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Interaction of cyanopentaamminechromium(III) with mercuric ion. Electrochemical, spectral and preparative study of adduct formation and linkage isomerism

Miroslav Rievaj, Dušan Bustin and Ján Mocák

Department of Chemistry, Slovak Technical University, Radlinského 9, 812 37 Bratislava (Slovakia)

Pietro Riccieri and Edoardo Zinato*

Dipartimento di Chimica, Università di Perugia, 06100 Perugia (Italy)

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Abstract

The reaction of $Cr(NH_3)_5(CN)^{2+}$ with Hg^{2+} was investigated in aqueous medium by various electrochemical techniques, as well as by absorption and emission spectrophotometry. Evidence was found for formation in solution of a stable 2:1 adduct, the polarographic and spectral properties of which indicate linkage isomerization (Cr–NC–Hg) of the cyano bridging group. In addition, two solids containing 4:1 and 2:1 Cr:Hg adduct species were isolated and characterized. The kinetics of adduct formation and subsequent Hg^{2+}-promoted CN^- aquation were studied by monitoring the phosphorescence of cyanopentaamminechromium(III) and by polarography, respectively. The former reaction obeys the rate law: $-d[Cr]/dt = k_1[Cr] + k_2[Cr]^2$, with k_1 independent of the $[Hg^{2+}]:[Cr]$ ratio in the 5–700 range, and k_2 decreasing as this ratio increases. The aquation rate is independent of both $[Hg^{2+}]$ and $[H_3O^+]$. The factors affecting the two reaction stages are briefly discussed.

Key words Electrochemistry, Chromium complexes; Ammine complexes; Cyano complexes; Mercuric ion complexes

Introduction

The linkage isomerism of cyanide has long been recognized in chromium coordination chemistry [1]. Among the methods employed for investigating this occurrence, voltammetry and polarography have proved particularly advantageous: as an example, a system that has been thoroughly characterized from this point of view is *cis*-$Cr(H_2O)_4(NO)(CN)^+$ [2–5]. Several new mixed-ligand cyano complexes of chromium(III), mainly cyano–am(m)ines, have been prepared during the past decade or so, especially with the aim of studying their excited-state properties [6]. Their ground-state solution chemistry has also been examined in some cases [7, 8], but possible cyano–isocyano rearrangements have not been looked for. The present study has explored the latter aspect by applying the above-mentioned techniques to the simplest member of this family, $Cr(NH_3)_5(CN)^{2+}$, and to its adducts with the Hg^{2+} ion in acidic aqueous medium.

Experimental

Materials and analyses

$[Cr(NH_3)_5(CN)](ClO_4)_2$ was prepared by a published procedure [7] and its purity was checked by analysis of Cr and CN^- and by the UV–Vis absorption spectrum, the maxima of which are reported in Table 1. Solutions of $Hg(ClO_4)_2$ were obtained by treating mercuric oxide with a small excess of perchloric acid. All other reagents

TABLE 1. Ligand-field absorption spectral data in acidic aqueous solution

Compound	Absorption maxima (nm)[a]		Reference
$Cr(NH_3)_5(CN)^{2+}$	451 (42.6)	347 (37.7)	7
$Cr(NH_3)_5(NC)^{2+}$ [b]	462 (40.2)	350 (40.5)	this work
$Cr(NH_3)_6^{3+}$	462 (38.9)	350 (33.5)	13
I[c]	458 (41.0)	348 (39.0)	this work
II[c]	462 (39.6)	350 (40.0)	this work
$Cr(NH_3)_5(H_2O)^{3+}$	480 (35.8)	359 (31.4)	7

[a] Extinction coefficients (M^{-1} cm^{-1}) in parentheses [b] Spectrum of solutions with $[Hg^{2+}]:[Cr(NH_3)_5(CN)^{2+}] \geqslant 0.5$, *c*. 2 min after mixing [c] Solid adduct

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*Author to whom correspondence should be addressed.

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were of analytical grade. Triply-distilled water was employed for the electrochemical measurements.

Chromium was determined spectrophotometrically at 374 nm (ϵ 4760 M^{-1} cm^{-1}) following oxidation of the complex to chromate with alkaline hydrogen peroxide Cyanide was analyzed polarographically after hydrolysis of the complex in 3 M HCl at room temperature in a closed system, in order to avoid possible loss of HCN The medium was then adjusted so as to record the anodic wave of CN^- The mercury content of the solid Cr–Hg adducts was measured by atomic absorption spectroscopy using a Perkin-Elmer 3100 apparatus.

Solid chromium–mercury compounds

Compound I

A 0.18 g portion of $[Cr(NH_3)_5(CN)](ClO_4)_2$ (0.50 mmol) was dissolved in 10 ml of 0.20 M $NaClO_4$ at pH 3 ($HClO_4$). Addition of 1.3 ml of 0.10 M $Hg(ClO_4)_2$ (0.13 mmol) caused progressive precipitation of a yellow solid. This was recovered (0.15 g) by centrifugation within 1–2 min, repeatedly washed with ethanol and ether, and then vacuum-dried.

