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THE INTERACTION OF MERCURY(II) CYANIDE WITH COORDINATIVELY SATURATED INERT CYANO COMPLEXES. I

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It was shown that $Hg(CN)_2$ can interact with coordinatively saturated inert cyano complexes in aqueous solution. By means of spectrophotometry and potentiometry, the stability constants of the heteropolynuclear complexes formed by the reaction of the $Hg(CN)_2$ with $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{3-}$ and $Ru(CN)_6^{4-}$ were determined at 25°C. It seems that the less the thermodynamic stability of the original cyano complex the more stable is the product.

INTRODUCTION

A good deal of evidence is to be found in the literature that polynuclear complexes can form by reaction of some coordinatively saturated inert complex, in which one or more ligands possess an unshared electron pair, with a metal ion having an affinity for such a ligand. As a result of the interaction a complex results with two or more nuclei, the ligand referred to forming a bridge between the original and the newly coordinated metal ions.

We shall mention only a few selected examples. Halogen bridges were demonstrated by Dollimore *et al.*[1] in the solid compounds $[MA_4X_2]X \cdot HX \cdot 2H_2O$ (M=Co, Cr, Rh; A = pyridine, $\frac{1}{2}$ en, $\frac{1}{2}$ bipy, $\frac{1}{2}$ o-phen; X=Cl, Br), and by Dawes and Kemmitt[2] in the adducts of mercury halogenides and cycloocta-1,5-diene rhodium complexes.

Dows *et al.*[3] found cyanide bridges in various solid cyano complexes. Shriver and Rupp[4,5] adsorbed compounds of a Lewis acid character (BF_3, $SnCl_4$, GeF_4, SiF_4) onto solid cyano complexes as onto Lewis bases; during the adsorption addition compounds were formed (e.g. $K_2Ni(CN)_4 \cdot 4BF_3$). They proved conclusively that the B, Sn, Ge or Si is always bonded to the nitrogen of the cyanide and a bridging linkage of the type $Ni-C\equiv N-BF_3$ is established.

Wasson and Trapp[6] found $Cr-NCS-M'$ bridges in heavy metal (Ag, Cd, Hg, Tl, Pb, Cu) salts of $Cr(NCS)_6^{3-}$. Oki *et al.*[7,8] showed the interaction of transition metal ions with the thiocyanate groups of Reinicke type complexes. They found uniformly that the new coordination occurs in every case at the sulphur end of the thiocyanate, and a $M-NCS-M'$ bridge is formed.

However, interactions of such kind are not found merely in the solid phase. Werner *et al.*[9] at the beginning of the century, and other research workers too[10-12] since then, have described for instance that in aqueous solution Ag^+ and Hg^{2+}, and H^+ too,[13] can coordinate to the thiocyanate group in thiocyanato —Co(III)-amine complexes, e.g. $Co(NH_3)_5NCS^{2+}$. The existence of Co—NCS—M bridges in the compounds formed during the reaction has been proved conclusively.

Schwarzenbach and Schellenberg[14] studied the complex-forming properties, likewise in aqueous solution, of the stable cation CH_3Hg^+, demonstrated the existence of among others $Co(NH_3)_5NCS-HgCH_3^{2+}$ and $Co(CN)_5-CN-HgCH_3^{2-}$, and determined their stability constants. According to unpublished data of Hohl and Geier,[15] CH_3Hg^+ forms polynuclear complexes with hexacyanoferrate(II) and hexacyanoferrate(III).

Kane,[16] in the middle of last century, and Strömholm,[17,18] at the beginning of this century, prepared several solid addition compounds from certain coordinatively saturated cyano complexes and mercury(II) cyanide:

$K_4Fe(CN)_6 \cdot 3Hg(CN)_2 \cdot 4H_2O$,

$K_2Ni(CN)_4 \cdot Hg(CN)_2 \cdot 2H_2O$ and
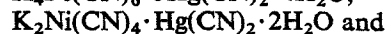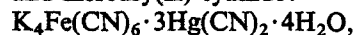
$K_2Pt(CN)_4 \cdot Hg(CN)_2 \cdot 2H_2O$. It was also mentioned that similar compounds could not be prepared from $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Cr(CN)_6$ or $K_4Mo(CN)_8$.

However, nothing can be found in the literature

referring to whether there is an interaction in aqueous solution between $Hg(CN)_2$ and co-ordinatively saturated cyano complexes. We set out to resolve this problem.

EXPERIMENTAL

The origin or methods of preparation of the cyano complexes studied are as follows:

$Hg(CN)_2$: Gehe and Co. AGDresden DAB 6, Ph. Ang. 1, Cod. Franc. 1937; Merck DAB 6 Cod. Franc. 1965; Mallinckrodt Anal. reag. $K_4Fe(CN)_6$: Reanal, anal. grade. $K_4Mo(CN)_8 \cdot 2H_2O$: prepared by the method of Furman and Miller.[19]
$K_3Mo(CN)_8$: prepared by the method of Kolthoff and Tomsicek[20] (only in solution). $K_2Pd(CN)_4$: prepared by the method of Bigelow.[21] $K_3Co(CN)_6$: prepared by the method of Bigelow.[22] $K_3Rh(CN)_6$: prepared by the method of Schmidtke.[23]
$K_2Ni(CN)_4$: prepared from $Ni(OH)_2$ with the stoichiometric amount of KCN. The product was purified by double recrystallization.

$K_4Ru(CN)_6 \cdot 3H_2O$: this was prepared by the following method, differing from the methods of Howe,[24] Krauss[25] and De Ford.[26] 1.4 g $RuCl_3$ (with a water content of 40%) was thoroughly dry mixed in a quartz crucible with 2.5 g KCN, and then a few drops of distilled water were added. There was a violent evolution of gas and on becoming warm the material turned dark green. When heated for a few minutes on an electric heater it became completely white (if heating was prolonged the separation of metallic Ru could be observed). The white $K_4Ru(CN)_6$ containing KCN and KCl was dissolved in 100 ml water, and the solution was heated on a water-bath and treated with active carbon. After two active carbon treatments the filterate was crystal-clear and colourless. This filtrate was evaporated almost to dryness when white crystals separated out. 50% ethanol was added to the cold mixture; the greater part of the KCN and KCl present was kept in solution while the $K_4Ru(CN)_6 \cdot 3H_2O$ was almost totally precipitated. The crystals were filtered off, washed with 50% ethanol until the filtrate was neutral, then with 96% ethanol, and dried at 60° C. After double recrystallization from water the product was in the form of white tabular crystals. Its aqueous solution was neutral and its spectrum agreed with that given in the literature.[25] Yield: 68%.

