

water it comprises 77% of the sum of the monoglycol species.

Although the relatively large rate which is interpreted here to be associated with reaction 2 is larger than the rate for the aquation reactions of most chromium(III) complexes, the rate coefficient ( $k_{-2} = 4.8 \times 10^{-3} \text{ sec}^{-1}$  at  $25^\circ$ )<sup>19</sup> is not the largest observed for such reactions. Other relatively large rate coefficients for aquation of chromium(III) species are those for perchloratochromium(III) ion ( $7.6 \times 10^{-3} \text{ sec}^{-1}$  extrapolated to  $25^\circ$ )<sup>20,21</sup> and for trifluoromethylsulfonatochromium(III) ion ( $7.6 \times 10^{-4} \text{ sec}^{-1}$  at  $25^\circ$ )<sup>21</sup>. Also pertinent for comparison to the present system is the large rate coefficient observed for conversion of the hydroxy-pentadentate EDTA chromium(III) complex to the corresponding tetradentate species ( $k = 4.8 \times 10^{-3} \text{ sec}^{-1}$  at  $25^\circ$ )<sup>22</sup>, a transformation which involves the opening of a chelate ring. Since the reactant species in this reaction involves hydroxide ion coordinated to chromium(III), a substitution for water which is known to cause greater lability, one cannot be sure of the cause of the greater lability.

The stability of diglycolchromium(III) ion is much lower than expected on a statistical basis; this trend is observed also for the cobalt(III)-ethylenediamine system.<sup>23</sup> Three different diglycolchromium(III) species are possible even if isomers are not considered:  $\text{CrG}_2(\text{OH}_2)_2^{3+}$ ,  $\text{CrG}_2(\text{OH}_2)_3^{3+}$ , and  $\text{CrG}_2(\text{OH}_2)_4^{3+}$ . From the values  $Q_I = 0.35$  and  $Q_{III} = 0.105$ , one would estimate on a statistical basis:  $Q_{22} \cong 0.022$ ,  $Q_{21} \cong 0.23$ , and  $Q_{11} \cong 0.15$ , in which the two subscripts denote the number of coordination sites occupied by each of

(19) Statistical correction gives  $2.4 \times 10^{-3} \text{ sec}^{-1}$ .

(20) K. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).

(21) A. Scott and H. Taube, *Inorg. Chem.*, **10**, 62 (1971).

(22) R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc. A*, 1494 (1971).

(23) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

the two coordinated glycol molecules. (The reactions forming a product with chelated glycol have the chelated monoglycol species as reactant.) With these values, one calculates that at  $Z \cong 0.73$ , the total concentration of species with two coordinated glycol molecules would be 41% of the total concentration of monoglycol species. The species in an equilibrated solution with this composition were separated by a column ion-exchange procedure; no diglycol species were detected, and correlations of spectral and  $\bar{n}$  data in this composition of solvent do not need the presence of diglycolchromium(III) species. At the highest glycol concentrations studied, species with two or more coordinated glycol molecules would be predominant if the several equilibrium quotients were related by the appropriate statistical factor. The spectral data suggest the presence of such species at the highest  $Z$  values studied, but certainly not in the statistically expected amounts.

The difference in light absorption by the two glycolchromium(III) species with the species having the larger molar absorptivity being assigned the chelate structure is consistent with the interpretation of corresponding differences for other systems.<sup>24</sup> The unstable chelated glycolatochromium(III) ion formed as the initial product in the oxidation of chromium(II) by pentaammineglycolatocobalt(III) ion has a larger molar absorptivity than the final product, which is predominantly the monodentate species.<sup>25</sup> Chelated tetraaquoethylenediaminechromium(III) ion has a larger molar absorptivity than the corresponding protonated monodentate complex.<sup>18</sup> In the chelated forms of each of these complexes, the greater distortion from octahedral symmetry results in lower forbiddenness of the transitions.

(24) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Amer. Chem. Soc.*, **80**, 4469 (1958).

(25) R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

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## Binding of Some Cyano- and Isocyanochromium(III) Complexes with Mercury(II), Silver(I), and Mercury Electrodes

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The reactions of  $\text{Cr}(\text{OH}_2)_5\text{CN}^{2+}$ , *cis*- $\text{Cr}(\text{OH}_2)_4(\text{CN})_2^+$ , and *fac*- $\text{Cr}(\text{OH}_2)_3(\text{CN})_3$  with  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  to form binuclear and trinuclear adducts have been investigated. Equilibrium quotients evaluated include  $\{[\text{CrNC})_2\text{Hg}^{6+}]/[\text{CrCN}^{2+}]^2[\text{Hg}^{2+}] = (1.3 \pm 0.6) \times 10^{15}$ ,  $\{[\text{CrNC})_2\text{Ag}^{6+}]/[\text{CrCN}^{2+}]^2[\text{Ag}^+] = (5.6 \pm 5) \times 10^{10}$ ,  $[\text{CrNC}^{2+}]/[\text{CrCN}^{2+}] = (4.8 \pm 1) \times 10^{-3}$ , and  $[\text{CrNCH}^{3+}]/[\text{CrCN}^{2+}][\text{H}^+] = 18 \pm 3$ . Electrochemical reduction of the heavy-metal adducts was utilized to generate a variety of the unstable isocyanochromium(III) isomers at mercury electrodes. No adsorptive binding of any of these complexes to the surface of the mercury electrodes could be detected. Possible reasons for the contrasting behavior displayed by the (nonadsorbing) isocyanochromium(III) and (strongly adsorbing) isothiocyanatochromium(III) complexes are examined.

The recent work of Espenson and coworkers<sup>1,2</sup> describing the reaction of  $\text{Cr}(\text{OH}_2)_5\text{CN}^{2+}$  with  $\text{Hg}^{2+}$  to form a stable binuclear adduct,  $(\text{H}_2\text{O})_5\text{CrNCHg}^{4+}$ , attracted our interest because of the possibilities it

suggested for substituting the positively charged surface of a mercury electrode for the  $\text{Hg}^{2+}$  ion to obtain the linkage-isomerized chromium(III) complex adsorbed on the electrode surface where its electrochemical behavior could be observed. The analogous system in which thiocyanate is the ligand by which

(1) J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968).

(2) J. H. Espenson and W. R. Bushey, *ibid.*, **10**, 2457 (1971).

mercury(II) is attached to chromium(III) has been studied in homogeneous solutions by Armor and Haim<sup>3</sup> and at the surface of mercury electrodes.<sup>4</sup> We were interested in testing whether the explanation proposed previously to account for the unusually strong bonding of the thiocyanato complexes to mercury electrodes<sup>4</sup> would also apply to the corresponding isocyanochromium(III) complexes.

In a previous study<sup>5</sup> the polarographic half-wave potential for  $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$  was given but an attempt to observe the reduction of the linkage isomer  $(\text{H}_2\text{O})_5\text{-CrNC}^{2+}$ , prepared *via* a homogeneous redox reaction, was not successful. We have found it possible to generate this isomer, as well as those obtainable from the di- and tricyano complexes, by electrochemical reduction of the heavy-metal ions in the mercury(II) or silver(I) adducts that result when the chromium(III)-cyanide complexes are exposed to  $\text{Hg}^{2+}$  or  $\text{Ag}^+$ . The electrochemical properties of the isocyno-linkage isomers are reported along with the composition and formation constants of the heavy-metal adducts from which the isocyno complexes were generated.

### Experimental Section

**Materials.**—Except as noted, commercially available chemicals of reagent grade quality were used without additional purification.  $[\text{Co}(\text{NH}_3)_5\text{CN}](\text{ClO}_4)_2$  was prepared according to Siebert.<sup>6</sup>

Commercial  $\text{K}_3\text{Cr}(\text{CN})_6$  (Alpha Inorganics) proved to be rather impure and gave solutions with spectra that differed significantly from those of pure samples even after repeated recrystallization. However, solutions of  $\text{CrCN}^{2+}$ ,  $\text{Cr}(\text{CN})_2^+$ , and  $\text{Cr}(\text{CN})_3$  prepared by hydrolysis of the impure  $\text{K}_3\text{Cr}(\text{CN})_6$  were indistinguishable from those obtained when spectroscopically pure  $\text{K}_3\text{Cr}(\text{CN})_6$ , prepared by slight modifications of published procedures,<sup>2,7</sup> was used.

Solutions of  $(\text{H}_2\text{O})_5\text{CrCN}^{2+}$ , *cis*- $(\text{H}_2\text{O})_4\text{Cr}(\text{CN})_2^+$ , and *fac*- $(\text{H}_2\text{O})_3\text{Cr}(\text{CN})_3$  were prepared from  $\text{Cr}(\text{CN})_6^{3-}$  by acid hydrolysis and separated by ion exchange.<sup>2,8</sup>  $\text{Cr}^{2+}$  prepared by electrolytic reduction of  $\text{Cr}(\text{ClO}_4)_3$  was used to catalyze the hydrolysis reaction leading to  $\text{CrCN}^{2+}$ . The ion-exchange resins employed were Bio-Rad AG 50W-X4, 100–200 mesh in the sodium form, and Bio-Rad AG-1-X2, 200–400 mesh in the perchlorate form. The resins were purified before use by treatment with warm, alkaline  $\text{H}_2\text{O}_2$  followed by thorough washing with  $\text{H}_2\text{O}$ . Sodium perchlorate solutions which had been passed through the purified resins yielded cyclic voltammograms with no evidence of adsorbable or electroactive impurities.

Solutions of the complexes were frozen and stored at  $-70^\circ$ . No decomposition of frozen solutions kept at  $-70^\circ$  was evident for periods up to 3 weeks. The concentrations of pure complexes in the solutions were determined spectrophotometrically either by direct methods using the published extinction coefficients<sup>2,8</sup> or after conversion of the Cr(III) to  $\text{CrO}_4^{2-}$ .<sup>9</sup>

Polarograms and cyclic voltammograms of solutions of  $\text{Cr}(\text{CN})_3$  invariably produced two closely spaced waves with relative heights that depended on the amount of time that had elapsed since the preparation of the complex. With solutions that are stored for 3 weeks at  $0^\circ$  the more anodic of the two waves becomes very prominent and only a vestigial remnant of the formerly sharp second wave remains. Such aged solutions also display spectral differences compared with freshly prepared solutions (fresh solutions: absorption maxima at 467 and 360 nm; aged solution: absorption maxima at 445 and 340 nm). Solutions stored at  $-70^\circ$  showed no similar spectral changes for storage periods as long as 3 weeks. We believe the double waves and

spectral shifts are both reflections of the presence of varying amounts of polymeric chromium-cyanide species in these solutions. Insoluble polymeric precipitates are formed by  $\text{Cr}(\text{CN})_3$  preparations upon repeated freezing and thawing of the solutions<sup>8</sup> and the soluble precursors to these precipitates are the likely sources of the observed behavior.

