Inorganica Chimica Acta, 26 (1978) 11–16

Study of Cyanoaquonitrosyl Complexes of Chromium.
IV.[a] Electrochemical Reactions and Complexation Equilibria of the $NO(H_2O)_4CrCN^+$ Adducts with Mercury(II)

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Received April 6, 1977

The electrochemical reactions of bond isomers cis-*$NO(H_2O)_4Cr$-CN^+ and* cis-*$NO(H_2O)_4Cr$-NC^+ and of their complexes with Hg^{2+} are described. The reaction schemes proposed are based chiefly on polarographic and coulometric measurements. The measurement of the potentials of the reversible reduction of Hg(II) complexed in $\{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+}$ was used for the calculation of the formation constant of this complex from $NO(H_2O)_4Cr$-NC^+ and Hg^{2+}, $K = 1.43 \times 10^{21}$ M^{-2} at 25 °C and an ionic strength of 1* M *(ClO_4^-, Na^+, H^+), and of the acid–base dissociation constant of $NO(H_2O)_4Cr$-NCH^{2+}, $K_a = 2.75 \times 10^{-2}$* M *for the same conditions. An analysis of the limiting diffusion current of reduction of the complexed Hg(II) yielded the value of the equilibrium constant for the reaction of Hg^{2+} with $\{NO(H_2O)_4Cr\text{-}NC\}_2$-$Hg^{4+}$, $Q = 7 \pm 4$ for 25 °C and an ionic strength of 1* M *(ClO_4^-, Na^+, H^+).*

Introduction

The existence of bond isomers of cyanide in complex compounds has been described in a number of works dealing mostly with substitution inert complexes of Co(III) and Cr(III) [1–7]. In all examples published so far, the Cr–CN bond was preferred over the Cr–NC bond. However, if heavy metal ions Hg^{2+} and Ag^+ are present in the solution, they react with cyanocomplexes with formation of bi- and trinuclear complexes with a cyanide bridge bonded to chromium through the nitrogen. The stoichiometry of the reactions of *cis*-$NO(H_2O)_4Cr(NC)^+$ with Hg^{2+} and Ag^+ and the equilibria involved are described in the previous paper in this series [1], where the spectral (electronic) changes taking place are also described.

The present paper deals with the study of the electrochemical reactions of bond isomers of *cis*-$NO(H_2O)_4Cr(CN)^+$ and of their polynuclear complexes with Hg^{2+}.

Experimental

Analytical grade reagents and triply-distilled water were employed. $NO(H_2O)_4Cr$-CN^+ was prepared in solution and analyzed according to procedures described earlier [1].

A Polarograph OH-102 (Radelkis, Budapest, Hungary) was used as an instrument for polarography and cyclic voltammetry. The dropping mercury electrode for polarographic measurements had a drop-time of 4.3 s and the flow rate was 1.65 mg s^{-1} in 0.1 *M* KCl in a short-circuit with saturated calomel electrode (SCE), at a mercury column height of 64 cm. A hanging mercury drop electrode according to Kemula, type E 69 b (Radiometer, Copenhagen, Denmark) was used as a stationary mercury electrode. Scan rate 4.63×10^{-2} V s^{-1} was used for cyclic voltammetric measurements.

Controlled potential coulometry was performed using the universal Coulometric Analyser OH-404 (Radelkis, Budapest, Hungary). A cylinder-shaped vessel equipped with two symmetrically placed auxiliary electrodes was used separated by sintered-glass/agar-impregnated diaphragms from the working space. The volume of the solution in the working electrode compartment was 50–70 ml. The mercury pool was used as the working electrode. This was kept in motion with a teflon stirrer, stirring also the electrolyzed solution.

Results

Polarographic Investigation of the Formation of a Polynuclear Complex of $NO(H_2O)_4CrCN^+$ with Hg^{2+}

In weakly acidic solutions ($[H^+] = 0.01$ *M*; I = 1 *M* ClO_4^-, Na^+, H^+), $NO(H_2O)_4CrCN^+$ is reduced under polarographic conditions in a diffusion-controlled

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[a] Part III of this series is ref. [1].