Experiments were carried out in pure aqueous solution at 25° C. Since $Hg(CN)_2$ behaves as a non-electrolyte its presence does not affect the ionic strength, and only in a few cases was the ionic strength adjusted with sodium perchlorate.

Spectrophotometric measurements were made with Perkin–Elmer 402 and Hitachi–Perkin–Elmer 139 spectrophotometers, and potentiometric measurements with a Radelkis OP–205 precision pH-meter.

Stability constants were calculated on an ODRA 1013 computer.

RESULTS

A. Spectrophotometric Measurements

Experiments with $K_4Fe(CN)_6$ The basic experimental observation was that the ultraviolet spectrum of a mixture of $K_4Fe(CN)_6$ and $Hg(CN)_2$ is not composed additively of the spectra of its components. The spectra obtained can be seen in Figure 1.
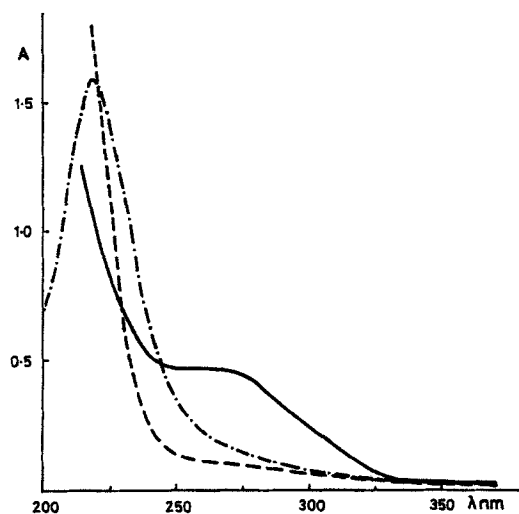
FIGURE 1   Effect of $Hg(CN)_2$ on the ultraviolet spectrum of $Fe(CN)_6^{4-}$. (—·—·—) 2 × 10^{-4} M $K_4Fe(CN)_6$; (— — —) 0.25 M $Hg(CN)_2$; (———) difference between the spectra of a 2 × 10^{-4} M $K_4Fe(CN)_6$ + 0.25 M $Hg(CN)_2$ mixture and of 0.25 M $Hg(CN)_2$.

The maximum difference between the corresponding spectra is at 265 nm.

The above spectral change shows conclusively that there *is* some interaction between aqueous solutions of hexacyanoferrate(II) and $Hg(CN)_2$.

(If not, the curve —— would be identical with —·——·.) However, there are several possibilities for the explanation of the effect. It must be taken into consideration that even concentrations of Hg^{2+}

FIGURE 2 Spectra of 2×10^{-4} M $K_4Fe(CN)_6$ and 2×10^{-4} M $Na_3Fe(CN)_5(OH_2)$.

of 10^{-7} M can catalyse the aquation of hexa-cyanoferrate(II).[27, 28] Thus it is conceivable that

(i) the spectral change is caused by aquation of the hexacyanoferrate(II) following the interaction with $Hg(CN)_2$;

(ii) $Fe(CN)_5(OH_2)^{3-}$ formed in a relatively fast aquation reacts with the $Hg(CN)_2$;
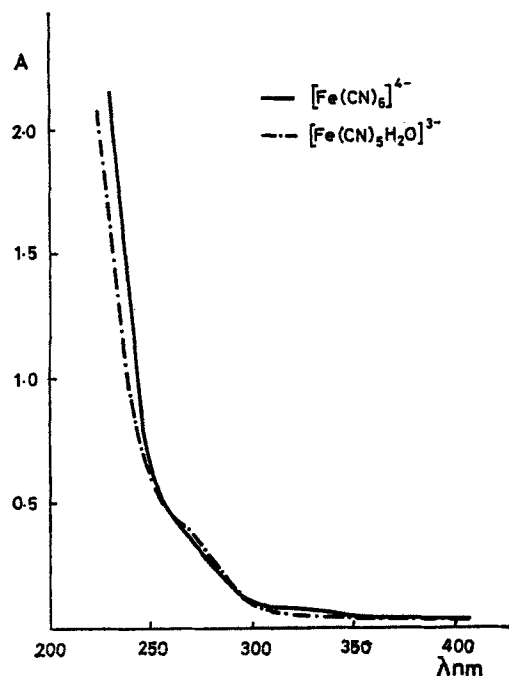
(iii) the $Hg(CN)_2$ coordinates directly to the hexacyanoferrate(II) and a polynuclear complex is formed.

In order to decide this question, the following experiments were carried out:

(a) The progress of the reaction was studied with regard to time (aquation generally requires a long time while formation of an addition compound is a very fast process).

It was observed that the extinction measured at 265 nm after the mixing of the reactants increases for about 1–2 minutes and then attains a constant value. Thus there is a certain time effect the

extent of which, however, is not characteristic of either type of interaction.

(b) Bearing in mind the high stability of $Hg(CN)_4^{2-}$, we added to a mixture of 2×10^{-4} M $Fe(CN)_6^{4-}$ and 0.21 M $Hg(CN)_2$ just sufficient 0·42 M KCN for the formation of $Hg(CN)_4^{2-}$.

