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# Study of the $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$ Equilibrium by Electronic and Vibrational Absorption Spectra; Effect of Fluoride Ion[1]

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Both the ultraviolet and infrared spectra of Ni(II) in 4 *m* KF–KCN mixtures show isosbestic points and can be fit exactly in terms of the two species, $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$. There is no evidence of formation of the hexacoordinated species $Ni(CN)_5F^{4-}$ or $Ni(CN)_6^{4-}$. The stepwise formation constant of $Ni(CN)_5^{3-}$ is 1.08 $m^{-1}$ at 25° and is independent of medium composition in KF–KCN mixtures, $\mu = 4\ m$. An ultraviolet peak assignable to $Ni(CN)_5^{3-}$ is found at 335 mμ.

Aqueous solutions containing $Ni(CN)_4^{2-}$ become an intense orange-red upon addition of excess cyanide ion. The color has been ascribed erroneously[2-4] to formation of $Ni(CN)_6^{4-}$ but is now known to be due to $Ni(CN)_5^{3-}$, one of the weakest complex species whose existence is unequivocally established.[5-7] The stepwise formation constant of $Ni(CN)_5^{3-}$ is small and increases with ionic strength, having the values: 0.19 mole$^{-1}$ l. at $\mu = 1.24$, 0.21 at $\mu = 2.5$, and 0.28 at $\mu = 4\ M$ in NaCN–$NaClO_4$ media.[5-7] As we shall show, the formation constant is dependent on the specific ions used to maintain constant ionic strength.

The color of solutions containing $Ni(CN)_5^{3-}$ is sensitive to the addition of various salts. Beck and Bjerrum recently measured changes in absorbance at 400 mμ.[8] They concluded that both KCl and KF had a specific effect on $Ni(CN)_5^{3-}$ as evidenced by increased visible absorption. The effect of fluoride was unexpectedly greater than that of chloride. However, in solutions containing only $Ni(CN)_4^{2-}$ plus halide, they found that the interaction between halide and $Ni(CN)_4^{2-}$ was in the opposite order, $I^- > Br^- > Cl^- > F^-$. Concurrent studies of infrared spectra at this laboratory had independently confirmed the effect of added NaCl.[6] In particular, substitution of $Cl^-$ for $ClO_4^-$ at constant ionic strength diminished the absorption at 2124 cm.$^{-1}$ due to $Ni(CN)_4^{2-}$ and increased the absorption at 2103 cm.$^{-1}$, the $Ni(CN)_5^{3-}$ position. The results were described in terms of formation of a new complex, $Ni(CN)_5Cl^{4-}$, which was considered to have an absorption maximum also near 2103 cm.$^{-1}$. It was recognized that these same results could also be described using the plausible alternative assumption that the formation constant of $Ni(CN)_5^{3-}$ varies with NaCl concentration at constant ionic strength.

The observations of Beck and Bjerrum suggested that $F^-$ would show either a larger specific interaction with $Ni(CN)_5^{3-}$ or cause a greater increase in the $Ni(CN)_5^{3-}/Ni(CN)_4^{2-}$ concentration quotient than does $Cl^-$. Our present study was undertaken to provide a clearer choice between the "new species" and "medium effect" descriptions. The more general interest was the understanding of complex formation in media of high electrolyte concentration.

We have continued to use infrared spectroscopy as a principal tool as in previous studies of aqueous cyanide complexes in this laboratory.[9] However, it has proved useful to supplement the infrared measurements with studies of the ultraviolet spectra, especially since

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) A. Job and A. Samuel, *Compt. rend.*, **177**, 188 (1923); *J. chim. phys.*, **40**, 247 (1943).

(3) M. S. Blackie and V. Gold, *J. Chem. Soc.*, 4033 (1959).

(4) V. Kosova and L. Cuprova, *Chem. Listy*, **52**, 1422 (1959); *Collection Czech. Chem. Commun.*, **24**, 862 (1959).

(5) R. L. McCullough, L. H. Jones, and R. A. Penneman, *J. Inorg. Nucl. Chem.*, **13**, 286 (1960).