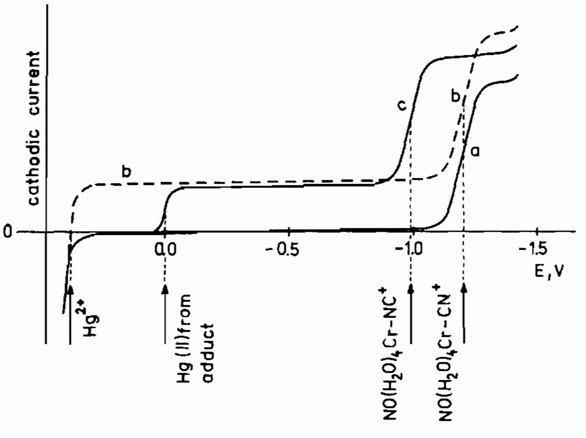

Figure 1. Schematic representation of the polarographic behaviour of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$; *a*) polarographic wave of $NO(H_2O)_4Cr\text{-}CN^+$ in concentration v; *b*) sum of polarographic wave *a* and Hg^{2+} in concentration 0.5 v; *c*) polarographic waves of reacted solution described under *b* (about 10 minutes after mixing).

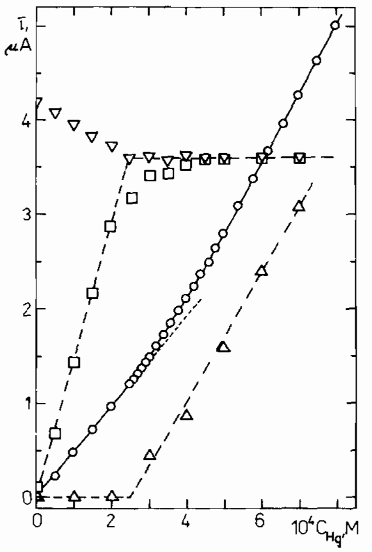

Figure 2. Dependence of polarographic limiting current on the concentration of added $Hg(ClO_4)_2$ (C_{Hg}); concentration of added $NO(H_2O)_4CrCN^+$ 5 × 10^{-4} *M*; 25 °C; ionic strength 1 *M*; $[H^+]$ = 0.01 *M*; current ($\bar{i}$) measured at +0.2 V *vs.* SCE △; at −0.5 V *vs.* SCE ○; current difference ($\Delta\bar{i}$) between potentials −1.1 V and −0.5 V *vs.* SCE □; −1.33 V and −0.5 V *vs.* SCE ▽.

wave (Fig. 1., curve a), whose height corresponds to the exchange of 3 electrons [8] and the half-wave potential is $E_{1/2} = -1.21_4$ V *vs.* SCE. Addition of Hg^{2+} and the formation of a polynuclear complex leads to a decrease in this polarographic wave and the formation of two more waves with half-wave potentials of about 0 V and -0.94_7 V *vs.* SCE ($[H^+] = 0.01$ *M*; I = 1 *M* ClO_4^-, Na^+, H^+). The original wave decreases and the two more positive waves increase with increasing concentration of Hg^{2+}, up to a Hg^{2+} concentration equal to one half the concentration of $NO(H_2O)_4CrCN^+$ (Fig. 1, curve b). At higher concentrations a current appears at potentials more positive than 0 V *vs.* SCE, owing to increased concentration of Hg^{2+} and the original wave of $NO(H_2O)_4CrCN^+$ disappears.