Anal. Calc. for $\{[Cr(NH_3)_5(NC)]_4Hg\}(ClO_4)_{10}$: Cr, 11.26; Hg, 10.86. Found: Cr, 11.1; Hg, 10.8±0.1%, corresponding to a Cr:Hg molar ratio of 3.96±0 05. Based on this formulation the yield was 65%.

Compound II

A 0.18 g amount of $[Cr(NH_3)_5(CN)](ClO_4)_2$ (0.50 mmol) was dissolved in 5 ml of aqueous 10^{-3} M $HClO_4$. This solution was added to 5.0 ml of 0.20 M $Hg(ClO_4)_2$ (1.00 mmol) with stirring, so as to prevent possible reprecipitation of the perchlorate salt of the reactant. After 2–3 min at room temperature, solid $NaClO_4$ (5.0 g) was added with stirring and a yellow precipitate started to form. Cooling to 0 °C completed precipitation. After 10 min the solid (0.08 g) was collected, washed and dried as above.

Anal. Calc. for $\{[Cr(NH_3)_5(NC)]_2Hg\}(ClO_4)_6$: Cr, 9.26; Hg, 17.85. Found: Cr, 9.0; Hg, 18.1±0.1%, corresponding to a Cr:Hg molar ratio of 1.92±0.05. The yield was 30%.

Instrumentation

Spectrophotometry was carried out by either a Specord UV–Vis (Zeiss, Jena) instrument or a Hewlett-Packard 8452A diode-array instrument. Emission spectra were measured by a Perkin-Elmer 650-10S spectrofluorometer, equipped with an R928 photomultiplier. Potentiometry made use of an OP-205 potentiometer (Radelkis, Budapest). For the titrations with Hg^{2+}, a hanging mercury drop electrode was employed, having as reference a saturated calomel electrode (SCE) with a 1 M $NaNO_3$ salt bridge. Polarography was performed by a PA 4 polarograph (Laboratórní prístroje, Praha); the dropping mercury electrode had a mercury flow rate of 1.65 mg s^{-1} and a drop time of 4.3 s (at a mercury reservoir height of 64 cm and in a short circuit with a SCE).

Kinetic measurements

The rates of adduct formation were determined by recording the decrease of the phosphorescence (under steady excitation) of $Cr(NH_3)_5(CN)^{2+}$ at 680 nm as a continuous function of time. Samples of 1.0 ml volume were made up in 1.0 cm fluorometer cells thermostated to ±0.2 °C. The complex concentration varied between 1.5×10^{-4} and 2.0×10^{-3} M. At the excitation wavelength of 466 nm (isosbestic point between reactant and product), the absorbance was in the 0.01–0 08 range, in order to ensure a uniform distribution of the emitted light from all points of the sample. The desired amounts of Hg^{2+} were added as 10–200 μl aliquots with stirring, so that reliable emission intensities could be measured within 2–3 s from mixing Since the reaction product does not luminesce, the intensity is proportional to the time concentration of the reactant. Rate constants were calculated from non-linear least-squares fits of the digitized emission traces extending to at least 90% conversion.

The rates of adduct aquation were determined spectrophotometrically under pseudo-first-order conditions, by monitoring the time dependence of the optical density at 462 nm of solutions 1×10^{-3} M in complex in the presence of various concentrations of $HClO_4$ and Hg^{2+}. These reaction rates were also measured by polarography through the decrease of the limiting current of the wave associated with the isocyano adduct.

Results and discussion

Polarographic behavior of $Cr(NH_3)_5(CN)^{2+}$ and $Cr(NH_3)_5(H_2O)^{3+}$

In moderately acidic solution ($[H_3O^+]=0.01$ M, $\mu=1.0$ M Na^+, H_3O^+, ClO_4^-) the cyanopentaamminechromium(III) ion is reduced under polarographic conditions in a diffusion-controlled irreversible wave, the limiting current of which corresponds to a one-electron exchange with a half-wave potential $E_{1/2}=-1\,02$ V versus SCE. The αz_α value (where α is the charge-transfer coefficient and z_α the number of electrons exchanged in the activating step of the electrode reaction), determined from the slope of the polarographic curve [9], is 0.80.

Under the same conditions, aquopentaamminechromium(III), the product of acid-catalyzed cyanide aquation (eqn. (1)), also undergoes irreversible one-electron

$$Cr(NH_3)_5(CN)^{2+} + H_3O^+ \longrightarrow Cr(NH_3)_5(H_2O)^{3+} + HCN \quad (1)$$

reduction with $E_{1/2} = -0.83$ V versus SCE and $\alpha z_\alpha = 0.75$.