(6) R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

(7) A. L. Van Geet and D. N. Hume, *Inorg. Chem.*, **3**, 523 (1964).

(8) M. Beck and J. Bjerrum, *Acta Chem. Scand.*, **16**, 2050 (1962).

(9) For previous infrared studies on cyanide complexes see the following: Ni(II)[5,6]; Ag(I) and Au(I)[10]; Cu(I)[11]; Tl(I)[12]; Zn(II), Cd(II), and Hg(II).[13] Fronaeus has used this technique successfully to study aqueous thiocyanate complexes.[14]

(10) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 965 (1954).

(11) R. A. Penneman and L. H. Jones, *ibid.*, **24**, 293 (1956).

(12) R. A. Penneman and E. Staritzky, *J. Inorg. Nucl. Chem.*, **6**, 112 (1958).

(13) R. A. Penneman and L. H. Jones, *ibid.*, **20**, 19 (1961).

(14) S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16**, 1447 (1962); *ibid.*, **16**, 1433 (1962).

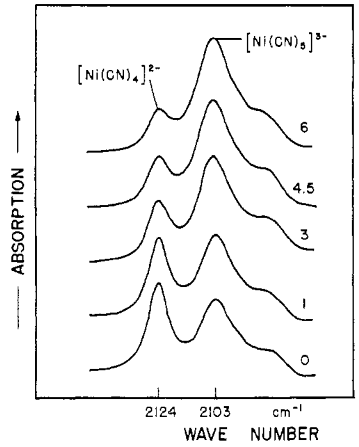

Figure 1.—Effect of KF on the infrared spectra of 0.05 *M* Ni(II) in 2 *m* KCN. The numbers with each curve refer to the KF molality.

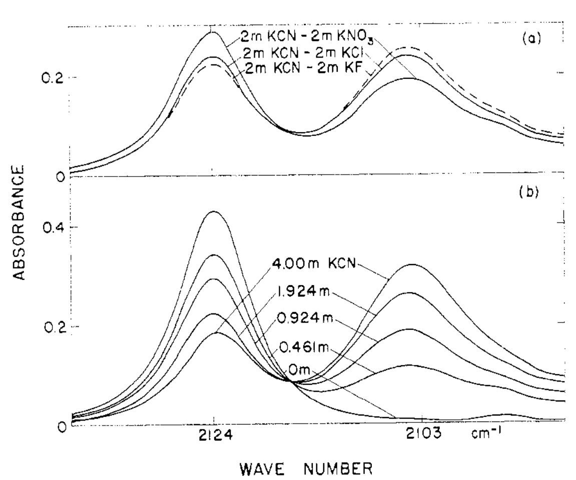

Figure 2.—Infrared spectra of 0.075 *M* Ni(II) in 4 *m* KCN–KX mixtures: (a) 2 *m* KCN + 2 *m* KX (X = $NO_3^-$, $Cl^-$, $F^-$); (b) various KF–KCN mixtures at $\mu = 4\ m$ (path length = 0.00625 cm., temperature *ca.* 30°).

absorbance measurements in the ultraviolet can be made to greater precision than is readily available in the infrared. Emphasis has also been given to measurements in the KF–KCN mixtures at constant total molality, with the absence of additional "inert" electrolyte, since medium effects may be anticipated to show the simplest functional dependence on composition under these conditions.

## Experimental

**Technique.**—Infrared spectra were recorded using a Perkin-Elmer Model 521 spectrometer. Sample and reference solutions were held between two $CaF_2$ optical flats spaced by tantalum foil in modified Perkin-Elmer "sealed liquid absorption cells." The path length of the empty cells was determined to be 62.5 μ by an interference technique.[6] The composition of the reference solutions was made the same as that of the sample solutions, except for the absence of $Na_2Ni(CN)_4$.

Ultraviolet absorption was measured using a Cary Model 14 spectrometer. Various KCN–KF mixtures were prepared by weight from 4.00 *m* stock solutions of KF and of KCN. One-half ml. aliquots of 0.120 *M* $Na_2Ni(CN)_4$ in 4 *m* KF were diluted to 50 ml. with these mixtures. Absorbance was read at each wave length directly from the recorder scales.