This polarographic behaviour is caused by the formation of polynuclear complexes between Hg^{2+} and $NO(H_2O)_4CrCN^+$. The experiments must be carried out in such a way that the effect of the subsequent decomposition of the polynuclear complex is avoided, *i.e.* separate solutions must be prepared for each Hg^{2+} concentration. This procedure is especially important because the formation of the polynuclear complex is rather slow and complete reaction takes several minutes. At the Hg^{2+} concentration equal to one half the $NO(H_2O)_4CrCN^+$ concentration, the wave with $E_{1/2} = -0.94_7$ V is about 14% lower than the original wave of chromium cyanonitrosyl, but is three times as high as the positive wave at 0 V. These changes in the wave heights are depicted in Fig. 2.

The wave with $E_{1/2} = -0.94_7$ V and the original $NO(H_2O)_4CrCN^+$ wave are polarographically irreversible, whereas the wave at 0 V is reversible. The reversibility of the latter wave was verified by using the Kalousek commutator (the formation of a typical anodic–cathodic wave), cyclic voltammetry on a hanging mercury drop electrode (the potential separation of the anodic and cathodic peaks typical of reversible processes) and an analysis of the wave shape. The analysis was carried out by transformation of the polarographic $\bar{i}$–E curve to the log $(\bar{i}_d - \bar{i}/\bar{i}^2)$ *vs.* E coordinates and verification of the linearity and the equality of the slope value with the value following from the equation for the reduction of Hg(II) complexes with two ligands [9, 10] at 25 °C,

$$E = E^{0'}_{Hg^{2+}} + 0.030 \log \frac{\bar{\kappa}'^2}{\bar{\kappa}^* K} + 0.059 \log \frac{K_a + [H^+]}{K_a} + 0.030 \log \frac{\bar{i}_d - \bar{i}}{\bar{i}^2} \qquad (1)$$

where $E^{0'}_{Hg^{2+}}$ is the formal potential of the mercury electrode, K is the overall formation constant of $Hg(CN)_2$ (formal), K_a is the dissociation constant of $NO(H_2O)_4CrNCH^{2+}$ (formal), $\bar{\kappa}'$ and $\bar{\kappa}^*$ are the mean values of the Ilkovič constant for $NO(H_2O)_4CrNC^+$ and $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$, respectively, $\bar{i}_d$ is the mean limiting diffusion current.

From the potential of the mercury drop electrode, the stability constant of the reduced complex and the dissociation constant of the protonated form of the ligand liberated on reduction can be calculated.

Using Eq. (1), the equation for the half-wave potential can be formulated as follows,

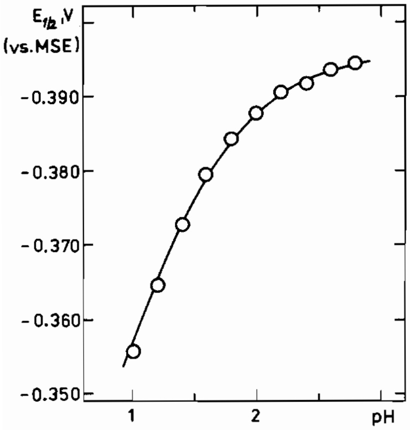

Figure 3. pH dependence of half wave potential $-E_{1/2}$ for 0.25 m*M* $\{NO(H_2O)_4CrCN\}_2Hg^{4+}$; ionic strength: 1 *M* (ClO_4^-, Na^+, H^+); 25 °C; solution 1 m*M* in $NO(H_2O)_4CrCN^+$ and 0.25 m*M* in Hg^{2+} reacted about 12 minutes before measurement at each $[H^+]$.

$$E_{1/2} = E^{o'}_{Hg^{2+}} + 0.059 \log \frac{\bar{\kappa}'}{\bar{\kappa}^*} - 0.030 \log \frac{cK}{2} - \\ - 0.059 \log \frac{K_a}{K_a + [H^+]}, \qquad (2)$$

where c is the concentration of the reduced Hg(II) complex.