Solutions of silver and mercury(II) perchlorates were prepared by dissolving the respective oxides in small excesses of perchloric acid. Solutions of 8 M  $\text{NaClO}_4$  were prepared by treating 9.5 M perchloric acid with solid sodium carbonate and heating the resulting solution on a steam bath overnight and filtering off the siliceous residue. The pH of the filtered solution was adjusted to be between 3 and 4 while stirring with nitrogen gas to remove  $\text{CO}_2$ .

For most of the electrochemical experiments the ionic strength was adjusted to 1.0 with  $\text{NaClO}_4$ . All solutions were prepared from triply distilled water and deaerated with prepurified nitrogen.

**Apparatus.**—The instrumental apparatus for cyclic voltammetry and chronocoulometry was essentially identical with one previously described.<sup>4</sup> Potentials were measured with respect to a NaCl-saturated calomel electrode but are reported *vs.* the usual KCl-saturated calomel electrode (*sce*). Controlled-potential electrolyses over stirred mercury pool electrodes were performed with a Wenking potentiostat (Model TR).

The hanging mercury drop electrodes used for cyclic voltammetry and chronocoulometry were the commercially available Kemula Model (Brinkman Instruments, Inc.). The electrode area was  $0.032 \text{ cm}^2$ . All voltammograms were recorded at a potential scan rate of 10 V/sec.

Spectra were obtained with Cary 14 or Cary 11 spectrophotometers. Concentrations of the chromium compounds were determined by means of a Beckman DU spectrophotometer equipped with a Gilford Absorbance Indicator, Model 220.

### Results

**Polarography and Cyclic Voltammetry.**—Polarograms and cyclic voltammograms of the three complexes  $\text{CrCN}^{2+}$ , *cis*- $\text{Cr}(\text{CN})_2^+$ , and *fac*- $\text{Cr}(\text{CN})_3$  were recorded in sodium perchlorate supporting electrolytes at pH values below 3 because above pH 3 the cyanide ion released at the electrode surface caused the local pH to increase to values where the unreduced complexes were rapidly hydrolyzed and the waves collapsed.

The polarograms and voltammograms correspond to totally irreversible reductions with half-wave and peak potentials that are independent of pH between pH 0 and 3. For each complex the peak potentials become *ca.* 60 mV more cathodic for each decade increase in sweep rate indicating that the transfer coefficients,  $\alpha$ , are close to 0.5 for all of the complexes. The half-wave and peak potentials for the three complexes as well as those for the hexaquo ion are collected in Table I.

TABLE I  
HALF-WAVE AND PEAK POTENTIALS<sup>a</sup>

Complex	$-E_{1/2},^b \text{ V}$	$-E_p,^c \text{ V}$	Complex	$-E_{1/2},^b \text{ V}$	$-E_p,^c \text{ V}$
	<i>vs. sce</i>	<i>vs. sce</i>		<i>vs. sce</i>	<i>vs. sce</i>
$\text{Cr}^{3+}$	0.87	1.07	$\text{Cr}(\text{CN})_2^+$	1.05	1.27
$\text{CrCN}^{2+}$	0.96 <sup>d</sup>	1.16	$\text{Cr}(\text{CN})_3$	1.15–1.20	1.36

<sup>a</sup> Supporting electrolyte was 1 M  $\text{NaClO}_4$  adjusted to a pH between 1 and 2 with  $\text{HClO}_4$ . <sup>b</sup> Dme characteristics: drop time 4.6 sec (0 V);  $m = 1.44 \text{ mg/sec}$ . <sup>c</sup> Sweep rate 10 V/sec. <sup>d</sup> The same value of  $E_{1/2}$  was obtained by Bustin and Earley<sup>5</sup> but the polarographic maxima they reported did not appear in our solutions.

With each complex an oxidation wave corresponding to the oxidation of  $\text{Cr}^{2+}$  to  $\text{Cr}^{3+}$  appeared at *ca.* 0 V during the anodic half of the cyclic voltammogram. Thus, the reduction products in each case appear to

(3) J. N. Armor and A. Haim, *J. Amer. Chem. Soc.*, **93**, 867 (1971).

(4) D. J. Barclay, E. Passeron, and F. C. Anson, *Inorg. Chem.*, **9**, 1024 (1970).

(5) D. I. Bustin and J. E. Earley, *ibid.*, **7**, 1238 (1968).

(6) H. Siebert, *Z. Anorg. Allg. Chem.*, **327**, 63 (1964).

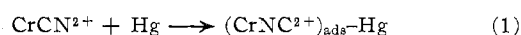
(7) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

(8) W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and W. F. Coleman, "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1967, p 117.

(9) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

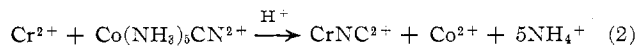
be the same, namely,  $\text{Cr}^{2+}$  and  $\text{HCN}$ . (Separate experiments with solutions containing the same concentrations of  $\text{H}^+$  and  $\text{CN}^-$  showed that  $\text{HCN}$  does not produce an anodic wave at pH values between 0 and 2.5.)

**The Search for Adsorption of the Complexes.**—One of our primary goals was to determine whether the cyano complexes of chromium(III) would mimic the behavior of the corresponding thiocyanato complexes by adsorbing on the surface of mercury electrodes.<sup>4</sup> The electrochemical technique of potential-step chronocoulometry<sup>4,10</sup> was employed to search for any adsorption at a series of initial potentials between +0.2 and -0.7 V. The known course of the homogeneous reaction between  $\text{CrCN}^{2+}$  and  $\text{Hg}^{2+}$ <sup>1,2</sup> made it seem quite likely that if adsorption were to occur, a linkage isomerization of the coordinated cyanide would be required.



In contrast with the adsorption of most ions on mercury, a reaction such as (1) could proceed fairly slowly so that the mercury electrode was exposed to solutions of the complex for periods up to 60 sec before the chronocoulometric determination of any adsorption was made. For both  $\text{CrCN}^{2+}$  and  $\text{Cr}(\text{CN})_2^+$  the intercepts of the chronocoulometric plots (charge *vs.* (time)<sup>1/2</sup>) matched the corresponding intercepts in chromium-free solutions within 0.2–0.5  $\mu\text{C}/\text{cm}^2$  for every initial potential and the match was not affected by increasing the length of time the mercury surface was exposed to the solution. Thus, no evidence for adsorption of  $\text{CrCN}^{2+}$  or  $\text{Cr}(\text{CN})_2^+$  was obtained. Solutions of  $\text{Cr}(\text{CN})_3$  could not be examined for possible adsorption by chronocoulometry because of the small potential separation between chromium(III) reduction and hydrogen ion reduction. However, electrocapillary curves (obtained from drop time measurements) for solutions of  $\text{Cr}(\text{CN})_3$  showed no evidence of adsorption.

**Electrochemical Preparation of the Linkage Isomer  $\text{CrNC}^{2+}$ .**—The failure of  $\text{CrCN}^{2+}$  to adsorb on mercury electrodes despite its ready homogeneous reaction with  $\text{Hg}^{2+}$  might be attributed to a much weaker tendency for the electrode surface to provoke the formation of the linkage isomer according to reaction 1. To examine this possibility we sought to prepare solutions containing reasonable concentrations of the linkage isomer,  $\text{CrNC}^{2+}$ , and to examine its adsorption on mercury. An established route to  $\text{CrNC}^{2+}$  is known<sup>11</sup> that utilizes the redox reaction



The resulting isocyanochromium(III) complex has a half-life of several hundred seconds at 0°, and we expected to be able to monitor it electrochemically with cyclic voltammetry carried out immediately on solutions prepared by mixing  $\text{Cr}^{2+}$  and  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ .<sup>12</sup> However, attempts to observe the electrochemical reduction of  $\text{CrNC}^{2+}$  prepared by reaction 2 were thwarted by the presence in the product solution of

(10) F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

(11) J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 1153 (1968).

(12) An earlier, unsuccessful attempt to observe  $\text{CrNC}^{2+}$  polarographically<sup>5</sup> was performed at a higher temperature, 15°, where the half-life of  $\text{CrNC}^{2+}$  would have been less than 70 sec.<sup>11</sup>

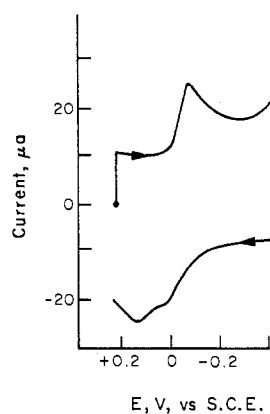
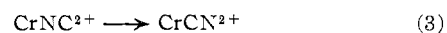


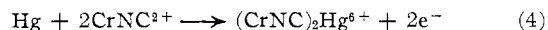
Figure 1.—Cyclic voltammogram obtained 3 min after treating 5 *M*  $\text{Cr}^{2+}$  with 4 *M*  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  in 0.1 *M*  $\text{HClO}_4$ –0.9 *M*  $\text{NaClO}_4$  at 2°.

an extremely active catalyst for hydrogen ion reduction. Reaction 2 needed to be carried out in solutions having pH values of 2 or less which yielded a large proton reduction wave commencing at about -0.7 V. This wave completely masked all electrode reactions occurring at more negative potentials such as the reduction of  $\text{CrCN}^{2+}$  and  $\text{CrNC}^{2+}$ .

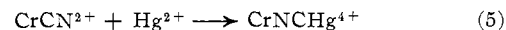
In separate experiments it was possible to obtain an entirely similar catalytic wave by adding sodium cyanide to acidic solutions containing  $\text{Co}^{2+}$  (but not *vice versa*). This and other evidence indicate that the active catalyst is a cyanocobalt complex which is apparently generated in small quantities by reaction 2 even when excess  $\text{Cr}^{2+}$  is used. Although no waves could be observed that were attributable to reduction of  $\text{Cr}(\text{III})$  species among the products of reaction 2, a new electroactive couple with anodic and cathodic waves centered about 0 V is apparent just after reaction 2 is complete (Figure 1). This couple gradually disappears at a rate comparable to that observed by Birk and Espenson<sup>11</sup> for the isomerization reaction



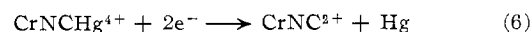
For reasons to be presented below the electrode processes that give rise to the waves in Figure 1 are believed to be reaction 4 and its reverse.



