ELECTROCHEMICAL STUDY OF *cis*-CYANOAQUOBIS(ETHYLENEDIAMINE)CHROMIUM(III) ION AND ITS ADDUCTS WITH Hg(II) AND Ag(I)

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Received December 2, 1991
Accepted March 3, 1992

The paper describes voltammetric and polarographic properties of the *cis*-cyanoaquobis(ethylenediamine)chromium(III) complex and the kinetics of its acid hydrolysis. The reactions of this complex with Hg(II) and Ag(I) ions were studied. Formation of di- and trinuclear adducts was found. Linkage isomerisation of CN bridging group in these adducts (Cr–NC–Hg and Cr–NC–Ag) was proposed on the basis of their electrochemical properties. The kinetics of formation and decomposition of $[Cr(CN)(en)_2(H_2O)]^{2+}$ adducts with Hg(II) and Ag(I) are described and the factors affecting them are discussed.

Voltammetric methods have yielded valuable information on the *cis*-cyanoaquonitrosyl chromium complexes studied in our previous papers[1 – 6]. This paper deals with the electrochemical reactions of *cis*-cyanoaquobis(ethylenediamine)chromium(III) and its oligonuclear complexes with Hg(II) and Ag(I).

EXPERIMENTAL

Reagents

Analytical grade reagents and triply-distilled water were employed. $[Cr(CN)(en)_2(H_2O)]^{2+}$ was prepared by acid hydrolysis of $[Cr(CN)_2(en)_2]^{2+}$ and was isolated in solution by conventional ion-exchange technique according to procedure described in the literature[7]. It was identified by its visible absorption spectrum and analysis of Cr and CN^- (ref.[7]). Chromium was determined spectrometrically in the stock solution of $[Cr(CN)(en)_2(H_2O)]^{2+}$, after oxidation of the complex to chromate by hydrogen peroxide in an alkaline medium. Cyanide was determined polarographically after hydrolysis of the complex in 3 mol dm^{-3} HCl and adjustment of the medium composition for the anodic wave of the CN^- registration. This procedure indicated 96% of the theoretical amount of CN^- in the sample. Molar ratio of chromium to cyanide was found to be 1 : 1.05.

Instruments

The spectrophotometric measurements were carried out on a Specord UV VIS (Zeiss, Jena) instrument; the kinetic experiments were performed in thermostatted cuvettes.

An OP-205 potentiometer (Radelkis, Budapest) was used for potentiometric measurements. Hanging mercury drop electrode (HMDE) and Ag-wire were used as working electrodes in titrations with Hg^{2+} or

Ag^+, respectively. Saturated calomel electrode (SCE) with a salt bridge containing 1 mol dm^{-3} $NaNO_3$ served as a reference electrode.

Voltammetric and polarographic measurements were carried out on an PA 4 polarograph (Laboratorní přístroje, Praha). The dropping mercury electrode used for polarographic measurements had a mercury flow-rate 1.65 mg s^{-1} and a drop time 4.3 s (at a mercury reservoir height of 64 cm and in a short circuit with a saturated calomel electrode). DPV measurements were carried out using HMDE with mercury drop area 1.64 mm^2. Scan rate 50 mV s^{-1}, pulse height −12.5 mV, pulse frequency 5 Hz.

RESULTS AND DISCUSSION

Voltammetric and Polarographic Properties of $[Cr(CN)(en)_2(H_2O)]^{2+}$ *and* $[Cr(en)_2(H_2O)_2]^{3+}$

Dirrect current polarography (DCP) and differential pulse voltammetry (DPV) were applied for determination of electrochemical behaviour of complex $[Cr(CN)(en)_2(H_2O)]^{2+}$ and $[Cr(en)_2(H_2O)_2]^{3+}$ as a product of its acid hydrolysis. In weakly acidic solutions (H^+ concentration 0.01 mol dm^{-3}, ionic strength 1 mol dm^{-3} ClO_4^-, Na^+, H^+) $[Cr(CN)(en)_2(H_2O)]^{2+}$ is reduced under polarographic conditions in a diffusion-controlled irreversible wave, the limiting current of which corresponds to the exchange of 1 electron and the half-wave potential is −0.95 V vs SCE. DPV peak of $[Cr(CN)(en)_2(H_2O)]^{2+}$ in the same medium has the potential −0.96 V vs SCE.

