422. An Infrared Study of Pentacyano-, Hexacyano-, and Chloropentacyano-nickelate(II) in Aqueous Solution.
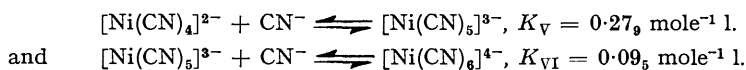
By R. A. Penneman, Ralph Bain, George Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy.

In 2M-aqueous ammonia, hexa-amminenickelate is converted quantitatively into disodium tetracyanonickelate by sodium cyanide. In the presence of an excess of sodium cyanide, the infrared absorption of the tetracyanonickelate ion at 2124 cm.$^{-1}$ is diminished and absorption from the pentacyanonickelate appears at 2103 cm.$^{-1}$. At very high free cyanide concentrations some hexacyanonickelate is formed, its absorption band being close to that position of the pentacyano-ion. Stepwise formation constants for these higher complexes were derived from quantitative infrared measurements in aqueous solution at ionic strength 4 and 25°:

$$[Ni(CN)_4]^{2-} + CN^- \rightleftharpoons [Ni(CN)_5]^{3-}, \quad K_V = 0.27_9 \text{ mole}^{-1} \text{ l.}$$

and $\quad [Ni(CN)_5]^{3-} + CN^- \rightleftharpoons [Ni(CN)_6]^{4-}, \quad K_{VI} = 0.09_5 \text{ mole}^{-1} \text{ l.}$

Corresponding values in ammoniacal (2M) solution are: $K_V' = 0.25_6$ and $K_{VI}' = 0.08_7$ mole^{-1} l.

The mixed ligand complex, $[Ni(CN)_5Cl]^{4-}$, is formed in solutions containing tetracyanonickelate, sodium cyanide, and sodium chloride. Its apparent formation constant from $[Ni(CN)_5]^{3-}$ and Cl$^-$ is 0.2_2 mole^{-1} l. The magnetic susceptibility of the products formed when cyanide reacts with tetracyanonickelate in aqueous solution have been investigated. The nature of the bonding in the penta- and hexa-co-ordinated complexes is discussed and correlated with magnetic and spectral data.

RECENTLY[1] we presented evidence for the reaction $[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$ in aqueous solution. The stepwise formation constant was found to be small, namely $K = 0.2$ mole^{-1} l. at 25° and ionic strength 1·24. The constant increased with ionic strength. The existence of this pentacyanonickel complex was shown by measurement of the absorption spectra in both the visible and the infrared region.

While our paper was in the press, two papers by Blackie and Gold [2,3] appeared, describing application of the proton relaxation technique to the study of nickel cyanide complexes in aqueous and ammoniacal solution. They interpreted their results to mean that $[Ni(CN)_6]^{4-}$ has an enormous formation constant and is formed quantitatively, to the exclusion of $[Ni(CN)_5]^{3-}$. Since their conclusions were contrary to ours, we have now investigated the $[Ni(CN)_4]^{2-} + CN^-$ equilibrium in both aqueous and ammoniacal solution, using the more accurate double-beam infrared technique.

[1] McCullough, Jones, and Penneman, *J. Inorg. Nuclear Chem.*, 1960, **13**, 286.
[2] Blackie and Gold, *J.*, 1959, 4033.
[3] Blackie and Gold, *J.*, 1959, 4037.

EXPERIMENTAL

Technique and Instrumentation.—The infrared technique involves observation of C≡N stretching frequencies in the 2000 cm.$^{-1}$ region. Optical-density measurements of cyanide complexes are made by using thin films (30—90 micron paths) of aqueous solution. Frequencies of individual cyanide complexes of a given metal are generally distinct from each other and shifted from that of the free CN$^-$ ion; examples of previous infrared work on aqueous cyanide complexes were on Ag(I) and Au(I),[4] Cu(I),[5] Tl(I),[6] Zn(II), Cd(II), and Hg(II).[7] Observation of a new infrared absorption band is unequivocal evidence for a new species.

The infrared portion of our previous study [1] was made with the single-beam Perkin-Elmer model 112 incorporating a lithium fluoride prism. The low formation constant of the penta-cyanonickelate(II) complex necessitates working at high free-cyanide concentrations. The resulting broad cyanide absorption causes some uncertainty in the optical density of the adjacent nickelate absorption. For the present study, the Perkin-Elmer model 221 instrument had become available; it incorporates a grating in the 2000 cm.$^{-1}$ region and has sufficient resolution. As a double-beam instrument it has the great advantage for this study that the absorption of water and of free cyanide ion can be cancelled by using an appropriate reference solution. Thus the absorption spectra of the nickel cyanide complexes can be displayed on a flat background, which permits considerably more precise measurements of optical density.

Reference and sample cells were similar and of the same path length. Modified Perkin-Elmer " sealed liquid absorption cells " were used. The windows were calcium fluoride optical flats separated by two-mil tantalum spacers. (The usual lead spacers were not used because of their reactivity with cyanide solutions.) When the tantalum spacers were sufficiently smooth and clean, the cells were liquid-tight.