**Infrared Results.**—Figure 1 illustrates the striking decrease in $Ni(CN)_4^{2-}$ absorption at 2124 cm.$^{-1}$ and increase in $Ni(CN)_5^{3-}$ absorption at 2103 cm.$^{-1}$ resulting from addition of KF to Ni(II) in 2 *m* KCN (ionic strength not constant). In Figure 2a are shown spectra of 0.075 *M* $Na_2Ni(CN)_4$ in constant ionic strength solutions ($\mu = 4\ m$) containing 2 *m* KCN + 2 *m* KX (X = F, Cl, $NO_3$). The effect tending to increase the $Ni(CN)_5^{3-}/Ni(CN)_4^{2-}$ ratio is clearly in the order $F^- > Cl^- > NO_3^-$.

A series of measurements (not shown) was made at constant ionic strength ($\mu = 4$) to determine the effect of substituting halide for nitrate over the range 0–2 *m;* KCN was held constant at 2 *m* and Ni(II) was constant at 0.05 *M*. KF (or KCl) was substituted for $KNO_3$ at intervals from 0 to 2 *m*. The apparent formation constant for the reaction $Ni(CN)_4^{2-} + CN^- = Ni(CN)_5^{3-}$ increased linearly as KF (or KCl) was substituted for $KNO_3$. Fluoride had a greater effect than chloride at all concentrations.

To determine whether halide interacted with $Ni(CN)_4^{2-}$ when no excess cyanide was present, $Na_2Ni(CN)_4$ was dissolved in solutions of halide salts. In pure water, the $Ni(CN)_4^{2-}$ ion has a strong, symmetric infrared absorption at 2124 cm.$^{-1}$ with a molar extinction coefficient, ε, of $\sim 10^3$ l. mole$^{-1}$ cm.$^{-1}$ and a half-width, $\Delta\nu_{1/2}$, of 8 cm.$^{-1}$. The absorbance of the complex ion obeys Beer's law. In 4 *m* KF there is no noticeable change; in 4 *m* KCl the change in ε and $\Delta\nu_{1/2}$ is less than 1%. In 4 *m* KBr, ε decreased by 6% but was compensated by an increase in half-width so that the integrated absorption was unchanged. (The product of ε and $\Delta\nu_{1/2}$ is roughly proportional to the integrated absorption coefficient.) In 4 *m* KI, ε decreased by 10% while the half-width increased by 30%. Here, then, we have infrared evidence for specific interaction between $I^-$ and $Ni(CN)_4^{2-}$. The $Br^- + Ni(CN)_4^{2-}$ interaction is slight and the $Cl^-$ or $F^-$ interaction with $Ni(CN)_4^{2-}$ is negligible.

The KF + KCN system was investigated in a series of measurements in which spectra were taken of 0.075 *M* Ni(II) in mixtures of KF + KCN at constant molality of 4. To obtain reproducible optical density values it was found necessary to record the spectra at a very slow scan rate; about 45 min. was required to scan the region shown in Figure 2 for each solution. An isosbestic point is clearly evident near 2116 cm.$^{-1}$ in Figure 2b. Quantitative treatment of these results will be described in a later section.

**Ultraviolet Results.**—A previously unreported absorption peak at about 335 mμ arises upon addition of KCN to solutions containing $Ni(CN)_4^{2-}$. The $Ni(CN)_4^{2-}$ peak at 308.5 mμ diminishes correspondingly as shown in Figure 3. Both the infrared and ultraviolet spectra exhibit well-defined isosbestic points, that of the electronic spectra occurring at 327 mμ. Additional measurements in KF–KCN mixtures are shown in Figure 4, the filled circles corresponding to absorbance readings made directly from the recorder scale at the fixed wave lengths shown.