In the polarographic study, as well as in the study of the reaction with Hg^{2+}, the acidity of the supporting electrolyte was sufficiently low to minimize aquation of $Cr(NH_3)_5(CN)^{2+}$ [7]. On the other hand, in view of the possible instability of $Hg(aq)^{2+}$ toward hydrolysis at low acidities, the H_3O^+ concentration was always above 5×10^{-3} M. The rate of reaction (1), determined by following the time change of the polarographic limiting diffusion current of either $Cr(NH_3)_5(CN)^{2+}$ or $Cr(NH_3)_5(H_2O)^{3+}$, was in agreement with the data previously obtained from spectral measurements. For example, the pseudo-first-order rate constant at $[H_3O^+] = 0.01$ M was 2.5×10^{-5} s^{-1} at 25 °C, comparable with the literature value of 2.62×10^{-5} s^{-1} [7].

Stoichiometry of the reaction of $Cr(NH_3)_5(CN)^{2+}$ with Hg^{2+}

The interaction of cyanopentaamminechromium(III) (the concentration of which is designated in the following as [Cr]) with mercuric ion was quantitatively studied by spectrophotometric, amperometric and potentiometric titrations.

The modification of the ligand-field spectrum of the complex upon addition of Hg^{2+} is illustrated in Fig. 1. Significant variations are observed up to an Hg:Cr molar proportion of 0.5; larger Hg^{2+} amounts have no further effect on the absorption curve. Table 1 reports the final, invariant spectral maxima for $[Hg^{2+}]:[Cr] \geqslant 0.5$.

The absorption changes induced by a given $[Hg^{2+}]$ are not instantaneous, however, but take place within about 1 min at room temperature. The lower part of Fig. 1 exemplifies a typical sequence of rapid-scan difference spectra recorded during this period of time. Isosbestic points indicate formation of either a single product or constant product ratios: that the latter occurrence is likely is suggested by the slight shift (by 1–2 nm) of the crossing points when $[Hg^{2+}]:[Cr]$ varies in the 0.1–0.5 range. The same time intervals were required to obtain stable current or potential signals. It was also necessary to avoid complications arising from the successive, slow decomposition of the species formed in this stage: therefore, each titration point was obtained in a separate experiment by mixing fresh reactants.

In the amperometric titrations, the potential of the indicator electrode was set at −0.6 V versus SCE, at which all forms of Hg(II) are reduced while Cr(III) remains electrochemically unchanged. Such titrations are based on the differences of the diffusion coefficients of free and variously bound Hg(II). At a given potential, the current increases linearly with the concentration of the titrant up to $[Hg^{2+}]:[Cr] = 0.5$. For higher ratios the increase becomes steeper.

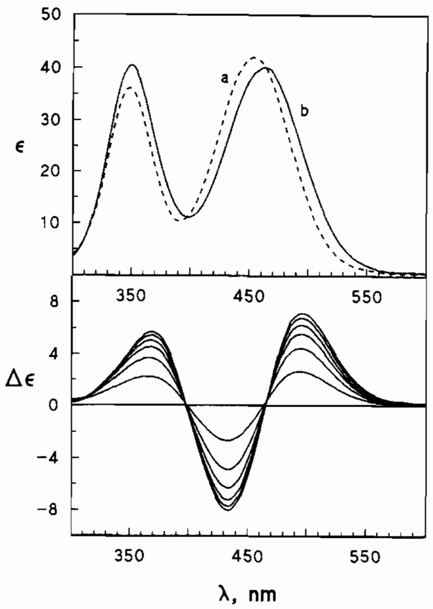

Fig 1. UV–Vis spectra of $Cr(NH_3)_5(CN)^{2+}$ in acidic aqueous solution. Upper part: (a) initial spectrum; (b) final, stable spectrum after Hg^{2+} addition, for $[Hg^{2+}]:[Cr] \geqslant 0.5$. Lower part: differential absorption during evolution from (a) to (b) at 25 °C; reading downward at 430 nm, the curves correspond to reaction times of 15, 30, 45, 60, 75 and 90 s.

In line with the above observations, the potentiometric titration curve also exhibits its inflection point corresponding to an $[Hg^{2+}]:[Cr]$ ratio of 0.5.

All these results are concordant in indicating formation in solution of a stable adduct with a Cr:Hg proportion of 2:1, according to eqn. (2):

$$2Cr(NH_3)_5(CN)^{2+} + Hg^{2+} \longrightarrow [Cr(NH_3)_5(NC)]_2Hg^{6+} \quad (2)$$

As discussed below, the association process is accompanied by isomerization of the cyano group. Such a rearrangement was not unexpected, in the light of the behavior of $Cr(H_2O)_5(CN)^{2+}$ [10, 11] and $Cr(H_2O)_4(NO)(CN)^+$ [2] in the presence of Hg^{2+}.