Under the same experimental conditions $[Cr(en)_2(H_2O)_2]^{3+}$ is reduced in a diffusion controlled irreversible wave, the limiting current of which corresponds to the exchange of 1 electron and the half-wave potential is −0.81 V vs SCE. DPV peak of $[Cr(en)_2(H_2O)_2]^{3+}$ has peak potential −0.82 V vs SCE under the experimental conditions given in the Experimental.

Acid Hydrolysis of $[Cr(CN)(en)_2(H_2O)]^{2+}$

In acidic solutions $[Cr(CN)(en)_2(H_2O)]^{2+}$ undergoes hydrolytic reaction.

$$[Cr(CN)(en)_2(H_2O)]^{2+} + H_3O^+ \xrightarrow{k} [Cr(en)_2(H_2O)_2]^{3+} + HCN \qquad (A)$$

The product of this reaction was identified as $[Cr(en)_2(H_2O)_2]^{3+}$ on the basis of comparison absorption spectrum of reacted solution with that published in ref.[7].

The kinetics of this reaction was followed evaluating *1*) the time-dependence of absorbance at 366 nm, *2*) the time-change of DPV peak current of $[Cr(CN)(en)_2(H_2O)]^{2+}$ at the potential −0.97 V vs SCE, *3*) the time-change of DPV peak current of $[Cr(en)_2(H_2O)_2]^{3+}$ at the potential −0.82 V vs SCE.

The rate constants determined by spectral and voltammetric method for solutions with different H^+ concentrations are given in Table I.

As it can be seen in Table I both sets of rate constants are in agreement. They enabled to optimize the H^+ concentration for the study of $[Cr(CN)(en)_2(H_2O)]^{2+}$ reaction with Hg(II) and Ag(I). The acid hydrolysis is competitive to this reaction, therefore it should be made negligible by lowering H^+ concentration.

Stoichiometry of the $[Cr(CN)(en)_2(H_2O)]^{2+}$ *Reaction with Hg(II) and Ag(I)*

Complex $[Cr(CN)(en)_2(H_2O)]^{2+}$ reacts with ions of heavy metals Hg(II), Ag(I) forming oligonuclear adducts.

From the analogy with Hg(II) reactions with of $[Cr(CN)(H_2O)_5]^{2+}$ (refs[8 – 10]) and $[Cr(CN)(H_2O)_4(NO)]^+$ (refs[3 – 6]) following scheme can be proposed for the reaction studied in which linkage isomerisation of cyano group takes place:

$$[Cr(CN)(en)_2(H_2O)]^{2+} + Hg^{2+} \rightleftharpoons [Cr(en)_2(H_2O)(NC)]_2Hg^{6+} \qquad (B)$$

The reaction with Ag(I) is analogous,

$$[Cr(CN)(en)_2(H_2O)]^{2+} + Ag^{+} \rightleftharpoons [Cr(en)_2(H_2O)(NC)]_2Ag^{5+} \qquad (C)$$

The stoichiometry of these reactions was examined by potentiometric titration of $[Cr(CN)(en)_2(H_2O)]^{2+}$ with corresponding heavy metal ion. Typical titration curves are given in Fig. 1. The potential stabilization required a certain time after each addition of the heavy metal ion. To avoid the effect of follow up decomposition of adduct:

$$[Cr(en)_2(H_2O)(NC)]_2Hg^{6+} + 2\,H_2O \longrightarrow Hg(CN)_2 + 2\,[Cr(en)_2(H_2O)_2]^{3+} \qquad (D)$$