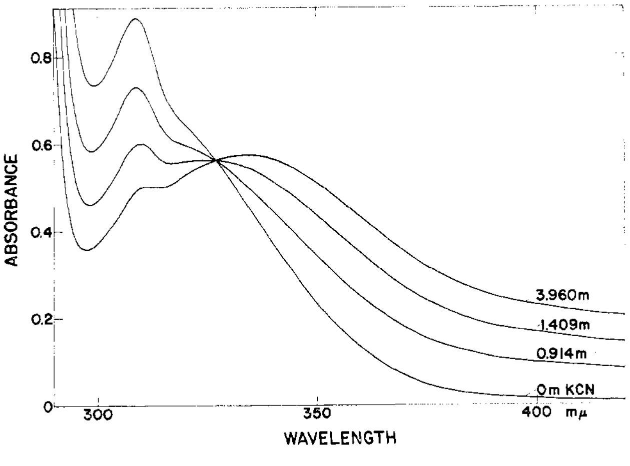

Figure 3.—Spectra of Ni(II) in 4 *m* KF–KCN mixtures (0.00120 *M* $Na_2Ni(CN)_4$, 1.00-cm. path length, 25°).

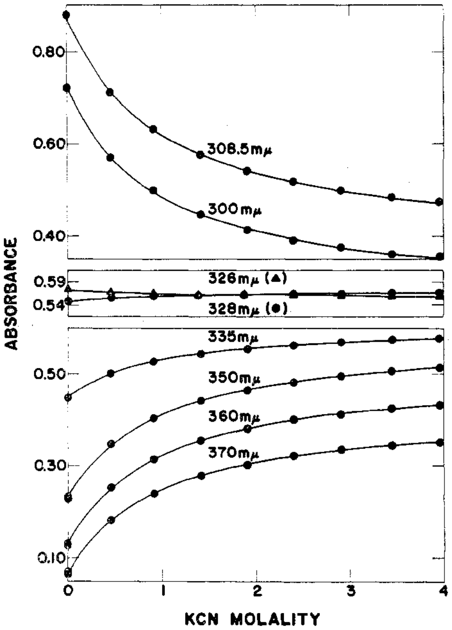

Figure 4.—Absorbance (*i.e.*, optical density) of 0.00120 $M$ $Na_2Ni(CN)_4$ at 25° in KCN–KF mixtures ($\mu = 4\ m$). Solid lines computed using eq. 5 with $K = 1.076\ m^{-1}$.

**Number of Ni-Containing Species.**—The occurrence of isosbestic points as in Figures 2 and 3 provides good evidence for the presence of only two Ni-containing species. The presence of the species $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$ has been established unequivocally in similar systems. However, plausible evidence was obtained previously[6] for occurrence of the additional species $Ni(CN)_6^{4-}$. A fourth, $Ni(CN)_5F^{4-}$, could be postulated on evidence similar to that suggesting occurrence of $Ni(CN)_5Cl^{4-}$ (see Figure 2a). The question was thus posed: Are additional species present with spectra similar to $Ni(CN)_5^{3-}$ and, indeed, with coincident extinction coefficients at the isosbestic points? More rigorous exclusion of such a possibility was desired using a test which would reveal trends in apparent extinction coefficients at wave lengths other than the isosbestic points and which would not depend on assuming invariance of any equilibrium quotients.

Such a test is provided by the relationship derived below between absorbances at arbitrary pairs of wave lengths.

Let $A_{m\lambda}$ be the absorbance of a $Na_2Ni(CN)_4$ solution at KCN concentration $m$ and wave length $\lambda$; $A_{0\lambda}$ equal the absorbance at the same $Na_2Ni(CN)_4$ concentration but [KCN] = 0, [KF] = 4 $m$; and $A_{\infty\lambda}$ equal the absorbance extrapolated to infinite KCN concentration; *i.e.*, absorbance deduced for a solution containing only the complex with the greater number of $CN^-$. Further, let $\Delta A_{m\lambda} = A_{m\lambda} - A_{0\lambda}$, and let $f_m$ be the fraction of Ni(II) present as the higher complex at KCN concentration $m$.