The experimental values of the half-wave potential for 1 X 10^{-3} *M* $NO(H_2O)_4CrCN^+$, 2.5 X 10^{-4} *M* Hg^{2+}, I = 1 *M* and 25 °C and for solutions with various hydrogen ion concentrations are given in Fig. 3. The value of $E^{o'}_{Hg^{2+}}$ obtained in this electrolyte against a mercurous sulphate electrode (MSE) was +0.120 V. The term involving the Ilkovič constants (the second term on the right-hand side of Eq. (2)) was calculated from the ratio of the limiting diffusion currents of $NO(H_2O)_4CrCN^+$ and of the negative wave of the 1:2 adduct at the Hg^{2+} concentration equal to one half of that of the ligand and was found to equal 0.007 V. In view of the assumed high value of K, the total Hg^{2+} concentration in the solution was substituted for c. The experimental points of the $E_{1/2}$ *vs.* $[H^+]$ dependence given in Fig. 3 are best fitted by the curve calculated from Eq. (2) for the values, K_a = 2.75 X 10^{-2} *M* and K = 1.43 X 10^{21} M^{-2} (for 25 °C and an ionic strength of 1 *M* (ClO_4^-, Na^+, H^+).

Further data on the character of the above polarographic waves were obtained on addition of excess halide or pseudohalide ions. It was found that an addition of I^- or CN^- (or HCN) in a hundred-fold molar excess to a solution of the polynuclear complex of pH 2.0 leads to a decrease in the more negative polarographic wave ($E_{1/2}$ = -0.94_7 V *vs.* SCE), which disappears within several minutes. The wave with $E_{1/2}$ = -1.21_4 V *vs.* SCE simultaneously increases; it corresponds to the reduction of $NO(H_2O)_4CrCN^+$ and within several minutes attains the limiting value corresponding to the three-electron reduction of this compound. An addition of a hundred-fold excess of Cl^- does not cause these changes in the polarographic behaviour.

Coulometric Measurements

Solutions with various Hg^{2+}-to-$NO(H_2O)_4CrCN^+$ ratios were electrolyzed on a mercury macroelectrode. In solutions containing Hg(II) in the amount equal to one half of the molar amount of $NO(H_2O)_4CrCN^+$ it was found that 2.00 ± 0.05 electrons are exchanged per Hg(II) ion during the reduction at a working electrode potential of –0.5 V *vs.* SCE. After completion of the electrolysis, the reduction wave at about 0 V *vs.* SCE (see Fig. 1) is absent, even the wave with $E_{1/2}$ = -0.94_7 V *vs.* SCE is missing, but a wave with $E_{1/2}$ = -1.21_4 V *vs.* SCE appears.

At a working electrode potential of –1.05 V the number of electrons exchanged in the reduction is higher; at the beginning of the electrolysis 7.8 electrons are exchanged per Hg(II) ion and this value gradually increases with increasing electrolysis time. The experimental results were in this case evaluated by predictive coulometric methods [12]. A similar increase in the number of electrons exchanged was observed in the coulometric reduction of $NO(H_2O)_4CrCN^+$, where the initial value was 3.

The course of the coulometric electrolysis and the number of electrons exchanged differ very much in the same solution depending on whether the electrolysis is carried out directly at –1.05 V or in two steps, first at about –0.5 V and then at –1.05 V. During the two-step electrolysis, 2 electrons are exchanged in the first step and the reduction current obtained after the increase in potential is very low.

Electrochemical Reduction of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ in a Solution of $Hg(CN)_2$

In the study of displacement equilibria and of the decomposition of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ to $Cr(H_2O)_5NO^{2+}$ and $Hg(CN)_2$, the problem of distinguishing between $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ and $Hg(CN)_2$ in the polarographic recording is encountered. As $Hg(CN)_2$ yields, *e.g.* at $[H^+]$ = 5 X 10^{-3} *M*, a wave about 200 mV more negative than that of the trinuclear complex, the two substances should give rise to independent waves. However, they gave a single wave with the half-wave potential corresponding to that of the $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ wave, if present together in a solution in concentrations of 5 X 10^{-4} *M*. It has been found that even in the presence of very small amounts of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ (one tenth the $Hg(CN)_2$ concentration) the $Hg(CN)_2$ is reduced in a wave by 200 mV more positive than the $Hg(CN)_2$ wave in the absence of the former substance.

