trolled. In this case the relative abundances in the reaction mixture might not reflect the relative thermodynamic stabilities of the complexes. The stability difference between the two forms could be measured if equilibrium were established. This would require inverting the coordinated amino acid. Inversion might occur in highly basic solution where hydroxide ions would remove protons from both the secondary N and α-carbon atoms of the amino acid. Unfortunately base-catalyzed hydrolysis of the amino acid preceded inversion. Hence the amino acid moiety is cleaved from the complex before inversion occurs.[4]

Recently, however, Yoshikawa[20] was able to measure the free energy difference between these two isomers by equilibration on activated charcoal and found the L-β_2-*RRS* isomer to be more stable than the D-β_2-*SSS* isomer by only 1.3 kcal/mol. This small energy difference is consistent with the conclusions based on the isomer geometries determined by X-ray analysis.

Acknowledgments.—The authors wish to thank Drs. A. M. Sargeson and D. A. Buckingham for their advice throughout this work and Dr. B. M. Foxman for helpful suggestions. We are also grateful to Dr. M. Sterns for kindly making her single-crystal X-ray camera facilities available to us. The calculations were carried out on the CDC 3200/3600 computers of the CSIRO Division of Computing Research in Sydney and Canberra and on an IBM 360/50 computer at the Computing Centre, Australian National University. The programs used for these calculations have been described in a previous publication.[6] The diffraction data were recorded on an automated diffractometer operated under Grant 65/15552 from the Australian Research Grants Committee.

(20) Professor S. Yoshikawa, private communication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540,
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On the Structure of $Ni(CN)_5^{3-}$. Raman, Infrared, and X-Ray Crystallographic Evidence[1a]

BY ARISTIDES TERZIS,[1b] KENNETH N. RAYMOND,[1c] AND THOMAS G. SPIRO*[1b]

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A single-crystal X-ray diffraction analysis has shown that in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ (tn = 1,3 propanediamine, space group *Pbca* with $a = 23.497$ (6), $b = 13.306$ (4), $c = 14.402$ (4) Å), the $Ni(CN)_5^{3-}$ anions are exclusively square pyramidal. The cyanide stretching bands of this complex have been assigned in the Raman and infrared spectra. Crystals of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$, which have previously been shown to contain both square-pyramidal and distorted trigonal-bipyramidal $Ni(CN)_5^{3-}$ units, give complicated spectra in the cyanide stretching region, which, however, simplify dramatically when the crystals are dehydrated: one set of bands disappears while the other set remains essentially unaltered. This latter set is attributable to square-pyramidal $Ni(CN)_5^{3-}$, while the former set is consistent with the distorted trigonal-bipyramidal units, which evidently convert to square-pyramidal geometry on dehydration of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. For $Ni(CN)_5^{3-}$ in aqueous solution the Raman and infrared evidence favors a square-pyramidal structure.

Introduction

One of the intriguing structural problems in inorganic chemistry is presented by the complex anion $Ni(CN)_5^{3-}$. That $Ni(CN)_4^{2-}$ adds a fifth ligand in concentrated aqueous cyanide solutions was demonstrated by the extensive spectrophotometric studies of Coleman, Petersen, and Penneman.[2] In the context of the rapid development of the field of pentacoordination, the fact that $Ni(CN)_5^{3-}$ remains among the few known complexes with five identical nonchelated ligands[3] lends considerable significance to the question of its structure.

Coleman, Petersen, and Penneman themselves favored a square-pyramidal structure based on a count of the infrared bands in the cyanide stretching region.[2] Recently Raymond and Basolo[4] obtained the first crystalline salts of $Ni(CN)_5^{3-}$ using $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ (en = ethylenediammine) as the counter ions. An X-ray diffraction study of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ was carried out by Raymond, Corfield, and Ibers,[5] who found that the unit cell contains *both* square-pyramidal and (somewhat distorted) trigonal-bipyramidal $Ni(CN)_5^{3-}$. They concluded that the energy difference between the two geometries is exceedingly small. When $Cr(tn)_3^{3+}$ (tn = 1,3-propanediamine) is the counterion, only square-pyramidal

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(1) (a) This investigation was supported by grants from the Public Health Service (National Institute of General Medical Sciences) and by the National Science Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund for partial support of this research. (b) Princeton University. (c) University of California.

(2) J. S. Coleman, H. Petersen, Jr., and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965).

