CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

Mixed-Ligand Complexes in Mercury(II)–Cyanide–Iodide Solutions: A Raman and Ultraviolet Study[1]

BY J. S. COLEMAN, R. A. PENNEMAN, L. H. JONES, AND I. K. KRESSIN

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Raman spectra of Hg(II) in aqueous NaCN–NaI show peaks unique to the mixtures at 2157, 2180–2200, and 318–330 cm^{-1}. The first of these is assigned to $Hg(CN)_3I^{2-}$ on the basis of observed trends with solution composition. The last two show variations in position with NaI concentration and have been assigned to the general composition $Hg(CN)_2I_x^{x-}$. Raman spectra of $Hg(CN)_2I_x^{x-}$ solutions show remarkable similarity to the spectrum of solid $KI \cdot Hg(CN)_2$ in which essentially linear $Hg(CN)_2$ groups are coordinated by equatorial iodides. Study of the disappearance of the 3225-Å peak of HgI_4^{2-}, when 5 *M* NaI solutions dilute in Hg(II) are made several millimolar in NaCN, indicates formation of $Hg(CN)I_3^{2-}$ and $Hg(CN)_2I_x^{x-}$. One additional mixed-ligand complex, namely, Hg(CN)I, is formed from $Hg(CN)_2$ and HgI_2 with a formation constant of 0.14. This new complex exhibits an ultraviolet peak at 2370 Å.

Introduction

Mercuric ion is a class B ion and forms strong complexes with both cyanide and iodide. The stepwise formation constants for the mono and di ligand complexes are about five orders of magnitude greater for cyanide than for iodide; the stepwise constants for the tri- and tetraligand complexes, in contrast, are of the same order of magnitude.[2] This paper reports a study of a number of the mixed-ligand complexes using Raman and ultraviolet spectrometry.

Experimental Section

Reagent grade $Hg(CN)_2$, NaI, HgI_2, and NaCN were used. Sodium cyanide solutions were assayed for CN before use. Solutions were examined shortly after preparation and at intervals thereafter to ensure that no time-dependent equilibria were present. Raman spectra were recorded using a Cary Model 81 Raman spectrometer.

Ultraviolet spectra were obtained using the Cary Model 14 spectrometer. For measurement of the formation of cyanide complexes in 5 *M* NaI, two sets of stock solutions were prepared. For each set, 5 *M* NaI was brought to pH 11.0 by addition of concentrated NaOH. Sodium arsenite (0.001 *M*) was added to reduce traces of triiodide ion to iodide. A total of 34 mixtures containing known amounts of HgI_2 and NaCN were prepared by weight. Samples were placed in 1-cm cells and brought to 25.0°. Portions of some of the mixtures were made 0.01 *M* in both sodium hydroxide and sodium arsenite to confirm that these reagents did not affect the observed absorbances.

Results

Raman Studies. (a) Addition of NaI to Solutions with 3 CN$^-$ per Hg(II).—A solution containing 1 *M* $Hg(CN)_2$ and 1 *M* NaCN shows Raman lines attributable to the well-characterized species $Hg(CN)_2$, $Hg(CN)_3^-$, and $Hg(CN)_4^{2-}$ (lowest curve, Figure 1). Addition of NaI leads to disappearance of these three lines and concomitant appearance of a new line at ~2153 cm^{-1}, between the positions of $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ (curve in Figure 1 labeled 1 *M* NaI). Further increase in the NaI concentration causes (1) appearance of a line attributable to free CN$^-$, (2) appearance of an incompletely resolved line near 2180 cm^{-1}, and (3) shift of the 2153-cm^{-1} line toward 2157 cm^{-1}.

In the middle-frequency region (250–450 cm^{-1}) $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ have broad Raman bands at ~365 and 335 cm^{-1}, respectively. A solution of stoichiometry 3 CN$^-$ per Hg saturated in iodide shows a slight shift from 365 to ~358 cm^{-1}. A solution of $Hg(CN)_4^{2-}$ saturated in iodide shows a very broad Raman band centered around 350 cm^{-1}.