Assembled with care, the cell windows were parallel (as determined visually by sodium-lamp interference fringes). The path length of the empty cell was found to be 62.5×10^{-4} cm. by observing the distance between interference peaks when run on the model 221 instrument.

Since the quantity of cyanide used by reaction with 0.075M-tetracyanonickelate was slight, the same concentration of sodium cyanide was used in the reference solution as in the sample. For each measurement, the cells were flushed with several volumes of the new solution.

Reagents.—The analysed hydrate, $Na_2Ni(CN)_4,3H_2O$, was prepared as previously described;[1,8] its aqueous solution was neutral. Analysed, reagent-grade sodium cyanide and aqueous ammonia were used. Solutions were made up by weight just before each measurement.

RESULTS

Infrared Measurements of Disodium Tetracyanonickelate(II) *in Water and Aqueous Ammonia.*—Aqueous solutions of this salt, with and without ammonia, were examined. Absolute positions of wavelength were determined by calibration against the spectrum of carbon monoxide which is a convenient standard for this region.[9] In 2M-ammonia, the tetra-cyanonickelate maximum at 2124 $\pm$ 1 cm.$^{-1}$ was not shifted from its position in water. This band is quite narrow and the optical density is slightly dependent on ionic strength since the peak broadens slightly. At constant ionic strength, however, this absorption obeyed Beer's law. Sodium perchlorate was used to maintain a constant ionic strength of 4 in all solutions.

Growth of Tetracyanonickelate from Hexa-amminenickelate with Added Cyanide.—Solutions of 0.1M-nickel sulphate in 2M-ammonia were examined in the infrared region at CN : Ni ratios from 0.5 : 1 to 4 : 1. The tetracyanonickelate absorption increased linearly up to a CN : Ni ratio of 4 : 1.

Effect of an Excess of Cyanide on Tetracyanonickelate.—Fig. 1 shows the effects of increasing concentrations of sodium cyanide on the infrared absorption of 0.075M-disodium tetracyano-nickelate solutions. Numerical results are given in Tables 1 and 2 (only those for aqueous solution are shown in Fig. 1; the curves in 2M-ammonia are qualitatively similar).

[4] Jones and Penneman, *J. Chem. Phys.*, 1954, **22**, 965.
[5] Penneman and Jones, *J. Chem. Phys.*, 1956, **24**, 293.
[6] Penneman and Staritzky, *J. Inorg. Nuclear Chem.*, 1958, **6**, 112.
[7] Penneman and Jones, *J. Inorg. Nuclear Chem.*, 1961, **20**, 19.
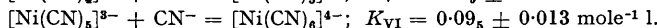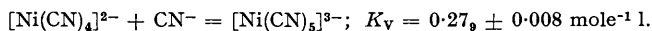[8] Fernelius and Burbage, *Inorg. Synth.*, 1946, **2**, 227.
[9] Plyler, Danti, Blaine, and Tidwell, *J. Res. Nat. Bur. Stand.*, 1960, **64**, 29.

Quantitative Treatment of the Absorption Data.—Since one new peak was observed as free cyanide was increased, we first assumed that only a single higher complex was formed.

To describe the equilibrium, $[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$, we use the following symbols: $(IV)_0$ = initial concentration of $Na_2Ni(CN)_4$, (IV) = equilibrium concentration of

TABLE 1.

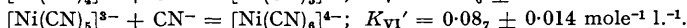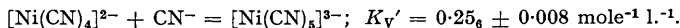Effect of sodium cyanide on the infrared spectrum of aqueous disodium tetracyanonickelate.

Initial concns. (mole l.$^{-1}$)		Optical density * at		Initial concns. (mole l.$^{-1}$)		Optical density * at	
NaCN	Na$_2$Ni(CN)$_4$	2124 cm.$^{-1}$	2103 cm.$^{-1}$	NaCN	Na$_2$Ni(CN)$_4$	2124 cm.$^{-1}$	2103 cm.$^{-1}$
0	0·07490	0·428	—	2·0036	0·07488	0·259	0·227
0·2608	0·07496	0·405	0·042	2·006	0·07522	0·260	0·223
0·5179	0·07462	0·373	0·073	2·202	0·07520	0·249	0·235
0·7606	0·07495	0·353	0·104	2·400	0·07519	0·237	0·249
1·002	0·07524	0·330	0·132	2·609	0·07521	0·227	0·260
1·0245	0·07494	0·315	0·132	2·818	0·07513	0·213	0·269
1·2492	0·07494	0·307	0·159	3·003	0·07521	0·208	0·282
1·498	0·07519	0·290	0·182	3·206	0·07513	0·199	0·291
1·5075	0·07490	0·285	0·187	3·399	0·07512	0·191	0·306
1·7586	0·07495	0·271	0·210	3·604	0·07517	0·180	0·315

$[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$; $K_V = 0.27_9 \pm 0.008$ mole^{-1} l.