(3) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(4) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 949 (1966).

(5) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

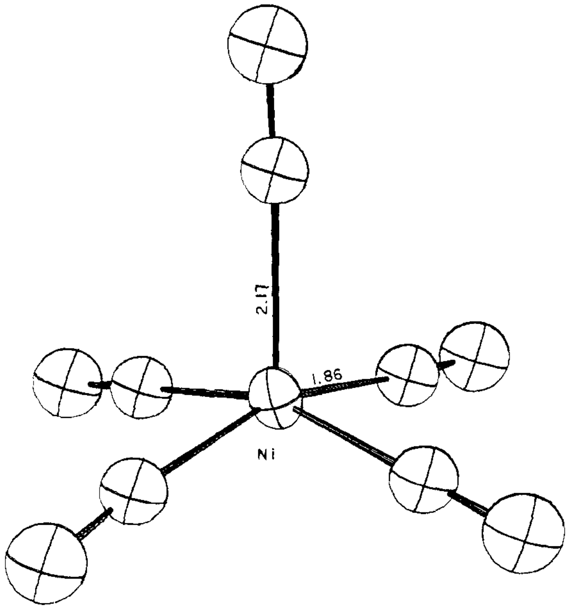

Figure 1.—A perspective drawing of the square-pyramidal $Ni(CN)_5{}^{3-}$ ion in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$. The shapes of the atoms represent 50% probability contours of the thermal motion.

$Ni(CN)_5{}^{3-}$ is found in the crystal as shown by an X-ray structure determination,[6] the results of which are reported herein.

We present also the results of a Raman and infrared study of $Ni(CN)_5{}^{3-}$ in solution and in $Cr(en)_3{}^{3+}$ and $Cr(tn)_3{}^{3+}$ crystalline salts. Acquisition of Raman spectra for these yellow and red materials was made possible by the use of He–Ne laser excitation.

Results and Discussion

$[Cr(tn)_3][Ni(CN)_3]\cdot 2H_2O$.—Large, red crystals of orthorhombic habit were obtained from aqueous solution. The space group and preliminary cell constants were obtained from precession and Weissenberg photographs (Mo Kα radiation). The systematic absences $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$, with *mmm* Laue symmetry favor the centric space group *Pbca*. The observed density (flotation) is 1.47 g/cm³. That calculated for eight formula units in the cell is 1.47 g/cm³. Accurate cell constants were determined by least-squares refinement of diffractometer setting angles and gave $a = 23.497$ (6), $b = 13.306$ (4), and $c = 14.402$ (4) Å.[4] Intensity data were collected by the θ–2θ scan technique on a four-circle computer-controlled diffractometer (Picker, FACS-1) and reduced to values of F^2. The structure was solved by direct methods and subsequent least-squares refinements and Fourier difference syntheses.[7]

For isotropic correction of thermal motion, the refinement for 1827 independent reflections above $\sigma(F^2)$ gives weighted and unweighted agreement factors (based on F) of 6.2 and 6.9%, respectively.

The $Ni(CN)_5{}^{3-}$ ion in this salt is virtually a perfect square pyramid (Figure 1) and identical with that previously observed in the $Cr(en)_3{}^{3+}$ salt.[5] All four of the basal Ni–C bond lengths are equal to within experimental error. The average basal Ni–C bond length is 1.86 (1) Å. The apical Ni–C bond length is 2.17 (2) Å. The C–Ni–C angles for opposite basal cyanides are 161.6 (6) and 162.0 (6)°. A comparison of these values and those for the square-pyramidal ion in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ is given in Table I.

TABLE I

COMPARISON OF SQUARE-PYRAMIDAL $Ni(CN)_5{}^{3-}$ GEOMETRIES

	$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$[a]	$[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$[b]
Av basal Ni–C bond, Å	1.86 (1)	1.86 (1)
Apical Ni–C bond, Å	2.17 (1)	2.17 (2)
Basal C–Ni–C angles (trans), deg	159.3 (5)	161.6 (6)
	159.7 (5)	162.0 (6)

[a] Reference 5. [b] Reference 6.