(b) Addition of NaCN to Solutions of Hg(CN)$_2$ in Saturated NaI.—Saturated NaI solutions containing 1 *M* $Hg(CN)_2$ show Raman emission near 2180 cm^{-1} (lowest curve, Figure 2). Some asymmetry is observed toward the low-frequency side. As NaCN is added, a new line arises at 2157 cm^{-1}. Further addition of NaCN causes appearance of free CN$^-$ emission and shifting of the peak initially at 2157 cm^{-1} toward the position of $Hg(CN)_4^{2-}$.

Along with the changes illustrated in Figure 2, two other effects occur attributable to the presence of HgI_4^{2-}. Concentrated NaI solutions containing 1 *M* $Hg(CN)_2$ are distinctly yellow. The color is discharged when the CN/Hg ratio is about 2.2. A detailed study of this effect in 5 *M* NaI is described later. The complex HgI_4^{2-} in saturated NaI solutions shows a highly polarized Raman line at 126 cm^{-1}. A line at 126 cm^{-1} with the identical polarization is observed in saturated NaI solutions containing 1 *M* $Hg(CN)_2$. This line also disappears when the CN/Hg ratio is increased to about 2.2.

(c) Hg(CN)$_2$ at Various NaI Concentrations. Comparison with Solids.—The Raman spectrum of $Hg(CN)_2$ in aqueous solution shows three prominent peaks: 2200 cm^{-1} (CN stretch), 412 cm^{-1} (Hg–C stretch), and 276 cm^{-1} (Hg–C–N bend). With increasing concentrations of NaI the strong Raman line of $Hg(CN)_2$ at 2200 cm^{-1} is shifted toward lower frequencies and the solubility of $Hg(CN)_2$ is greatly increased over its solubility in water. The emission at 2200 cm^{-1} does not occur together with a new line; instead, the shift is a gradual one to the position (2180

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[1] This work was carried out under the auspices of the U. S. Atomic Energy Commission.

[2] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, Burlington House, London, 1964.

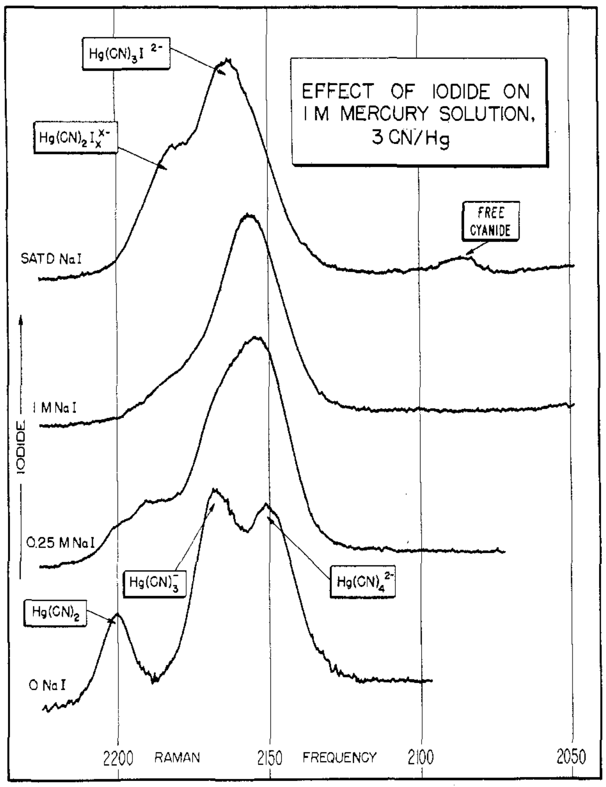

Figure 1.—Effects of adding NaI to a solution containing 3 CN^- per Hg.