The break in the amperometric titration plot is congruent with an expectedly smaller diffusion coefficient for the trinuclear product of eqn. (2) than for either 'free' Hg^{2+} or a possible 1:1 adduct arising from reaction (3):

$$[Cr(NH_3)_5(NC)]_2Hg^{6+} + Hg^{2+} \longrightarrow 2Cr(NH_3)_5(NC)Hg^{4+} \quad (3)$$

This subsequent reaction has indeed been considered in the above-mentioned related cases [2, 11]; however, spectrophotometry does not provide any indication as to whether or not it is actually occurring here, since the spectral changes are only due to changes within the Cr(III) moiety.

Supplementary information is given by emission spectral measurements: the fairly intense phosphorescence of $Cr(NH_3)_5(CN)^{2+}$ centered at 680 nm [7] is gradually reduced by Hg^{2+} addition and vanishes precisely at $[Hg^{2+}]:[Cr] = 0.5$. This is clearly due to consumption of the cyano complex and not to an 'external' quenching effect of the heavy metal, as the emission fading that follows the mixing is not immediate but takes place at the same rate as the absorption changes.

An additional possibility to be taken into account specially when a large excess of Hg^{2+} is mixed with the cyano complex, is direct formation of the dinuclear species:

$$Cr(NH_3)_5(CN)^{2+} + Hg^{2+} \longrightarrow Cr(NH_3)_5(NC)Hg^{4+} \qquad (4)$$

as believed in the case of the above-mentioned cyanoaquo compounds [5, 10].

Linkage isomerism: polarographic study

The movement to the red of the ligand-field absorption maxima of the product of reaction (2) and of compounds **I** and **II** (*vide infra*) relative to $Cr(NH_3)_5(CN)^{2+}$, is consistent with cyano–isocyano rearrangement about Cr(III). Spectral shifts in the same direction have been noted earlier in the $Cr(H_2O)_5(CN)^{2+}$–Hg^{2+} system and have been ascribed to bond isomerization of CN^- [10–12]. The inference that, in the present case, the initial CrN_5C chromophore is converted to CrN_6 is corroborated by the closeness of the spectrum of the adduct with that of $Cr(NH_3)_6{}^{3+}$, taken as a model [13] (Table 1).

Polarography provides further evidence for linkage isomerism. Upon addition of mercuric ion to aqueous $Cr(NH_3)_5(CN)^{2+}$, the polarographic behavior is rapidly modified as shown in Fig. 2. A progressive lowering of the wave of the original complex with $E_{1/2} = -1.02$ V (curve a) is accompanied by the increase of a new wave with $E_{1/2} = -0.76$ V versus SCE (curve b). This is attributed to the trinuclear adduct of eqn. (2). As was concluded in the previous study of the monocyanonitrosyl complex [3], a less negative potential denotes the one-electron reduction of the less stable Cr–NC linkage isomer liberated at the electrode upon cathodic reduction of Hg(II) bound in the adduct.

Reaction (2) is followed by slow decomposition of the adduct leading to the aquopentaamminechromium(III) ion (eqn. (5)), the accrual of which is indicated by the growth of its polarographic wave with $E_{1/2} =$

$$[Cr(NH_3)_5(NC)]_2Hg^{6+} + 2H_2O \longrightarrow 2Cr(NH_3)_5(H_2O)^{3+} + Hg(CN)_2 \qquad (5)$$

-0.83 V versus SCE (curve c). Reaction (5) could, in principle, be studied by detection of $Hg(CN)_2$ at more positive potentials. The wave for the latter process, however, was not sufficiently resolved with respect to that for Hg(II) reduction of $[Cr(NH_3)_5(NC)]_2Hg^{6+}$, strongly affected by a kind of polarographic maximum.

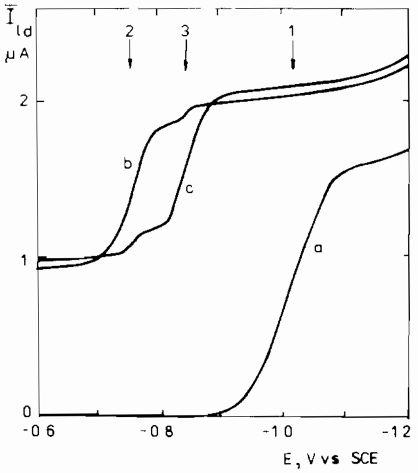

Fig. 2. Schematic representation of the polarographic behavior of aqueous 1.00 mM $Cr(NH_3)_5(CN)^{2+}$ in the presence of 0.5 mM Hg^{2+}. $[H_3O^+] = 0.01$, $\mu = 1.00$ M (ClO_4^-, Na^+, H_3O^+, Hg^{2+}); $t = 25$ °C. Waves (a) before Hg^{2+} addition, (b) 10 min after Hg^{2+} addition, (c) 120 min after Hg^{2+} addition. Half-wave reduction potentials: (1) $Cr(NH_3)_5(CN)^{2+}$, (2) $Cr(NH_3)_5(NC)^{2+}$; (3) $Cr(NH_3)_5(H_2O)^{3+}$