Because of the difficulties which ensue when reaction 2 is used to generate  $\text{CrNC}^{2+}$ , a number of alternate routes for the preparation of the complex were investigated. The most suitable preparation for our purposes was based upon the homogeneous reaction between  $\text{CrCN}^{2+}$  and  $\text{Hg}^{2+}$ <sup>1,2</sup>



Electrochemical reduction of the  $\text{Hg}(\text{II})$  in the binuclear cation produced in reaction 5 would be expected to yield  $\text{CrNC}^{2+}$  according to



If the reduction were carried out with a mercury electrode, the metallic mercury would be incorporated into the electrode and the electrochemistry of the  $\text{CrNC}^{2+}$  produced at the electrode surface could readily be studied at the same electrode.

To test these expectations single-sweep and cyclic

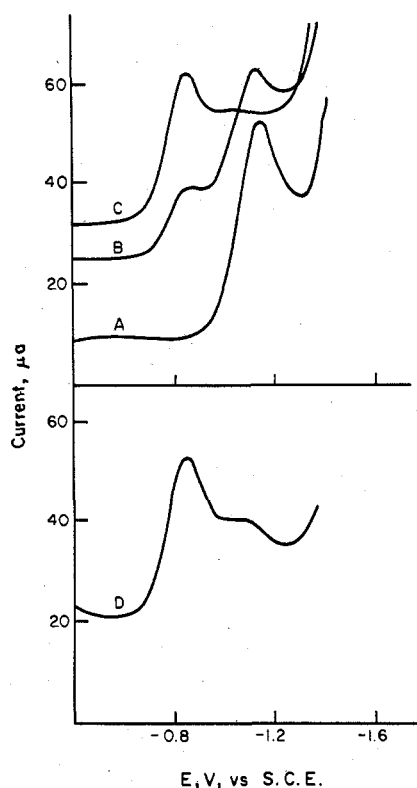
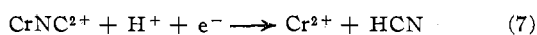


Figure 2.—Cathodic voltammograms: A, 1 mM CrCN<sup>2+</sup>; B, 1 mM CrCN<sup>2+</sup>+2 mM Hg<sup>2+</sup>, 2 min after mixing; C, as in B, 10 min after mixing; D, 1.15 mM CrCN<sup>2+</sup>+0.58 mM Ag<sup>+</sup>, 15 min after mixing. Supporting electrolyte 0.1 M HClO<sub>4</sub>-0.9 M NaClO<sub>4</sub>; temperature 22°.

voltammograms were recorded in solutions of CrCN<sup>2+</sup> to which small excesses of Hg<sup>2+</sup> were added. Figure 2 shows the results. When the current-potential curve is recorded within 20–30 sec after addition of the Hg<sup>2+</sup> to the solution of CrCN<sup>2+</sup>, reaction 5 has proceeded very little (the initial reaction rate is  $9 \times 10^{-6} M \text{ sec}^{-1}$  under the conditions prevailing in Figure 2<sup>2</sup>) and the wave corresponding to reduction of unisomerized CrCN<sup>2+</sup> (curve A in Figure 2) is virtually unaffected by the presence of the mercury(II). When more time is allowed for reaction 5 to proceed, the chromium(III) reduction wave splits into two waves: a new wave with a peak potential of -0.9 V grows at the expense to the original wave at -1.1 V. This process is shown in curves B and C of Figure 2 which was obtained by maintaining the electrode for 1–2 sec at an initial potential (-0.4 V) where the reduction of CrNCHg<sup>2+</sup> is diffusion controlled before commencing the potential scan in order to allow the current arising from mercury(II) reduction to decay sufficiently so that the relative magnitudes of the subsequent waves are more readily measured. Note that 10 min after mixing (curve C, Figure 2) the new wave at -0.9 V has become the major wave with only a small remnant remaining of the wave corresponding to the reduction of CrCN<sup>2+</sup>.

A number of lines of evidence can be cited to support the assertion that the new wave at -0.9 V is due to the reduction of the isocyano complex



It was verified that the product of the reduction reaction for this wave is Cr<sup>2+</sup> by reversing the direction

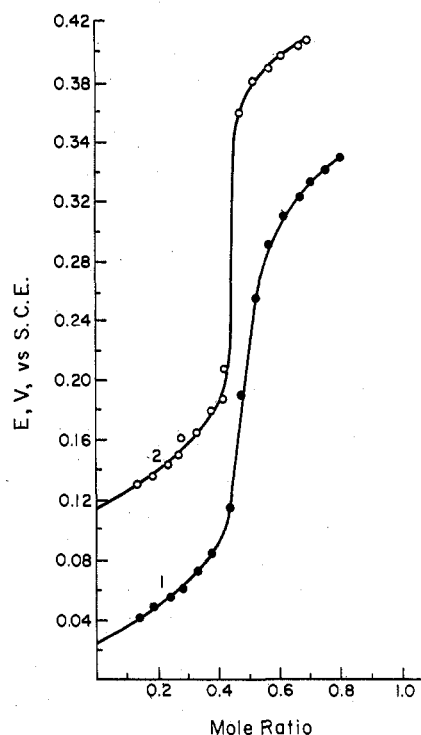


Figure 3.—Potentiometric titrations of CrCN<sup>2+</sup> with Hg<sup>2+</sup> and Ag<sup>+</sup>: (1) 124.5 µmol of CrCN<sup>2+</sup> in 25 ml of 0.1 M HClO<sub>4</sub>-0.9 M NaClO<sub>4</sub> titrated with 0.030 M Ag<sup>+</sup>; (2) 126 µmol of CrCN<sup>2+</sup> in 25 ml of 0.1 M HClO<sub>4</sub>-0.9 M NaClO<sub>4</sub> titrated with 0.030 M Hg<sup>2+</sup>. The abscissa gives the moles of heavy-metal cation added per mole of CrCN<sup>2+</sup> initially present.

of the potential scan in a solution containing chloride ion and observing the characteristic chloride-catalyzed Cr<sup>2+</sup> oxidation wave<sup>13</sup> during the anodic scan. If the direction of the potential scan from -0.4 V is anodic rather than cathodic with a solution such as the one that gave curve C in Figure 2, the same pair of anodic-cathodic waves (centered at 0 V) is found that was obtained when CrNC<sup>2+</sup> was generated *via* reaction 2 (Figure 1). In addition, the rate at which the peak currents grow following the addition of Hg<sup>2+</sup> matches the growth rate of the new cathodic wave at -0.9 V, as it should if both the anodic and cathodic waves involve diffusion to the electrode of the same reaction product, CrNC<sup>2+</sup>.

Silver ion also reacts with CrCN<sup>2+</sup> to yield spectral changes resembling those obtained with Hg<sup>2+</sup>: a mixture containing 1 mol of Ag<sup>+</sup> per mole of CrCN<sup>2+</sup> yields a spectrum with maxima at 556 and 399 nm. The same mixture prepared with Hg<sup>2+</sup> has maxima at 565 and 401 nm<sup>1,2</sup> and pure CrCN<sup>2+</sup> has maxima at 525 and 393 nm.<sup>8</sup> Reduction of the Ag<sup>+</sup> adducts at mercury electrodes (the Ag<sup>+</sup> is reduced to silver metal which dissolves in the mercury) followed by a linear potential scan yields the same cathodic and anodic voltammograms that are obtained when Hg<sup>2+</sup> is used. Thus, the same product, namely, CrNC<sup>2+</sup> appears to result from the reduction of the heavy-metal cation in both adducts.

CrCN<sup>2+</sup> reacts considerably faster with Ag<sup>+</sup> than with Hg<sup>2+</sup> and the resulting complex appears to aquate much less rapidly (*e.g.*, negligible aquation of the Ag<sup>+</sup> complex during a period when 50% of the Hg<sup>2+</sup> com-

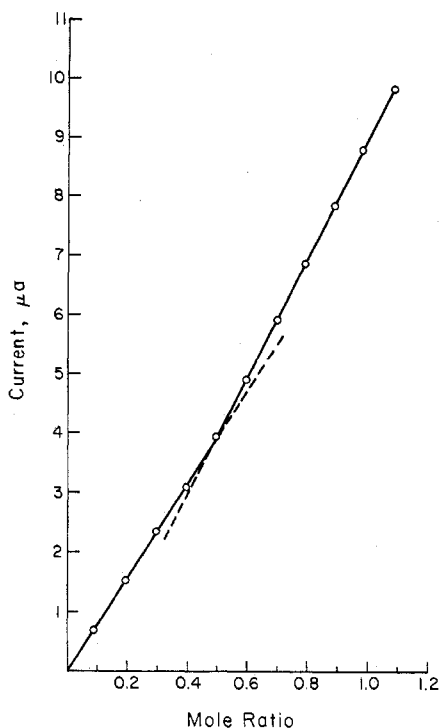


Figure 4.—Amperometric titration of  $\text{CrCN}^{2+}$  with  $\text{Hg}^{2+}$ ;  $60.8 \mu\text{mol}$  of  $\text{CrCN}^{2-}$  in  $40 \text{ ml}$  of  $0.1 \text{ M HClO}_4$ – $0.9 \text{ M NaClO}_4$  titrated with  $0.030 \text{ M Hg}^{2+}$ . The dme was maintained at  $-0.5 \text{ V vs. sce}$ . The abscissa gives the moles of  $\text{Hg}^{2+}$  added per mole of  $\text{CrCN}^{2+}$  initially present.

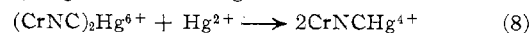
plex aquates). For these reasons  $\text{Ag}^+$  was utilized most often to generate  $\text{CrNC}^{2+}$  at electrode surfaces.

