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

Miroslav RIEVAJ, Elena KORGOVÁ and Dušan BUSTIN

Department of Analytical Chemistry,
Slovak Technical University, 812 37 Bratislava, The Slovak Republic

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Electrochemical properties of $[Cr(CN_2)(en)_2]^+$ are described. Reactions of this complex with Hg(II) and Ag(I) were studied. Their stoichiometry (1 : 1) was determined using potentiometric and amperometric titrations. Differential pulse voltammetry (DPV) was applied to identify their products – dinuclear adducts. It was concluded on the basis of DPV experiments that linkage isomerization of bridding cyano ligand occurs in the process of adducts formation. The decomposition (aquation) of these adducts was followed and the influence of H^+ and Hg^{2+} concentration on its rate was measured and discussed. The paper also deals with a spontaneous isomerization of unstable CN linkage isomers $Cr(NC)_2$ and Cr(NC)(CN) to the stable isomer $Cr(CN)_2$.

In our previous papers the linkage isomerization of the cyano group was studied occurring in the process of adducts formation of Hg(II) and Ag(I) with $[Cr(CN)(H_2O)_4(NO)]^+$ (refs[1 – 4]) and $[Cr(CN_2)(H_2O)_3(NO)]$ (ref.[5]). In the case of $[Cr(CN)(H_2O)_4(NO)]^+$ the situation was rather simple because only a few substances were involved in the process. A great variety of possible multinuclear complexes may arise during formation of adducts of $[Cr(CN_2)(H_2O)_3(NO)]$ with the above mentioned heavy metals.

In the present paper our attention was foccused on the processes taking place in reacting solution of $[Cr(CN_2)(en)_2]^+$ in the presence of Hg(II) and Ag(I) ions. Similarly to the case of $[Cr(CN_2)(H_2O)_3(NO)]$ (ref.[5]), several complexes had to be taken into consideration in this study. Voltammetric methods were predominantly used for their investigation.

EXPERIMENTAL

Analytical grade reagents and triply-distilled water were employed.

cis-$[Cr(CN)_2(en)_2]Cl \cdot H_2O$ was prepared by published method[6]. It was identified by its visible absorption spectrum and by analysis of Cr and CN. Chromium was determined spectrometrically in stock solution of $[Cr(CN)_2(en)_2]^+$, after oxidation of the complex to chromate by hydrogen peroxide in an alkaline medium. Cyanide was determined polarographically after hydrolysis of the complex in HCl (3 mol dm^{-3}) and following adjustment of the solution composition for CN^- anodic wave registration. This procedure indicated the presence of 97% theoretical amount of CN^- in the sample; consequently the molar ratio of chromium to cyanide is 1 : 2.

Spectrophotometric measurements were carried out on a Specord UV VIS (Zeiss, Jena) instrument; 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 a PA4 polarograph (Laboratorní přístroje, Praha). The dropping mercury electrode 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 SCE). All DPV measurements were carried out using hanging mercury drop electrode HMDE with mercury drop area 1.64 mm^2. Scan rate 50 mV s^{-1}, pulse height −12.5 mV, pulse repetition frequency 5 Hz.

RESULTS AND DISCUSSION

Electrochemical Properties of $[Cr(CN)_2(en)_2]^+$

Polarography and differential pulse voltammetry (DPV) were used for electrochemical characterization of $[Cr(CN)_2(en)_2]^+$. In weakly acidic solutions (H^+ concentration 0.01 mol dm^{-3}; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+ , H^+)) $[Cr(CN)_2(en)_2]^+$ is reduced under polarographic conditions in a diffusion controlled irreversible wave, the height of which corresponds to the exchange of 1 electron and the half wave potential is $E_{1/2}$ = −1.11 V vs SCE. In the same medium DP voltammogram of 1 . 10^{-3} mol dm^{-3} $[Cr(CN)_2(en)_2]^+$ exhibits its maximum peak current at the potential E_p = −1.12 V vs SCE.

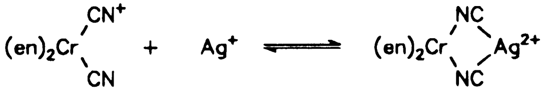
Potentiometric and Amperometric Determination of Stoichiometry of $[Cr(CN)_2(en)_2]^+$ *Reaction with Hg(II) and Ag(I)*

The stoichiometry of the reaction of $[Cr(CN)_2(en)_2]^+$ with Hg(II) and Ag(I) was examined by potentiometric titration. For molar ratios $c(Hg(II)) : c([Cr(CN)_2(en)_2]^+) < 1.0$ reading of potential required certain time interval after each addition of the heavy metal ion. Also it was necessary to avoid the effect of slow follow up aquation of adduct leading to $[Cr(en)_2(H_2O)_2]^{3+}$ and $Hg(CN)_2$. Each point of potentiometric titration curve was obtained in separate experiment, by measuring the potential after mixing reactants in the corresponding molar ratio. As the analogous aquation of Ag(I) adduct was much slower, this procedure was unnecessary in titrations with Ag(I). The molar ratios corresponding to the inflection points on the potentiometric titration curves of $[Cr(CN)_2(en)_2]^+$ with Ag(I) and Hg(II), support the formation of dinuclear complexes in both cases.