It is well-known from the literature [10] that $Hg(CN)_2$ is reduced with an overvoltage in acidic solutions of pH < 5. From the known stability constant of $Hg(CN)_2$ [10, 11] and the dissociation constant of HCN, the apparent stability constant can be calculated for $Hg(CN)_2$ at $[H^+] = 10^{-2}$ *M*; analogously, the apparent stability constant for $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ at the same hydrogen ion concentration can be calculated from the K and K_a values determined above. From the two stability constants, the equilibrium constant for the displacement reaction,

$$2\,NO(H_2O)_4CrNC^+ + Hg(CN)_2 \rightleftharpoons \{NO(H_2O)_4CrNC\}_2Hg^{4+} + 2\,CN^- \qquad (3)$$

can be calculated; it equals 2.38 for $[H^+] = 10^{-2}$ *M*. Hence the equilibrium is slightly shifted to the right in the absence of excess HCN. On reduction of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$, $NO(H_2O)_4CrNC^+$ is liberated in the vicinity of the indicator electrode and forms again the reduced complex by reaction (3). Thus even the Hg(II) bound in $Hg(CN)_2$ is reduced at the potential of the reduction of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$. Participation of equilibrium (3) in this phenomenon was verified by potentiostatic electrolysis in the bulk solution studied. If the working mercury electrode potential equalled the half-wave potential of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$, the nitrogen passing through the solution electrolyzed did not contain HCN, provided that the solution contained only $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ or only $Hg(CN)_2$. However, if the solution contained both these substances simultaneously, the nitrogen passing through the solution contained HCN at the same electrode potential.

The Limiting Diffusion Current of the More Positive Polarographic Wave and Equilibria of the Hg(II) Complexes

As already pointed out, when the Hg^{2+} concentration exceeds one half of the original concentration of $NO(H_2O)_4CrCN^+$, the current begins to increase at more positive potentials (Fig. 2). This current corresponds to the reduction of uncoordinated Hg^{2+}. It might seem that the measurement of this current could serve for the calculation of the equilibrium constant of the reaction,

$$\{NO(H_2O)_4CrNC\}_2Hg^{4+} + Hg^{2+} \overset{Q}{\rightleftharpoons} 2NO(H_2O)_4CrNCHg^{3+} \qquad (4)$$

However, the reduction of Hg^{2+} depletes the vicinity of the dropping mercury electrode, which may affect equilibrium (4).

Therefore, it is more advantageous to employ the limiting diffusion current at about –0.5 V *vs.* SCE (see Fig. 1) for quantitative expression of equilibrium (4). The measurement and the equilibrium constant calculation are then based on different diffusion coefficients of the Hg-containing components participating in the equilibrium.

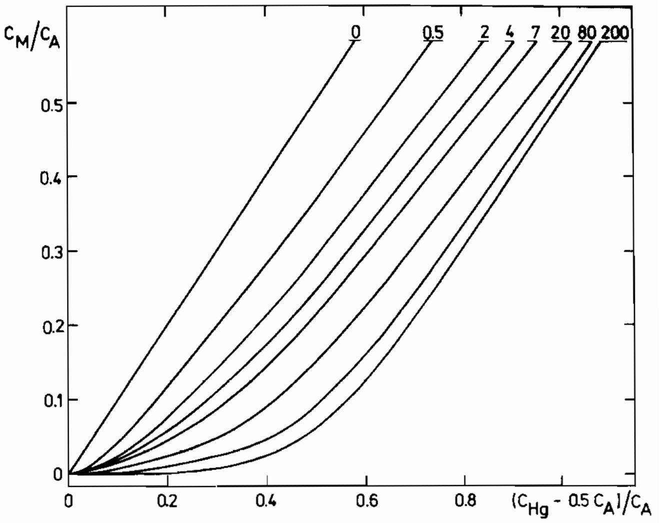

Figure 4. Curves of C_M/C_A *vs.* $(C_{Hg} - 0.5\ C_A)/C_A$ dependence calculated according to eq. (10) for different Q (specified with the curves).