**Composition and Stability of the  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  Adducts.**—The voltammetric wave for reduction of  $\text{CrCN}^{2+}$  is converted almost completely into the wave corresponding to  $\text{CrNC}^{2+}$  reduction in solutions containing only  $0.5 \text{ mol}$  of  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  per mole of  $\text{CrCN}^{2+}$  (Figure 2, curve D). This observation indicated that the formation of the heavy-metal adducts in solutions not containing excesses of the heavy-metal ions might involve a different stoichiometry than the simple 1:1 complexation of reactions such as (5). Espenson and Bushey<sup>2</sup> alluded to the same possibility but did not pursue it quantitatively. Potentiometric titrations of  $\text{CrCN}^{2+}$  solutions with  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  using Hg or Ag electrodes, respectively, were therefore performed to investigate the stoichiometries of the adduct formation reactions at low concentrations of heavy metal.

Figure 3 shows some typical titration curves. The rate of reaction between  $\text{CrCN}^{2+}$  and the heavy metal ions is fairly slow so that several minutes was required before steady potential readings were obtained after each addition of reactant. The rather long times required for the adduct formation to reach equilibrium caused no problems in the case of the  $\text{Ag}^+$  adduct because of its much slower aquation rate. With the  $\text{Hg}^{2+}$  adduct, however, considerable aquation occurred during the time ( $\sim 60 \text{ min}$ ) required to complete a titration. To overcome this problem the complete titration curve was assembled from a series of titrations which commenced with successively higher amounts of added mercury(II). That the steady potentials eventually achieved corresponded to a true equilibrium was supported by the fact that the inflec-

tion points in the titration curves occurred at the same stoichiometric ratio of reactants regardless of the direction in which titration was performed.

The inflection points in the potentiometric titration curves correspond to the formation of the adducts  $(\text{CrNC})_2\text{Hg}^{6+}$  and  $(\text{CrNC})_2\text{Ag}^{5+}$ . Additional evidence supporting this trinuclear stoichiometry for the adducts was obtained from amperometric titrations. Figure 4 shows the current at a dropping mercury electrode held at  $-0.5 \text{ V}$  where no reduction of any Cr(III) species occurs but the  $\text{Hg}(\text{II})$  contained in the adduct is reduced. The titration utilizes the fact that the diffusion coefficient of  $(\text{CrNC})_2\text{Hg}^{6+}$  is significantly smaller than those of  $\text{CrNCHg}^{4+}$  and  $\text{Hg}^{2+}$ . During the first half of the titration the current increases at a rate proportional to the concentration of  $(\text{CrNC})_2\text{Hg}^{6+}$ . During the second half of the titration the current increases more rapidly because reaction 8 begins to become important and leads to the partial conversions of the  $(\text{CrNC})_2\text{Hg}^{6+}$  to  $\text{CrNCHg}^{4+}$



The intersection of the two linear segments should correspond to the maximum concentration of  $(\text{CrNC})_2\text{Hg}^{6+}$ . The fact that it occurs at a stoichiometric ratio of  $0.5 \text{ Hg}^{2+}$  per  $\text{CrCN}^{2+}$  is strong evidence that this is the mole ratio in the adduct.

An amperometric titration with the  $\text{Ag}^+$ – $\text{CrCN}^{2+}$  system could not be performed in the same way because of interference by polarographic maxima. To avoid the maxima a solution of  $\text{Ag}^+$  was titrated with  $\text{CrCN}^{2+}$  and the electrode was maintained at  $-0.8 \text{ V}$  where both  $\text{CrNC}^{2+}$  and the  $\text{Ag}^+$  adduct but not  $\text{CrCN}^{2+}$  contributed to the diffusion-limited current. The first intersection point appeared at a  $\text{Ag}(\text{I})$  to  $\text{Cr}(\text{III})$  mole ratio somewhat less than the value expected for formation of  $\text{CrNCAg}^{3+}$  but the second intersection occurred at a mole ratio of  $\text{Cr}(\text{III})$  per  $\text{Ag}(\text{I})$  corresponding to quantitative formation of  $(\text{CrNC})_2\text{Ag}^{5+}$ .

The potentiometric titration data can be utilized to evaluate equilibrium quotients for formation of the adducts. Analysis of the data by the procedure outlined in the Appendix produced the equilibrium quotients listed in Table II

TABLE II  
EQUILIBRIUM QUOTIENTS FOR ADDUCTS WITH  $\text{Hg}^{2+}$  AND  $\text{Ag}^+$

Reaction	Equilibrium quotient
(I) $\text{CrCN}^{2+} + \text{Hg}^{2+} = \text{CrNCHg}^{4+}$	$Q_I = (3 \pm 0.7) \times 10^7$
(II) $\text{CrCN}^{2+} + \text{HgCN}^+ = (\text{CrNC})_2\text{Hg}^{6+}$	$Q_{II} = (4 \pm 2) \times 10^7$
(III) $\text{CrCN}^{2+} + \text{Ag}^+ = \text{CrNCAg}^{3+}$	$Q_{III} = (5 \pm 2) \times 10^5$
(IV) $\text{CrCN}^{2+} + \text{AgCN}^+ = (\text{CrNC})_2\text{Ag}^{5+}$	$Q_{IV} = (11 \pm 10) \times 10^4$

**Protonation of  $\text{CrNC}^{2+}$ .**—In contrast with the behavior of  $\text{CrCN}^{2+}$ , the cathodic voltammograms for the complex generated from either the  $\text{Hg}^{2+}$  or the  $\text{Ag}^+$  adduct display peak potentials that are pH dependent. The existence of this pH dependence and the fact that both heavy-metal adducts lead to products with the same pH dependence are taken as added evidence that the same species,  $\text{CrNC}^{2+}$ , is being produced in both cases. Figure 5 shows the experimentally observed pH dependence along with that to be expected<sup>14</sup> if the

(14) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

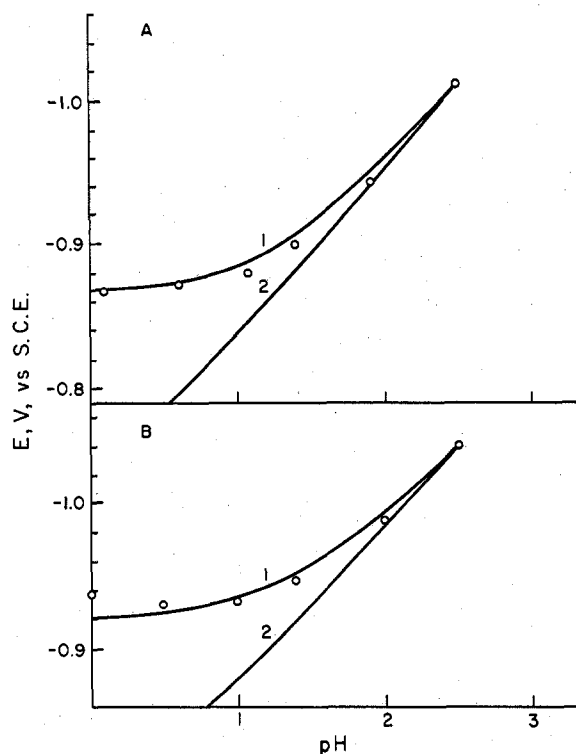
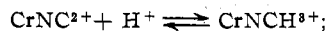


Figure 5.—pH dependence of voltammetric peak potentials, for reduction of  $\text{CrNC}^{2+}$ . The plotted points are the experimental peak potentials. The curves were calculated from a simplified version of eq 75 of ref 14

$$E = E_r - \frac{RT}{\alpha F} \left[ \ln \left( \frac{Q_p [\text{H}^+]}{1 + Q_p [\text{H}^+]} \right) - \ln \left( \frac{Q_p [\text{H}^+]_r}{1 + Q_p [\text{H}^+]_r} \right) \right]$$

where  $E_r$  is the peak potential when  $[\text{H}^+] = [\text{H}^+]_r$ . The peak potential at the highest pH was chosen as  $E_r$ . The values of  $Q_p$  used to calculate curves 1A and 1B were obtained from least-squares fitting of the data to this equation. Curves 2A and 2B were calculated using the estimate  $Q_p = 0.94$ .<sup>11</sup> The supporting electrolyte concentration was maintained at 1 M with  $\text{NaClO}_4$ ; A, 25°; B, 2°.

electrode reaction were preceded by protonation of the isocyano complex



$$Q_p = [\text{CrNCH}^{3+}]/[\text{CrNC}^{2+}][\text{H}^+] \quad (9)$$

Curve 2 in Figure 5A was obtained by using Birk and Espenson's kinetically estimated value for the equilibrium quotient for reaction 9,  $Q_p = 0.94$ .<sup>11</sup> Curve 1 in Figure 5A which gives the best fit of the experimental data to the appropriate theoretical equation<sup>14</sup> was obtained by using a value of 18.7 for  $Q_p$ . Thus, these data suggest that  $Q_p$  may be considerably larger than the previous estimate.<sup>11</sup> A second series of voltammograms was recorded at 2° where the isocyano complex is more stable. The data, shown in Figure 5B, indicate that at 2°  $Q_p$  is ca. 28.6.

The product of the values of  $Q_I$  and  $Q_{II}$  in Table II is slightly larger than the corresponding formation quotient for  $\text{HgCl}_2$  but much smaller than the quotient for  $\text{HgI}_2$ .<sup>15</sup> It follows that excess iodide ion but not excess chloride ion should decompose solutions of  $\text{Hg}(\text{CN-Cr})_2^{\delta+}$  into  $\text{CrNC}^{2+}$  and the mercury halide complex. These expectations were borne out in experimental tests and the rapid reaction between  $\text{Hg}(\text{CNCr})_2^{\delta+}$  and

(15) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Chemical Society London, 1964.