TABLE I

Pseudo-first order rate constants for the reaction of $[Cr(CN)(en)_2(H_2O)]^{2+}$ with H_3O^+. Ionic strength 1.00 mol dm^{-3} (ClO_4^-, H^+, Na^+); T 298 K. Values are average of three measurements

$[H^+]$, mol dm^{-3}	$k \cdot 10^4$, s^{-1} [a]	$k \cdot 10^4$, s^{-1} [b]
0.01	0.49 ± 0.05	0.52 ± 0.05
0.03	1.50 ± 0.15	1.37 ± 0.15
0.10	4.26 ± 0.45	4.40 ± 0.50
0.30	13.8 ± 1.5	13.5 ± 1.5

[a] Voltammetric determination; [b] spectrophotometric determination.

each point of the titration curve was obtained in a separate experiment by measuring the potential after mixing the reactants at the appropriate molar ratio. As the reaction analogous to Eq. (*D*) is much slower with Ag(I), this procedure was unnecessary in titrations with Ag(I). The molar ratio corresponding to the inflection points on the potentiometric titration curves (Fig. 1) indicates the formation of trinuclear complexes.

The stoichiometry of the reaction of $[Cr(CN)(en)_2(H_2O)]^{2+}$ with the heavy metal ions was further studied by amperometric titration. The indicator electrode potential was −0.5 V vs SCE at which both the free and the bound heavy metal ions were reduced, but Cr remained electrochemically unchanged. The titration is based on the differences of the diffusion coefficients for Ag(I) and Hg(II) bound in various complexes. Figure 2 shows that current increases linearly with increasing concentration of titrant, up to the molar ratio of the heavy metal ion to $[Cr(CN)(en)_2(H_2O)]^{2+}$ equal to 0.5. The proportionality coefficient of this linear dependence is the Ilkovič constant for the given trinuclear adduct. On further increase in Hg^{2+} and Ag^+ concentrations, following reactions take place

$$[Cr(en)_2(H_2O)(NC)]_2Hg^{6+} + Hg^{2+} \rightleftarrows 2\ [Cr(en)_2(H_2O)(NC)]Hg^{4+} \qquad (E)$$

$$[Cr(en)_2(H_2O)(NC)]_2Ag^{5+} + Ag^{+} \rightleftarrows 2\ [Cr(en)_2(H_2O)(NC)]Ag^{3+} \qquad (F)$$

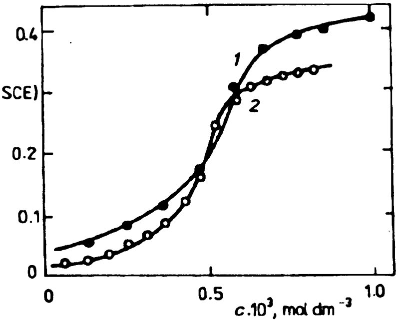

FIG. 1

Potentiometric titrations of 1.0 mmol dm^{-3} $[Cr(CN)(en)_2(H_2O)]^{2+}$ with *1* Hg(II) and *2* Ag(I). $c(H^+)$ 0.01 mol dm^{-3}; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+). Concentration of heavy metal ion given in abscissa