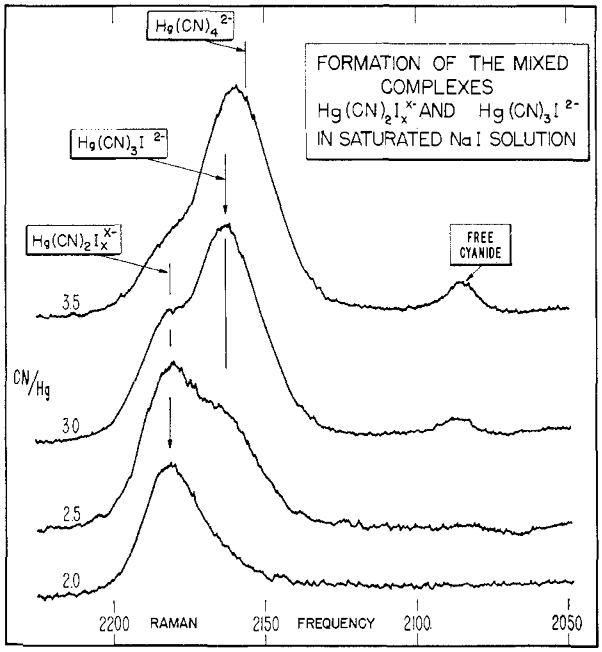

Figure 2.—Effects of adding NaCN to $Hg(CN)_2$ dissolved in saturated NaI solution.

cm^{-1}) observed in saturated NaI. A new peak, however, was reported at about 330 cm^{-1} [3] when NaI is added to $Hg(CN)_2$ solutions. A solution containing 1 *M* NaI and 1 *M* $Hg(CN)_2$ shows this peak shifted down to about 324 cm^{-1}; it is the most intense in the 250–500-cm^{-1} region. The other two peaks in this region now appear at 398 and 283 cm^{-1}, respectively. At 2 *M* NaI (and 1 *M* $Hg(CN)_2$) the peaks occur at 385, 318, and 288 cm^{-1}, the middle one being much more intense than the other two. At higher iodide concentrations the peaks become broader and less well defined and the background scattering increases considerably.

We note that the spectrum of a solution of 2 *M* NaI and 1 *M* $Hg(CN)_2$ bears a remarkable similarity to that of the crystalline $KI \cdot Hg(CN)_2$[4] and $NaI \cdot Hg(CN)_2 \cdot 2H_2O$[5] as seen in Table I.

TABLE I

RAMAN FREQUENCIES (IN CM^{-1}) FOR CRYSTALLINE $MI \cdot Hg(CN)_2$ (*M* = Na or K) AND NaI–$Hg(CN)_2$ SOLUTION

Solid $NaI \cdot Hg(CN)_2 \cdot 2H_2O$	Solid $KI \cdot Hg(CN)_2$	Solution 2 *M* NaI + 1 *M* $Hg(CN)_2$
2186 s	2183 s	2180 s
399 s	392 m	385 m
327 m	304 s	318 s
288 s	288 m	288 m
60 s[a]	43 s[a]	(126)[b]

[a] Lattice vibrations. [b] This peak arises from HgI_4^{2-}.

Ultraviolet Spectra. (a) **HgI_2 in Aqueous $Hg(CN)_2$.**—The ultraviolet spectra of solutions containing both HgI_2 and $Hg(CN)_2$ differ markedly from the spectrum of either $Hg(CN)_2$ or HgI_2 alone in water. Spectra of 4.7×10^{-5} *M* HgI_2 solutions are shown in Figure 3.

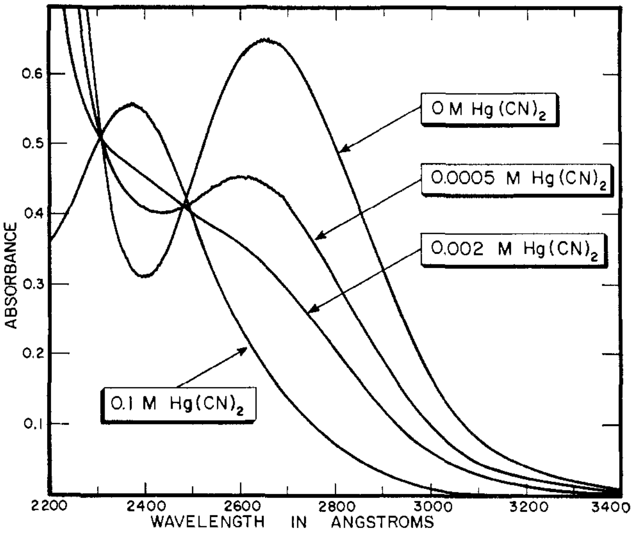

Figure 3.—Ultraviolet spectra of 4.7×10^{-5} *M* HgI_2 solutions containing various amounts of $Hg(CN)_2$.