$[Ni(CN)_5]^{3-} + CN^- = [Ni(CN)_6]^{4-}$; $K_{VI} = 0.09_5 \pm 0.013$ mole^{-1} l.

* Optical densities at 2124 and 2103 cm.$^{-1}$ in 0·075M-Na$_2$Ni(CN)$_4$ solution as a function of added NaCN ($\mu = 4$ with NaClO$_4$, path length = $62·5 \times 10^{-4}$ cm.).

TABLE 2.

Effect of sodium cyanide on the infrared spectrum of ammoniacal disodium tetracyanonickelate.

Initial concns. (mole l.$^{-1}$)		Optical density * at		Initial concns. (mole l.$^{-1}$)		Optical density * at	
NaCN	Na$_2$Ni(CN)$_4$	2124 cm.$^{-1}$	2103 cm.$^{-1}$	NaCN	Na$_2$Ni(CN)$_4$	2124 cm.$^{-1}$	2103 cm.$^{-1}$
0·2532	0·07490	0·395	0·035	2·341	0·07510	0·254	0·213
0·5058	0·07492	0·368	0·066	2·415	0·07532	0·248	0·220
0·7571	0·07494	0·352	0·093	2·503	0·07486	0·241	0·235
1·001	0·07490	0·337	0·108	2·609	0·07532	0·236	0·230
1·012	0·07496	0·329	0·117	2·815	0·07537	0·228	0·240
1·253	0·07485	0·320	0·142	2·998	0·07485	0·217	0·272
1·508	0·07486	0·297	0·166	3·003	0·07502	0·222	0·250
1·510	0·07505	0·297	0·151	3·011	0·07525	0·217	0·260
2·007	0·07503	0·272	0·195	3·206	0·07530	0·213	0·265
2·010	0·07523	0·263	0·207	3·264	0·07488	0·205	0·275
2·012	0·07485	0·265	0·207	3·406	0·07537	0·206	0·277
2·211	0·07524	0·254	0·210	3·511	0·07490	0·196	0·298
2·265	0·07484	0·253	0·222	4·001	0·07485	0·173	0·314

$[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$; $K_V' = 0.25_6 \pm 0.008$ mole^{-1} l.$^{-1}$.

$[Ni(CN)_5]^{3-} + CN^- = [Ni(CN)_6]^{4-}$; $K_{VI}' = 0.08_7 \pm 0.014$ mole^{-1} l.$^{-1}$.

* As for Table 1 but for 2M-NH$_3$ solution.

$[Ni(CN)_4]^{2-}$, (V) = equilibrium concentration of $[Ni(CN)_5]^{3-}$ (all concns. in mole l.$^{-1}$), and $K_V = (V)/(IV)(CN^-)$.

Since $(IV)_0 = (IV) + (V)$, and $(V) = K_V(IV)(CN^-)$, we have

$$1/(IV) = [1/(IV_0)][1 + K_V(CN^-)]. \qquad (1)$$

The plot of eqn. 1 (with optical densities proportional to concentration at constant path length) is very nearly linear up to about 2·5M-sodium cyanide (see Fig. 2). It deviates progressively from linearity at higher free cyanide concentrations, indicating that residual tetracyanonickelate is smaller than that calculated on the basis that only pentacyanonickelate is formed. The ratio of the optical density of the 2103 cm.$^{-1}$ peak to that of tetracyanonickelate shows the same behaviour when plotted against free cyanide (plot not shown). These results suggest the formation of an additional higher complex.

Assuming, therefore, that the equilibrium is between $[Ni(CN)_4]^{2-}$, $[Ni(CN)_5]^{3-}$, and $[Ni(CN)_6]^{4-}$, and using $(VI) = [Ni(CN)_6]^{4-} = K_{VI}(V)(CN^-)$, we write:

$$(IV)_0 = (IV) + (V) + (VI),$$

Thus, $(IV)_0 = (IV)[1 + K_V(CN^-) + K_V K_{VI}(CN^-)^2],$

and $[(IV)_0 - (IV)]/(IV)(CN^-) = K_V + K_V K_{VI}(CN^-).$ (2)

A plot of the left-hand side of eqn. 2 against cyanide concentration should give a straight line of intercept K_V and a slope of $K_V K_{VI}$. For K_{VI} to be zero, the slope has to be zero. Fig. 3 shows a plot of the above function for the studies both in water and in 2M-aqueous ammonia.
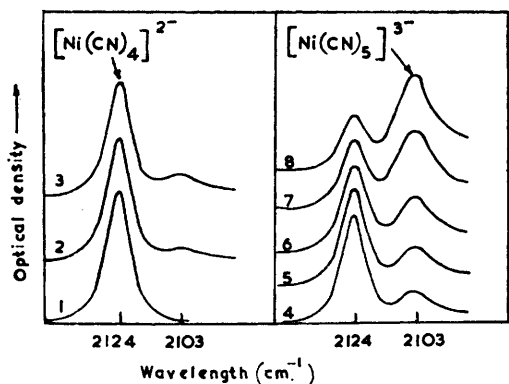