If only $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$ are present (or, more precisely, if the spectrum in the KF–KCN mixtures is a weighted sum of the limiting spectra described by $A_{0\lambda}$ and $A_{\infty\lambda}$), then the absorbances at wave lengths $\alpha$ and $\beta$ are given by eq. 1a and 1b.

$$A_{m\alpha} = f_m A_{\infty\alpha} + (1 - f_m)A_{0\alpha} \qquad (1a)$$

$$A_{m\beta} = f_m A_{\infty\beta} + (1 - f_m)A_{0\beta} \qquad (1b)$$

Since $f_m$ is independent of wave length, it may be eliminated, giving eq. 2.

$$\Delta A_{m\alpha}/\Delta A_{m\beta} = \Delta A_{\infty\alpha}/\Delta A_{\infty\beta} \qquad (2)$$

The right-hand side of eq. 2 is a constant independent of solution composition and is denoted by $S_{\alpha\beta}$. Equation 2 may then be rewritten

$$\Delta A_{m\alpha} = S_{\alpha\beta}\Delta A_{m\beta} \qquad (3)$$

Plots of $\Delta A_{m\alpha}$ for a particular wave length, $\alpha$, against the values of $\Delta A_{m\lambda}$ for other selected wave lengths were constructed for both the ultraviolet and infrared results. Nine different KCN–KF mixtures 0.00120 $M$ in Ni(II) were examined in the ultraviolet region and five mixtures 0.0750 $M$ in Ni(II) were examined in the infrared. Both $\Delta A_{m\lambda}$ *vs.* $\Delta A_{m\alpha}$ plots gave families of excellent straight lines intersecting at zero as required by eq. 3. In the ultraviolet, the value of $S_{\alpha\beta}$ reversed sign between 326 and 328 mμ and was indistinguishable from zero at the isosbestic point, 327 mμ. Similarly, $S_{\alpha\beta}$ reversed sign in the infrared between 2117 and 2115 cm.$^{-1}$ and was indistinguishable from zero at 2116 cm.$^{-1}$.

**Invariance of Equilibrium Quotient.**—Equation 3 can be satisfied even if $f_m$ is a very complicated function of the solution composition; *e.g.*, if the formation constant for $Ni(CN)_5^{3-}$ depends strongly on solution composition. The absorbance measurements were next tested for consistency with two more restrictive assumptions: (1) only a single equilibrium need be considered; namely, $Ni(CN)_4^{2-} + CN^- = Ni(CN)_5^{3-}$ and, further (2) that the equilibrium quotient $K$ defined by eq. 4 is *independent* of solution composition in KF–KCN mixtures of constant total

$$K = [Ni(CN)_5^{3-}]/[Ni(CN)_4^{2-}]\{CN^-\} \qquad (4)$$

molality. The braces in eq. 4 refer to concentration on a molal basis and the brackets to concentration on a volume basis. With the two above assumptions, the absorbance at each wave length and KCN concentration is given by eq. 5. Although $CN^-$

$$\Delta A_{m\lambda} = K\{CN^-\}\Delta A_{\infty\lambda}/(1 + K\{CN^-\}) \qquad (5)$$

and $F^-$ concentrations were maintained on a molal basis, the Ni concentration was maintained at constant total molarity so that the usual form of Beer's law would apply to the measured absorbances. The concentration units for the Ni-containing species cancel in eq. 4, so that $K$ is expressed in units of reciprocal molality.

The solid lines shown in Figure 4 were computed using eq. 5, taking $K = 1.076$, $A_{0\lambda}$ as the average of measurements of KCN-free solutions prepared in duplicate, and using the observed values of $S_{\alpha\beta}$ to compute the remaining values of $A_{\infty\lambda}$ from the value, 0.379, at 308.5 mμ. The excellent fit to the observed experimental points demonstrates that this equation represents the measurements in the ultraviolet region with gratifying precision. The average absolute value of the deviation between the calculated and observed results is slightly less than the estimated scale reading error of 0.001 absorbance unit. The parameters appearing above were obtained using standard numerical techniques. The interdependence of the parameters was examined graphically using normalized curves in the manner described by Sillén.[15] This method is convenient for visual estimation of uncertainties. Our best estimate of the maximum uncertainty in $K$ due to random scattering of the results is ±0.02. The measurements of Figure 2b in the infrared region were treated similarly. The cyanide concentration was corrected for the amount found in the complex. The solutions were allowed to reach a steady-state temperature (~30°) in the infrared beam. It did not prove feasible to hold the temperature at 25° for the infrared measurements. The equilibrium quotient is smaller due to the negative $\Delta H$ for this reaction. The value of the equilibrium quotient derived from the infrared measurements is $0.83 \pm 0.1\ m^{-1}$.