For total Hg^{2+} concentrations lower than one half the concentration of $NO(H_2O)_4CrCN^+$ (C_A), exclusive and quantitative formation of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ is assumed and its concentration (C_B) equals the total Hg(II) concentration (C_{Hg}) (a high value of the overall formation constant for $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ is assumed). The measured mean limiting diffusion current, $\bar{i}_l$, is given by the Ilkovič equation, $\bar{i}_l = \bar{\kappa}_B C_B = \bar{\kappa}_B C_{Hg}$ (in the abbreviated form), from which the mean Ilkovič constant for $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$, $\bar{\kappa}_B$, can be determined.

If C_{Hg} exceeds 1/2 C_A, equilibrium (4) begins to participate significantly and the current is the sum of the currents of all components present,

$$\bar{i}_2 = \bar{\kappa}_B C_B + \bar{\kappa}_D C_D + \bar{\kappa}_M C_M \qquad (5)$$

where subscripts D and M refer to $NO(H_2O)_4CrNCHg^{3+}$ and uncomplexed Hg^{2+}, respectively.

On combination of Eq. (5) with the material balance for Hg^{2+} and $NO(H_2O)_4CrCN^+$,

$$\begin{aligned} C_{Hg} &= C_B + C_D + C_M \\ C_A &= 2C_B + C_D \end{aligned} \qquad (6)$$

and introduction of $\Delta\bar{i} = (\bar{i} - 0.5\ \bar{\kappa}_B)$, the relationship,

$$\Delta\bar{i} = (2\bar{\kappa}_D - \bar{\kappa}_B)(C_{Hg} - 0.5\ C_A) + (\bar{\kappa}_B + \bar{\kappa}_M - 2\bar{\kappa}_D)\,C_M \qquad (7)$$

is obtained.

C_M depends on $(C_{Hg} - 0.5\ C_A)$ according to the relationship,

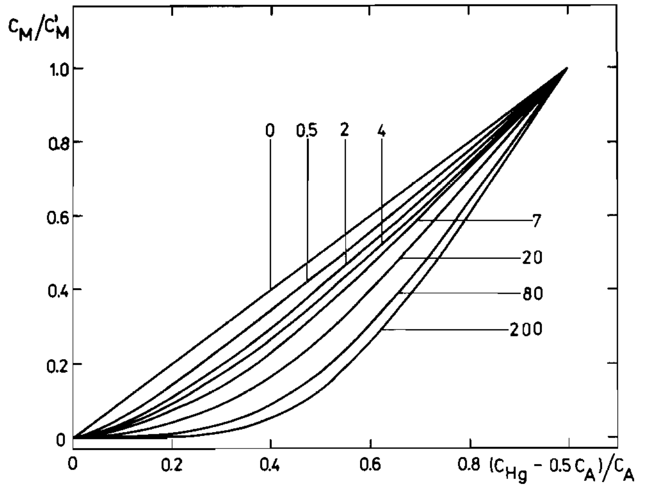

Figure 5. Curves of C_M/C'_M *vs.* $(C_{Hg} - 0.5\ C_A)/C_A$ dependence calculated according to eq. (10) for different Q (specified with the curves); C'_M denotes the C_M value for $(C_{Hg} - 0.5\ C_A)/C_A = 1$.

$$(4 - Q)C_M^2 + (Q - 8)(C_{Hg} - 0.5\ C_A)C_M - 0.5\ Q\ C_A\ C_M + 4(C_{Hg} - 0.5\ C_A)^2 = 0 \quad (8)$$

which follows from the defining equation for Q and from material balance (6). This dependence is plotted for various values of Q in Fig. 4. From the point of view of the precision of the evaluation, it is advantageous to modify the calculated curves of the C_M *vs.* $C_{Hg} - 0.5\ C_A$ dependence by introducing relative coordinate C_M/C'_M, where for C'_M *e.g.* the value, $(C_{Hg} - 0.5\ C_A)/C_A = 1$, can be substituted. The curves thus modified are depicted in Fig. 5.