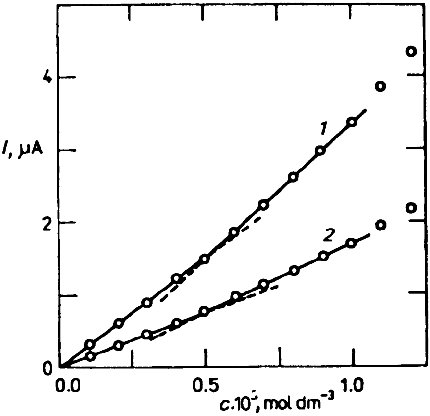

FIG. 2

Amperometric titration of 1.0 mmol dm^{-3} $[Cr(CN)(en)_2(H_2O)]^{2+}$ with *1* Hg(II) and *2* Ag(I). Concentration of heavy metal ion indicated in abscissa or Hg^{2+} or Ag^{+} are accumulated in solution. This causes a sharper current increase with increasing heavy metal ion concentration at the molar ratio higher than 0.5. Higher value of the diffusion coefficient for the product of reaction (*E*) and for Hg^{2+}, compared to that for $[Cr(en)_2(H_2O)(NC)]_2Hg^{6+}$ (and analogously for silver) which follows from the shape of the curves in Fig. 2 is in agreement with the expectation. The position of the breaks on the titration curves also supports the assumption that trinuclear adducts are formed. The effect of reaction (*D*) on the amperometric titrations was avoided in the same way as in the potentiometric titration.

Potentiometric data describing titration of $[Cr(CN)(H_2O)(NO)]^{+}$ with Hg(II) were used for calculation of the equilibrium constant of resulting trinuclear adduct formation[3]. However, in the case of $[Cr(CN)(en)_2(H_2O)]^{2+}$, the rate constant of adduct decomposition reaction (*D*) is approximately 10 times higher (vide infra), therefore potentiometry does not allow calculation of equilibrium constant for reaction (*C*) with sufficient accuracy.

Voltammetric Investigation of $[Cr(CN)(en)_2(H_2O)]^{2+}$ Reaction with Hg(II)

An addition of Hg(II) to the solution of $[Cr(CN)(en)_2(H_2O)]^{2+}$ leads to the decrease of its peak at the potential –0.97 V vs SCE and to the formation of a new one at the potential –0.76 V vs SCE. Similarly to the formerly studied monocyanonitrosyl chromium complex[3 – 6] this voltammetric behaviour is caused by the formation of di- or trinuclear adduct with mercury(II) (Eq. (*B*)). DPV peak at the potential –0.76 V vs SCE corresponds to the one-electron reduction of $[Cr(en)_2(H_2O)(NC)]^{2+}$, which is formed at the electrode by the cathodic reduction of Hg(II) bound in the di- or trinuclear adduct (Fig. 3, curve *b*).

Consecutively to the reaction (*B*), the decomposition of the adduct (Eq. (*D*)) takes place and finally $[Cr(en)_2(H_2O)_2]^{3+}$ is formed. This species demonstrates itself by DPV peak at the potential –0.82 V vs SCE (Fig. 3, curve *c*).

Rate of Formation and Decomposition of the $[Cr(CN)(en)_2(H_2O)]^{2+}$ Adducts with Hg^{2+}

The time dependence of the DPV peak current can be evaluated as to determine rate constants of di- or trinuclear adduct formation and its decomposition. If Hg(II) concentration is comparable with the concentration of $[Cr(CN)(en)_2(H_2O)]^{2+}$ the half-time of the formation reaction (*B*) is about 100 s at room temperature. Under the pseudomonomolecular condition $c(Hg(II)) > 10\ c([Cr(CN)(en)_2(H_2O)]^{2+})$, the half-time amounts several seconds. DPV is, therefore, unable to provide sufficiently precise data for the evaluation of formation rate constant.

As already mentioned, the $[Cr(CN)(en)_2(H_2O)]^{2+}$ adduct with Hg^{2+} undergoes a relatively slow decomposition in which $[Cr(en)_2(H_2O)_2]^{3+}$ and $Hg(CN)_2$ are formed. This reaction is expressed by Eq. (*D*) for trinuclear adduct; for the binuclear adduct it can be formulated as follows

$$[Cr(en)_2(H_2O)(NC)]Hg^{4+} + H_2O \longrightarrow [Cr(en)_2(H_2O)_2]^{3+} + [Hg(CN)]^+ \qquad (G)$$

Reactions (*D*) and (*G*) were studied using the time-change of the DPV peak current of $[Cr(en)_2(H_2O)_2]^{3+}$ at a potential −0.82 V vs SCE.