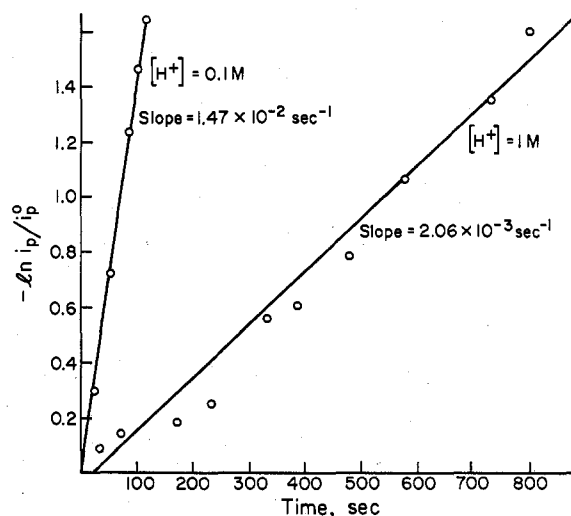


Figure 6.—Rate of conversion of  $\text{CrNC}^{2+}$  into  $\text{CrCN}^{2+}$  at pH 0 and 1.0. The peak currents,  $i_p$ , corresponding to the reduction of  $\text{CrNC}^{2+}$  were measured and the ratio of  $i_p$  at each time to the first value of  $i_p$ ,  $i_p^0$ , was used in plotting the ordinate. (Solutions were prepared by treating 2 mM  $\text{Hg}^{2+}$  with 2 mM  $\text{CrNC}^{2+}$  at 22°, waiting 10 min, and then cooling to 2° and making the solution 25 mM in  $\text{NaI}$ .) The supporting electrolyte concentration was maintained at 1 M with  $\text{NaClO}_4$ . (Data point at 1050 sec,  $-\ln(i_p/i_p^0) = 2.2$ , not shown but included in data analysis for 1 M  $[\text{H}^+]$ .)

excess iodide ion was used to generate homogeneous solutions of  $\text{CrNC}^{2+}$  which were used to measure the kinetics of its isomerization to  $\text{CrCN}^{2+}$  at 2°. (At room temperature the rate was inconveniently rapid.) The rate was followed by measuring the peak currents of the voltammetric waves for reduction of the  $\text{CrNC}^{2+}$  remaining at various time intervals after addition of the iodide. Rate data at two different pH values are plotted in Figure 6. The pH dependence of this isomerization rate has been explained by Birk and Espenson as arising from the protonation of  $\text{CrNC}^{2+}$  to form  $\text{CrNCH}^{3+}$  which isomerizes much more slowly.<sup>11</sup> Accordingly, they wrote  $k_{\text{obsd}} = \{1/(1 + Q_p [\text{H}^+])\} k_i$  where  $k_{\text{obsd}}$  is the observed isomerization rate constant,  $Q_p$  is the protonation quotient (reaction 9), and  $k_i$  is the rate constant for isomerization of the unprotonated complex. The ratio of the two values of  $k_{\text{obsd}}$  obtained from the slopes of the lines in Figure 6 yields a value of 21 for  $Q_p$  at 2°. The reasonable agreement between these estimates of  $Q_p$  derived from the pH dependences of both the voltammetric peak potentials (Figure 5) and the isomerization kinetics (Figure 6) supports the reliability of the larger values for  $Q_p$  resulting from these measurements. Accordingly, the estimate of the protonation quotient obtained at 22°,  $Q_p = 18.7$ , will be used in the discussion to follow.

**Spontaneous Isomerization of  $\text{CrCN}^{2+}$ .**—Espenson and Birk<sup>16</sup> gave 0.048 as an estimate of the upper limit for the equilibrium quotient for reaction 10. This



value is large enough for the concentration of the isocyano isomer present at equilibrium in a sufficiently concentrated solution of  $\text{CrCN}^{2+}$  to be determined electrochemically. For example, a 10 mM solution of  $\text{CrCN}^{2+}$  should contain 0.48 mM  $\text{CrNC}^{2+}$  which is

(16) J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 2266 (1968).

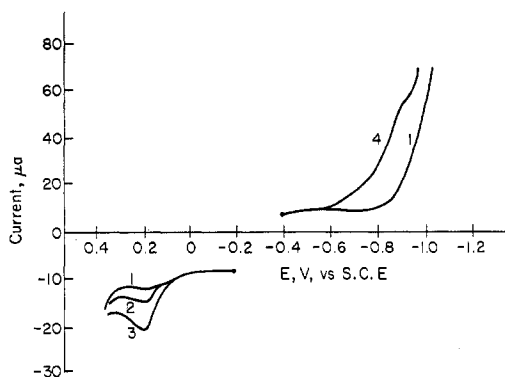


Figure 7.—Voltammograms of a 10 mM  $\text{CrCN}^{2+}$  solution at (1) pH 2, (2) pH 1, (3) pH 0.5, and (4) pH 0. The supporting electrolyte also contained 0.9 M  $\text{NaClO}_4$  (except at pH 0); temperature 22°.

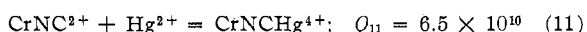
enough to yield detectable voltammetric waves corresponding to the isocyano isomer as in Figures 1 and 2. Figure 7 contains a set of voltammograms obtained with a 10 mM solution of  $\text{CrCN}^{2+}$  at several pH values. The expected cathodic and anodic waves corresponding to  $\text{CrNC}^{2+}$  are observed and their peak currents are used in Table III to evaluate the

TABLE III  
ESTIMATION OF  $Q_{10}$  FROM PEAK CURRENTS FOR Hg  
OXIDATION (REACTION 4) AND  $\text{CrNC}^{2+}$  REDUCTION IN A  
10 mM SOLUTION OF  $\text{CrCN}^{2+}$

pH	Anodic peak current, $\mu\text{A}$	Cathodic peak current, <sup>a</sup> $\mu\text{A}$	$10^3 Q_{10}^b$
2	4	c	7.2
1	6	c	4.7
0.5	11	c	3.7
0	35	c	4.4
0		34	4.2
		Av	$4.8 \pm 1$

<sup>a</sup> Corrected for the current resulting from reduction of  $\text{CrCN}^{2+}$  at the potential where the peak current was measured. <sup>b</sup> Calculated from  $i_p = i_p^0 \alpha$ , where  $i_p$  is the observed peak current (anodic or cathodic),  $i_p^0$  is the total peak current corresponding to the reduction of all isomers of Cr(III) present (480  $\mu\text{A}$  for the experimental conditions employed), and  $\alpha$  is the fraction of the Cr(III) present in the two isocyano forms  $\text{CrNC}^{2+}$  and  $\text{CrNCH}^{3+}$ ;  $\alpha = Q_{10}(Q_p[\text{H}^+] + 1)/(1 + Q_2 Q_{10}[\text{H}^+] + Q_{10})$ . <sup>c</sup> The small cathodic wave was too close to the main reduction wave of  $\text{CrCN}^{2+}$  for accurate estimation of the peak current at these pH values.

equilibrium quotient for spontaneous linkage isomerization,  $Q_{10}$ . The average value obtained in this way,  $Q_{10} = (4.8 \pm 1) \times 10^{-3}$ , is compatible with but about one-tenth as large as the previously estimated upper limit.<sup>16</sup> Combining this value of  $Q_{10}$  with  $Q_1$ , the equilibrium quotient for reaction 5, leads to a value for the equilibrium quotient for the binding of  $\text{Hg}^{2+}$  to the isocyanochromium(III) complex



This value is consistent with the estimated lower limit on this quotient of  $2 \times 10^6$  given by Espenson and Bushey.<sup>2</sup>

**Nonadsorption of  $\text{CrNC}^{2+}$  on Mercury.**—Of the two methods described for generating significant concentrations of  $\text{CrNC}^{2+}$  at the surface of a mercury electrode (electroreduction of the heavy-metal adducts or reaction of the  $\text{Hg}^{2+}$  adduct with excess iodide ion) the electroreduction route was selected for experiments

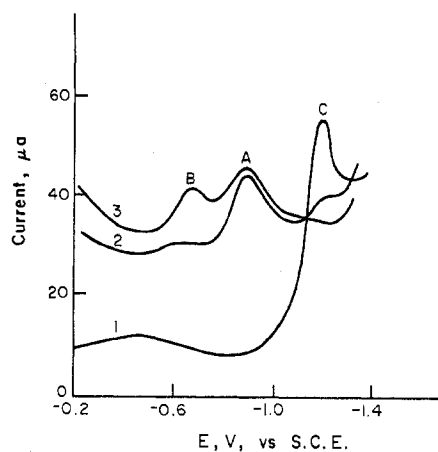


Figure 8.—Voltammograms: (1) 1 mM  $\text{Cr(CN)}_2^+$ ; (2) 1 mM  $\text{Cr(CN)}_2^+ - 1 \text{ mM Hg}^{2+}$ , 3 min after mixing; (3) as in 2, 20 min after mixing—no further changes occur. Supporting electrolyte 0.1 M  $\text{HClO}_4 - 0.9 \text{ M NaClO}_4$ .

designed to search for possible adsorption of  $\text{CrNC}^{2+}$  in order to eliminate interference from competitive adsorption by iodide. It was necessary to modify the usual chronocoulometric procedure for measurement of adsorbed, electroactive species.<sup>10</sup> First, the potential of the mercury electrode was stepped to a value where the  $\text{Hg(II)}$  in the  $\text{Hg(CNCr)}_2^{6+}$  complex was reduced to metallic mercury and the surface of the electrode was exposed to the  $\text{CrNC}^{2+}$  that resulted. After sufficient isocyano complex had been generated at the electrode to yield a measurable adsorption, if it were adsorbed, the electrode potential was stepped to a value where the  $\text{CrNC}^{2+}$  (as well as the small amounts of  $\text{CrCN}^{2+}$  produced by reisoimerization) was reduced to  $\text{Cr}^{2+}$  along with the additional amount of  $\text{Hg(CNCr)}_2^{6+}$  that continued to diffuse to the electrode. Appropriate analysis<sup>17</sup> of the charge-time behavior obtained from the sum of the two electrode reactions leads to linear chronocoulometric plots with intercepts that measure the amount of adsorbed  $\text{CrNC}^{2+}$ , if any. The intercepts obtained with solutions containing no  $\text{CrCN}^{2+}$  matched those obtained in the presence of chromium with  $0.2 \mu\text{C}/\text{cm}^2$  indicating that no more than  $2 \times 10^{-12} \text{ mol}/\text{cm}^2$  of the complex is adsorbed. Similar results were obtained at both 2 and 25° and when  $\text{Ag}^+$  was substituted for  $\text{Hg}^{2+}$  in generating the  $\text{CrNC}^{2+}$ . Under the experimental conditions employed, the amount of  $\text{CrNC}^{2+}$  produced at the electrode surface was 3–4 times more than would be needed to form a monolayer on the electrode, *i.e.*, an ample amount to have resulted in adsorption if it were favored.