The stoichiometry of adduct formation was further studied by amperometric titrations. The indicator electrode potential (−0.5 V vs SCE) was selected so that both free and bound heavy metal ions were reduced, but Cr remained electrochemically unchanged. The titration was based on the differences in diffusion coefficients for free and bound Hg(II) or Ag(I). The current increases linearly with increasing concentration of heavy metal ion added to the solution of $[Cr(CN)_2(en)_2]^+$ up to the molar ratio 1.0. The proportionally coefficient of this linear dependence is the Ilkovič constant for the dinuclear adduct. Further increase in Hg(II) and Ag(I) concentration caused sharper current increase corresponding to higher value of the diffusion coefficients for free Hg(II) or Ag(I) ions. The position of breaks on titration curves also supports the dinuclear adducts formation.

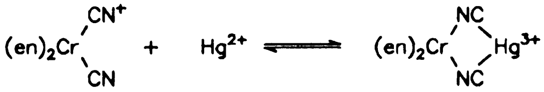
Formation of $[Cr(CN)_2(en)_2]^+$ adducts with Ag(I) was studied spectrophotometrically by Heatherington at al.[7].

Authors reported the formation of adduct.



(*A*)

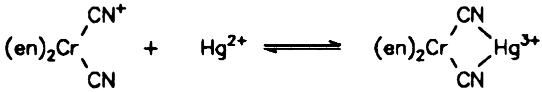
On the basis of described stoichiometric studies taking into account similarity of voltammograms of Hg(II) and Ag(I) adduct with $[Cr(CN)_2(en)_2]^+$ (vide infra), it is possible to propose the linkage isomerisation also for analogous reaction with mercury.



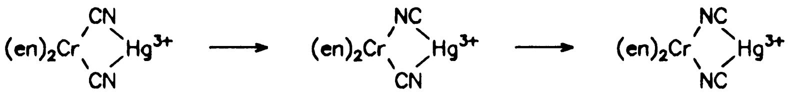
(*B*)

Voltammetric Investigation of the Reaction of $[Cr(CN)_2(en)_2]^+$ with Hg(II)

Differential pulse voltammetry was applied to study the reaction of $[Cr(CN)_2(en)_2]^+$ with Hg(II) ions. This reaction is connected with subsequent formation of dinuclear complexes with CN bridges. On the basis of the analogous reactions of $[Cr(CN)_2(H_2O)_4]^+$ with Hg(II) and Ag(I) studied by Frank and Anson[8] we propose the following scheme for reaction of $[Cr(CN)_2(en)_2]^+$ with Hg(II).



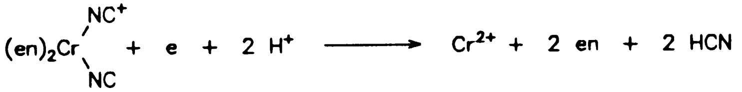
(*C*)



(*D*)

The DP voltammograms taken in different stages of reaction of $[Cr(CN)_2(en)_2]^+$ with Hg(II) are depicted in Fig. 1. Electrode reaction equations for adduct formed in the reaction (*B*) are as follows.

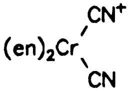
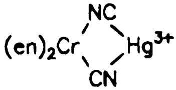
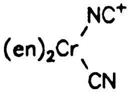
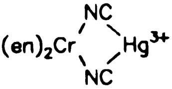
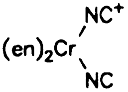
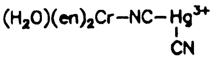
(*E*)



(*F*)

TABLE I

DPV peak potentials of complexes occurring in reacting solution of $[Cr(en)_2(CN)_2]^+$ with Hg(II). H^+ concentration 0.01 mol dm^{-3}; ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}); *T* 298 K. Parameters for DPV are given in Experimental

No.	Parent species	Electroactive species	E_p V vs SCE	Reference
1			−1.12	this work
2			−0.87	this work
3			−0.65	this work
4		$[Cr(CN)(en)_2(H_2O)]^{2+}$	−0.97	9
5	 $(H_2O)(en)_2Cr{-}NC{-}\underset{CN}{\underset{\mid}{Hg^{3+}}}$	$[Cr(en)_2(H_2O)(NC)]^{2+}$	−0.76	9
6		$[Cr(en)_2(H_2O)_2]^{3+}$	−0.82	9

Dinuclear adducts formed in the course of reaction (*D*) are analyzed on the basis of their reduction peaks (Eq. (*F*)) growing on the Hg(II) reduction current backround (Eq. (*E*)). Possible dinuclear complexes occurring in the reacting solution in the process of formation and decomposition of adduct of $[Cr(CN)_2(en)_2]^+$ with Hg(II) are listed in Table I.