As $Hg(CN)_2$ is added, the HgI_2 absorption at 2650 Å decreases. At the same time, a new peak is formed with a maximum at 2370 Å. The absorption of $Hg(CN)_2$ is small and decreases monotonically in this region; its effect was removed through use of $Hg(CN)_2$ solutions in the spectrometer reference compartment. As shown in Figure 3, the absorbance remains constant at 2480 and 2310 Å.

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(3) R. P. J. Cooney and J. R. Hall, *J. Inorg. Nucl. Chem.*, **28**, 1679 (1966).

(4) F. H. Kruse, *Acta Cryst.*, **16**, 105 (1963).

(5) Crystals of $NaHg(CN_2)I \cdot 2H_2O$ are triclinic needles elongated in the *c*-axis direction. Twinning on a plane parallel to the *c* axis is common. The unit cell has $a = 6.57$, $b = 9.88$, $c = 3.41$ Å, $\alpha = 89° 51'$, $\gamma = 103° 20'$. The unit cell contains one formula weight.

A 0.4 *M* solution of $Hg(CN)_2$ was saturated with HgI_2 by stirring with an excess for 1 week at 25°. A similar solution was prepared containing a lesser but known concentration of HgI_2 (0.00110 *M*). The absorbance of the saturated solution was 21% greater at all wavelengths. We conclude that the solubility of HgI_2 in 0.4 *M* $Hg(CN)_2$ is 0.00133 *M*. The reported solubility of HgI_2 in water at 25° is 0.000105 *M*.[6]

To throw further light on the nature of the new complex species, portions of the saturated solution of HgI_2 in 0.4 *M* $Hg(CN)_2$ were diluted with water by factors of 2.5, 5, 10, and 25. The spectra were recorded using cells of different path lengths so that the product of Hg concentration and path length remained constant. The resulting spectra were superimposable.

(b) Addition of NaCN to 5 *M* NaI Solutions Containing HgI_4^{2-}.—As noted earlier, yellow solutions of Hg(II) in concentrated NaI become colorless upon addition of NaCN. The color is due to the HgI_4^{2-} ion which has an absorption maximum at 3225 Å with absorption extending into the visible region. The effect of NaCN addition to 4×10^{-5} *M* Hg(II) in 5 *M* NaI is illustrated in Figure 4.

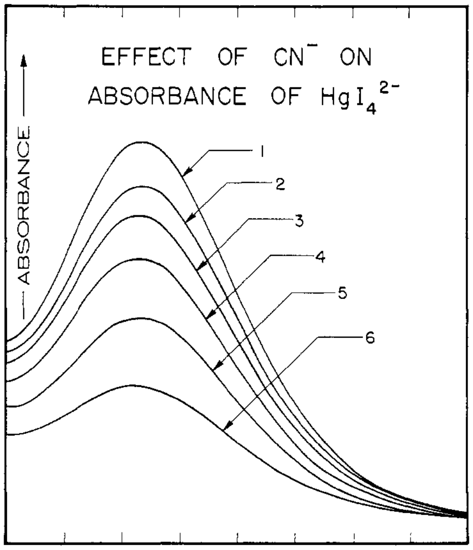

Figure 4.—Diminution of HgI_4^{2-} on addition of NaCN; 5 *M* NaI and 4.07×10^{-5} *M* Hg: 1, [CN] = 0; 2, [CN] = 3.1×10^{-4} *M;* 3, [CN] = 4.5×10^{-4} *M;* 4, [CN] = 6.3×10^{-4} *M;* 5, [CN] = 8.9×10^{-4} *M;* 6, [CN] = 1.4×10^{-3} *M.*

The results of quantitative measurements are shown in Table II. The tabulated values of observed absorbance are the differences between the readings at 3225 and 3650 Å. This procedure eliminates the influence of small variations in optical zero point. The corresponding extinction coefficient for HgI_4^{2-} ($\epsilon_{3225} - \epsilon_{3650}$), as measured in cyanide-free solutions, is 19,690 M^{-1} cm^{-1}.