Instead of the spectrum characteristic of the interaction, the original spectrum of 2×10^{-4} M $Fe(CN)_6^{4-}$ was recovered. This means that neither (i) nor (ii) but the presence of the addition compound formed during the $Fe(CN)_6^{4-} - Hg(CN)_2$ interaction is responsible for the spectral effect; that is, the reaction occurring on the addition of the cyanide is:

$$Fe(CN)_6 \cdot Hg(CN)_2^{4-} + 2CN^- \longrightarrow$$
$$Fe(CN)_6^{4-} + Hg(CN)_4^{2-} \quad (1)$$

This finding is supported by experiment (3).

(c) The spectra of identical concentrations of $Fe(CN)_6^{4-}$ and $Fe(CN)_5(OH_2)^{3-}$ were taken in the presence and absence of $Hg(CN)_2$. As can be seen in Figures 2 and 3, in the absence of $Hg(CN)_2$ the spectra of $Fe(CN)_6^{4-}$ and $Fe(CN)_5(OH_2)^{3-}$ solu-
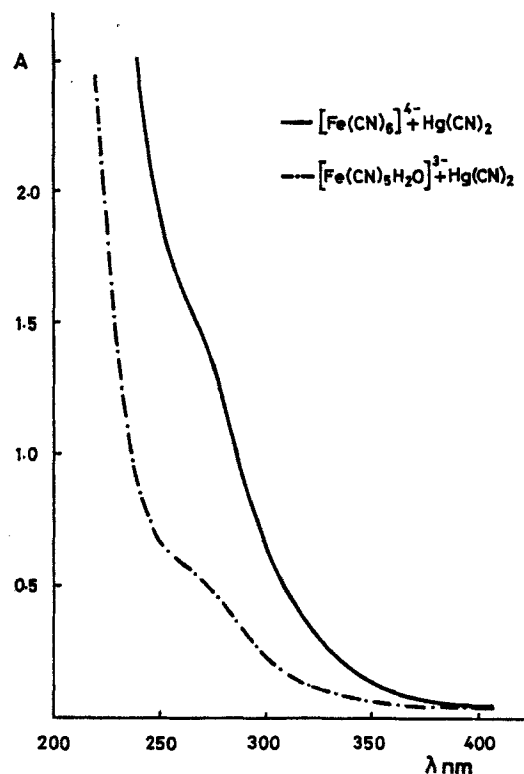

FIGURE 3 Effect of 0.25 M $Hg(CN)_2$ on the spectra of 2×10^{-4} M $K_4Fe(CN)_6$ and 2×10^{-4} M $Na_3Fe(CN)_5(OH_2)$

tions are very similar, whilst in the presence of $Hg(CN)_2$ there is a considerable difference in just the critical wavelength region. Thus, if $Hg(CN)_2$ does react with $Fe(CN)_5(OH_2)^{3-}$ the large spectral change observed is not caused by this process.

In this way it could be decided that of the three possibilities mentioned only the third, the direct

$Fe(CN)_6^{4-}$—$Hg(CN)_2$ system. However, since the number of $Hg(CN)_2$ molecules coordinated in the solid addition compounds is never more than half the number of cyano groups in the parent complex, it would not be reasonable to assume the formation of polynuclear complexes containing more than three $Hg(CN)_2$ molecules.

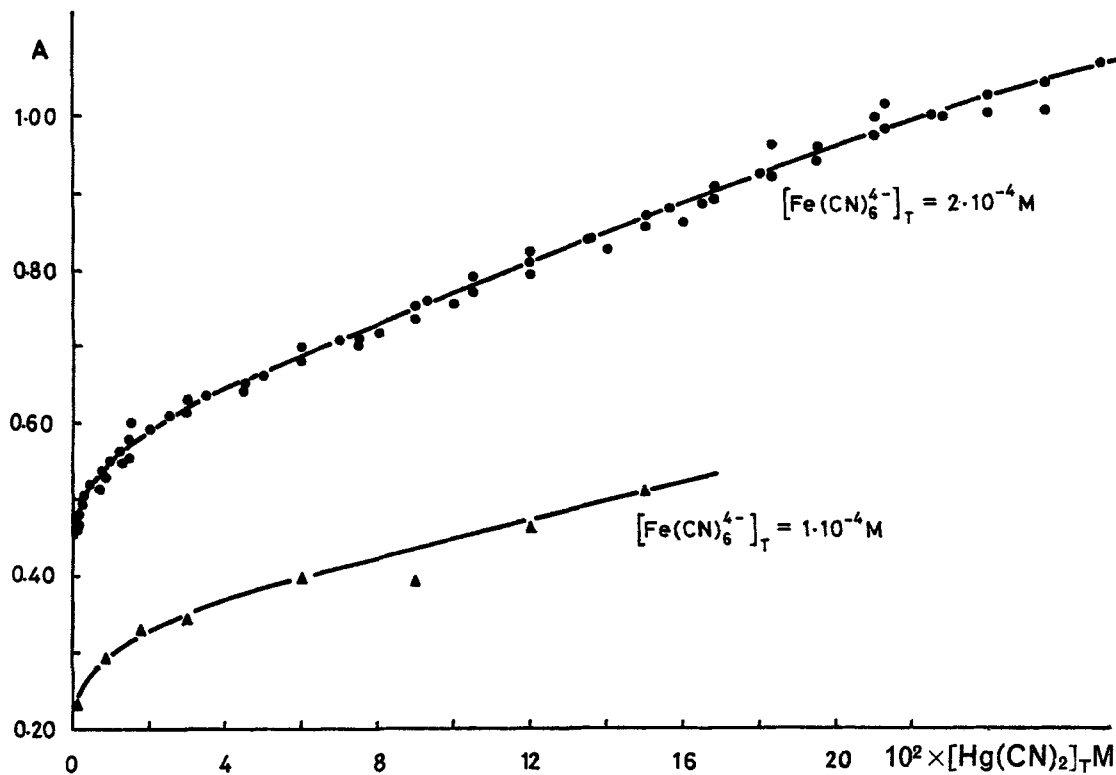FIGURE 4   Effect of $Hg(CN)_2$ on the extinction of $K_4Fe(CN)_6$ at 265 nm.

coordination of $Hg(CN)_2$ to $Fe(CN)_6^{4-}$, leads to the spectral difference.