FIG. 1. Infrared absorption of 0·075M-Na₂Ni(CN)₄ solutions containing concentrations of NaCN increasing as follows: (1) 0, (2) 0·25M, (3) 0·50M, (4) 0·75M, (5) 1·0M, (6) 1·5M, (7) 2·6M, and (8) 3·6M-NaCN. Constant ionic strength, μ = 4, was maintained with NaClO₄.
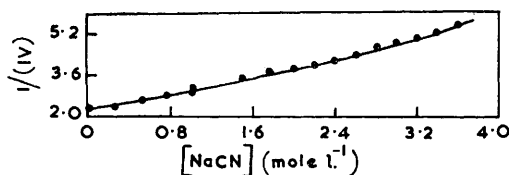

FIG. 2. The reciprocal of the optical density of $[Ni(CN)_4]^{2-}$ plotted as a function of NaCN (data from Table 1).

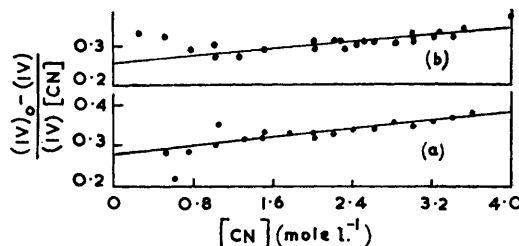FIG. 3. A plot of the equation $[(IV)_0 - (IV)]/(IV)(CN^-) = K_V + K_V K_{VI}(CN^-)$, (a) in water, and (b) in 2M-aqueous ammonia.

In both instances the slopes are positive and different from zero, indicating that hexacyanonickelate is being formed in addition to the pentacyanonickelate.

Such a plot of eqn. 2 illustrates that two complexes are formed. However, it emphasises errors at low cyanide concentrations when $(IV) \approx (IV)_0$. Thus, for computation, the power series $(IV)_0 = (IV)[1 + K_V(CN^-) + K_V K_{VI}(CN^-)^2]$ was used, with optical-density data, to obtain least squares values for K_V and K_{VI}.

Formation Constants of Penta- and Hexa-cyanonickelate.—The above treatment of the optical density gives the following values of the formation constants ($\pm$ values are standard deviations):

In aqueous solution, $\mu = 4$: $[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}$, $K_V = 0·27_9 \pm 0·008$ mole⁻¹ l.; and $[Ni(CN)_5]^{3-} + CN^- = [Ni(CN)_6]^{4-}$, $K_{VI} = 0·09_5 \pm 0·013$ mole⁻¹ l.

Values for the corresponding equilibria in 2M-ammonia, at $\mu = 4$, are denoted by primes: $K_V' = 0·25_6 \pm 0·008$ and $K_{VI}' = 0·08_7 \pm 0·014$ mole⁻¹ l.

We did not observe a shift in $[Ni(CN)_4]^{2-}$ absorption in water, 2M-ammonia, or 0·1M-sodium hydroxide, so we conclude that the formation constant for a complex such as $[Ni(CN)_4(NH_3)]^{2-}$ or $[Ni(CN)_4OH]^{3-}$ must be small. This is further borne out by the similarity of K_V and K_{VI} in aqueous solution and in 2M-ammonia. The effect of hydroxide ion on the equilibrium of 2M-sodium cyanide and 0·075M-disodium tetracyanonickelate was also determined. Addition of sodium hydroxide up to a concentration of 0·5M had no apparent effect. This concentration far exceeds any contribution from the hydroxide impurity in the cyanide or from its hydrolysis. Thus, the contribution from a complex such as $[Ni(CN)_5OH]^{4-}$ can be neglected. Although hydroxide ion had no effect on the equilibrium, addition of chloride ion had a marked effect, as described in the next section.

Formation Constant of Chloropentacyanonickelate.—Addition of sodium chloride to 2M-sodium cyanide and 0·075M-disodium tetracyanonickelate significantly diminished the absorption due to $[Ni(CN)_4]^{2-}$ and increased the absorption of the broad peak at 2103 cm.$^{-1}$. When the sodium chloride concentration was increased from 0 to 2M [at constant total Ni(II) concentration in 2M-sodium cyanide] the reciprocal of the optical density of $[Ni(CN)_4]^{2-}$ gave a straight line of the form $1/(IV) = A + B(Cl^-)$.

This linear function tempts one into a quantitative treatment of the effect. It is true that one can fit the results by assuming that the formation constant K_V (for $[Ni(CN)_5]^{3-}$) varies linearly with chloride concentration. However, since this linear behaviour is also that expected for a 1 : 1 complex [see eqn. (1)], we prefer to regard it as evidence for mixed-ligand complex formation.