In C_{4v} symmetry four cyanide stretching modes are expected, classified as $\Gamma_{CN} = 2\ A_1 + B_2 + E$. All are Raman active and the A_1 and E modes are infrared active as well. Some qualitative intensity arguments can be made from the form of the normal coordinates, illustrated in Figure 2. Of the two A_1 modes, one involves the apical cyanide primarily, while the other is essentially the breathing mode of the basal cyanides. In the Raman spectrum the latter should be more intense than former, by roughly a factor of 4, since it involves four cyanide groups vibrating in phase. In the infrared spectrum, on the other hand, the apical cyanide mode should have appreciable intensity whereas the basal cyanide breathing mode should be quite weak. If the basal cyanides were coplanar with the nickel atom and in the absence of potential coupling with the apical C–N and Ni–C modes, the breathing mode would have zero intensity in the infrared spectrum. Similarly the E mode, which involves asymmetric stretching of the basal cyanides, should be weak in the Raman spectrum and would be absent if the basal $Ni(CN)_4$ group were square planar.

With these considerations in mind, we can readily assign the Raman and infrared spectra, which are shown in Figures 3 and 4. The strongest Raman band, at 2127 cm^{-1}, is clearly the basal cyanide breathing mode. It is weak in the infrared spectrum. The strongest infrared band, at 2100 cm^{-1}, is assigned to the E mode. It shows evidence of splitting, attributable to the site symmetry (C_1) of the $Ni(CN)_5{}^{3-}$ units in the crystal lattice. This mode is quite weak in the Raman spectrum, as expected. Of the two remaining modes, at 2113 and 2076 cm^{-1}, the latter is much the stronger in the infrared spectrum and is assigned to the A_1 apical cyanide stretch. The weak infrared band at 2113 cm^{-1} is reasonably assigned to the infrared-forbidden B_2 mode, rendered active because of the site symmetry. These assignments are summarized in Figure 2.

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(6) F. A. Jurnak and K. N. Raymond, to be submitted for publication.

(7) The standard deviation in the least significant digits is given in parentheses. Programs for the PDP 8-I computer were those of Busing and Levy, used as received from the Picker Corp. In addition to local programs for the CDC 6400 computer, modifications of Zalkin's FORDAP Fourier program, Busing and Levy's ORFLS least-squares program, and Long's REL direct methods program were used.

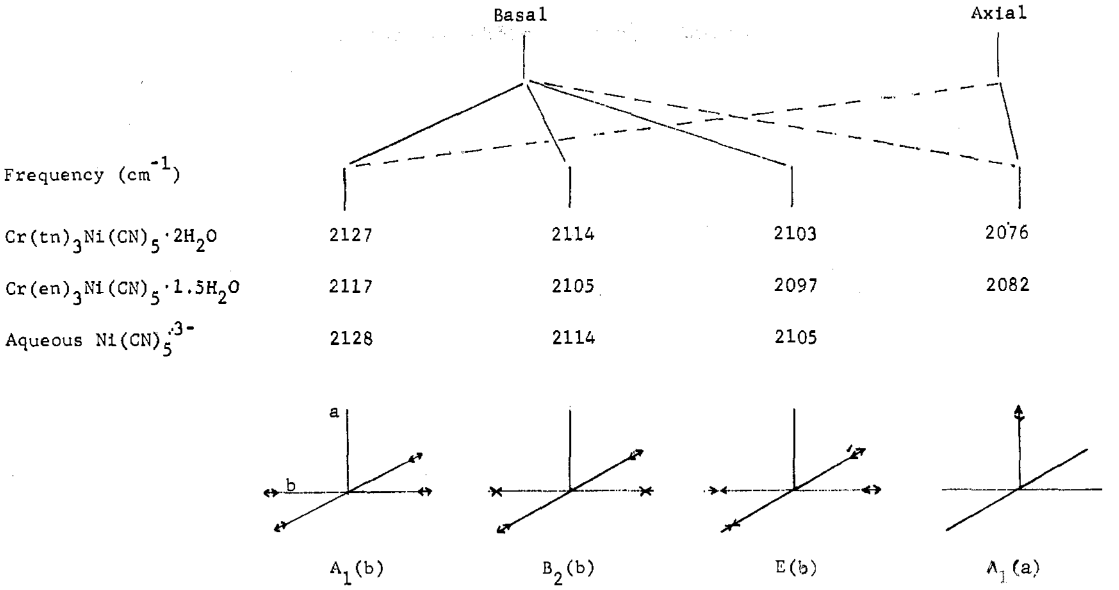

Figure 2.—Schematic representation and assignments of C–N stretching normal coordinates for square-pyramidal (C_{4v}) $Ni(CN)_5^{3-}$.