The rate constants are given in Table II for various concentrations of mercury and hydrogen ions. It can be seen from the Table II that the rate constant of aquation, k_a, does not depend on the hydrogen ion concentration for $c(Hg^{2+}) > 0.5\ c([Cr(CN)(en)_2(H_2O)]^{2+})$. The independence of adduct aquation rate on H^+ concentra-

TABLE II

Rate constants for the aquation of adducts of $[Cr(CN)(en)_2(H_2O)]^{2+}$ with Hg(II) for different Hg(II) and H^+ concentrations. *T* 298 K, ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}); initial concentration of $[Cr(CN)(en)_2(H_2O)]^{2+}$ 1 mmol dm^{-3}

$c(H^+)$, mol dm^{-3}	$c(Hg^{2+})$, mol dm^{-3}	$k_a \cdot 10^3$, s^{-1} [a]
$5 \cdot 10^{-1}$	$5 \cdot 10^{-4}$	1.24 ± 0.11
$5 \cdot 10^{-2}$	$5 \cdot 10^{-4}$	1.31 ± 0.12
$5 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	1.32 ± 0.10
$5 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	1.23 ± 0.12
$5 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	1.34 ± 0.15
$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	1.31 ± 0.15

[a] Values are average of 3 measurements.

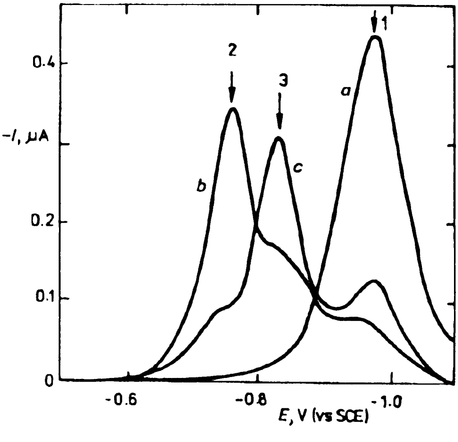

FIG. 3

DPV voltammograms of reacting solution of 1 mmol dm^{-3} $[Cr(CN)(en)_2(H_2O)]^{2+}$ and 0.5 mmol dm^{-3} Hg(II). $c(H^+)$ 0.01 mol dm^{-3}; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}). *T* 298 K. *a* before Hg(II) addition, *b* 10 min after Hg(II) addition, *c* 60 min after Hg(II) addition, 1 reduction of $[Cr(CN)(en)_2(H_2O)]^{2+}$, 2 reduction of $[Cr(en)_2(H_2O)(NC)]^{2+}$, 3 reduction of $[Cr(en)_2(H_2O)_2]^{3+}$

tion indicates that protonation of the bridging CN group is energetically unfavourable and substantially more difficult than the protonation of CN groups in $[Cr(CN)(en)_2(H_2O)]^{2+}$. This is possibly caused by the high positive charge on the adduct, but also unfavourable electronic structure.

The rate constant of adduct aquation does not change either with a variation in Hg^{2+} concentration over a wide range 0.05 mol dm^{-3} $c(Hg^{2+}) > 0.0005$ mol dm^{-3} (with 1 mmol dm^{-3} $[Cr(CN)(en)_2(H_2O]^{2+}$). From its constancy it can be concluded that the decompositions of the di- and trinuclear adducts Eqs (*D*) and (*G*) proceed at the same rates.

Some problems were reported[3] when reaction with Ag(I) was followed spectrophotometrically. The problems were caused by AgCN precipitate which appears in solution due to the aquation of Ag(I) adduct. This precipitate is probably responsible for disturbances which were observed on DPV voltammograms registered in case of Ag(I) adducts. Nevertheless it can be estimated that the rates of decomposition of the Ag(I) adducts are substantially (more than 100 times) lower than those for Hg(II) adduct. In case of decomposition of analogous adducts of $[Cr(CN)(H_2O)_4(NO)]^+$ with heavy metal ions studied in our previous work[3] the decomposition rate constant of the Ag(I) adduct was only 10 times lower than that for Hg(II) adduct.

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Translated by the author (D.B.).