We first thought that this diminution of tetracyanonickelate concentration resulted from the reaction, $[Ni(CN)_4]^{2-} + Cl^- = [Ni(CN)_4Cl]^{3-}$, which can be studied separately. We carefully measured the spectra of tetracyanonickelate in water, and as a function of sodium perchlorate and sodium chloride concentrations. The nickelate absorption in water is quite narrow; it broadens slightly and shifts just detectably (0·5 cm.$^{-1}$) as the ionic strength increases to 2M (NaCl or NaClO$_4$). The effects of perchlorate and chloride anions were indistinguishable. From this we conclude that complex formation between Cl^- and $[Ni(CN)_4]^{2-}$ is small.

Since added sodium chloride has essentially no effect on the optical density of tetracyanonickelate unless sodium cyanide is also present, the marked effect when sodium chloride is added to a solution containing both tetra- and penta-cyanonickelate is logically ascribed to formation of a mixed-ligand complex: $[Ni(CN)_5]^{3-} + Cl^- = [Ni(CN)_5Cl]^{4-}$. We determined the apparent formation constant, K_{VCl}, for this reaction in the following manner:

$$\text{Total [nickel]} = (IV)_0 = (IV) + (V) + (VI) + (VCl),$$

and $$(IV)_0/(IV) = 1 + K_V(CN^-) + K_VK_{VI}(CN^-)^2 + K_VK_{VCl}(CN^-)(Cl^-). \qquad (3)$$

At constant CN^-, this has the form, $(IV)_0/(IV) = \text{Intercept} + \text{Slope}(Cl^-)$, where the slope = $K_VK_{VCl}(CN^-)$.

We assumed, as before, that the optical density at 2124 cm.$^{-1}$ is due to " free " tetracyanonickelate and obtained the least-squares value of $K_{VCl} = 0·2_2 \pm 0·03$. Table 3 summarises the results.
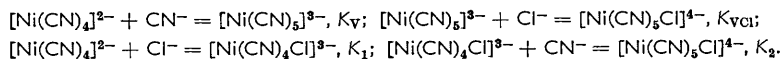
TABLE 3.

Effect of sodium chloride on the infrared spectrum of aqueous disodium tetracyanonickelate in 2M-sodium cyanide.

Initial [NaCl] (mole l.$^{-1}$)	Optical density * at		Initial [NaCl] (mole l.$^{-1}$)	Optical density * at		Initial [NaCl] (mole l.$^{-1}$)	Optical density * at	
	2124 cm.$^{-1}$	2103 cm.$^{-1}$		2124 cm.$^{-1}$	2103 cm.$^{-1}$		2124 cm.$^{-1}$	2103 cm.$^{-1}$
0·1957	0·239	0·227	0·8002	0·233	0·234	1·5040	0·229	0·256
0·2550	0·248	0·240	1·0020	0·238	0·242	1·6001	0·217	0·253
0·4116	0·233	0·226	1·0113	0·230	0·243	1·7530	0·226	0·260
0·5020	0·244	0·239	1·2051	0·226	0·240	1·8123	0·212	0·254
0·6033	0·233	0·231	1·2530	0·233	0·253	1·9986	0·209	0·260
0·7530	0·241	0·239	1·4029	0·225	0·241	2·0000	0·220	0·265

$[Ni(CN)_5]^{3-} + Cl^- = [Ni(CN)_5Cl]^{4-}$, $K_{VCl} = 0·2_2 \pm 0·03$ mole^{-1} l.

* Optical densities of 2124 and 2103 cm.$^{-1}$ in 0·075M-Na$_2$Ni(CN)$_4$ + 2·01M-NaCN as a function of added NaCl.

The above treatment assumes that the amount of the ion $[Ni(CN)_4Cl]^{3-}$ is small. However, its formation constant cannot be zero. Consider the following parallel paths:

$$[Ni(CN)_4]^{2-} + CN^- = [Ni(CN)_5]^{3-}, K_V; \quad [Ni(CN)_5]^{3-} + Cl^- = [Ni(CN)_5Cl]^{4-}, K_{VCl};$$

$$[Ni(CN)_4]^{2-} + Cl^- = [Ni(CN)_4Cl]^{3-}, K_1; \quad [Ni(CN)_4Cl]^{3-} + CN^- = [Ni(CN)_5Cl]^{4-}, K_2.$$

Then, $K_1K_2 = K_VK_{VCl}$. By independent measurement we know only that $K_V = 0·28$. Taking into account the additional species $[Ni(CN)_4Cl]^{3-}$ would add a term $K_1(Cl^-)$ to eqn. (3). As long as the ion $[Ni(CN)_4Cl]^{3-}$ does not absorb at the position of $[Ni(CN_4)]^{2-}$, the treatment is the same as before except that the slope now involves $[K_VK_{VCl}(CN^-) + K_1]$. Thus, K_{VCl} would be smaller than 0·2, if K_1 is not negligible compared with $0·56K_{VCl}$.