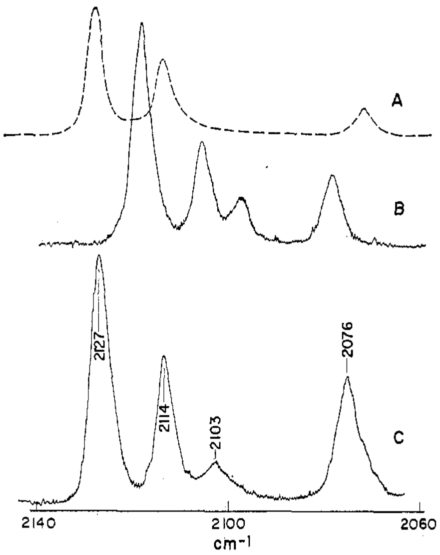

Figure 3.—Raman spectra of crystalline $Ni(CN)_5^{3-}$ species: (A) $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ (see Figure 6) after subtraction of the peaks which remain on dehydration; (B) $[Cr(en)_3][Ni(CN)_5]$ (anhydrous); (C) $[Cr(tn)_3][Ni(CN)_5] \cdot 2H_2O$.

$[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$.—This compound contains two types[5] of $Ni(CN)_5^{3-}$, one of which is square pyramidal and structurally identical with the complex found in $[Cr(tn)_3][Ni(CN)_5] \cdot 2H_2O$ (Table I). The other is roughly trigonal bipyramidal, with substantial distortion in the equatorial triangle (Figure 5). The axial Ni–C bonds are nearly collinear. The cyanide stretching region of the Raman and infrared spectra of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$, shown in Figure 6, are very complicated, as might be expected. While it might be hoped that one could select the features due to square-pyramidal $Ni(CN)_5^{3-}$ by comparison with the $[Cr(tn)_3][Ni(CN)_5] \cdot 2H_2O$ spectra, this procedure cannot be followed with confidence, since the bands are closely spaced, and frequency shifts are expected between different crystal lattices even for isostructural units. It appears, however, that decomposition of the spectra can be achieved by the simple expedient of dehydrating the sample. When the red crystals of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ are placed under vacuum, they readily lose their water of hydration and turn to a yellow powder. We confirmed that the yellow product was the dehydrated salt, as previously characterized,[4,8] by weight loss measurements and by microanalysis. The possibility that HCN was lost leaving $Ni(CN)_4^{2-}$ is excluded both by the analytical data and by the Raman and ir spectra, which differ unmistakably from those of $Ni(CN)_4^{2-}$.[9]

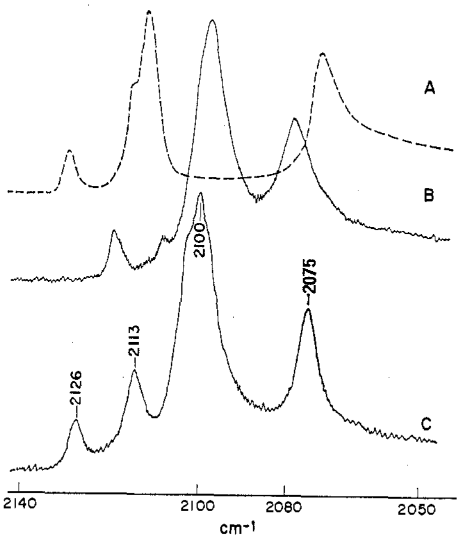

Figure 4.—Infrared spectra of crystalline $Ni(CN)_5^{3-}$ species. Labels are the same as for Figure 3.

The changes in the cyanide stretching region on dehydration of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ are dramatic