Another experiment substantiates the occurrence of Cr–CN/Cr–NC isomerism: if a large excess of iodide ion is added to the adduct (obtained either by solution mixing or by dissolving **I** and **II**), wave b disappears, being replaced by wave a, which shows regeneration of $Cr(NH_3)_5(CN)^{2+}$. Evidently, because of the high stability of $HgI_4{}^{2-}$ [14], equilibrium (6) is shifted to the right with prompt conversion of the displaced,

$$[Cr(NH_3)_5(NC)]_2Hg^{6+} + 4I^- \rightleftharpoons HgI_4{}^{2-} + 2Cr(NH_3)_5(NC)^{2+} \qquad (6)$$

unstable isocyano complex to the stable cyano form:

$$Cr(NH_3)_5(NC)^{2+} \longrightarrow Cr(NH_3)_5(CN)^{2+} \qquad (7)$$

Also the spectrum of the latter is restored: only the 451 nm maximum is apparent though, as the higher-energy band is obscured by the intense absorption of $HgI_4{}^{2-}$.

The stabilization of the Cr–NC bonding mode by Hg^{2+} association is readily understood in terms of the high affinity of the softer-base C end of cyanide for the soft acid Hg^{2+} [10, 11].

Cr–Hg adduct isolation

Two distinct solids, containing Cr–Hg adduct species, can be isolated under different conditions. Compound **I** is obtained by adding Hg^{2+} to $Cr(NH_3)_5(CN)^{2+}$ in the presence of excess ClO_4^-, and precipitates as long as $[Hg^{2+}]:[Cr] < c.\ 0.3$: the Hg:Cr molar ratio in this salt is 1:4. Its prompt redissolution when more Hg^{2+} is added, is suggestive of a definite composition.

Compound **II** can be precipitated by adding ClO_4^- to solutions where $[Hg^{2+}]:[Cr] > c.\ 2$: the Hg:Cr ratio is, in this case, 1:2.

The IR spectra of the solids in the CN stretching region (Fig. 3) are quite different from that of the parent complex: more importantly, the two compounds differ tangibly from each other. While in $[Cr(NH_3)_5(CN)](ClO_4)_2$ the stretching appears as a narrow peak at 2140 cm^{-1} [7], in **I** and **II** broader and considerably more intense bands are observed at 2192 and 2242 cm^{-1}, respectively. The indication is that there are actually two different species, excluding the possibility that **I** be a co-precipitate of **II** and cyanopentaamminechromium(III).

On the basis of polarography, elemental analysis and IR data, **I** and **II** are assigned the formulae $\{[Cr(NH_3)_5(NC)]_4Hg\}(ClO_4)_{10}$ and $\{[Cr(NH_3)_5(NC)]_2Hg\}(ClO_4)_6$. With regard to the IR spectra, the following comparisons are particularly significative. (i) The CN stretchings of $Hg(CN)_4^{2-}$ and $Hg(CN)_2$ occur at 2143 and 2193 cm^{-1}, respectively: i.e. as usual the frequency regularly increases with decreasing number of coordinated cyanides [15]. (ii) CN bridging between metal ions generally involves a 30–50 cm^{-1} shift to higher energies for such vibrations [16]. The two adducts can therefore be viewed as tetra- and di-coordinated Hg(II) species having Cr(III) isocyano complexes as ligands: the CN bonding interaction is, naturally, weaker in the bulkier compound **I** than in **II**.

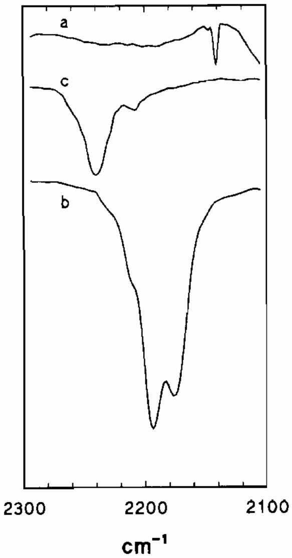

Fig. 3. IR spectra in the CN stretching region: (a) $[Cr(NH_3)_5(CN)](ClO_4)_2$, (b) compound **I** (Cr:Hg = 4:1); (c) compound **II** (Cr:Hg = 2:1).