Constancy of the Extinction Coefficient of Tetracyanonickelate.—The molar extinction co-efficient of tetracyanonickelate, ε_{IV}, was calculated for each optical density value listed in Tables 1 and 2. Values for the equilibrium constants appearing below each table were used to calculate concentrations of $[Ni(CN)_4]^{2-}$ in each solution. The results can be summarised as follows:

(*a*) From the optical density of tetracyanonickelate in 4M-sodium perchlorate (in the absence of an excess of sodium cyanide), $\varepsilon_{IV} = 914$ l. mole^{-1} cm.$^{-1}$. The mean value in 0·25—3·5M-sodium cyanide, calculated from the 19 optical-density values of Table 1, is $\bar{\varepsilon}_{IV} = 914\cdot6 \pm 2\cdot5$ (standard deviation of the mean).

(*b*) The mean value in 2M-ammonia, calculated from the 26 optical-density values in Table 2, is $\bar{\varepsilon}_{IV} = 912\cdot8 \pm 2\cdot5$ (standard deviation of the mean).

Treatment of the Absorption Data of the Peak at 2103 cm.^{1}.—The absorption maximum of tetracyanonickelate occurs a few wavenumbers higher than that of pentacyanonickelate even though we were not able to resolve it. This was shown by dissolving disodium tetracyano-nickelate in nearly saturated aqueous sodium cyanide so that the nickel was primarily distributed between the two higher complexes. The peak broadened and the absorption maximum shifted from 2103 to 2105 cm.$^{-1}$.

Over the cyanide range used in our study, the contribution of hexacyanonickelate was not sufficient to cause an observable shift in the position of the absorption maximum of the penta-cyano-complex. The optical density at the maximum of the broad absorption peak at 2103 cm.$^{-1}$ was assumed equal to the sum of the contributions of penta- and hexa-cyano-complexes. The extinction coefficients of the two species were then calculated from the optical-density measurements given in Table 1, by using concentrations calculated from the equilibrium constants. The following least-squares values were obtained $\bar{\varepsilon}_V = 1240 \pm 20$ l. mole^{-1} cm.$^{-1}$ at 2103 cm.$^{-1}$, and $\bar{\varepsilon}_{VI} = 900 \pm 70$ l. mole^{-1} cm.$^{-1}$ at 2103 cm.$^{-1}$.

Observation of a Second Absorption Frequency for Pentacyanonickelate.—As shown in previous sections, the prominent absorption maximum of pentacyanonickelate occurs at 2103 cm.$^{-1}$ with an extinction coefficient of 1240. Symmetry considerations show that two other cyanide vibrations are infrared-active and might be observable in this region. Searching for this obviously weaker absorption at the cyanide position (not shown in our drawings) we noticed some positive absorption. Since cyanide is consumed in complex formation, the sample should have shown a " negative " background (*i.e.*, free cyanide in the sample should have been " over-compensated " by the sodium cyanide control). This is not the case and was

TABLE 4.

Magnetic susceptibilities, found and calculated from the susceptibilities of the components, at 25·5°.

K$_2$Ni(CN)$_6$ (M)	1·50	1·04	0·65	1·01
KCN (M)	1·00	2·18	2·60	4·08
10$^{-6}\chi$ found	−0·604	−0·619	−0·620	−0·602
calc.	−0·602	−0·618	−0·626	−0·602

checked carefully by using matched cells with the same sodium cyanide concentration in each to give a flat background. Addition of disodium tetracyanonickelate increased absorption at ~2080 cm.$^{-1}$ instead of decreasing it. This slight absorption increased as the concentration of pentacyanonickelate increased, approximately linearly with cyanide concentration. It arises from one or both of the other vibrations of the pentacyanonickelate.

Magnetic Data.—As shown in Table 4 the aqueous complexes which we prepared are diamagnetic. Magnetic measurements were carried out on the apparatus described by Figgis and Nyholm.[10]

DISCUSSION

In ammoniacal solution, addition of sodium cyanide to disodium hexa-amminenickelate(II) yields disodium tetracyanonickelate quantitatively until a CN : Ni ratio of 4 : 1 is reached. Our results agree with this part of the work of Blackie and Gold.[2] However, our conclusions are completely different from their conclusions based on proton

[10] Figgis and Nyholm, *J.*, 1959, 331.

relaxation studies [2,3] concerning the formula of the major higher complex in an excess of sodium cyanide and the magnitude of its formation constant.
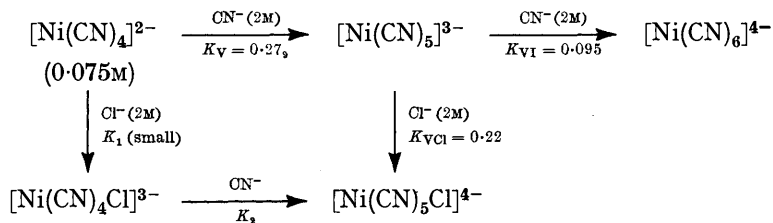
The curves in Fig. 1 show that even with a ten—twenty-fold excess of sodium cyanide, most of the nickel remains in the form $[Ni(CN)_4]^{2-}$ absorbing at 2124 cm.$^{-1}$. Therefore the formation constant of a higher complex cannot be large. From Blackie and Gold's [2,3] results, tetra- should have been completely converted into hexa-cyanonickelate when the ratio $NaCN : Na_2Ni(CN)_4$ exceeded 2 : 1.