In the following, with a constant concentration of $K_4Fe(CN)_6$ the concentration of $Hg(CN)_2$ was varied and the extinction of the mixture measured at 265 nm. In the preparation of the mixtures the following amounts of the appropriate solutions were measured from microburettes:

1.0 ml 2×10^{-3} M or 1×10^{-3} M
$K_4Fe(CN)_6$ + x ml 0.3 M $Hg(CN)_2$ + $(9 - x)$ml water. The results obtained can be seen in Figure 4.

From the shapes of the curves it can be concluded that the presence of definitely more than one complex species must be considered in the

Thus, the following stepwise equilibria must be considered:

$$Fe(CN)_6^{4-} + Hg(CN)_2 \overset{K_1}{\rightleftharpoons} Fe(CN)_6 \cdot Hg(CN)_2^{4-} \quad (2)$$

$$Fe(CN)_6 \cdot Hg(CN)_2^{4-} + Hg(CN)_2 \overset{K_2}{\rightleftharpoons} Fe(CN)_6 \cdot 2Hg(CN)_2^{4-} \quad (3)$$

$$Fe(CN)_6 \cdot 2Hg(CN)_2^{4-} + Hg(CN)_2 \overset{K_3}{\rightleftharpoons} Fe(CN)_6 \cdot 3Hg(CN)_2^{4-} \quad (4)$$
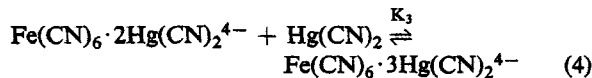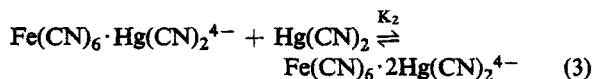
The curves shown in Figure 4 were used for the determination of the stability constants.

Since the extinction of $Hg(CN)_2$ is negligible at this wavelength (265 nm), and since it appears from the shape of the curves that K_3 is very small

(which means that the formation of the complex product of reaction (4) can be neglected), the following relations are valid:

$$A = \epsilon_0[Fe(CN)_6^{4-}] + \epsilon_1 K_1[Fe(CN)_6^{4-}][Hg(CN)_2] + \\ + \epsilon_2 K_1 K_2[Fe(CN)_6^{4-}][Hg(CN)_2]^2 \quad (5)$$

$$[Fe(CN)_6^{4-}]_T = [Fe(CN)_6^{4-}](1 + K_1[Hg(CN)_2] \\ + K_1 K_2[Hg(CN)_2]^2) \quad (6)$$

$$[Hg(CN)_2]_T = [Hg(CN)_2](1 + K_1[Fe(CN)_6^{4-}] \\ + 2K_1 K_2[Fe(CN)_6^{4-}][Hg(CN)_2]) \quad (7)$$

where

$$\epsilon_0 = \epsilon_{Fe(CN)_6^{4-}} \ i \quad \epsilon_1 = \epsilon_{Fe(CN)_6 \cdot Hg(CN)_2^{4-}} \ i$$

$$\epsilon_2 = \epsilon_{Fe(CN)_6 \cdot 2Hg(CN)_2^{4-}}$$

The solution of these equations was obtained with a computer by iteration. The constants obtained were:

for 2×10^{-4} M $K_4Fe(CN)_6$:

$$\epsilon_1 = 2960 \pm 20 \ M^{-1} cm^{-1}$$
$$K_1 = 240 \pm 25 \ M^{-1}$$

for 9.82×10^{-5} M $K_4Fe(CN)_6$:

$$\epsilon_1 = 2950 \pm 20 \ M^{-1} cm^{-1}$$
$$K_1 = 240 \pm 25 \ M^{-1}$$

Due to the limited accuracy of the experimental data and to theoretical difficulties arising in the calculation of K_2 and ϵ_2, their values could not be obtained exactly: however, it is possible to say that $0 < K_2 \leqslant 7.0 \ M^{-1}$ and $\epsilon_2 \gg 3000 \ M^{-1} \ cm^{-1}$. The extinction values calculated using K_1 and ϵ_1 agree with the curves drawn in Figure 4 in the $Hg(CN)_2$ concentration range $0 - 10^{-2}$ M.

From all this it can be stated that in aqueous solution $Fe(CN)_6^{4-}$ reacts with $Hg(CN)_2$ to give heteropolynuclear complexes. The stability constant at 25° C of the first complex formed is $K_1 = 240 \ M^{-1}$ and this is independent of the hexacyanoferrate(II) concentration.

It must be noted that in the experiments carried out with $Hg(CN)_2$ from Merck a reaction took place which was completely different from that described above. After the addition of $Hg(CN)_2$ the instantly obtained high extinction at 265 nm decreased quickly and continuously, and in about 20 minutes the originally almost colourless solution became blue (Prussian blue). This different reaction was probably caused by some heavy metal impurity in the $Hg(CN)_2$ since mercuric cyanide containing

quite a high proportion of basic mercuric cyanide did not lead to a similar effect.

Experiments with $K_4Ru(CN)_6$ In the presence of $Hg(CN)_2$ a similar change was observed in the ultraviolet spectrum of an aqueous solution of $K_4Ru(CN)_6$ as in the spectrum of hexacyanoferrate(II). The spectra obtained are given in Figure 5.
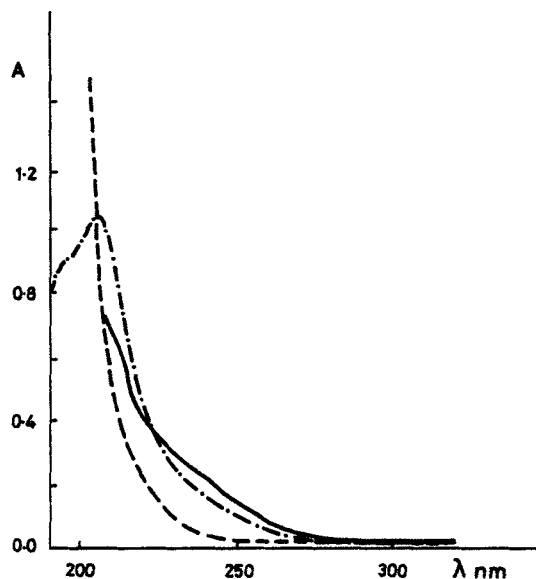
FIGURE 5. Effect of $Hg(CN)_2$ on the ultraviolet spectrum of $K_4Ru(CN)_6$. (—.—.) spectrum of 0.27 M $Hg(CN)_2$; (———) spectrum of 1×10^{-4} M $K_4Ru(CN)_6$; (———) difference between the spectra of a 0.27 M $Hg(CN)_2$ + 1×10^{-4} M $K_4Ru(CN)_6$ mixture and of 0.27 M $Hg(CN)_2$.