Actual electroactive species for the characterisation of dinuclear adducts (parent species) are the corresponding chromium complexes.

It can be seen at Fig. 1 that predominant process is formation of adduct of $[Cr(CN)_2(en)_2]^+$ with Hg(II) with a stepwise linkage isomerisation of CN ligands (Eqs (*C*) and (*D*)). This demonstrates itself by decrease of the peak current at the potential −1.12 V vs SCE corresponding to the reduction of original complex $[Cr(CN)_2(en)_2]^+$. Simultaneously, two another peaks appear, one at the potential −0.87 V vs SCE corresponding to substance *2* reduction (Table I) and the second at the potential −0.65 V vs SCE in which species *3* (Table I) is assumed to be reduced. Peaks of species *2* and *3* (Table I) were assigned on the basis of the potential difference of analogous isomers of $[Cr(CN)_2(H_2O)_4]^+$ (ref.[8]) and on the basis of time changes of these peaks in the course of $[Cr(CN)_2(en)_2]^+$ reaction with Hg(II). Peak of substance *2* is dominant in early stages of this reaction when the intermediate complex (Eq. (*D*)) $[Cr(CN)(en)_2(NC)Hg]^{3+}$ is likely formed (Fig. 1, curve *b*). Subsequently (Fig. 1, curve *c*) the peak of the reduction of substance $[Cr(en)_2(NC)_2]^+$ prevails.

On typical DP voltammograms in Fig. 1 three minor peaks at potentials −0.76, −0.82, −0.97 V vs SCE can also be seen. They were assigned (Table I) on the basis of our previous paper[9] dealing with the study of reaction $[Cr(CN)(en)_2(H_2O)]^{2+}$ with Hg(II). All of these substances occur in the reacting solution as a consequence of relatively fast aquation reactions of $[Cr(CN)_2(en)_2]^+$ adduct with Hg(II).

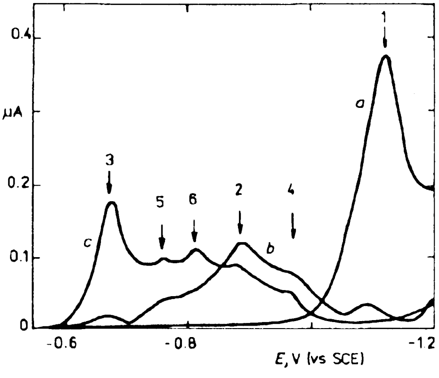
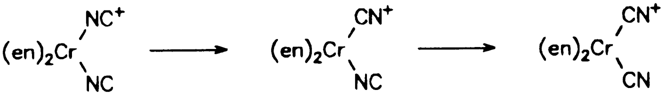


FIG. 1

DPV voltammograms of the reacting solution of 1 mmol dm^{-3} $[Cr(CN)_2(en)_2]^+$ with 1 mmol dm^{-3} Hg(II); H^+ concentration 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* 3 min after Hg(II) addition, *c* 30 min after Hg(II) addition. 1 peak of $[Cr(CN)_2(en)_2]^+$, 2 peak of $[Cr(CN)(en)_2(NC)]^+$, 3 peak of $[Cr(NC)_2(en)_2]^+$, 4 peak of $[Cr(CN)(en)_2(H_2O)]^{2+}$, 5 peak of $[Cr(en)_2(H_2O)(NC)]^{2+}$, 6 peak of $[Cr(en)_2(H_2O)_2]^{3+}$

The height of the peak of $[Cr(en)_2(NC)_2]^+$ at the potential −0.65 V vs SCE has never reached the peak height of the original complex $[Cr(CN)_2(en)_2]^+$. This can be partially caused by lower diffusion coefficient of Hg(II) adduct as compared to $[Cr(CN)_2(en)_2]^+$ (mentioned in the above section describing amperometric titration of $[Cr(CN)_2(en)_2]^+$ with Hg^{2+}), lower electrode reaction rate constant or possible adsorption on the electrode surface. Another explanation might be based on the fact that the time passed untill the peak potential of the Cr-component is reached in voltammetric polarization, may be long enough for their partial spontaneous linkage isomerization to more stable isomers.

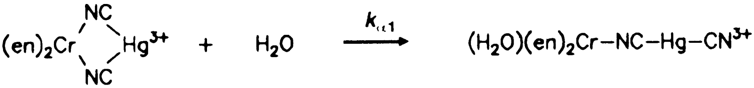

(*G*)

This assumption is supported by the observation that the higher is the polarisation rate the higher is the ratio of peak heights of less stable to more stable isomers.