**$Ni(CN)_5^{3-}$ Absorption at 2124 cm.$^{-1}$.**—The ratio between $\Delta A$ at the $Ni(CN)_4^{2-}$ peak near 2124 cm.$^{-1}$ and $\Delta A$ at the $Ni(CN)_5^{3-}$ peak at 2103 cm.$^{-1}$ was found to be −0.80. This value is in excellent agreement with that observed in 4 $M$ NaCN–$NaClO_4$ mixtures.[6] The value deduced for $A_{\infty\lambda}$ at 2103 cm.$^{-1}$ is 0.410, corresponding to a molar extinction coefficient for $Ni(CN)_5^{3-}$ of 875 $M^{-1}$ cm.$^{-1}$. Using these numbers, we calculate $A_{\infty\lambda}$ = 0.100 at the position of the $Ni(CN)_4^{2-}$ peak. Similar calculations at closely spaced wave lengths in this region confirm the presence of a maximum in the absorption spectrum of $Ni(CN)_5^{3-}$ at 2123

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[15] L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).

± 3 cm.$^{-1}$. Other absorptions assignable to $Ni(CN)_5^{3-}$ vibrations primarily involving CN stretching include the prominent peak at 2103 cm.$^{-1}$ and a peak (which appears as a well-defined shoulder on the 2103 peak) near 2083 cm.$^{-1}$.

## Discussion

In our previous infrared study of Ni(II) cyanide complexes,[6] we observed a change in apparent $Ni(CN)_4^{2-}$–$Ni(CN)_5^{3-}$ equilibrium constant on substituting NaCN for $NaClO_4$ as well as on substituting NaCl for $NaClO_4$ at fixed NaCN concentration. These effects were interpreted as resulting from formation of the hexacoordinated Ni(II) species $Ni(CN)_6^{4-}$ and $Ni(CN)_5Cl^{4-}$ with formation constants smaller than that of $Ni(CN)_5^{3-}$. However, it is now possible from quantitative treatment of the absorbance data obtained from KF–KCN mixtures to decide between higher complex formation and those effects due to changing ionic media. The new data show that two species, $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$, are sufficient to account exactly for the observed spectra. There is no evidence for higher complexes such as $Ni(CN)_5F^{4-}$ or $Ni(CN)_6^{4-}$ in the 4 *m* KF–KCN mixtures. The added finding that the formation constant of $Ni(CN)_5^{3-}$ is the same at all KF/KCN ratios ($\mu = 4m$) makes it particularly unnecessary to postulate any specific interaction between $F^-$ and $Ni(CN)_5^{3-}$. As shown by Beck and Bjerrum the effect on $Ni(CN)_5^{3-}$ is in the order $F^- > Cl^-$; this can now be shown to reside in a medium effect best described in terms of activity coefficient changes. The otherwise unusual attraction order (fluoride > chloride) for the anion, $Ni(CN)_5^{3-}$, need not be rationalized.

The spectra obtained in this study show remarkable simplicity. The extinction coefficients of each species remain constant over the full range of composition of 4 *m* KF–KCN mixtures. Re-examination of the results of earlier studies in this laboratory confirms that the $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$ extinction coefficients are not at all sensitive to medium changes despite substantial changes in the apparent association quotients. This conclusion holds both for the vibrational and the electronic spectra.

The constancy of the extinction coefficients is graphically obvious at the is osbesticpoints. Extension to other wave lengths is based on the observed linearity of $\Delta A_{m\alpha}$ *vs.* $\Delta A_{m\beta}$ plots. Use of such plots or, equivalently, use of eq. 3 has been too rarely reported in the literature; such relationships provide an important generalization from the occurrence of isosbestic points and permit more substantial test of the usual assumptions of constancy of extinction coefficients and presence of only two species.[16]

Applicability of eq. 3 does not require invariance of the equilibrium quotient. For example, the previously reported measurements of infrared absorbance of Ni(II) in $NaCN$–$NaClO_4$ mixtures[6] show substantial changes in *K* with $NaCN/NaClO_4$ ratio. However, these measurements follow eq. 3 precisely. These results do not follow eq. 5, which demands *both* two species and an invariant equilibrium constant.

