the trigonal bipyramid, D_{3h}, there should again be four CN stretches but with quite different selection rules $[(2A_1' + A_2'' + E')$; Raman modes are $(2A_1' + E)$ with A_1' polarised and E depolarised; the two i.r.-active modes will be $(A_2'' + E')$, only one coincident with a Raman mode $E']$.

The Raman spectra of solutions of $Na_2[Ni(CN)_4]$ in sodium cyanide were studied in the 2000—2200 cm^{-1} range, with the CN : Ni ratio varying from 4 : 1 up to 100 : 1. As this ratio increases the two Raman bands due to $[Ni(CN)_4]^{2-}$ at 2148 (polarised) and 2139 cm^{-1} (depolarised) drop in intensity and four new Raman bands appear (at 2130, 2117, 2106, and 2090 cm^{-1}) which become stronger relative to the $[Ni(CN)_4]^{2-}$ modes; the free CN^- stretch at 2081 cm^{-1} also of course increases with increasing CN : Ni ratios. These four new bands must be associated with $[Ni(CN)_5]^{3-}$ since this is the only major species other than $[Ni(CN)_4]^{2-}$ and CN^- present in the solutions; [2] the appearance of four rather than three bands together with their i.r. counterparts (see Table) is consistent with C_{4v} symmetry rather than D_{3h} for $[Ni(CN)_5]^{3-}$. These spectra are not, of course, able to tell us whether the ion is aquated in solution to $[Ni(CN)_5(H_2O)]^{3-}$; this latter complex would have the same C_{4v} symmetry. No useful information is provided by the low-frequency Raman spectra (300—700 cm^{-1}) since overlapping of the broader Ni–C stretching and Ni–C–N bending modes makes assignment very difficult. The possibility that the C_{4v} and D_{3h} forms coexist in the solution as in the solid cannot be absolutely excluded, but it is highly unlikely; the spectra of the solutions and of the solid are very different, and it would be necessary to invoke several coincidences of bands to explain the spectra on the basis of such a mixture.

Assuming C_{4v} symmetry for $[Ni(CN)_5]^{3-}$ we may assign the strong polarised Raman mode at 2130 cm^{-1} to the symmetric stretch of the equatorial cyanide ligands; the corresponding i.r. mode is the weak one at 2123 cm^{-1}. The other polarised Raman mode at 2090 cm^{-1} is presumably the A_1 mode for the axial ligand (i.r. 2083 cm^{-1}); this is expected to be weaker than the equatorial one since the latter involves the stretching of four ligands. The strong i.r. band at 2112 cm^{-1} is clearly the asym-

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[1] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.

[2] J. S. Coleman, H. Petersen, and R. A. Penneman, *Inorg. Chem.*, 1965, **4**, 135; R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 1963, 2266.

metric CN stretch (E) with a weak and depolarised Raman counterpart at 2106 cm^{-1}, and this leaves the fourth depolarised Raman mode at 2117 cm^{-1} as the B_1 mode (i.r.-inactive). Although a case could be made for reversing the assignments of the 2117 and 2106 Raman bands, the sequence A_1 (equatorial)–B_1–E–A_1 (axial) for decreasing CN frequencies is found for the CO frequencies in $Re(CO)_5X$ (X = Cl or Br)[3] and $Mn(CO)_5X$ (X = Cl, Br, and I); the relative Raman and i.r. intensities are similar for $[Ni(CN)_5]^{3-}$ and $Mn(CO)_5Br$[4] for which Raman and i.r. solution data are also available, so we propose that the 2117 cm^{-1} Raman band is of the B_1 type.

Vibrational spectra for $[Ni(CN)_5]^{3-}$ and $[Co(CN)_5]^{3-}$ ions

Mode	$[Ni(CN)_5]^{3-}$ aq.		$[Cr(en)_3][Ni(CN)_5]$ (solid)		$[Co(CN)_5]^{3-}$ (aq. methanol)	
(assignments for C_{4v} symmetry)	Raman	I.r.[a]	Raman	I.r.	Raman	I.r.[b]
A, (Raman, pol; ν_{CN} (equatorial)	2130 (10)p[c]	2123w	2136 (10)	2123vs[d]	2115 (10)p	2105m
B_1 (Raman, dp)	2117 (1) dp		2114 (½)		2110w	
E (Raman, dp; i.r.)	2106 (1) dp	2112vs	2106 (1)	2111vs[d]	2096 (½) dp	2095vs,b
A_1 (Raman, pol; i.r.) ν_{CN} (axial)	2090 (2) p	2083w	2087 (1)	2095m	2080 (1) p	2085m

Other strong bands for solid $[Cr(en)_3][Ni(CN)_5]$: Raman 2147 (8); 2124 (2); 2078 (½); I.r. 2140s, 2079w.

[a] Ref. 2. [b] Ref. 5. [c] Relative Raman intensities in parentheses. p = Polarised, dp = depolarised. Frequencies in cm^{-1}. [d] Complex splitting of this band found under high resolution.

The vibrational spectra of solid $[Cr(en)_3][Ni(CN)_5]$ are complex since both C_{4v} and D_{3h} anions are present, but by assuming that there is not a large shift between solid and solution frequencies for the C_{4v} anion we may provisionally assign the 2147, 2124, and 2078 Raman bands of this salt to the two A_1' and E modes of the D_{3h} anion respectively, the i.r. modes at 2140 and 2079 being perhaps the A_2'' and E' modes. A factor group analysis for the anion shows that 10 Raman-active (A_g,B_g) and 10 i.r.-active (A_u,B_u) CN stretches could arise for the solid; hence the complexity of the spectrum and the lack of coincidences of some Raman and i.r. bands.

We similarly assign the Raman spectra of $[Co(CN)_5]^{3-}$ solutions which also exhibit four bands; since the i.r. spectrum of the solution shows only one broad band at 2095 cm^{-1}[5] and it is difficult to obtain good Raman spectra the assignments are necessarily more tentative. It is clear from recent electronic and e.s.r. studies[6] that $[Co(CN)_5]^{3-}$ is square-based pyramidal in solution (possibly with some slight distortion); the evidence from that work[6] and also from kinetic evidence[7] is that in solution there is no solvent molecule to complete the octahedron.

EXPERIMENTAL

Sodium tetracyanonickelate(II) was made from stoicheiometric quantities of nickel and sodium cyanides and recrystallised; the $[Ni(CN)_5]^{3-}$ solutions were then made up from this salt and sodium cyanide solutions to give CN : Ni ratios of 4 : 1 to 100 : 1. The optimum ratio for observation of the Raman spectra is 40 : 1. The salt $[Cr(en)_3][Ni(CN)_5]$ was made as described in the literature.[8] Solutions of $[Co(CN)_5]^{3-}$ were made from pure $Na_6[Co_2(CN)_{10}]$ in an inert atmosphere in pure methanol or methanol–water (1 : 1), and the Raman spectra were run as quickly as possible in short repetitive scans.

Raman spectra were measured on a Cary 81 spectrophotometer equipped with a CRL 52MG mixed gas (krypton–argon) laser; yellow excitation at 5648 Å was used for the nickel solutions and green excitation at 5145 Å for cobalt. The Raman spectrum of solid $[Cr(en)_3][Ni(CN)_5]$ was run on the red 6471 Å line: i.r. spectra were measured in Nujol mulls on a Perkin-Elmer 325 instrument.

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