It can be seen that the greatest difference from additivity occurs at 238 nm. When an amount of KCN just sufficient to convert the $Hg(CN)_2$ to $Hg(CN)_4^{2-}$ was added to a mixture of $Ru(CN)_6^{4-}$ and $Hg(CN)_2$, the corresponding $Ru(CN)_6^{4-}$ spectrum was recovered quantitatively. Thus, in this case too the formation of heteropolynuclear complexes similar to those above must be considered.

With the $K_4Ru(CN)_6$ concentration constant at 2×10^{-4} M the $Hg(CN)_2$ concentration was varied. The extinctions measured at 238 nm are given in Figure 6. The mixtures were prepared as for hexacyanoferrate(II). The value of the extinction became constant practically at once and after this did not change.

From the shape of the curve it appears that in this case the formation of several, but for the reasons mentioned for hexacyanoferrate(II) a maximum of three, complexes must be considered. The equilibria and the other relevant relations can be described by equations similar to (2)–(7). The

spectrum of an aqueous $K_4Mo(CN)_8$—$Hg(CN)_2$ mixture. On the addition of just sufficient KCN to form $Hg(CN)_4{}^{2-}$ the original spectrum of $K_4Mo(CN)_8$ was recovered. The maximum difference between the appropriate spectra, and thus the most suitable wavelength for the determination
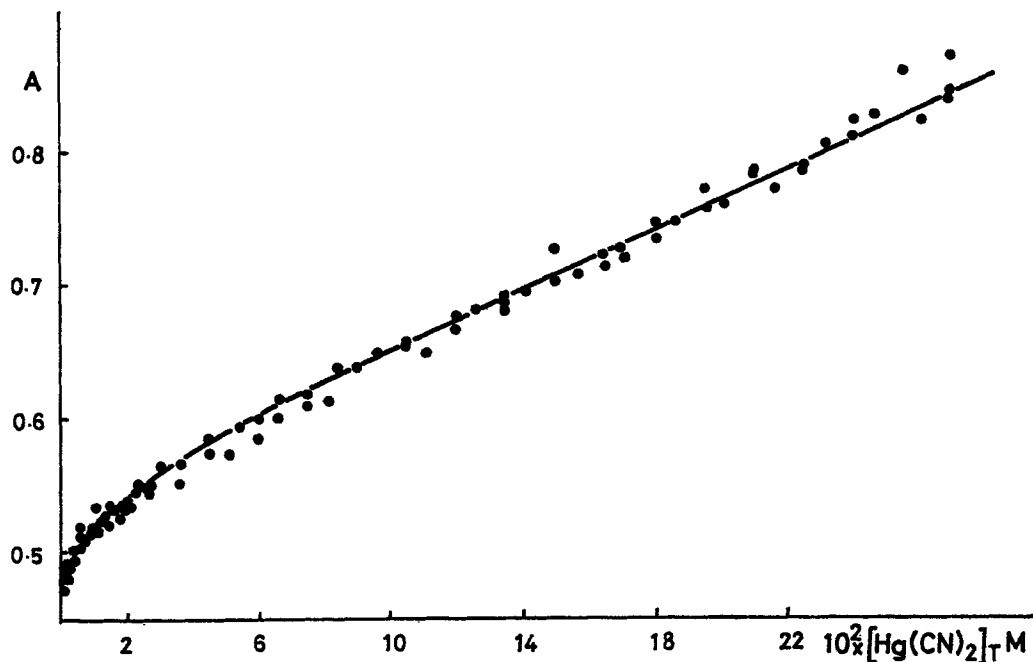
FIGURE 6   Effect of $Hg(CN)_2$ on the extinction of 2×10^{-4} M $K_4Ru(CN)_6$ at 238 nm.

calculation of the constants was done on a computer with an iteration method, and when the extinction values were recalculated using the constants K_1 and ϵ_1 they agreed with the curve drawn in Figure 6 in the $Hg(CN)_2$ concentration range $0–2.1 \times 10^{-2}$ M. The values of the constants are:

$\epsilon_0 = 4.70 \times 10^3$ M^{-1} cm^{-1};
$\epsilon_1 = 5840 \pm 50$ M^{-1} cm^{-1}; $K_1 = 78 \pm 8$ M^{-1};
$\epsilon_2 \geqslant 6 \times 10^3$ M^{-1} cm^{-1}; $0 < K_2 \leqslant 2$. For the reasons mentioned the values of K_2 and ϵ_2 could only be estimated.

With $Ru(CN)_6{}^{4-}$ too the Merck $Hg(CN)_2$ gave a totally different reaction. The extinction changed continuously and during the reaction the appearance of drops of mercury in the mixture could be observed under the microscope.

Experiments with $K_4Mo(CN)_8$ A difference from additivity was also observed in the ultraviolet

of the stability constants, was at 265 nm. The above is shown in Figure 7.

The extinctions of mixtures prepared as described for $K_4Fe(CN)_6$ and containing a constant initial concentration of $K_4Mo(CN)_8$ of 6.4×10^{-4} M were measured at 265 nm as a function of the concentration of added $Hg(CN)_2$. The results are given in Figure 8.

The character of this curve is similar to those already discussed and so the values of the corresponding constants were calculated from the analogous equilibria and equations to (2)–(7).