Strictly speaking, adherence of the measurements to eq. 3 requires only that the absorbing species fall into two classes—those having spectra indistinguishable from $Ni(CN)_4^{2-}$ and those having spectra indistinguishable from $Ni(CN)_5^{3-}$. Since a principal conclusion of the present paper is the nonexistence of $Ni(CN)_5F^{4-}$ and $Ni(CN)_6^{4-}$, it is well to ask whether such species might have spectra nearly identical with that of $Ni(CN)_5^{3-}$. The changes in the spectrum of $Ni(CN)_4^{2-}$ upon association with $CN^-$ to form $Ni(CN)_5^{3-}$ are clear and unmistakable even though the association is weak. The appearance of new electronic and vibrational energy levels reflects the pronounced redistribution of the bonding electrons necessary to allow bonding with an additional ligand. We suggest that binding of a sixth anion in any well-defined configuration could not result in absorption spectra having the *same* extinction coefficients over a broad range of wave lengths. We believe that such a criterion for nonexistence of species should be applicable using either vibrational or electronic spectra. Use of both as in this study provides particularly convincing evidence for the absence of "outer-orbital" as well as "inner-orbital" complex species having $CN^-$ or $F^-$ bound as a sixth ligand.

The results of this study show another feature quite unexpected in its simplicity—the invariance of the equilibrium quotient. Heistand and Clearfield[17] have shown that formation of $FeCl^{2+}$ in concentrated perchlorate solutions is strongly affected by substitution of $NaClO_4$ for $HClO_4$ and appreciably affected even by substitution of $LiClO_4$ for $HClO_4$. The effect is described as a medium effect and may be expected at concentrations sufficiently high that the ionic strength principle does not hold. A similar effect was illustrated in Figure 2a of this paper resulting from substitution of KF or KCl for $KNO_3$ at a total $K^+$ concentration of 4 *m*. The effects of nitrate ions, described here as "indirect effects," are substantially different from those of $F^-$. However, in KF–KCN mixtures the expected variation of association quotient with composition vanishes. In other words, the indirect effects of $F^-$ are indistinguishable from those attributable to $CN^-$.

Certainly $F^-$ and $CN^-$ behave very differently as ligands; the nature and strength of the complex ions formed with the transition elements shows little in common between the two anions. The halogenoid character of $CN^-$ will become more evident when $\pi$-bonding is unimportant. The "indirect effects" on complex ion equilibria should be such a case. It is not surprising that substitution of $CN^-$ for $F^-$ would cause less change in the quotient *K* than would substitution of $NO_3^-$ for $F^-$. However, the invariance of the equilibrium quotient was not anticipated in KF–KCN mixtures and is, in a sense, coincidental.

The absence of complex formation between $Ni(CN)_5^{3-}$ and $F^-$, $CN^-$, or, very likely, $H_2O$ is consistent

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[16] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).

[17] R. N. Heistand and A. Clearfield, *J. Am. Chem. Soc.*, **85**, 2566 (1963).

with the findings of Adamson[18] that Co(II) in concentrated aqueous cyanide solutions is present as pentacoordinated $Co(CN)_5^{3-}$ rather than $Co(CN)_5H_2O^{3-}$. In fact, the tendency of d$^8$ ions such as Ni(II) to bind additional ligands should be even smaller than for a d$^7$ ion such as Co(II). Adamson reported the preparation of the diamagnetic salt $K_3Co(CN)_5$, earlier misidentified as $K_4Co(CN)_6$. In contrast, no Ni(II) cyanides have been isolated containing more than four $CN^-$ per Ni(II); $K_2Ni(CN)_4$ is obtained from Ni(II) solutions saturated with KCN, even though the principal species in solution is $Ni(CN)_5^{3-}$. In the case of the other d$^8$ ions, Pd(II), Pt(II), and Au(III), no complex cyanide ion higher than $M(CN)_4^{n-}$ is observed.[19]

Two chemically reasonable structures can be suggested for $Ni(CN)_5^{3-}$—a square pyramid of $C_{4v}$ symmetry and a trigonal bipyramid of $D_{3h}$ symmetry. The presence of three infrared-active CN-stretching vibrations is expected for a structure of $C_{4v}$ symmetry and excludes the bipyramidal structure.