The ligand-field absorption maxima of these compounds in water are included in Table 1. The spectrum of **II** is virtually identical with that of solutions where $[Hg]:[Cr] \geq 0.5$, attributed to the $Cr(NH_3)_5(NC)^{2+}$ chromophore. The spectrum of **I** is intermediate between those of the Cr–CN and Cr–NC isomeric forms. The emission properties are congruent with the absorption properties: in **II** the 680 nm phosphorescence of $Cr(NH_3)_5(CN)^{2+}$ is totally extinguished, whereas in **I** it is reduced to *c.* one-half of its original intensity.

Once redissolved, both **I** and **II** are unstable like the solutions from which they are separated, and slowly decompose to eventually give $Cr(NH_3)_5(H_2O)^{3+}$.

The solution behavior and the observations on the solid compounds reveal complexity of equilibria among various adducts in the liquid phase. For low Hg:Cr proportions, formation of at least some $[Cr(NH_3)_5(NC)]_4Hg^{10+}$ is plausible, given the coordination properties of Hg^{2+}. Precipitation of **I** would displace the equilibrium toward this highly charged species; its redissolution on increasing $[Hg^{2+}]$ is in agreement with the high solution stability (implied by the spectral and electrochemical results) of $[Cr(NH_3)_5(NC)]_2Hg^{6+}$. Also when solid **I** is redissolved, a shift would take place in favor of the more stable 2:1 adduct, accompanied by the liberation of stoichiometric amounts of $Cr(NH_3)_5(CN)^{2+}$.

The composition and the spectrum of **II** confirm the importance of the 2:1 adduct at higher Hg:Cr solution ratios, but do not completely rule out the possibility that a less charged, conceivably more soluble 1:1 species be formed (eqn. (3)), especially for very high Hg:Cr proportions.

Rate of adduct formation

The chromium–mercury association reaction is too fast to be characterized kinetically by polarography. Moreover, the absorption changes involved (Fig. 1) are relatively small, so that spectrophotometry was also inadequate. The fact that the reactant phosphoresces while the product does not, suggested an unusual, fairly sensitive procedure. The disappearance of $Cr(NH_3)_5(CN)^{2+}$ could be conveniently monitored through the decline of its emission at 680 nm. Steady excitation corresponded to an isosbestic point between reactant and product: consequently, the light absorption by the sample and the emission geometry remained constant during the reaction.

Several sets of experiments were run, with [Cr] ranging between 1.5×10^{-4} and 2.0×10^{-3} M, and 5- to 700-

fold molar excess of Hg^{2+}. It may be noted that, at pH 2.0 (and $\mu = 1.0$ M), the potentially competitive acid-catalyzed loss of CN^- (eqn. (1)) [7] is fully negligible as it is 3 orders of magnitude slower than the reaction in question. The subsequent aquation can equally be ignored within this time scale.

Plots of $[Cr(NH_3)_5(CN)^{2+}]$ versus time conform to first-order kinetics only to a first approximation: the deviations from this behavior are not large, but are systematic. By a more precise treatment based on iterative non-linear regressions over at least 100 points, the data are found to obey very well the rate law:

$$-d[Cr]/dt = k_1[Cr] + k_2[Cr]^2 \tag{8}$$

the integrated expression of which is:

$$[Cr] = \frac{[Cr]_0 k_1 \exp(-k_1 t)}{k_1 + k_2[Cr]_0(1 - \exp(-k_1 t))} \tag{9}$$

where $[Cr]_0$ is the known initial concentration. The correlation coefficients of the fittings to eqn. (9) were always better than 0.999. In the concentration intervals examined, variations of the experimental rate constants depend, within error limits, only on the $[Hg^{2+}]$:$[Cr]_0$ proportion and not on the absolute $[Hg^{2+}]$ and $[Cr]_0$, the latter changing up to 13 times. Therefore, the values of k_1 and k_2, obtained at 25 °C for various combinations of $[Cr]_0$ and $[Hg^{2+}]$ are grouped in Table 2 as a function of the reactant ratio.

The kinetic suggestion is that the Cr–CN moiety competitively disappears through two parallel pathways, the rate-determining steps of which involve either one or two molecules at a time. Equations (10) and (11) offer a reasonable picture of the reactive sequence under the present conditions, consistent with the experimental rate expression of eqn. (8).

$$Cr(NH_3)_5(CN)^{2+} + Hg^{2+} \overset{K'}{\rightleftharpoons} Cr(NH_3)_5(CN)Hg^{4+} \xrightarrow{k'} Cr(NH_3)_5(NC)Hg^{4+} \tag{10}$$

$$2Cr(NH_3)_5(CN)^{2+} + Hg^{2+} \overset{K''}{\rightleftharpoons} [Cr(NH_3)_5(CN)]_2Hg^{6+} \xrightarrow{k''} [Cr(NH_3)_5(NC)]_2Hg^{6+} \tag{11}$$

Immediate association with Hg^{2+} would produce equilibrium mixtures of labile, non-isomerized $Cr(NH_3)_5(CN)Hg^{4+}$ and $[Cr(NH_3)_5(CN)]_2Hg^{6+}$ ions, whose Cr units would retain their original absorption and emission spectral properties. Linkage isomerization of the two associated species would then ensue with comparable (and measurable) rates.