The lack of adsorption of  $\text{CrNC}^{2+}$  on mercury contrasts with the behavior of  $\text{CrNCS}^{2+}$  although the latter cation is only weakly adsorbed.<sup>4</sup> Much stronger adsorption is obtained with  $\text{Cr(NCS)}_2^+$  and  $\text{Cr(NCS)}_3^4$  and it therefore seemed desirable to try to prepare the isocyano analogs of the di- and trithiocyanato complexes to see if they were adsorbed in detectable amounts.

**Electrochemical Generation of  $\text{Cr(NC)}_2^+$  and  $\text{NC-CrNC}^+$ .**—When  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  is added to solutions of  $\text{Cr(CN)}_2^+$ , new voltammetric reduction waves slowly develop as the original wave corresponding to the re-

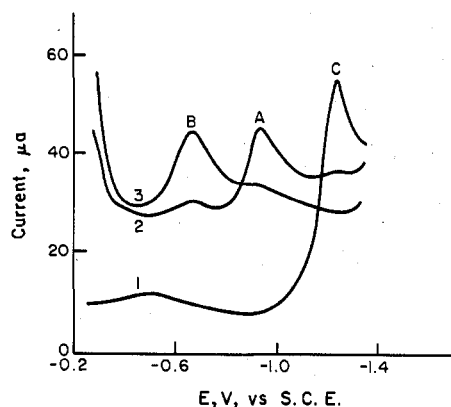


Figure 9.—Voltammograms: (1) 1 mM  $\text{Cr}(\text{CN})_2^+$ ; (2) 1 mM  $\text{Cr}(\text{CN})_2^+$ +1 mM  $\text{Ag}^+$ , 15–30 sec after mixing; (3) as in 2, 9 min after mixing. Supporting electrolyte 0.1 M  $\text{HClO}_4$ –0.9 M  $\text{NaClO}_4$ ; temperature 2°.

duction of  $\text{Cr}(\text{CN})_2^+$  decays (Figures 8, 9). (New anodic waves corresponding to mercury oxidation in the presence of the isocyanochromium(III) complexes also appear but they were not extensively investigated.) The two cathodic waves developed by the addition of  $\text{Hg}^{2+}$  appear at potentials on either side of the single wave that develops in solutions of  $\text{CrCN}^{2+}$ . Figure 8 shows the temporal development of the two waves. Wave A appears first. Wave B develops somewhat later and continues to increase in magnitude even after the original  $\text{Cr}(\text{CN})_2^+$  reduction wave, C, has disappeared completely, which indicates that wave B results from a continuing reaction between the  $\text{Hg}^{2+}$  added and the species responsible for wave A. At 25° approximately 20 min is required for the wave heights to stop changing and their final relative magnitudes depend upon the mole ratio of  $\text{Hg}^{2+}$  to  $\text{Cr}(\text{CN})_2^+$  employed; wave B increases and wave A decreases in magnitude as the mole ratio is increased from 1 to 2.0.

Soon after the relative wave heights become stable, the peak potential of wave A begins to shift in an anodic direction and eventually moves to the potential characteristic of  $\text{CrNC}^{2+}$ . This suggests that mercury-induced aquation of  $\text{Cr}(\text{CN})_2^+$  is proceeding as does the fact that the shift in peak potential occurs more rapidly at higher concentrations of  $\text{Hg}^{2+}$ .

Silver ion reacts with  $\text{Cr}(\text{CN})_2^+$  much more rapidly than does  $\text{Hg}^{2+}$ , and with 1 mol of  $\text{Ag}^+$  added to each mole of  $\text{Cr}(\text{CN})_2^+$  at 25° there appears only a single new cathodic wave, identical with wave B obtained from  $\text{Hg}^{2+}$  addition (Figure 8). By cooling the solution, however, the intermediate appearance of a second new wave, apparently identical with wave A in Figure 8, becomes visible (Figure 9). In fact, at 2°, the second wave, A, develops within 10–20 sec and several minutes is required before wave A decays and wave B appears. In contrast to the behavior with  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$  leads eventually to an essentially complete conversion to wave B even at a mole ratio of 1  $\text{Ag}^+$  per  $\text{Cr}(\text{CN})_2^+$ .

The potentials of both waves A and B are pH dependent as is true of the wave for  $\text{CrNC}^{2+}$  but not of the waves for  $\text{CrCN}^{2+}$  or  $\text{Cr}(\text{CN})_2^+$ , suggesting that the two waves correspond to the complexes  $\text{NCCrNC}^+$  and  $\text{Cr}(\text{NC})_2^+$ . To examine the stoichiometry of the adduct-forming reaction, potentiometric titrations such as those performed with the monocyano complex were

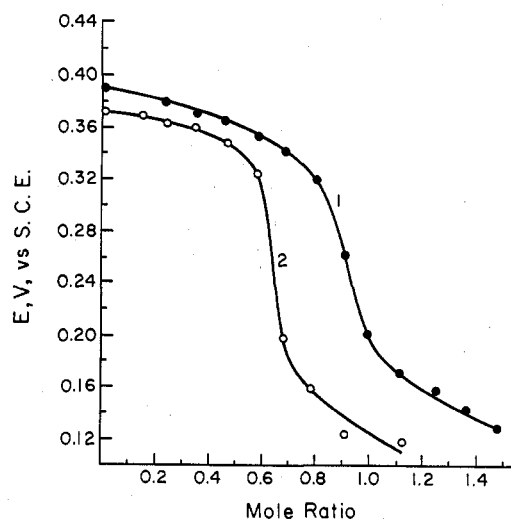


Figure 10.—Potentiometric titrations of  $\text{Ag}^+$  with  $\text{Cr}(\text{CN})_2^+$  and  $\text{Cr}(\text{CN})_3$ : (1) 45  $\mu\text{mol}$  of  $\text{Ag}^+$  in 29 ml of 0.1 M  $\text{HClO}_4$ –0.9 M  $\text{NaClO}_4$  titrated with 0.0258 M  $\text{Cr}(\text{CN})_2^+$ ; (2) 30  $\mu\text{mol}$  of  $\text{Ag}^+$  in 33 ml of 0.1 M  $\text{HClO}_4$ –1 M  $\text{NaClO}_4$  titrated with 0.0171 M  $\text{Cr}(\text{CN})_3$ . The abscissa gives the moles of  $\text{Cr}(\text{III})$  added per mole of  $\text{Ag}(\text{I})$  present.

attempted at 25° where the rate of adduct formation is reasonably rapid. The aquation rate of the complexes in the presence of mercury(II) proved to be too rapid for the attainment of steady potentials but successful titrations were obtained with the less rapidly aquating silver adducts. Curve 1 in Figure 10 shows the titration of  $\text{Ag}^+$  with  $\text{Cr}(\text{CN})_2^+$ . The inflection in the curve occurs at a mole ratio of 0.9 indicating a stoichiometry close to 1 mol of  $\text{Cr}(\text{CN})_2^+$  per mole of  $\text{Ag}^+$  which contrasts with the 2:1 stoichiometry obtained for the same titration with  $\text{CrCN}^{2+}$  (Figure 3).

The voltammograms obtained from solutions containing equimolar quantities of  $\text{Ag}^+$  and  $\text{Cr}(\text{CN})_2^+$  display only the single wave, B. However, as more  $\text{Cr}(\text{CN})_2^+$  is added, wave B is decreased in magnitude and wave A develops. This behavior is in accord with that expected if  $\text{Cr}(\text{NC})_2^+$  were generated from solutions containing molar excesses of  $\text{Ag}^+$  over the complex, but  $\text{NCCrNC}^{2+}$  resulted when the converse were true.

The slow rates of attainment of equilibria and the multiplicity of species present prevented the use of the potentiometric titration data for evaluation of equilibrium quotients for the formation of these heavy-metal adducts with the dicyanochromium(III). It was possible, however, to obtain estimates of the relative stabilities of the mercury(II) and silver(I) adducts by comparing the equilibrium voltammograms obtained with the two heavy metals. The curves numbered 3 in Figures 8 and 9 show such a comparison and lead to the conclusion that the stability of the silver(I) precursor to the electrogenerated  $\text{Cr}(\text{NC})_2^+$  ion (responsible for wave B) is greater than that of its mercury(II) counterpart.

Qualitative experiments showed that small excesses of iodide but not chloride ion decomposed the heavy-metal adducts and thus eliminated waves A and B (Figures 8 and 9) from voltammograms. The adducts formed with the dicyano complex therefore are not very much more stable than those obtained with the monocyano complex.



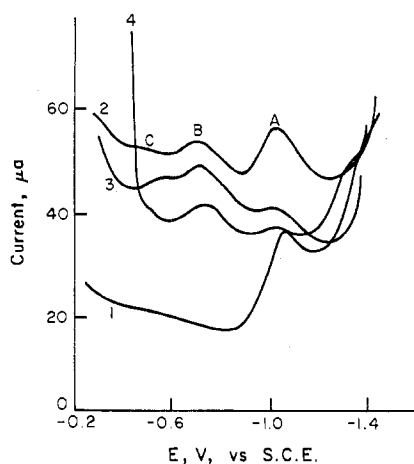


Figure 11.—Voltammograms: (1) 1 mM  $\text{Cr}(\text{CN})_3$ -1.8 mM  $\text{Hg}^{2+}$ ; (2) as in (1), 10 min after mixing; (3) as in (1), 20 min after mixing—no further changes occur; (4) 1 mM  $\text{Cr}(\text{CN})_3$ -1 mM  $\text{Ag}^+$ , 10 min after mixing. Supporting electrolyte 0.1 M  $\text{HClO}_4$ -0.9 M  $\text{NaClO}_4$ ; temperature 22°.

Chronocoulometry was used to investigate the possible adsorption of the two isocyano complexes generated at the electrode surface by reduction of the heavy-metal adducts. The silver(I) adduct was employed to obtain  $\text{Cr}(\text{NC})_2^+$  and the mercury(II) adduct to obtain  $\text{NCCrNC}^+$ . Neither of these two complexes was adsorbed on the mercury electrodes in a detectable amount from millimolar solutions.