The extinction values calculated back with the constants K_1 and ϵ_1 thus obtained agree with the curve drawn in Figure 8 in the $Hg(CN)_2$ concentration range $0–2.5 \times 10^{-2}$M. The constants obtained were: $\epsilon_0 = 1.71 \times 10^{-3}$ M^{-1} cm^{-1};
$\epsilon_1 = 1900 \pm 20$ M^{-1} cm^{-1}; $K_1 = 19.8 \pm 2$ M^{-1};
$\epsilon_2 \geqslant 2.2 \times 10^3$ M^{-1} cm^{-1}; $0 < K_2 \leqslant 1$.

It is interesting to note that $Hg(CN)_2$ signi-

ficantly affects the photochemical reactions of aqueous $Mo(CN)_8^{4-}$ which have been studied by many authors.[29]
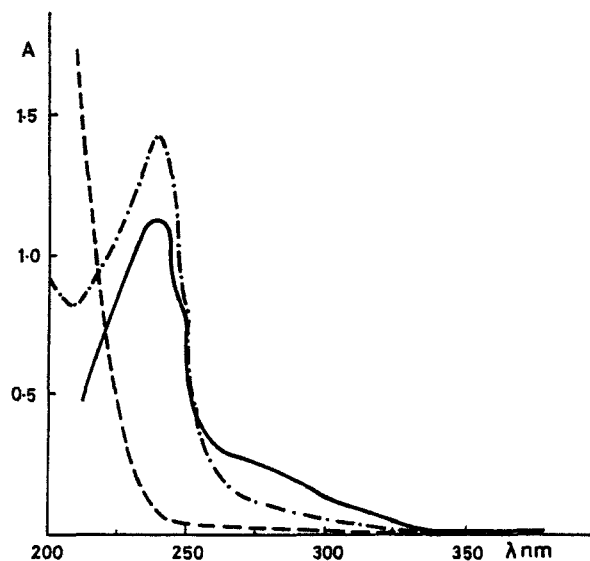

FIGURE 7 Effect of $Hg(CN)_2$ on the ultraviolet spectrum of $K_4Mo(CN)_8$. (— — —) sprectrum of 0.25 M $Hg(CN)_2$; (—·—·—) spectrum of 1×10^{-4} M K_4Mo $(CN)_8$; (———) difference between the spectra of a 0.25 M $Hg(CN)_2$ + 1×10^{-4} M $K_4Mo(CN)_8$ mixture and of 0.25 M $Hg(CN)_2$.

As is well-known, in the absence of $Hg(CN)_2$ the original yellow colour of an aqueous solution of $Mo(CN)_8^{4-}$ is very rapidly changed by ultraviolet light (250 nm $< \lambda <$ 400 nm) and in a few minutes the solution is red. At the same time the pH of the solution increases significantly. If irradiation is stopped, the effects of heat or KCN are to turn the solution yellow again. On further irradiation of the red solution it becomes yellow, then green and blue. This process is irreversible and takes place during a much longer time (several hours) than the former. In the presence of $Hg(CN)_2$ on prolonged (10–15 hours) irradiation the solution remains yellow but finally slowly becomes a little blue. Thus it can be seen that the $Mo(CN)_8^{4-}$—$Hg(CN)_2$ interaction strongly affects the photochemical reaction. Because of the extreme complexity of the reaction, however, there are so far no reliable conclusions as to its mechanism.

With the Merck $Hg(CN)_2$ a reaction differing from that described was observed; during this the appearance of mercury drops could be detected under the microscope.

Other complexes In an analogous way the spectra were taken of aqueous solutions of $K_3Fe(CN)_6$, $K_3Mo(CN)_8$, $K_2Ni(CN)_4$, $K_3Co(CN)_6$,
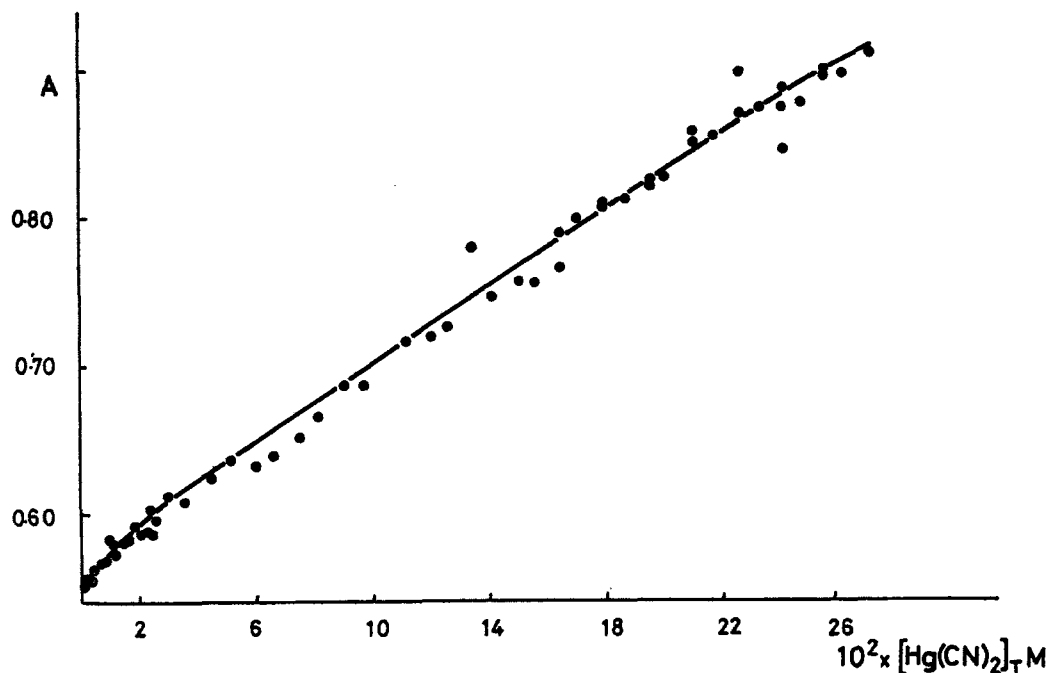

FIGURE 8 Effect of $Hg(CN)_2$ on the extinction of 6.4×10^{-4} M $K_4Mo(CN)_8$ at 265 nm.