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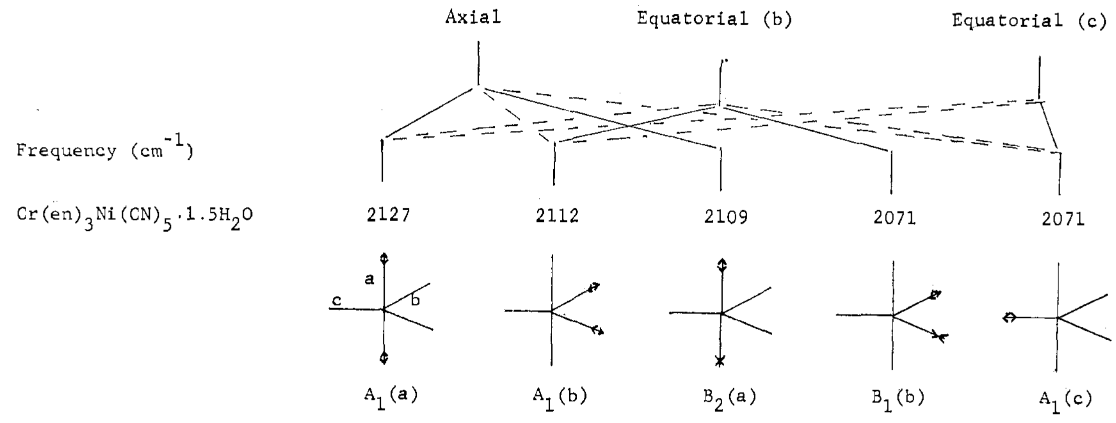
[8] W. E. Hatfield, R. Whyman, R. C. Fay, K. N. Raymond, and F. Basolo, *Inorg. Syn.*, **11**, 47 (1968); K. N. Raymond, Ph.D. Dissertation, Northwestern University, 1968.

[9] D. Jones, I. J. Hyams, and E. R. Lippincott, *Spectrochim. Acta, Part A*, **24**, 973 (1968).



Ni-C Parameters (C_{2v} averaged values, from ref. 8)

a = 1.84Å b = 1.91Å c = 1.99Å

<aa = 173° <ab = 92° <ac = 89° <bb = 141° <bc = 109°

Figure 5.—Schematic representation and assignments of C–N stretching normal coordinates for distorted trigonal-bipyramidal (C_{2v}) $Ni(CN)_5^{3-}$.

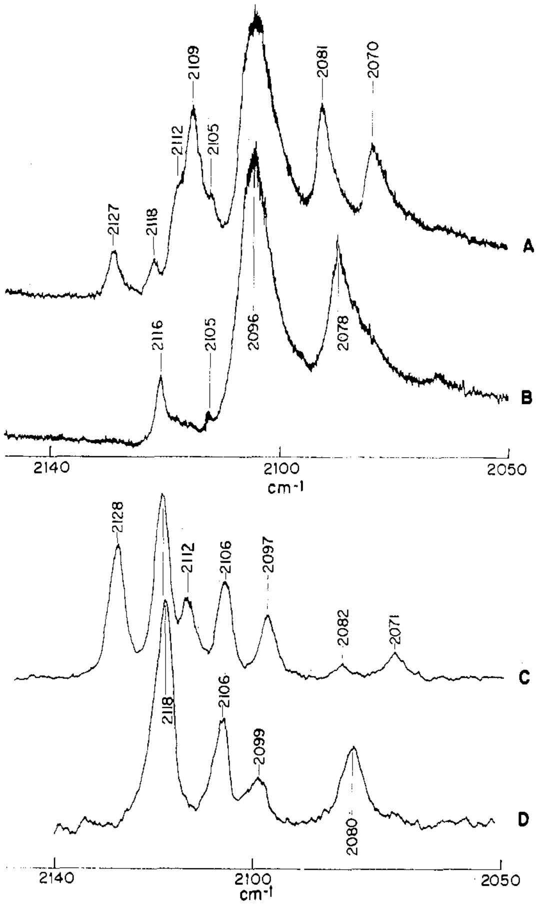


Figure 6.—Vibrational spectra of $Cr(en)_3^{3+}$ salts of $Ni(CN)_5^{3-}$: A and B, infrared spectra of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ before and after dehydration, respectively; C and D, Raman spectra of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ before and after dehydration, respectively.

and produce a marked simplification of the spectra, as shown in Figure 6. Three Raman and four infrared bands are eliminated. There are no noticeable changes in band frequencies during dehydration, except that the two lowest frequency bands appear to move slightly toward each other as the lower band diminishes. The disappearance of an entire set of bands implies a pronounced change in the $Ni(CN)_5^{3-}$ structure, and the fact that the band positions are not appreciably altered during the transformation strongly suggests that one of the two structural forms in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ is converted into the other.