Table II

Effect of CN^- on Absorbance at 3225 Å of Hg(II) in 5 *M* NaI

CN added, $M \times 10^3$	Hg added, $M \times 10^5$	*A*		CN added, $M \times 10^3$	Hg added, $M \times 10^5$	*A*	
		Obsd	Calcd			Obsd	Calcd
0.311	4.074	0.702	0.700	1.131	7.958	0.684	0.690
0.378	7.958	1.312	1.316	1.131	7.958	0.688	0.690
0.378	7.958	1.313	1.316	1.131	7.958	0.690	0.690
0.378	7.958	1.313	1.316	1.132	4.040	0.326	0.337
0.445	4.074	0.636	0.636	1.180	4.041	0.320	0.322
0.554	4.074	0.582	0.582	1.226	4.042	0.309	0.308
0.629	4.074	0.546	0.545	1.270	4.043	0.320	0.296
0.709	4.074	0.508	0.507	1.346	4.044	0.272	0.276
0.751	7.958	0.970	0.976	1.500	7.958	0.491	0.494
0.751	7.958	0.973	0.976	1.500	7.958	0.496	0.494
0.751	7.958	0.973	0.976	1.500	7.958	0.508	0.494
0.764	4.074	0.482	0.482	1.408	4.045	0.257	0.261
0.831	4.074	0.454	0.452	1.482	4.047	0.242	0.244
0.892	4.074	0.433	0.427	1.687	4.050	0.202	0.204
0.904	4.074	0.409	0.407	1.881	7.958	0.352	0.358
0.958	4.037	0.383	0.397	1.881	7.958	0.357	0.358
1.086	4.039	0.341	0.352	1.881	7.958	0.371	0.358

Additional solutions were prepared free of NaCN with the Hg(II) concentration adjusted so that the absorption at 3225 Å matched that of selected cyanide-containing solutions. The resulting pairs of spectra coincided at all wavelengths greater than 3200 Å. Separate experiments demonstrated that the observed absorbances are unaffected by sodium hydroxide and sodium arsenite up to concentrations of 0.01 *M*, 10 times the concentrations used for the main series of solutions.

Discussion

Raman Spectra and the Species $Hg(CN)_3I^{2-}$ and $Hg(CN)_2I_x^{x-}$.—The species $Hg(CN)^{3-}$ is known[7] to disproportionate according to

$$2Hg(CN)_3^- = Hg(CN)_2 + Hg(CN)_4^{2-} \qquad (1)$$

The Raman spectrum of 1 *M* NaCN–1 *M* $Hg(CN)_2$ thus exhibits lines from three species in the CN-stretch region as shown in Figure 1, lower curve. Addition of NaI causes these lines to merge to a single line at a position between those of $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$. We assign this new line to the mixed-ligand complex $Hg(CN)_3I^{2-}$ partially overlapped by $Hg(CN)_4^{2-}$. Further addition of NaI displaces some of the cyanide from the complex as shown by the appearance of emission attributable to free CN^-. At the same time a new line appears at 2180 cm^{-1} which is assigned to a mixed complex with less than 3 CN^- per Hg.

Appearance of a line at the same position (2180 cm^{-1}) in 1 *M* $Hg(CN)_2$-saturated NaI establishes that this additional mixed complex contains two cyanides (see Figure 2). The slight asymmetry toward lower energies may be attributed to the presence of some $Hg(CN)_3I^{2-}$ formed along with the HgI_4^{2-} which is known to be present. The remaining spectra of Figure 2 appear consistent with formation of $Hg(CN)_3I^{2-}$ and, finally, some $Hg(CN)_4^{2-}$ as NaCN is added. Similar considerations also allow assignment of the new low-frequency line at 318 cm^{-1} observed in 1 *M* $Hg(CN)_2$–2 *M* NaI to a mixed-ligand complex containing 2 CN^- per Hg.