$K_3Rh(CN)_6$ and $K_2Pd(CN)_4$ in the absence and the presence of $Hg(CN)_2$, but no spectral effect could be observed. For this reason we attempted to detect an interaction by using a different independent experimental method.
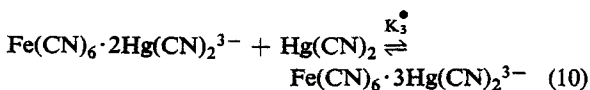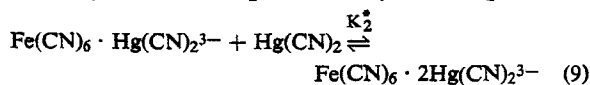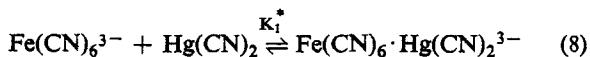
As the $Fe(CN)_6^{3-}$—$Fe(CN)_6^{4-}$ and $Mo(CN)_8^{3-}$—$Mo(CN)_8^{4-}$ systems are reversible redox systems, this offers a possibility by the measurement of their redox potentials. In the following, experimental results are reported in this connection.

B. Potentiometric Measurements

Experiments with $K_3Fe(CN)_6$ The e.m.f. of the following galvanic cell was measured at 25° C:
$Pt|0.01$ M $Fe(CN)_6^{3-}$, 0.01 M $Fe(CN)_6^{4-}$;
X M $Hg(CN)_2\|0.1$ M $NaClO_4\|$ satd. $KCl|$ satd. calomel; in the concentration range $X = 0$–0.2 M.

If it is assumed that there is no interaction between $Hg(CN)_2$ and $Fe(CN)_6^{3-}$, the effect of $Hg(CN)_2$ on the e.m.f. of the cell is to make it increase because as a result of the $Fe(CN)_6^{4-}$—$Hg(CN)_2$ interaction the concentration of free $Fe(CN)_6^{4-}$ in the solution decreases. The thus expected, calculated e.m.f. and that measured are given in Figure 9. The large difference can only be explained by the $Hg(CN)_2$ reacting not only with $Fe(CN)_6^{4-}$ but also with $Fe(CN)_6^{3-}$, and the free $[Fe(CN)_6^{3-}]:[Fe(CN)_6^{4-}]$ ratio therefore does not change to the extent expected from the calculation. The fact that an increase of e.m.f. is observed shows that the complex formed with $Fe(CN)_6^{4-}$ is more stable than that formed with $Fe(CN)_6^{3-}$.

In the aqueous solutions simultaneously containing $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ and $Hg(CN)_2$ the following equilibria must be considered in addition to (2), (3) and (4):

$$Fe(CN)_6^{3-} + Hg(CN)_2 \overset{K_1^*}{\rightleftharpoons} Fe(CN)_6 \cdot Hg(CN)_2^{3-} \quad (8)$$

$$Fe(CN)_6 \cdot Hg(CN)_2^{3-} + Hg(CN)_2 \overset{K_2^*}{\rightleftharpoons} \\ Fe(CN)_6 \cdot 2Hg(CN)_2^{3-} \quad (9)$$

$$Fe(CN)_6 \cdot 2Hg(CN)_2^{3-} + Hg(CN)_2 \overset{K_3^*}{\rightleftharpoons} \\ Fe(CN)_6 \cdot 3Hg(CN)_2^{3-} \quad (10)$$

If the complexes containing three molecules of $Hg(CN)_2$ are disregarded because of their very low stabilities, the following relations are valid:

$$E = E° + 0.059 \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]} \quad (11)$$

$$[Fe(CN)_6^{4-}]_T = [Fe(CN)_6^{4-}] \\ \{1 + K_1[Hg(CN)_2] + K_1K_2[Hg(CN)_2]^2\} \quad (12)$$

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{3-}] \\ \{1 + K_1^*[Hg(CN)_2] + K_1^*K_2^*[Hg(CN)_2]^2\} \quad (13)$$

$$[Hg(CN)_2]_T = [Hg(CN)_2]\{1 + K_1^*[Fe(CN)_6^{3-}] \\ + K_1[Fe(CN)_6^{4-}] + 2(K_1^*K_2^*[Fe(CN)_6^{3-}] \\ + K_1K_2[Fe(CN)_6^{4-}])[Hg(CN)_2]\} \quad (14)$$

As K_1 and K_2 known, there is a possibility of the calculation of K_1^* and K_2^*. This was done by computer using the least squares method and K_1^* was found to be 170 ± 20 M^{-1}. Because of the
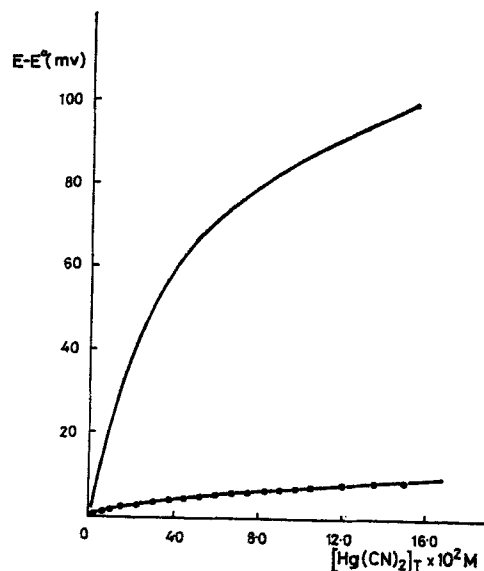

FIGURE 9. Effect of $Hg(CN)_2$ on the redox potential of the $Fe(CN)_6^{3-}$ — $Fe(CN)_6^{4-}$ system. $[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{4-}]_T = 0.01$ M. Upper curve: Change of the redox potential values as a function of the $Hg(CN)_2$ concentration, taking into consideration the $Fe(CN)_6^{4-}$ — $Hg(CN)_2$ interaction. Lower curve: The experimentally measured redox potential values as a function of the $Hg(CN)_2$ concentration.

complexity of the calculation and the limited accuracy of the experimental data, K_2^* could be estimated as $0 < K_2^* \leqslant 5$ M^{-1}.