Addition of fluoride to solutions containing $Ni(CN)_4^{2-}$ without free cyanide has negligible effect on the infrared absorption of $Ni(CN)_4^{2-}$. However, iodide ion does show significant interaction with $Ni(CN)_4^{2-}$ based on the increase in integrated absorption coefficient even though no separate new peak is found. This parallels the findings of Bjerrum and Beck,[8] who showed that of the halides, iodide causes the greatest increase in the visible absorption of $Ni(CN)_4^{2-}$. In this latter case, therefore, there is evidence for iodide occupying the fifth coordination position.

[18] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

[19] L. H. Jones, J. M. Smith, and R. A. Penneman, unpublished work at Los Alamos Scientific Laboratory, 1963.

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# Near-Infrared Spectra of Some Pseudotetrahedral Complexes of Cobalt(II) and Nickel(II)

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Electronic spectra in the near-infrared region are reported for some pseudotetrahedral complexes of cobalt(II) and nickel(II) of the types $MLX_3^-$ and $ML_2X_2$, where L = quinoline, benzimidazole, triphenylphosphine, triphenylphosphine oxide, or triphenylarsine oxide, and X = Cl, Br, I, or NCS. The results are discussed in terms of the distortions of the ligand fields from $T_d$ symmetry.

## Introduction

Following the calculations of Liehr and Ballhausen[1] and the preparation during recent years of a variety of tetrahedral complexes of nickel(II), the criteria for the recognition of this type of complex have become well established. Even where the symmetry is no higher than $C_{2v}$, the observed visible spectra are in quite good agreement with the theoretical predictions for $T_d$ symmetry. During recent work on tetrahedral complexes of nickel halides with benzimidazole,[2] a study of the near-infrared spectra suggested that the $^3T_1(F) \rightarrow {}^3T_2$ transition was much more sensitive to deviations from $T_d$ symmetry. We have therefore examined the spectra in this region of a number of nickel(II) complexes with distorted tetrahedral structure. The near-infrared spectra of analogous cobalt(II) complexes have also been studied for comparison with the nickel compounds.

## Experimental

**Preparation of Compounds.**—The quinoline complexes of cobalt(II) halides were prepared by the following general method: quinoline was added to the hydrated cobalt salt in ethanol. The crystalline precipitate was filtered off, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd. for $C_{18}H_{14}Cl_2CoN_2$: C, 55.71; H, 3.64. Found: C, 55.63; H, 3.65. Calcd. for $C_{18}H_{14}Br_2CoN_2$: C, 45.31; H, 2.96. Found: C, 44.90; H, 3.46. Calcd. for $C_{18}H_{14}CoI_2N_2$: C, 37.86; H, 2.47. Found: C, 38.14; H, 2.33.

The preparation of $(C_2H_5)_4N[Ni(C_7H_6N_2)Br_3]$ and $Ni(C_7H_6N_2)_2X_2$ (X = Br, I) will be reported elsewhere.[2] The other compounds have been described previously.[3-7]

**Physical Measurements.**—Reflectance spectra were obtained with a Beckman DK2 spectrometer and X-ray powder photographs with an Enraf–Nonius Guinier–De Wolff camera No. II or with a Philips Debije–Scherrer powder camera type PW 1024.

## Results

The compounds we have studied are listed in Table I, together with the positions of their electronic absorption bands, obtained by the reflectance technique, in the near-infrared region down to 4000 cm.$^{-1}$. Most of the complexes show absorption in this region due to vibrational overtones, which were identified by comparison with the spectra of the free ligands, of the

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