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[6] W. F. Linke, "Solubilities; Inorganic and Metal Organic Compounds," Vol. 1, 4th ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p 1232.

[7] R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, **20**, 19 (1961).

The positions of the lines associated with iodide species containing 2 CN^- per Hg vary with NaI concentration. The similarities between the Raman spectra of NaI–$Hg(CN)_2$ solutions and that of KI·$Hg(CN)_2$ (see Table I) provide an interesting clue to the nature of the dicyanide complexes. Solid KI·$Hg(CN)_2$ is known to contain essentially linear $Hg(CN)_2$ groups with each Hg surrounded by a slightly puckered ring of four iodides normal to the CN groups.[4] It seems likely then that mixed-ligand dicyanide complexes form in solution with essentially linear $Hg(CN)_2$ groups loosely coordinated to one or more iodide ions. The variations of line positions can be rationalized as resulting from mixtures of species of the general composition $Hg(CN)_2I_x^{x-}$.

The emission around 318 cm^{-1} from $Hg(CN)_2I_x^{x-}$ may arise from an MCN bending vibration which is inactive in the Raman spectrum of linear $Hg(CN)_2$ but which is made active by change in the symmetry caused by association with the iodides. The ν_6 fundamental of $Hg(CN)_2$, for example, appears in the infrared at 341 cm^{-1} but is normally inactive in the Raman.[8] The other two bands, at 385 and 288 cm^{-1}, for $Hg(CN)_2I_x^{x-}$ no doubt arise from Hg–C stretch and HgCN bend found at 412 and 276 cm^{-1} for $Hg(CN)_2$. The Raman bands of $Hg(CN)_3^-$, $Hg(CN)_4^{2-}$, and $Hg(CN)_3I^{2-}$, at 365, 335, and 358 cm^{-1}, respectively, probably arise from Hg–C stretching vibrations. It is interesting that the Hg–C frequency becomes lower in the order $Hg(CN)_2$ (412 cm^{-1}), $Hg(CN)_3^-$ (365 cm^{-1}), and $Hg(CN)_4^{2-}$ (335 cm^{-1}).

In the Hg–I stretching region, 100–150 cm^{-1}, no Raman lines were observed for any of the $Hg(CN)_xI_y$ complexes other than that of HgI_4^{2-} at 126 cm^{-1}. This is perhaps not too surprising because the polarizability of such complexes may be associated primarily with the CN group. In such a case, the Hg–I stretch may have little change in polarizability associated with it and thus would be quite weak in the Raman spectrum.

Ultraviolet Results. Formation of $Hg(CN)I_3^{2-}$ and $Hg(CN)_2I_x^{x-}$ in 5 *M* NaI.—Our experiments show the absorption in the 3200–4000-Å region is ascribable entirely to the species HgI_4^{2-} in 5 *M* NaI. The cyanide-containing complexes absorb only at shorter wavelengths. The results of Table II show the amount of HgI_4^{2-} remaining after formation of cyanide complexes and can be used to compute formation quotients for whatever cyanide complexes are indicated by the concentration dependence of the absorption.

The results of Table II could be represented only by assuming formation of both monocyanide–iodide and dicyanide–iodide complexes (but not the dicyanide complex alone). In this case the absorbance, *A*, is related to the concentrations of NaCN, HgI_2, and the cell path length, *t*, by eq 2 and 3, where brackets indicate stoichiometric concentrations and parentheses represent species concentration. The equilibrium quotients β_1 = (monocyanide)/(HgI_4^{2-})(CN^-) and β_2 = (dicyanide)/(HgI_4^{2-})$(CN^-)^2$ apply only to 5 *M* NaI. The measured value of ϵ is 19,690 M^{-1} cm^{-1}, where $\epsilon = \epsilon_{3225} - \epsilon_{3650}$ for HgI_4^{2-} in 5 *M* NaI.