Experiments with $K_3Mo(CN)_8$ The redox potential was measured as a function of $Hg(CN)_2$ concentration in solutions containing 0.01 M $K_4Mo(CN)_8$, 0.01 M $Na_3Mo(CN)_8$, 0.1 M $NaClO_4$ and various amounts of $Hg(CN)_2$ (the cell arrangement was similar as for $K_3Fe(CN)_6$). Because of the extreme

light-sensitivity of $Mo(CN)_8^{3-}$, the experiments were carried out in a darkened room in the diffuse light of a table lamp. In the absence and presence of $Hg(CN)_2$ $(7.5 \times 10^{-3}.- 0.229 M)$, identical values were found for E, 0.790 V. Since the spectrophotometric study showed that $Mo(CN)_8^{4-}$ forms a complex with $Hg(CN)_2$, the unchanged value of the e.m.f. shows that $Mo(CN)_8^{3-}$ interacts with $Hg(CN)_2$ to the same extent as does $Mo(CN)_8^{4-}$.

The existence of the interaction is supported by the fact that $Hg(CN)_2$ also affects the photochemical reactions of $Mo(CN)_8^{3-}$. In the absence of $Hg(CN)_2$, the effect of irradiation is to turn an aqueous solution of $Mo(CN)_8^{3-}$ rapidly (2–3 minutes) from yellow to green, then reddish-brown and dark brown and turbid; however, in the presence of $Hg(CN)_2$ the solution is still yellow after 20 minutes. Nevertheless, on prolonged irradiation this too turns brown.

DISCUSSION OF THE RESULTS

It could be shown that in aqueous solution $Hg(CN)_2$ interacts with coordinatively saturated inert cyano complexes and as a result heteropolynuclear complexes are formed.

As has already been mentioned in connection with the results obtained for hexacyanoferrate(II), it appears from the composition of the solid adducts that in the compounds formed one $Hg(CN)_2$ is bonded to two cyano groups of the parent complex; this assumption is supported by the fact that in chloroform/ethanol solution dicyano-bis(1,10-phenanthroline)-iron(II) forms only a single complex, $Fe(II)(o\text{-phen})_2(CN)_2 \cdot Hg(CN)_2$ with $Hg(CN)_2$[30].

At first sight it appears obvious that the bond is formed with an unshared electron pair of the cyano nitrogen. This would mean, however, that in the bridging system
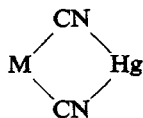
the structure of the cyano group can not be linear. Linearity can be achieved in three ways:

(a) if the $Hg(CN)_2$ coordinates to only one cyano group and an M—CN—Hg bridge is formed;

(b) if the mercury is bonded to the carbon atom of the cyano groups:
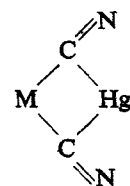
(c) if the mercury is bonded to the π-electrons of the cyano groups.

An X-ray study of the solid addition compounds is now under way to decide this question.

It was observed that interaction is not necessarily accompanied by a spectral effect. It occurs only in those cases when there is a possibility for the increase of the oxidation number of the central metal ion, i.e. with $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$. At such time the interaction probably takes place with a partial electron transfer and this causes the spectral effect.

This is supported by the experimental observation[31] that $Co(CN)_5^{3-}$ reacts stoichiometrically with $Hg(CN)_2$ and as the end-products of a true redox reaction $Co(CN)_6^{3-}$ and metallic mercury are formed.

It may be assumed that there is a relation between the stability constant of a heteropolynuclear complex formed with $Hg(CN)_2$ and the thermodynamic stability of the coordinatively saturated inert cyano complex acting as parent complex. It seems that the greater the thermodynamic stability of the parent complex, the smaller the "residual" affinity of the bound cyanide for the $Hg(CN)_2$, and so a polynuclear complex of lower stability is formed.

The data available are not in contradiction with this assumption. If the mean stability constant $\log {}^N\!\sqrt{\beta_N}$ is accepted as a numerical measure of the thermodynamic stability, this may be compared with the experimentally found stability constants. Such a comparison may be seen in Table I.

As a result of the lack of literature data referring to the thermodynamic stabilities of the other coordinatively saturated inert cyano complexes, a wider comparison could not be made.

The experimental results showed that it is not possible to find a clear-cut connection between the formation of the solid addition compounds and the interactions in solution. In aqueous solution $Hg(CN)_2$ forms complexes with $K_3Fe(CN)_6$, $K_4Mo(CN)_8$, $K_4Fe(CN)_6$ and $K_4Ru(CN)_6$, but

solid addition compounds can be prepared only in the cases of $K_4Fe(CN)_6$ and $K_4Ru(CN)_6$[32].

The fact that interactions could not be detected in the cases of $Ni(CN)_4^{2-}$, $Co(CN)_6^{3-}$, $Rh(CN)_6^{3-}$ and $Pd(CN)_4^{2-}$ with $Hg(CN)_2$ does not necessarily

TABLE I

Comparison of the stability constants of polynuclear complexes formed by $Hg(CN)_2$ with the "mean stability constants" of the parent complexes.

Parent complex	$\log \sqrt[N]{\beta_N}$	$K_1 M^{-1}$	$\log K_1$[a]	$\log K_2$[a]
$Fe(CN)_6^{4-}$	5, 9	240	7.66	7.12
$Fe(CN)_6^{3-}$	7, 3	170	4.13	3.76

[a] The stability constants of the complexes formed with methylmercury ion at 20°C and an ionic strength of 0.1 M[15]

mean that complexes are not formed, but merely that the experimental methods so far used were not able to show their presence. From the high thermodynamic stabilities of these complexes, however, it may be presumed that if heteropolynuclear complexes are formed with $Hg(CN)_2$ at all, their stabilities should be very low.

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