Quantitative infrared measurements of the optical density of tetracyanonickelate in solutions containing increasing amounts of free cyanide are best interpreted in terms of formation of penta- and hexa-cyanonickelate. The values of the stepwise formation constants are: $K_V = 0.27_9$ and $K_{VI} = 0.09_5$. The formation constants in 2M-ammonia are only slightly different (0.25_6 and 0.08_7, respectively).

Absorption from a new complex occurs at 2103 cm.$^{-1}$ and increases approximately linearly as the free cyanide concentration increases. This absorption at 2103 cm.$^{-1}$ results primarily from pentacyanonickelate which is the predominant higher complex (*e.g.*, only 6% of the total nickel is in the form of hexacyanonickelate in 2M-sodium cyanide). The infrared absorptions of the penta- and hexa-cyano-complexes occur too close together to be resolved. Consequently, evidence for hexacyano-complex was based on quantitative treatment of the absorption of the tetracyano-species.

Chloride apparently does not form a mixed-ligand complex from sodium tetracyano-nickelate. However, once the pentacyano-complex is formed, chloride appears to add more readily to it than does another cyanide. The formation constant for $[Ni(CN)_5]^{3-} + Cl^- = [Ni(CN)_5Cl]^{4-}$ appears to be about twice as large as that for $[Ni(CN)_5]^{3-} + CN^- = [Ni(CN)_6]^{4-}$. This is a reversal of the usual complex-forming tendencies of cyanide and chloride, but has been observed also with thallium(I).[6]

Structure of Five- and Six-co-ordinate Complex Anions.—The annexed chart summarises the reactions for the maximum concentrations of reagents employed. The products pose

$$[Ni(CN)_4]^{2-} \xrightarrow[K_V = 0.27_9]{CN^- (2M)} [Ni(CN)_5]^{3-} \xrightarrow[K_{VI} = 0.095]{CN^- (2M)} [Ni(CN)_6]^{4-}$$

$$(0.075M)$$

$$\downarrow{\substack{Cl^- (2M) \\ K_1 \text{ (small)}}} \qquad\qquad \downarrow{\substack{Cl^- (2M) \\ K_{VCl} = 0.22}}$$

$$[Ni(CN)_4Cl]^{3-} \xrightarrow[K_2]{CN^-} [Ni(CN)_5Cl]^{4-}$$

some interesting problems. In particular, one seeks possible explanations for: (1) apparent variations in co-ordination numbers (4, 5, 6); (2) the relative sizes of the various equilibrium constants; (3) the magnetic data [can six-co-ordinated nickel(II) be diamagnetic?], and (4) the stereochemistry of the products.

If we consider complexes having the d^8 spin-paired, non-bonding configuration we find that the co-ordination number is very sensitive to the oxidation state and the effective electronegativity of the metal atom. In general, five-co-ordination predominates for the lower oxidation states, *e.g.*, $[Cr^{-II}(CO)_5]^{2-}$, $[Mn^{-I}(CO)_5]^-$, $Fe^0(CO)_5$, $[Co^{+I}(PhNC)_5]^+$, whereas four-co-ordination is more common with the higher oxidation state of $+2$, *e.g.*, the preferred $[Ni(CN)_4]^{2-}$ ion.

As we pass from Ni^{II} to Pd^{II} to Pt^{II} or from Co^I to Rh^I the trend is again in favour of the lower co-ordination number. It was proposed [11] that, as the formal charge or the effective electronegativity of the metal atom decreases, the separation between $(n-1)d$-, ns-, and np-orbitals decreases, leading to greater similarity with metal-carbonyl-type behaviour, with a tendency to reach the nearest inert-gas configuration and hence to form stable five-co-ordinate complexes with polarisable ligands.

[11] Nyholm, *Proc. Chem. Soc.*, 1961, 273.

This does not preclude six-co-ordination with more electronegative ligands to complete the co-ordination sphere. For example, the complex ions $[M^{II}$ Diarsine$_2]^{2+}$ $[M^{II} = Ni^{II},$ Pd^{II}, Pt^{II}; Diarsine $= o\text{-}C_6H_4(AsMe_2)_2]$ all readily attach one halide ion in nitromethane and crystallise in a tetragonal structure with two long, essentially M^{II}–Hal bonds normal to the square. There are other examples in which ligands attached to the same metal atom can be divided into two groups, one group being attached by strong covalent bonds, the other by essentially ionic or ion–dipole bonds.