The value of Q is determined by comparing the experimental dependence with the calculated curves, from the best matching curves. For the experimental dependence (Fig. 2), modified to the form $\Delta\ \bar{I}$ *vs.* $(C_{Hg} - 0.5C_A)$, to reflect the C_M dependence on $(C_{Hg} - 0.5\ C_A)$, it is necessary, in accordance with Eq. (7), to subtract the values proportional to $(C_{Hg} - 0.5\ C_A) - px(C_{Hg} - 0.5\ C_A)$ from the values of $\Delta\ \bar{I}$. After normalization of the dependence, similar to the calculated curves, it is compared with the calculated curves given in Fig. 5 (Fig. 5 contains only examples of the calculated curves; for the comparison, the curves for 50 values of Q were used). During the comparison, coefficient p is varied until the best match is attained. If the experimental dependence is modified using an incorrectly estimated p, it intersects several calculated curves, whereas with correct p the points are statistically scattered around a single calculated curve over the whole range of C_{Hg}.

The current values measured and plotted in Fig. 2 were treated in this way and a value of Q = (7 ± 4) was obtained for 25 °C, an ionic strength of 1 *M* (ClO_4^-, Na^+, H^+, Hg^{2+}) and $[H^+] = 0.01\ M$. For the same conditions, values of $\bar{\kappa}_B = 2.4 \times 10^{-3}\ AM^{-1}$ and $\kappa_D = \bar{\kappa}_B/2 + p/2 = 3.8 \times 10^{-3}\ AM^{-1}$ were obtained and from an independent experiment without $NO(H_2O)_4CrCN^+$ a value of $\bar{\kappa}_M = 5.8_4 \times 10^{-3}\ AM^{-1}$ (the constants of the dropping electrode used are given in the experimental part).

The solution given cannot be used if $\bar{\kappa}_D = 0.5\ (\bar{\kappa}_M + \bar{\kappa}_B)$ and its precision increases with $\bar{\kappa}_D$ departing from this value (Eq. (8)). As it can be assumed that $\bar{\kappa}_M > \bar{\kappa}_D > \bar{\kappa}_B$, the maximum value of $\bar{\kappa}_M - \bar{\kappa}_B$ will be favourable from the point of view of the precision.

Discussion

The described polarographic behaviour of the solutions of $NO(H_2O)_4Cr\text{-}CN^+$ and Hg^{2+} can be explained on the basis of a scheme involving the formation of a complex with three metal ions and bridge CN ligands. On addition of Hg^{2+} to solution of $NO(H_2O)_4Cr\text{-}CN^+$ in the amount equal to one half of that of the latter substance, the trinuclear complex is formed by the reaction,

$$2\ NO(H_2O)_4Cr\text{-}CN^+ + Hg^{2+} \rightleftharpoons \{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+} \quad (9)$$

The assumption of conversion of the Cr–C bond into the Cr–N bond during reaction (9) was made [1] on the basis of the discussion of changes in the visible spectrum and of the low rate of reaction (9). The polarographic behaviour of $\{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+}$ supports this assumption. The complexed Hg(II) is reduced at a potential close to 0 V *vs.* SCE,

$$\{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+} + 2e \rightleftharpoons 2\ NO(H_2O)_4Cr\text{-}NC^+ + Hg \quad (10)$$