The formation of adduct was also observed voltammetrically in the case of Ag(I). Observed voltammograms resembled those in Fig. 1. Dominant formation of $[Cr(en)_2(NC)_2Ag]^{2+}$ demonstrates itself in the DPV peak at −0.65 V vs SCE , which is evidently identical with the peak of $[Cr(en)_2(NC)_2]^+$ formed also in the case of Hg(II) dinuclear adduct. The decrease rate of this peak, however, is much slower indicating that dinuclear complex of Ag(I) is more stable. The height of the −0.65 V vs SCE peak did not reach the peak height of the original complex similarly as in the case of Hg(II).

Decomposition of Adducts of $[Cr(CN)_2(en)_2]^+$ with Hg(II)

Formation of $[Cr(en)_2(NC)_2Hg]^{3+}$ in the presence of excess Hg(II) is too fast to be studied by voltammetry or polarography. These techniques provided, however, valuable information about decomposition kinetics. It evidently proceeds in two subsequent steps.


(*H*)

$$(H_2O)(en)_2Cr{-}NC{-}Hg{-}CN^{3+} + H_2O \xrightarrow{k_{d2}} [Cr(en)_2(H_2O)_2]^{3+} + Hg(CN)_2 \qquad (I)$$

The rate of the reaction expressed by Eq. (*H*) was followed as a decrease of $[Cr(en)_2(NC)_2]^+$ reduction peak at the potential −0.65 V vs SCE while rate of the second decomposition step (Eq. (*I*)) was followed as an increase of $[Cr(en)_2(H_2O)_2]^{3+}$ peak at the potential −0.82 V vs SCE. In the second case the evaluation was done in the stage of reaction when the influence of reaction (*H*) was negligible. The kinetics has been found to obey the monomolecular rate law. Rate constants of both steps for different H^+ and Hg^{2+} concentrations are given in Table II. The independence of adduct aquation rate on H^+ concentration indicates that protonation of the bridging CN group is energetically unfavourable and substantially more difficult than the protonation of CN 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. Rate constants found for the first step of decomposition (Eq. (*H*) were about 20% higher than those corresponding to the second one. Both sets depend neither on the proton concentration nor on the excess of Hg(II) ions, which is in agreement with the schemes (*H*) and (*I*) proposed for decomposition steps.

Rate constants for the second step (*I*) agrees reasonably with the rate constant found in our previous paper[9] for decomposition of $[Cr(CN)(en)_2(H_2O)]^{2+}$ adduct with Hg(II). This fact supports the above given assignment of decomposition steps.

Spontaneous Isomerisation of $[Cr(en)_2(NC)_2]^+$

Since the stability constants of HgI_2 is much higher than that of $[Cr(en)_2(NC)_2Hg]^{3+}$, reaction

$$[Cr(en)_2(NC)_2Hg]^{3+} + 2\ I^- \rightleftharpoons HgI_2 + [Cr(en)_2(NC)_2]^+ \qquad (J)$$

TABLE II

Rate constants of decomposition reaction $k_{\alpha 1}$ (Eq. (*H*)) and $k_{\alpha 2}$ (Eq. (*I*) of $[Cr(CN)_2(en)_2]^+$ adduct with Hg(II) for different H^+ and Hg^{2+} concentrations. *T* 298 K, ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}); initial concentration of $[Cr(CN)_2(en)_2]^+$ 1 mmol dm^{-3}

$c(H^+)$, mol dm^{-3}	$c(Hg^{2+})$, mol dm^{-3}	$k_{\alpha 1} \cdot 10^3$, s^{-1}	$k_{\alpha 2} \cdot 10^3$, s^{-1} [a]
$5 \cdot 10^{-1}$	$1 \cdot 10^{-3}$	1.45 ± 0.20	1.21 ± 0.15
$5 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	1.40 ± 0.15	1.25 ± 0.13
$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	1.40 ± 0.15	1.23 ± 0.12
$5 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	1.45 ± 0.13	1.32 ± 0.15
$5 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	1.50 ± 0.15	1.35 ± 0.15

[a] Values are average of 3 measurements.

could be used to generate the unstable linkage isomer in the bulk of solution. Polarography was used to measure rate constant of spontaneous isomerisation of $[Cr(H_2O)_4(NC)(NO)]^+$ in our paper[4]. In the case of $[Cr(en)_2(NC)_2]^+$ both steps of linkage isomerisation (Eq. (*G*)) are too fast to be measured polarographically. That is why reaction (*J*) followed by reaction (*G*) could only be used to prove polarographically the composition of adduct $[Cr(en)_2(NC)_2Hg]^{3+}$. Addition of excess KI to its solution leads to a full recovery of polarographic wave of $[Cr(CN)_2(en)_2]^+$.

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