The spectra of the dehydrated $Cr(en)_3^{3+}$ salt are reproduced in Figures 3 and 4 for comparison with the spectra of $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$. It is clear that, although there are significant frequency shifts, the relative intensities of both the Raman and ir features correspond very well. The same assignments are clearly applicable, and we conclude that only square-pyramidal $Ni(CN)_5^{3-}$ units are present in the dehydrated salt. The spectra of the trigonal-bipyramidal units in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ can then be obtained by subtracting the bands associated with the square-pyramidal units from the original spectra. The results are shown in Figures 3 and 4.

The distortions in the trigonal-bipyramidal structure are pronounced.[5] There are three distinct sets of Ni–C bond distances, one equatorial bond being nearly 0.1 Å longer than the other two (see Figure 5). The complex has nearly C_{2v} symmetry. One expects, therefore, three A_1 modes associated with the three different groups of cyanides, and we assign the three observed Raman frequencies to these modes.

For square-pyramidal $Ni(CN)_5^{3-}$ in $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$, the A_1 CN stretch for the basal cyanides is 50 cm^{-1} higher than for the apical cyanide, while the Ni–C distances are 0.3 Å shorter. The stretching frequency of free cyanide is shifted to higher frequency on coordination to metal ions,[10] in contrast to the behavior of carbon monoxide, and the increase in cyanide stretching frequency with increasing Ni–C bond

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(10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 166.

strength is presumably an extension of this general behavior. (An apical–basal CN interaction force constant could also force the A_1 frequencies apart, but a separation as large as 50 cm^{-1} is unlikely from this source alone.) It seems probable that the A_1 frequencies for the trigonal-bipyramidal complex also vary inversely with the Ni–C distances. Consequently we assign the highest frequency, 2127 cm^{-1}, to the symmetric stretch of the axial cyanides, which have the shortest Ni–C distances (1.84 Å). The Raman intensity for this mode is high but the ir intensity is quite low, as expected, since the axial cyanides are not far from collinearity (C–Ni–C = 173°). For the antisymmetric stretch of the axial cyanides (B_1 in C_{2v}) the intensities should be reversed, and we therefore assign the strong, noncoincident ir band, at 2109 cm^{-1}, to this mode. The lowest frequency mode, at 2071 cm^{-1}, is assigned to the unique equatorial cyanide, which has the longest Ni–C distance (1.99 Å). The middle-frequency Raman band, at 2112 cm^{-1}, is assigned to the symmetric stretch of the remaining pair of equatorial cyanides, whose Ni–C distances (1.90 Å) are intermediate. The corresponding ir band appears as a shoulder on the B_1 band and is fairly weak, consistent with a rather large (141°) C–Ni–C angle. There must be an asymmetric stretch (B_2) for this pair of cyanides, which should appear strongly in the infrared and weakly in the Raman spectrum. Since all observed bands are already assigned, we conclude that this mode must be accidentally degenerate with one of the others. It is unlikely that it is coincident with the A_1 mode of the same pair of cyanides, a condition which would require a zero interaction force constant between them. In all other cases, *e.g.*, the axial cyanides of the same complex or the basal cyanides of the square-pyramidal complexes, the frequencies for a given set of cyanides are significantly separated. A positive interaction constant requires that the B_2 mode be lower than the A_1 mode, and we suggest that the B_2 mode is coincident with the unique equatorial cyanide stretch at 2071 cm^{-1}, which is quite strong in the infrared spectrum. These assignments are illustrated in Figure 5.

Aqueous Ni(CN)$_5^{3-}$.—Raman and infrared spectra for 0.12 *M* $K_2Ni(CN)_4$ solutions saturated with KCN (7.8 *M*) are shown in Figure 7. The strong polarized Raman emission at 2082 cm^{-1} is characteristic of uncoordinated cyanide, as is the ir band at the same frequency. The weak Raman band at 2144 cm^{-1} is associated with $Ni(CN)_4^{2-}$, which is incompletely converted to $Ni(CN)_5^{3-}$ even in saturated KCN. The tetracyanide complex is probably also responsible for the weak ir band at 2123 cm^{-1} (*vide infra*). Raman and infrared spectra of aqueous $K_2Ni(CN)_4$ are included in Figure 7 for comparison.