The exchange of two electrons in this reduction was verified coulometrically. Therefore, the Cr–N bond isomer is the product of reaction (10) and is reduced in a following wave with $E_{1/2} = -0.94_7$ V *vs.* SCE. The reduction takes place at a potential about 270 mV more positive than that of the reduction of $NO(H_2O)_4Cr\text{-}CN^+$. This is in good agreement with the assumptions concerning the stabilities of the two isomers. As already mentioned, the Cr–C form is substantially more stable (Q_i is high) and thus its irreversible reduction occurs at the more negative potential. A similar difference in the peak potentials, 200 mV, was observed [6] during the voltammetry of the bond isomers of pentaaquocyanochromium(III) ion. As pointed out, the polarographic wave at $E_{1/2} = -0.94_7$ *V vs.* SCE is about 14% lower than the wave for the corresponding concentration of $NO(H_2O)_4CrCN^+$. This fact can be explained by a greater value of the diffusion coefficient of $NO(H_2O)_4Cr$-CN^+ compared with $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ whose diffusion controls not only the polarographic wave of the reduction of Hg(II) bound in the complex, but also the wave of the product, $NO(H_2O)_4CrNC^+$. From the comparison of the limiting currents of the two waves, the scheme

$$NO(H_2O)_4CrNC^+ + 2H_2O + 5H^+ + 3e \rightleftharpoons Cr(H_2O)_6^{2+} + NH_3OH^+ + HCN \qquad (11)$$

can be proposed for the reduction of $NO(H_2O)_4$-$CrNC^+$. The three-electron reduction of $NO(H_2O)_4$-$CrNC^+$ also follows from the described coulometric experiments (the comparison of the electrolysis at −0.5 and −1.05 V *vs.* SCE), similar to $NO(H_2O)_4$-$CrCN^+$. The increase in the number of electrons exchanged at the end of the electrolysis is probably caused by a slow reaction of Cr^{2+} with water or NH_3OH^+.

The changes in the polarographic behaviour of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ on addition of large excesses of HCN and I^- are caused by the reactivity of NO-$(H_2O)_4CrNC^+$, which is liberated by the reaction

$$\{NO(H_2O)_4CrNC\}_2Hg^{4+} + 4I^- \rightleftharpoons HgI_4^{2-} + 2NO(H_2O)_4CrNC^+ \qquad (12)$$

From a comparison of the formation constants of HgI_4^{2-} and $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ it follows that equilibrium (12) is strongly shifted to the right. Large excesses of HCN are required for the formation of Cr–N and $Hg(CN)_2$ and addition of Cl^- does not lead to a reaction analogous to (12). The $NO(H_2O)_4$-$CrNC^+$ liberated by reaction (12) (or by the analogous reaction with HCN) isomerizes to the more stable $NO(H_2O)_4CrCN^+$, which is reflected in the gradual decrease of the wave at -0.94_7 V and the increase of the more negative wave of the Cr – C isomer.

This relatively slow isomerization is not detected polarographically, as $NO(H_2O)_4Cr$-NC^+ is generated on the mercury drop whose life-time is short compared with the half-time of the isomerization reaction. However, if a mercury macroelectrode is used for the electrolytic generation under coulometric conditions with a common electrolysis time, the isomerization is complete and the only Cr-containing product in the electrolysate is $NO(H_2O)_4CrCN^+$. In this way the different courses of the coulometric macroelectrolysis at −1.05 V and in two steps at −0.5 and then at −1.05 V *vs.* SCE can also be explained. The current in the second step is low, because the $NO(H_2O)_4$-$CrNC^+$ generated electrolytically in the first step isomerizes quantitatively to $NO(H_2O)_4CrCN^+$ before the start of the second step; the latter yields only a very low current at −1.05 V *vs.* SCE (see Fig. 1).

The limiting diffusion current at −0.5 V *vs.* SCE was used for quantitative characterization of equilibrium (4). The current balance is based on the relatively large differences in the diffusion coefficients of the components, which werc observed in the introductory experiments. The value of Q obtained by this method is not very precise, but is in a good agreement with the value obtained from potentiometric measurements [1], within this precision.

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