$$A = \epsilon[\mathrm{Hg}]t/\{1 + \beta_1(\mathrm{CN}^-) + \beta_2(\mathrm{CN}^-)^2\} \qquad (2)$$

$$[\mathrm{CN}] = (\mathrm{CN}^-) + [\mathrm{Hg}]\{\beta_1(\mathrm{CN}^-) + 2\beta_2(\mathrm{CN}^-)^2\}/\{1 + \beta_1(\mathrm{CN}^-) + \beta_2(\mathrm{CN}^-)^2\} \qquad (3)$$

The free cyanide ion concentration (CN^-) may be eliminated by combining eq 2 and 3, but the resulting equation is awkward. In the present case, (CN^-) differs from [CN] by less than 10%, so that a successive approximation method could be devised which converged rapidly. Initial estimates β_1 and β_2 were obtained graphically. The values of *A* (calcd) in Table II were obtained using β_1 = 185 and β_2 = 980,000.

Values of β_1 and β_2 were optimized graphically using a plot displaying the deviations resulting from a preliminary choice of β_2. For this purpose, eq 2 is rearranged and both sides are divided by β_2', the preliminary value chosen for β_2

$$\frac{\epsilon[\mathrm{Hg}]t - A}{\beta_2' A(\mathrm{CN}^-)} - (\mathrm{CN}^-) = (\beta_1/\beta_2') + \left(\frac{\beta_2}{\beta_2'} - 1\right)(\mathrm{CN}^-) \qquad (2')$$

The left-hand side of eq 2′ was plotted *vs.* (CN^-); the slope of the best straight line is $(\beta_2/\beta_2') - 1$ and the intercept is β_1/β_2'. This procedure shares with somewhat more elaborate computer methods the virtue of displaying the extent of correlation in the uncertainties of the two parameters. We conclude $\beta_1 = 185 \pm 40$ and $\beta_2 = 980{,}000 \pm 50{,}000$. The calculated *A*'s of Table II differ from those observed by an average of 0.004 unit. Values of *A* computed using the extreme pairs β_1 = 145, β_2 = 1,030,000, and β_1 = 225, β_2 = 930,000 differ from the observed values by 0.008 unit on the average. The results at 4×10^{-5} *M* Hg(II) are in agreement with those at 8×10^{-5} *M* Hg(II).

The most striking feature of these results is that the formation quotient for the dicyanide complex is enormously higher than than for the monocyanide. This behavior suggests that a change in coordination number occurs upon addition of the second cyanide.

Formation of HgI(CN).—The spectra of Figure 3 show that a new species absorbing at 2370 Å is formed when $Hg(CN)_2$ is added to aqueous solutions of HgI_2. The isosbestic points indicate clearly that only one new absorbing species is formed. The dilution experiments described in the Results section were designed to distinguish between monomeric and polymeric complexes. The observed series of superimposable spectra are to be expected if, but only if, the new complex is monomeric, that is, if it contains only a single Hg(II) atom. All of our experiments are consistent with formation of HgI(CN). They do not rule out formation of mixtures such as $HgCN^+$ plus $HgI_2(CN)^-$ if one of the species does not absorb light in the 2200–3400-Å region. Uncharged mixed mercuric halides are well known;[9] therefore, formation of an uncharged complex in the present system seems likely. We conclude that HgI(CN) is formed by the reaction $HgI_2 + Hg(CN)_2 \rightarrow 2HgI(CN)$.

Our experiments provide two separate measures of the formation constant, *K*, for HgI(CN) where *K* =

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(8) L. H. Jones, *J. Chem. Phys.*, **27**, 665 (1957).

(9) T. G. Spiro and D. N. Hume, *J. Am. Chem. Soc.*, **83**, 4305 (1961).

$[HgI(CN)]^2/[HgI_2][Hg(CN)_2]$. From the solubility of HgI_2 measured in 0.4 *M* $Hg(CN)_2$, we compute K = 0.14. The concentration of the species HgI_2 is assumed to be equal to 1.05×10^{-4} *M*, the measured solubility in water. From the spectra of Figure 4 we compute K = 0.13. The spectra labeled 0 and 0.1 *M* $Hg(CN)_2$ are taken to be those of the species HgI_2 and HgI(CN), respectively. Beck and Gazier[10] report that K = 0.2 in dioxane and 0.11 in water.