**Electrochemical Generation of Isocyano Complexes from  $\text{Cr}(\text{CN})_3$ .**—The voltammetry of  $\text{Cr}(\text{CN})_3$  solutions containing mercury(II) or silver(I) is very similar to that just described for  $\text{Cr}(\text{CN})_2^+$ . Addition of mercury(II) (1.8 mmol per millimole of  $\text{Cr}(\text{CN})_3$ ) causes the original  $\text{Cr}(\text{CN})_3$  reduction wave to disappear within 5 min at 25° followed by a more gradual development of new reduction waves (Figure 11). The wave that develops at the most positive potential (wave C in Figure 11) overlaps with the reduction wave for the mercury(II) adduct itself which causes it to be somewhat less distinct. The peak potentials of the three new waves that develop differ from those obtained in solutions of  $\text{CrCN}^{2+}$  or  $\text{Cr}(\text{CN})_2^+$  and display different pH dependences. They appear to correspond to three different new complexes, presumably  $(\text{NC})_2\text{CrNC}$ ,  $\text{NCCr}(\text{NC})_2$ , and  $\text{Cr}(\text{NC})_3$  in the order of increasingly positive peak potentials. As was true with the mercury(II) adduct of  $\text{Cr}(\text{CN})_2^+$ , significant aquation of the tricyano complex takes place after ca. 30-min exposure to mercury(II). At this point waves with peak potentials matching those obtained with solutions of  $\text{Cr}(\text{CN})_2^+$  and  $\text{CrCN}^{2+}$  begin to appear.

The silver(I) adducts of  $\text{Cr}(\text{CN})_3$  are formed more rapidly than the Hg(II) adducts, and two new reduction waves with the same peak potentials as those obtained with Hg(II) result (Figure 11, curve 4). The voltammetric data thus indicate that the same three species are generated by electroreduction of the mercury(II) and silver(I) adducts.

Potentiometric titration of solutions of  $\text{Cr}(\text{CN})_3$  with  $\text{Ag}^+$  could be completed before significant aquation occurred. A typical titration curve is shown in Figure 10, curve 2. The inflection point appears at a mole ratio of 0.64 Cr(III) per Ag(I).

Chronocoulometry could not be used to measure any adsorption of the complexes generated from the heavy-metal adducts of  $\text{Cr}(\text{CN})_3$  because the various waves were too poorly separated. However, electrocapillary measurements indicated no adsorption of any of the isocyano species on mercury electrodes.

### Discussion

The voltammetric and titrimetric data (Figures 1-4) leave little doubt that the same species,  $\text{CrNC}^{2+}$ , that results from the reaction between  $\text{Cr}^{2+}$  and  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  is also generated by electroreduction of the mercury(II) and silver(I) adducts of  $\text{CrCN}^{2+}$ . The existence of both the binuclear and trinuclear adducts  $\text{MCNCr}$  and  $\text{M}(\text{CNCr})_2$  seems clearly established (Figure 3).

The values of the equilibrium quotients obtained from the potentiometric titration data were summarized in Table II. The fact that the equilibrium quotients for reactions I and II and for reactions III and IV are not very different emphasizes the minor influence of coulombic repulsion on the stability of the adducts. The rather surprising stabilities of the adducts despite their high charges seems best understood in terms of the natural affinity of the carbon end of the cyanide ligand for the very soft cations  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ .<sup>2,3</sup> The equilibrium quotients for reactions II and IV in Table II show  $(\text{CrNC})_2\text{Ag}^{5+}$  to be less stable than  $(\text{CrNC})_2\text{Hg}^{6+}$ . The difference in stability is also reflected in the spectra and relative aquation rates of the two adducts. The more stable  $\text{Hg}^{2+}$  adduct aquates more rapidly because of its weaker Cr(III)-N bond<sup>2</sup> and, correspondingly, its d-d absorption band appears at a longer wavelength ( $\lambda_{\text{max}}$  565 and 556 nm for the binuclear  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  adducts, respectively).

The failure of any of the isochromium(III) complexes to adsorb on mercury was surprising to us. The analogous thiocyanato complexes are strongly adsorbed<sup>4</sup> and in most other respects there is considerable similarity in the homogeneous coordination chemistry displayed by both sets of chromium complexes in their binding to mercury(II). To understand a possible basis for the differences in the adsorptive properties of the isocyano and thiocyanato complexes the data collected in Table IV are useful. The first point to note is that attachment of  $\text{Cr}^{3+}$  to  $\text{HgCN}^+$  destabilizes the mercury-cyanide bond much more than the mercury-sulfur bond is destabilized when  $\text{Cr}^{3+}$  is attached to  $\text{HgSCN}^+$ . This difference has been attributed<sup>2</sup> to a greater decrease in the  $\sigma$ -donating ability of the carbon end of cyanide than of the sulfur end of thiocyanate when chromium(III) is attached to the remote end of the ligand.

The adsorption data in Table IV show that uncoordinated thiocyanate ions are adsorbed much more strongly on both neutral and positively charged mercury surfaces than are cyanide ions. Thus, in adsorptive binding to a mercury surface the two anions behave differently from what they do in their coordination to mercury(II) cations. The same reversal in the order of binding strengths also obtains (Table IV) for iodide, bromide, and azide ions compared with cyanide ion. The origin of the difference presumably lies in the very stable mercury-carbon  $\sigma$  bond that is formed when Hg(II) and cyanide combine in homo-

TABLE IV  
 COMPARISONS OF ION BINDING TO MERCURY(II) AND  
 MERCURY ELECTRODES

X <sup>m</sup>	[HgX <sup>2+m</sup> ]/ [Hg <sup>2+</sup> ][X <sup>m</sup> ]	10 <sup>-11</sup> Γ, <sup>a</sup> mol/cm <sup>2</sup>			
		Ref	q <sup>m</sup> = 0	q <sup>m</sup> = +10	Ref
CN <sup>-</sup>	1 × 10 <sup>18</sup>	d	4.5	10	j
I <sup>-</sup>	7.4 × 10 <sup>12</sup>	e	12	26	k
NCS <sup>-</sup>	1.2 × 10 <sup>9</sup>	f	10	21	l
Br <sup>-</sup>	1.1 × 10 <sup>9</sup>	e	7.2	19	m
N <sub>3</sub> <sup>-</sup>	3 × 10 <sup>7</sup>	g	5.2	16	n
Cl <sup>-</sup>	5.5 × 10 <sup>9</sup>	e	2.8	13	o
CNCr <sup>2+</sup>	6.5 × 10 <sup>10</sup>	h	0 <sup>b</sup>	0 <sup>b</sup>	h
SCNCr <sup>2+</sup>	1.6 × 10 <sup>4</sup>	i	1.0 <sup>c</sup>	1.3 <sup>c</sup>	p

<sup>a</sup> For 0.1 M solutions of the anion; q<sup>m</sup> is the value of the electronic charge on the mercury surface in μC/cm<sup>2</sup>. <sup>b</sup> For 1 mM solutions of the adsorbent. <sup>c</sup> For 0.5 mM solutions of the adsorbent. <sup>d</sup> G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957). <sup>e</sup> Reference 15. <sup>f</sup> L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta*, **4**, 312 (1970). <sup>g</sup> T. R. Musgrave and R. N. Keller, *Inorg. Chem.*, **4**, 1793 (1965). <sup>h</sup> This work. <sup>i</sup> Reference 3. <sup>j</sup> H. Wroblowa, Z. Kovac, and J. O'M. Bockris, *Trans. Faraday Soc.*, **61**, 1523 (1965). <sup>k</sup> D. C. Grahame, *J. Amer. Chem. Soc.*, **80**, 4201 (1958). <sup>l</sup> R. Parsons and D. C. Symons, *Trans. Faraday Soc.*, **64**, 1077 (1968). <sup>m</sup> J. Lawrence, R. Parsons, and R. Payne, *J. Electroanal. Chem.*, **16**, 193 (1968). <sup>n</sup> C. V. D'Alkaine, E. R. Gonzalez, and R. Parsons, *ibid.*, **32**, 57 (1971). <sup>o</sup> D. C. Grahame and R. Parsons, *J. Amer. Chem. Soc.*, **83**, 1291 (1961). <sup>p</sup> Reference 4.

geneous solution. The analogous bond on the mercury surface must be much less stable because the 6s orbital on mercury remains essentially filled even at high positive surface charge densities (at a surface charge of +10 μC/cm<sup>2</sup> the average charge per mercury atom on the surface is only ca. 0.06) which makes it difficult for the cyanide ion to approach the surface atoms as closely as is required for the formation of the very stable mercury-carbon bond. The large sulfur atom in thiocyanate leads to a mercury-sulfur bond length in Hg(SCN)<sub>4</sub><sup>2-</sup> of 2.5 Å<sup>18</sup> which is considerably longer than the 2.0-Å mercury-carbon bond in Hg(CN)<sub>2</sub><sup>19</sup> so that the presence of the filled 6s orbital in the mercury surface should produce less destabilization of the mercury-sulfur bond than it does of the mercury-carbon bond in the case of cyanide.

The explanation for the nonadsorption of CrNC<sup>2+</sup> to which this line of reasoning leads is then the following. The attachment of Cr(III) to cyanide produces a great decrease in the mercury-carbon bond strength in HgCNCr<sup>4+</sup>. The same effect, acting on the already weaker mercury-carbon bond in adsorbed cyanide, leads to a bond strength so weak that the adsorption drops below the level of detectability. Thus, the two adsorption-inhibiting factors, namely, the presence of the electrons in the essentially antibonding 6s orbital of mercury(0) and the partial withdrawal by the attached chromium(III) of the electron pair on cyanide that are used in forming the σ bond to mercury combine to prevent the adsorption. The same two obstacles to adsorption are also faced by CrNCS<sup>2+</sup> but the larger ligand more easily accommodates the presence of the 6s electrons, and the (presumed) weakening of the chromium-nitrogen σ bond produced by attachment to the mercury surface is partially compensated by an increased metal-to-ligand π bonding indicated by the bathochromic shift in the d-d

absorption band when Hg<sup>2+</sup> attaches to CrNCS<sup>2+</sup>.<sup>8</sup> The corresponding bond in CrNC<sup>2+</sup> shifts to higher wavelengths upon attachment of Hg<sup>2+</sup> (from <535 to 565 nm) indicating a loss instead of a gain in ligand field stabilization energy. Assuming that a shift in the same direction would result from adsorption on a positively charged mercury surface, this factor would also act to decrease the tendency for CrNC<sup>2+</sup> to adsorb.