The following features are clearly attributable to $Ni(CN)_5^{3-}$: a strong polarized Raman band at 2128 cm^{-1}, a broad depolarized Raman band centered at 2114 cm^{-1}, and a strong ir band at 2105 cm^{-1}. Coleman, *et al.*,[2] also reported two other ir bands, at 2083 and 2123 cm^{-1}, for this species and on this basis concluded that its symmetry was C_{4v} (only one ir band being expected for D_{3h} symmetry). There is some question about the authenticity of these extra bands since their observation required careful compensation for free CN$^-$ in the first case and for $Ni(CN)_4^{2-}$ in the second. Our measurements, with a cyanide excess twice that used by Coleman, *et al.*, suggest that the entire absorbance at 2123 cm^{-1} is due to $Ni(CN)_4^{2-}$. Furthermore the A_1 mode, to which this frequency would be assigned, is shown in the Raman spectrum to be 5 cm^{-1} higher.

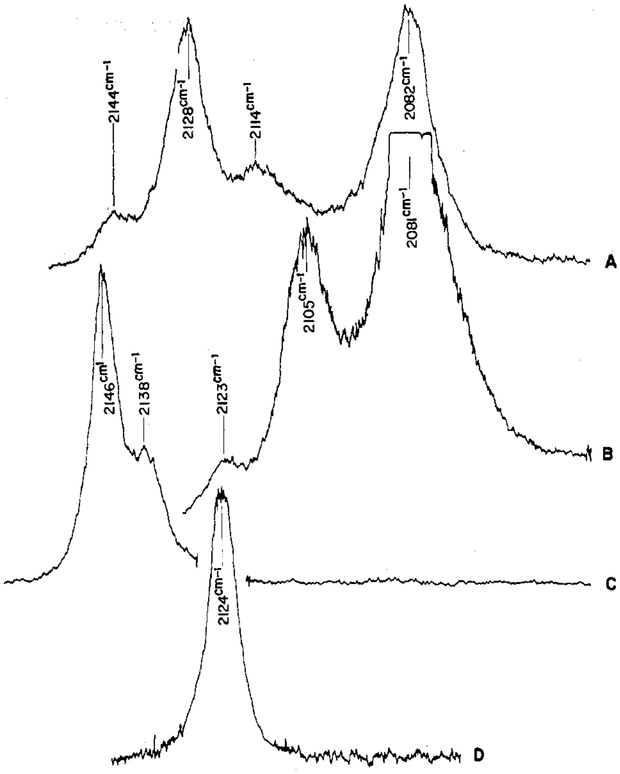

Figure 7.—Vibrational spectra of aqueous $Ni(CN)_5^{3-}$ and $Ni(CN)_4^{2-}$: A and B, Raman and infrared spectra, respectively, of $K_2Ni(CN)_4$ (0.12 *M*) in 7.8 *M* KCN; C and D, Raman and infrared spectra, respectively, of $K_2Ni(CN)_4$ in water.

In any case these extra ir bands could not exclude a *distorted* trigonal-bipyramidal structure, with ir-active A_1 vibrations, of the type found in $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. We conclude nevertheless that aqueous $Ni(CN)_5^{3-}$ is indeed square pyramidal. There is an excellent match, both in frequency and in relative intensity, with the spectra of $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$. Furthermore the observation of a *depolarized* Raman band at 2114 cm^{-1} which is missing in the infrared spectrum means that there is a nontotally symmetric mode which is ir-inactive, or nearly so. The only possible mode that fulfills these requirements is the B_2 vibration of a square pyramid (see Figure 2). All of the modes of either a regular or a distorted trigonal bipyramid would either be polarized in the Raman spectrum or have appreciable ir intensity, or both. It is of course possible that other solution structures (such as C_{2v}) exist in equilibrium with the C_{4v} structure. In this perspective the evidence favors a distribution dominated by the C_{4v} structure. Also the distribution must be narrow, or else the spectra (particularly the A_1 Raman band) would be more diffuse than is observed.

Conclusions

The cyanide stretching modes for $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$ are readily assignable on the basis of the square-pyramidal geometry for the $Ni(CN)_5^{3-}$ complex determined by single-crystal X-ray diffraction. Dehydration of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ is accompanied by conversion of the distorted trigonal-bipyramidal units, known to be present in the sesquihydrate, to square-pyramidal geometry, as deduced by comparison of the Raman and infrared spectra with those of $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$. The reason for this transformation is not apparent. The sesquihydrate crystal structure shows that both $Ni(CN)_5^{3-}$ units are hydrogen bonded to water, and there is no structural feature to suggest that one of them would be more sensitive to loss of water than the other. The spectra of the trigonal-bipyramidal complex can be obtained by subtraction of the square-pyramid spectra, and the bands can be tentatively assigned with the aid of the crystallographically determined molecular parameters.