Conclusions

The following picture appears consistent with both the ultraviolet and Raman results: (1) At low CN^- concentrations, but in concentrated NaI, tetrahedral HgI_4^{2-} reacts to give the mixed complex, $Hg(CN)I_3^{2-}$, of likely C_{3v} symmetry. (2) At slightly higher CN^- concentrations (and well before formation of $Hg(CN)I_3^{2-}$ is complete), formation of a dicyanide complex with a linear $Hg(CN)_2$ group becomes dominant, with iodides bound in equatorial positions. (3) These dicyanide complexes are still present at free CN^- concentrations of a few tenths molar, but $Hg(CN)_3I^{2-}$ predominates.

The results of this study provide no quantitative estimate for the number of iodide ions which are bound in mixed-ligand dicyanide complexes. Coordination with iodide in solid $KI \cdot Hg(CN)_2$ gives an equatorial ring of four iodides. It seems plausible, from stoichiometric considerations and from the fact that "free" $Hg(CN)_2$ is not observed, that the number of bound iodides in solution is <4 for the species we have designated $Hg(CN)_2I_x^{x-}$, in all but perhaps the most concentrated NaI solutions.

Monomeric HgI(CN) is formed when HgI_2 is dissolved in aqueous $Hg(CN)_2$ solutions.

Acknowledgments.—Professor John C. Bailar, Jr., provided helpful suggestions both for the experimental design and the interpretation of the results. Crystallographic properties of $NaI \cdot Hg(CN)_2 \cdot 2H_2O$ were determined by Professor A. Rosenzweig.

[10] M. T. Beck and F. Gazier, *J. Inorg. Nucl. Chem.*, **26**, 1755 (1964).

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY

Four- and Five-Coordinated Complexes of Cobalt(II) and Nickel(II) with Tridentate Schiff Bases

BY L. SACCONI AND I. BERTINI

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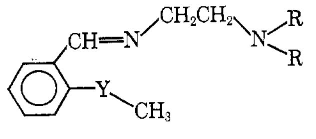
The Schiff bases derived from *o*-methoxybenzaldehyde (MOB) and N,N-dialkylethylenediamines ($MOBenNR_2$) and N,N-dialkyltrimethylenediamines ($MOBtnNR_2$) (both with the potential set of donor atoms ONN), or ethylenediamine ($(MOB)_2en$) and 1,2-propylenediamine ($(MOB)_2pn$) (both with the potential set of donor atoms ONNO), form adducts with cobalt(II) and nickel(II) salts of the general formula MLX_2. All of the complexes are of the high-spin type. The cobalt complexes are pseudo-tetrahedral. The nickel ones are five coordinated or pseudo-tetrahedral depending on the nature of the R substituent. The nickel complexes in solution with inert solvents often give rise to equilibria between the two species.

Introduction

After the recent discovery in this laboratory of some pentacoordinate, high-spin, Schiff-base complexes of nickel(II)[1,2] and cobalt(II),[2,3] a systematic study of this type of compound has been undertaken with the purpose of extending the available information on pentacoordinate complexes.

It has been found that the tridentate ligand $MABenNEt_2$ (I, Y = NH, R = C_2H_5) is particularly well suited to form high-spin pentacoordinate complexes with cobalt(II) and nickel(II) salts of the formula MLX_2.[4] In this instance the donor atom set is NNN. It is quite general to find that high-spin pentacoordinate complexes are formed with ligands containing nitrogen and/or oxygen donor atoms.[5] When the donor atoms are phosphorus or arsenic atoms, the pentacoordinate complexes formed are of the low-spin type.[6]



I

The ligand $MSBenNEt_2$ (I, Y = S, R = C_2H_5) has a donor atom set SNN and it too forms high-spin pen-

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[1] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

[2] L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **87**, 3102 (1965); L. Sacconi and I. Bertini, *ibid.*, **88**, 5182 (1966).

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