This raises the question of whether aqueous tetracyanonickelate is properly called an example of four-co-ordination or whether it is six-co-ordinated with two weakly bound water molecules. However, whether or not the true co-ordination is altered on addition of one or two cyanide ligands, it is more important to recognise that these last ligands are not equivalent to the first four.

The tetracyanonickelate structure is a very stable configuration with a large formation constant. Addition of one cyanide ion to form pentacyanonickelate enables the atom to approach the so-called inert-gas configuration. However, addition of this fifth ligand is obviously not very favourable even for cyanide which co-ordinates readily and can participate in π-bonding. The fact that there is, in a Ni^{2+} ion, a large $3d$–$4s$–$4p$ separation means that the five bonds are by no means equivalent. If we consider the pentacyano-complex as a tetragonal pyramid of C_{4v} symmetry, there should be three infrared-active cyanide stretching vibrations. One of these would be strongly absorbing, namely, the doubly degenerate vibration of the four basal cyanide ligands which we observe at 2103 cm.$^{-1}$. Another is the symmetric vibration of the basal cyanide group which we expect to be very weak and of a frequency about the same as, or slightly higher than, that of the degenerate vibration. Therefore, we assign the weakly absorbing peak at $\sim$2080 cm.$^{-1}$ to the third infrared-active vibration of $[Ni(CN)_5]^{3-}$, namely, the apical cyanide stretch. If this fifth cyanide were held to the nickel about as strongly as the other four, the intensity of its absorption band should be about one-fourth of that at 2103 cm.$^{-1}$. However, its intensity is much less than one-fourth of that of the degenerate vibration. This indicates that this fifth cyanide group is indeed held much less strongly than the other four, thus acting more like free cyanide ion which absorbs weakly at 2080 cm.$^{-1}$.

The diamagnetism of these aqueous complexes also supports the non-equivalence of the ligands. It is important to emphasise that there are many examples now known of diamagnetic five- and six-co-ordinate derivatives [11] of nickel(II), palladium(II), and platinum(II) since it is often erroneously assumed that six-co-ordinate nickel(II) is necessarily paramagnetic. Diamagnetism can arise, however, if there is a considerable tetragonal distortion from regular octahedral symmetry.

From a ligand-field point of view, five- and six-co-ordinated nickel(II) can be diamagnetic as long as the fifth and the sixth ligand are not equivalent to the four planar ones. Certainly (in a d^8-case) the d_{z^2}-orbital is energetically preferred for the fourth electron pair. Addition of a fifth ligand (bonding stronger than that of water) will tend to bring the d_{z^2}- and the $d_{x^2-y^2}$-orbitals closer in energy but still the d_{z^2}-orbital is preferred. Addition of chloride as the sixth ligand would also allow this asymmetry. The crux of the matter is reached with hexacyanonickelate. We find that this ion is diamagnetic; therefore the six cyanide groups cannot be equivalent, as demanded by octahedral symmetry, otherwise d_{z^2}- and $d_{x^2-y^2}$-orbitals would have the same energy and thus the two electrons would be unpaired.*

We have presented evidence that while chloride is attached more readily than cyanide to pentacyanonickelate it is obviously attached to tetracyanonickelate less readily than is cyanide. It is true that our infrared method may not be sensitive to interaction of chloride

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* It was found by Blackie and Gold that the cyano-adduct of the $[Ni(CN)_4]^{2-}$ ion which they took to be the $[Ni(CN)_6]^{4-}$ entity had a "magnetic dipole moment very small or zero." [2] However, they concluded that $[Ni(CN)_6]^{4-}$ relaxed protons as effectively as if it had a moment of 1·58 B.M., behaviour generally attributed to paramagnetic ions.

and tetracyanonickelate ions in relatively dilute (0—2M) chloride solutions. It would be extremely helpful to determine the constant for $[Ni(CN)_4]^{2-} + Cl^- = [Ni(CN)_4Cl]^{3-}$ independently, *e.g.*, by a study of a band dependent upon M–Cl attachment such as the 4700 Å band observed in [Ni Diarsine$_2$Hal]$^+$ complexes.[12]

With regard to the stereochemistry of the various species one can only speculate in the absence of X-ray data. Considering first the $[Ni(CN)_5]^{3-}$ ion we favour the square, pyramidal arrangement, partly because one cyanide ion differs from the other four, and, secondly, by analogy with the known structure of NiBr$_2$Triarsine, where Triarsine = Me$_2$As·[CH$_2$]$_3$·AsMe·[CH$_2$]$_3$·AsMe$_2$, which has this shape.[13] The square-pyramidal arrangement holds only for the five cyanide ligands because we consider it likely that there is a water molecule in the sixth (octahedral) position. The hexacyano- and the chloropenta-cyano-derivative are then formed by replacement of the water molecule by a cyanide or a chloride ion respectively.

[12] Harris, Nyholm, and Phillips, *J.*, 1960, 4379.
[13] Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415.