For aqueous $Ni(CN)_5^{3-}$ three out of the four or five possible cyanide stretching modes have been observed, the remainder of the spectrum being obscured by free cyanide ion. The evidence strongly favors a square-pyramidal structure and rests on the observation of a depolarized Raman band which is missing in the infrared spectrum (consistent only with assignment of the band to the out-of-phase symmetric stretch (B_2) of the basal cyanides of a square pyramid) and on the excellent correspondence with the spectra of $[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$.[10a]

Experimental Section

$K_2Ni(CN)_4\cdot H_2O$.—This salt was prepared according to Fernelius and Burbage.[11] It was dissolved in water and in saturated (7.8 *M*) potassium cyanide for the solution measurements.

$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$.—This was prepared using the method described by Raymond and Basolo.[8] Large well-formed red crystals were obtained. *Anal.* Calcd for $NiCrN_{11}C_{11}H_{24}\cdot 1.5H_2O$: Ni, 13.12; N, 34.40; C, 29.45; H, 6.02. Found: Ni, 13.27; N, 34.36; C, 29.36; H, 5.91.

Anhydrous $[Cr(en)_3][Ni(CN)_5]$.—When placed under a high vacuum at room temperature, $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ readily loses all its water. For two samples the per cent weight losses were 6.26 and 6.23, corresponding to 1.50 and 1.49 mol of H_2O per mol of salt. The yellow powder remaining analyzed well for the anhydrous salt. *Anal.* Calcd for $NiCrN_{11}C_{11}H_{24}$: N, 36.58; C, 31.35; H, 5.71. Found: N, 36.34; C, 30.99; H, 5.54.

$[Cr(tn)_3][Ni(CN)_5]\cdot 2H_2O$.—This was prepared by a method similar to that used for $[Cr(en)_3][Ni(CN)_5\cdot 1.5H_2O$.[8] Details are given in ref 6.

Spectra.—Infrared spectra were recorded with a Beckman IR-12 double-beam spectrophotometer. Solids were run as Nujol mulls. For the aqueous solutions, a liquid cell with CaF_2 windows and Teflon gaskets was used. The path length was measured by the fringe method. A matching reference cell contained water.

Raman spectra were obtained with a spectrometer[12] equipped with an He–Ne laser source (6328 Å). The scattered light was collected at 90° from the incident beam. For solutions a Perkin-Elmer multipass cell was used. The anhydrous $Cr(en)_3Ni(CN)_5$ powder and small crystals of $Cr(tn)_3Ni(CN)_5\cdot 2H_2O$ were placed between glass plates. For $Cr(en)_3Ni(CN)_5\cdot 1.5H_2O$, care was needed to prevent loss of water by heating from the laser beam. A large single crystal was used and an extra filter was inserted before the sample to reduce the intensity of the exciting radiation.

Acknowledgment.—We thank Miss Frances Jurnak for helpful discussions regarding the X-ray structure analysis.

[10a] NOTE ADDED IN PROOF.—Since submission of this article for publication, another report on the Raman spectrum of aqueous $Ni(CN)_5^{3-}$ has appeared: R. A. Spragg, H. Stammreich, and Y. Kawano, *J. Mol. Struct.*, **5**, 359 (1970). The authors inferred a trigonal-bipyramidal structure for the complex, but they did not have the advantage of detailed comparisons with crystal spectra. Their reasoning rests on the assignment of a weak Raman band at 2162 cm^{-1} (not observed by us, but our solutions were considerably more dilute in nickel than theirs) to a fundamental mode of $Ni(CN)_5^{3-}$, an assignment we are inclined to doubt. Spragg, *et al.*, acknowledged that this band is absent in the infrared spectrum of $Cr(en)_3Ni(CN)_5\cdot 1.5H_2O$, where it would be expected to appear, and the present study shows that it is absent as well in the Raman spectrum of this material.

[11] W. C. Fernelius and J. J. Burbage, *Inorg. Syn.*, **2**, 227 (1946).

[12] R. E. Miller, D. L. Rousseau, and G. E. Leroi, Technical Report Nó. 22, ONR Contract 1858(27), NR 014-203, May 1967 (available from Defense Documentation Center, Cameron Station, Alexandria, Va. 22314)