**Multiple Linkage Isomers.**—The electrochemical behavior of the products obtained upon reduction of the heavy-metal adducts of *cis*-Cr(CN)<sub>2</sub><sup>+</sup> and *fac*-Cr(CN)<sub>3</sub> (Figures 8, 9, 11) is consistent with the linkage isomerization of one, two, or three of the cyano groups depending upon the ratio of heavy metal to complex and the time elapsed after the addition of the heavy metal. In the case of *cis*-Cr(CN)<sub>2</sub><sup>+</sup> the strong implication is that both NCCrNCM and Cr<sup>NC</sup><sub>NC</sub>>M (M = Ag<sup>+</sup> or Hg<sup>2+</sup>) are formed and, when reduced, yield NCCrNC<sup>+</sup> and Cr(NC)<sub>2</sub><sup>+</sup>, respectively. (A similar complex, *cis*-Cr<sub>Cl</sub>>Hg<sup>3+</sup>, has been proposed as an intermediate in the mercury(II)-catalyzed aquation of CrCl<sub>2</sub><sup>20</sup>.)

Spectral evidence can be marshaled to support the conclusion that a species containing three isocyano groups results when Ag<sup>+</sup> is added to *fac*-Cr(CN)<sub>3</sub> solutions in a ratio of 1.5 mol of Ag<sup>+</sup> per mole of Cr(III) or greater. Table V gives absorption maxima for d-d bands in several complexes and values of 10Dq that are calculated from the spectra and assigned to the respective ligands. These values of ligand 10Dq values are used in Table V to calculate the expected positions of

 TABLE V  
 Calculated<sup>a</sup> Values of 10Dq for the Ligands AgCN  
 and H<sub>2</sub>O on Cr(III) (d-d Band Maxima)

Complex	λ <sub>max</sub> , nm	10Dq, cm <sup>-1</sup>	
		Obsd	Calcd <sup>b</sup>
Cr(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	575	17,391	
Cr(H <sub>2</sub> O) <sub>5</sub> CN <sup>2+</sup>	525	19,048	(H <sub>2</sub> O = 17,391) CN = 27,327
Cr(H <sub>2</sub> O) <sub>5</sub> NCAg <sup>3+</sup>	556	17,986	NCAg = 20,961 (H <sub>2</sub> O = 17,391)

Comparison of Observed d-d Band Maxima for  
 the Ag(I) Adducts of Cr(CN)<sub>2</sub><sup>+</sup> and Cr(CN)<sub>3</sub> with  
 Those Calculated from the Values of 10Dq Listed Above

Mixture	λ <sub>max</sub> (obsd), nm	Possible isomer present	λ <sub>max</sub>
			(calcd), nm
2 mM Cr(H <sub>2</sub> O) <sub>3</sub> (CN) <sub>3</sub> - 3 mM Ag <sup>+</sup>	527	Cr(H <sub>2</sub> O) <sub>3</sub> (CN) <sub>2</sub> (NCAg) <sup>+</sup>	475 <sup>c</sup>
		Cr(H <sub>2</sub> O) <sub>3</sub> (CN)(NCAg) <sub>2</sub> <sup>2+</sup>	497 <sup>c</sup>
1 mM Cr(H <sub>2</sub> O) <sub>4</sub> (CN) <sub>2</sub> <sup>+</sup> - 1 mM Ag <sup>+</sup>	540	Cr(H <sub>2</sub> O) <sub>3</sub> (NCAg) <sub>3</sub> <sup>3+</sup>	522 <sup>c</sup>
		Cr(H <sub>2</sub> O) <sub>4</sub> (CN)(NCAg) <sub>2</sub> <sup>2+</sup>	513 <sup>c</sup>
		Cr(H <sub>2</sub> O) <sub>4</sub> (NCAg) <sub>2</sub> <sup>3+</sup>	538 <sup>c</sup>

<sup>a</sup> According to the procedure outlined by B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 236. <sup>b</sup> (10Dq)<sub>calcd</sub> = 6(10Dq)<sub>obsd</sub> - (5 × 17,391). <sup>c</sup> 1/λ<sub>max</sub>(calcd) = (10Dq)<sub>calcd</sub> = [17,391x + 27,327y + (6 - x - y)20,961]/6 where x and y are the number of aquo and cyano groups, respectively, in the isomer.

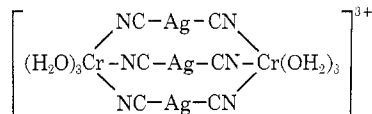
band maxima for heavy-metal adducts containing the possible combinations of cyano and isocyano groups. The experimental spectra are included for comparison and the agreement between the calculated and experi-

(18) H. Scouloudi, *Acta Crystallogr.*, **6**, 651 (1953).

(19) A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed, Oxford Press, London, 1962, p 892.

(20) J. P. Birk, *Inorg. Chem.*, **9**, 735 (1970).

mental values is best for the fully linkage-isomerized cases. The spectra of mixtures of  $\text{Cr}(\text{CN})_3$  and  $\text{Ag}^+$  become constant when the molar ratio of  $\text{Ag}(\text{I})$  to  $\text{Cr}(\text{CN})_3$  is 3:2 or greater. The corresponding potentiometric titration (Figure 10) shows an inflection at this same ratio. These observations indicate the presence of a rather stable adduct having the stoichiometry  $\text{Ag}_3[\text{Cr}(\text{CN})_3]_2$  and a symmetrical structure such as

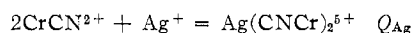


suggests itself.

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### Appendix

The derivation of the formulas used to evaluate the equilibrium quotients will be given for the case of silver ion only because the treatment for mercury(II) is identical. During the early stages of the titration of solutions of  $\text{CrCN}^{2+}$  with  $\text{Ag}^+$  (or  $\text{Hg}^{2+}$ ) the concentration of the heavy-metal cation is controlled by the equilibrium



The value of  $[\text{Ag}^+]$  was evaluated from

$$[\text{Ag}^+] = 10^{\left( \frac{E_{\text{Ag}} - 0.543}{0.059} \right)} = \theta \quad (\text{A1})$$

where  $E_{\text{Ag}}$  is the equilibrium potential assumed by the silver electrode, and 0.543 V is the experimentally observed formal potential of the  $\text{Ag}^+/\text{Ag}$  couple in the 1 M  $\text{NaClO}_4$ -0.1 M  $\text{HClO}_4$  supporting electrolyte employed (the corresponding value for the  $\text{Hg}^{2+}/\text{Hg}$  couple is 0.525 V).

The equilibrium concentrations of  $\text{Ag}(\text{CNCr})_2^{5+}$  at each point in the titration were evaluated from the known analytical concentrations of  $\text{CrCN}^{2+}$  and  $\text{Ag}^+$

$$[\text{Ag}(\text{CNCr})_2^{5+}] = C_{\text{Ag}}^0 - [\text{Ag}^+] \quad (\text{A2})$$

where  $C_{\text{Ag}}^0$  is the total (analytical) concentration of silver present. The equilibrium concentration of  $\text{CrCN}^{2+}$  was calculated from

$$[\text{CrCN}^{2+}] = C_{\text{Cr}}^0 - 2[\text{Ag}(\text{CNCr})_2^{5+}] \quad (\text{A3})$$

where  $C_{\text{Cr}}^0$  is the total (analytical) concentration of  $\text{CrCN}^{2+}$  initially present.

The numerical value of  $Q_{\text{Ag}}$  was calculated from (A4).

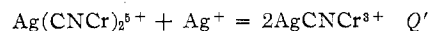
$$Q_{\text{Ag}} = \frac{C_{\text{Ag}}^0 - \theta}{\theta(C_{\text{Cr}}^0 - 2C_{\text{Ag}}^0 + 2\theta)^2} \quad (\text{A4})$$

A typical set of data for the  $\text{Ag}^+$  adduct is shown in Table VI.

TABLE VI  
POTENTIOMETRIC TITRATION OF 4.41 mM  $\text{CrCN}^{2+}$   
(IN 1 M  $\text{NaClO}_4$ -0.1 M  $\text{HClO}_4$ ) WITH 0.030 M  $\text{Ag}^+$

$C_{\text{Cr}}^0$ , mM	$C_{\text{Ag}}^0$ , mM	$E$ , mV (vs. sce)	$10^4\theta$	$10^{10}Q_{\text{Ag}}$
4.34	0.472	41	2.71	1.5
4.30	0.703	44	3.05	2.8
4.26	0.93	50	3.06	4.2
4.23	1.15	60	5.72	5.4
4.20	1.37	73	9.53	6.7
4.17	1.59	91	19.3	8.4
4.14	1.80	132	96.9	6.4
				Av 5.1
			$10^4\theta$	$Q'$
4.01	2.63	322	1.69	3.2
3.99	2.83	334	2.71	3.3
3.96	3.02	342	3.72	3.7
3.93	3.21	349	4.89	3.9
3.87	3.59	360	7.54	4.2
3.85	3.78	364	8.82	4.5
				Av 3.9

When the potentiometric titrations are carried well beyond the equivalence point for formation of the trinuclear complexes, the following equilibrium becomes important



Equation A1 continues to apply and the excess of silver present ensures that the concentration of  $\text{CrCN}^{2+}$  will be negligibly small so the concentrations of the trinuclear and binuclear complexes are given by

$$[\text{AgCNCr}^{3+}] = 2(C_{\text{Ag}}^0 - 1/2C_{\text{Cr}}^0 - \theta) \quad (\text{A5})$$

and

$$[\text{Ag}(\text{CNCr})_2^{5+}] = (C_{\text{Cr}}^0 - C_{\text{Ag}}^0 + \theta) \quad (\text{A6})$$

$Q'$  was therefore evaluated from

$$Q' = \frac{4(C_{\text{Ag}}^0 - 1/2C_{\text{Cr}}^0 - \theta)^2}{\theta(C_{\text{Cr}}^0 - C_{\text{Ag}}^0 + \theta)} \quad (\text{A7})$$

A typical set of data are shown in Table VI.

Finally, the values of  $Q_{\text{III}}$  and  $Q_{\text{IV}}$  in Table II were calculated from the experimentally measured values of  $Q_{\text{Ag}}$  and  $Q'$  according to the relations given by

$$Q_{\text{III}} = (Q'Q_{\text{Ag}})^{1/2} \quad (\text{A8})$$

$$Q_{\text{IV}} = (Q_{\text{Ag}}/Q')^{1/2} \quad (\text{A9})$$