Figure 4 plots the observed rate constants k_1 and k_2 versus $[Hg^{2+}]$:[Cr]. The k_1 values do not show any significant change over the whole range of Hg(II) and Cr(III) concentrations explored (within a maximum uncertainty of ±17% arising mainly from the two-parameter mathematical treatment rather than from experimental reproducibility). As to k_2, the variability is much larger (up to ±40%) due to the smaller weight of this parameter in the curve-fitting procedure. This

TABLE 2. Observed rate constants at 25 °C for the reaction of $Cr(NH_3)_5(CN)^{2+}$ with Hg^{2+} at $[H_3O^+] = 0.01$ M and $\mu = 1.00$ M[a]

$[Hg^{2+}]$:[Cr][b]	$10^2 \times k_1$ (s^{-1})	$10^4 \times k_2$ ($M^{-1}\ s^{-1}$)
5	1.73±0.30	4.3±1.0
10	1.64±0.23	3.6±0.4
15	1.94±0.22	2.8±0.3
25	1.60±0.22	2.3±0.3
30	1.90±0.25	2.2±0.2
40	1.73±0.20	2.0±0.2
45	1.46±0.12	1.6±0.2
55	1.60±0.27	1.3±0.1
70	1.52±0.24	1.3±0.6
75	1.53±0.08	1.4±0.1
90	1.75±0.12	1.0±0.3
120	1.43±0.18	1.4±0.3
140	1.62±0.07	0.85±0.19
150	1.52±0.05	0.77±0.15
280	1.52±0.07	0.58±0.14
690	1.58±0.10	0.34±0.12

[a] Each entry is the average of at least 3 kinetic runs. [b] Concentration ranges $[Cr(NH_3)_5(CN)^{2+}] = 1.5 \times 10^{-4}$–$2.0 \times 10^{-3}$ M; $[Hg^{2+}] = 0.01$–0.10 M.

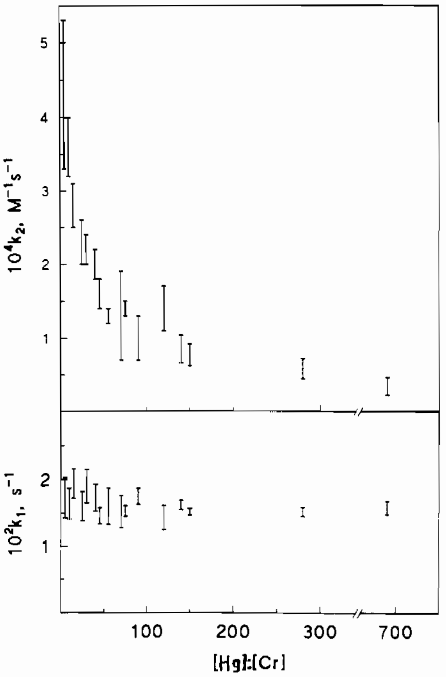

Fig. 4. Plots of k_1 (lower part) and k_2 (upper part) vs. $[Hg^{2+}]$:$[Cr(NH_3)_5(CN)^{2+}]$ at 25 °C, $[H_3O^+] = 0.01$ and $\mu = 1.00$ M.

notwithstanding, a definite trend is now apparent: the higher $[Hg^{2+}]:[Cr]_0$, the less important reaction path (11), in agreement with expectation (it should be kept in mind that k_1 and k_2 are not mechanistic, but experimental parameters that may or may not be concentration dependent).

In consideration of the intricacy of this system, k_1 and k_2 are regarded as merely empirical quantities indicating the relative importance of reactions (10) and (11) under different circumstances, and no attempt is made at a more detailed analysis of the isomerization process. Yet, some remark appears possible in the framework of the mechanism that has been proposed earlier for the same reaction step of $Cr(H_2O)_5(CN)^{2+}$ [10] and $Cr(H_2O)_4(NO)(CN)^+$ [5]. The isomerization rates of these two systems were found to obey first-order kinetics and were interpreted in terms of Cr–Hg association pre-equilibria involving 1:1 adducts only, analogous to eqn. (10) and described by a relation of the type:

$$k_1 = k'K'[Hg^{2+}]/(1 + K'[Hg^{2+}]) \qquad (12)$$

In both cases, k_1 increased with $[Hg^{2+}]:[Cr]$, and from such an increase respective K' values of 28 M^{-1} [10] and 6×10^2 M^{-1} [5] were derived. The present virtual constancy of k_1 is taken to indicate a substantially higher degree of association in this stage (i.e. $K' > 10^3$; $k_1 \simeq k'$): practically all Cr molecules would be engaged with Hg^{2+} even at low $[Hg^{2+}]:[Cr]$ proportions. This is plausible, since CN^- bound to a CrN_5-type fragment is presumed to be a stronger Lewis base than CN^- bound to CrO_5- and CrO_4N-type fragments. The proton uptake ability is, in fact, higher for $Cr(NH_3)_5(CN)^{2+}$ [7] than for $Cr(H_2O)_5(CN)^{2+}$ [17].

Rate of adduct aquation

Adduct decomposition, that is, Hg^{2+}-catalyzed cyanide aquation leading to $Cr(NH_3)_5(H_2O)^{3+}$ (eqn. (5)), is *c.* 100 times slower than adduct formation. The process was studied by measuring the decrease in time of the polarographic wave of the Cr–NC isomer with $E_{1/2} = -0.76$ V versus SCE. It could also be studied by following the increase of the limiting current at the constant potential of -0.6 V versus SCE, at which Hg(II) bound in all possible complexes is reduced (such an increase is due to formation of species with higher diffusion coefficients).

Spectrophotometry confirmed the polarographic results through monitoring of the changes in absorbance at 462 nm. These arise from the shift of the low-energy maximum to 480 nm, which identifies aquopentaamminechromium(III) (Table 1).

As discussed above, the 1:1 adduct (eqns. (3) and (4)) and hence its aquation (eqn. (13)) should also be

$$Cr(NH_3)_5(NC)Hg^{4+} + H_2O \longrightarrow Cr(NH_3)_5(H_2O)^{3+} + Hg(CN)^+ \qquad (13)$$

considered. Reactions (5) and (13), however, cannot be distinguished on the basis of the available polarographic and spectral results, both related to properties of the Cr(III) component, regardless of its association ratio with Hg^{2+}.

The pseudo-first-order rate constants, k_A, determined by the two methods for various concentrations of mercuric and hydrogen ions are collected in Table 3. There is satisfactory agreement between the two groups of data.

It is seen that, provided $[Hg^{2+}] > 0.5[Cr]$, the k_A values are independent of $[H_3O^+]$ within experimental error. The invariance indicates that protonation of the bridging cyano group is hindered in comparison with protonation of CN^- in $Cr(NH_3)_5(CN)^{2+}$. This can be explained by the high positive charge of the adduct and especially by an unfavourable electronic structure, as both lone pairs of cyanide are now employed in metal coordination. On the grounds that the electrochemical and spectral variations connected with reaction (2) are complete at $[Hg^{2+}]:[Cr] = 0.5$, an at least 90% extent of Cr–Hg association may be estimated, setting a lower limit of 10^4–10^5 M^{-2} to the stability constant of the adduct. This is to be compared with the value of 0.08 M^{-1} (25 °C, $\mu = 1.0$ M) previously determined for the protonation constant of $Cr(NH_3)_5(CN)^{2+}$ [7]. Process (2) is, therefore, strongly competitive with proton uptake, i.e. adduct formation protects the complex from rapid acid-catalyzed aquation. While the half-life for aquation of cyanopentaamminechromium(III) in 2.0 M $HClO_4$ is approximately 2 min [7], that for decomposition of the adduct(s) in the same medium is 25 times as long.

Besides being pH-independent, k_A does not depend on $[Hg^{2+}]$ over a fairly wide range (0.5–50) of $[Hg^{2+}]:[Cr]$, where both 2:1 and 1:1 adducts should

TABLE 3. Pseudo-first-order rate constants for adduct aquation at 25 °C[a]

$[H_3O^+]$ (M)	$[Hg^{2+}]$ (M)	$10^4 \times k_A$[b] (s^{-1})	$10^4 \times k_A$[c] (s^{-1})
5×10^{-1}	5×10^{-4}	2.24 ± 0.1	2.26 ± 0.20
5×10^{-2}	5×10^{-4}	2.31 ± 0.1	2.30 ± 0.15
5×10^{-3}	5×10^{-4}	2.32 ± 0.1	2.24 ± 0.12
5×10^{-1}	5×10^{-3}	2.23 ± 0.1	2.36 ± 0.13
5×10^{-2}	5×10^{-3}	2.34 ± 0.2	2.31 ± 0.10
5×10^{-2}	5×10^{-2}	2.31 ± 0.3	2.21 ± 0.15

[a] Ionic strength 1.00 M (ClO_4^-, Na^+, H_3O^+, Hg^{2+}); initial concentration of $Cr(NH_3)_5(CN)^{2+}$ 1.0 mM. Values are the average of 3 determinations. [b] Polarographic measurements. [c] Spectrophotometric measurements.

occur. The constancy implies very similar rates for reactions (5) and (13).

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