Polarographic Study of the Reactions of *cis*- and *trans*-Dicyanochromium(III) Complexes with Hg²⁺ Ions

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Potentiometry and polarography were used to study the reactions of some *cis*- and *trans*-dicyanochromium(III) complexes with $Hg(ClO_4)_2$. Potentiometric investigation revealed the different stoichiometry of the reactions of *cis* and *trans* complexes. The results of polarographic study were consistent with the potentiometric investigations of the reaction stoichiometry and enabled to propose the course of the reaction and the structure of the reaction products. It was found that the configuration of the cyano groups *cis* or *trans* of the chromium(III) complex plays a crucial role in the structure of oligonuclear compounds. It is supposed that *cis*-dicyano complexes may associate either through single or double bridges. The latter circumstance is not incurred with *trans*-dicyano complexes obviously because of the unfavourable cyano groups position.

In our previous papers the reactions of some monocyanochromium(III) complexes with either Hg²⁺ or Ag⁺ ions were studied. The formation of adducts was found to be accompanied by the linkage isomerization (Cr—NC—Hg) of the cyanide bridging group. In the case of monocyano complexes $[Cr(H_2O)_4(NO)(CN)]^+$ [1—4], $[Cr(en)_2(H_2O)(CN)]^+$ [5], $[Cr(en)(H_2O)_2(NO)(CN)]^+$ [6], and $[Cr(NH_3)_5(CN)]^{2+}$ [7] the situation was rather simple because only a few substances were involved in the process. A great variety of possible oligonuclear complexes may arise in case of dicyano complexes with the above-mentioned heavy metal ions. It would be optimal to study the reactions of the same dicyano complex *cis* and *trans* analogues. We were unable to find out in literature the procedures for such pair complexes preparation. So our investigation was limited to some *cis*- and *trans*-dicyanochromium(III) complexes of similar composition of the ligand sphere: *cis*-$[Cr(en)(H_2O)(NO)(CN)_2]$, *cis*-$[Cr(H_2O)_3(NO)(CN)_2]$, *cis*-$[Cr(en)_2(CN)_2]^+$, and *trans*-$[Cr(NH_3)_4(CN)_2]^+$ with reported preparation procedures. It was believed that some general conclusions could be made even on the basis of these investigations.

EXPERIMENTAL

All chemicals were of anal. grade. Triply-distilled water was used. The following complexes were prepared by reported procedures: *cis*-$[Cr(en)(H_2O)(NO)(CN)_2]$ [8], *cis*-$[Cr(H_2O)_3(NO)(CN)_2]$ [9], *cis*-$[Cr(en)_2(CN)_2]Cl \cdot H_2O$ [10], and *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$

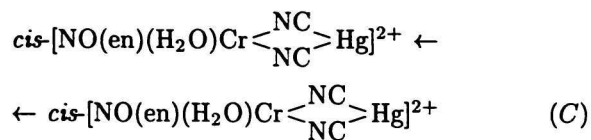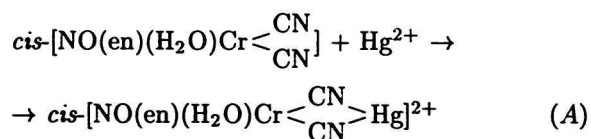[11]. They were identified on the basis of the spectral measurements as it was described in the original papers.

A potentiometer (model 250 Denver Instrument Comp., USA) was used for potentiometric measurements. Hanging mercury drop electrode (HMDE) served as an indicator electrode in potentiometric titrations with $Hg(ClO_4)_2$. Polarographic measurements were carried out on a PAR Model 273 A (Princeton Applied Research, USA) on line with computer PC-AT 80 486. Electrochemical software ECHEM (PAR EG & G) enabled data acquisition and processing thus ensuring automation, flexibility, and convenience of performing analysis. 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 an SCE). Saturated calomel electrode (SCE) connected to the sample solution by a salt bridge was applied as a reference electrode in potentiometric and also polarographic measurements.
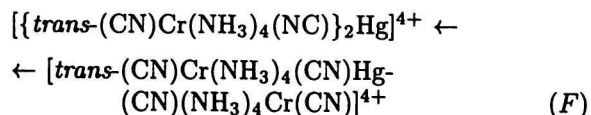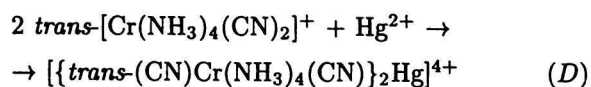
RESULTS AND DISCUSSION

Reactions of dicyanochromium(III) complexes with Hg²⁺ ions were investigated in the weak acidic medium pH (equal to 3) of which was optimized to be convenient for the stability of all species involved in the reaction. In this medium protonation reactions of complexes are relatively slow and also Hg²⁺ is stable enough. The stoichiometry of the reactions was examined by potentiometric titrations. To avoid the in-

terference of the competing slow aquation reactions of reactants and also decomposition reactions of reaction products, each point of titration curve was obtained from fresh reactants added in different mole ratio. Stabilization of the equilibrium potential of the indicator electrode was slow indicating the complexity of the reactions. Equilibrium potential was reached in about 15—20 s and its value could easily be determined. Another much slower potential drift proceeded probably due to the decomposition of the reaction products. The phenomenon of about 20 s stabilization of equilibrium potential was also observed in our previous studies of monocyano complexes [1—7] and was explained by rearrangement of the reaction products coordination sphere by the linkage isomerization of the bridging cyano ligand from Cr—CN—Hg to Cr—NC—Hg configuration. The observed reaction stoichiometry of Cr—Hg association of the *cis*-dicyano complexes differed from that found for *trans*-dicyano complexes. Inflection points of the potentiometric titration curves for all investigated *cis*-dicyano complexes *cis*-[Cr(en)(H$_2$O)(NO)(CN)$_2$], *cis*-[Cr(en)$_2$(CN)$_2$]$^+$, and *cis*-[Cr(H$_2$O)$_3$(NO)(CN)$_2$] were observed at the mole ratio of the complex to Hg(ClO$_4$)$_2$ equal to 1:1 while for *trans*-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ to Hg(ClO$_4$)$_2$ at the mole ratio equal to 2:1.

Based on analogy with monocyano complexes [1—7] the following reaction scheme written for *cis*-[Cr(en)(H$_2$O)(NO)(CN)$_2$] as an example for all *cis*-complexes studied was proposed
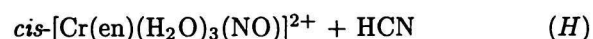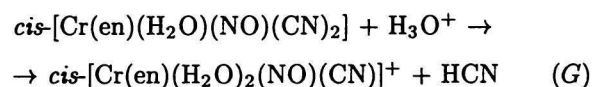
$$\textit{cis-}[\text{NO(en)}(\text{H}_2\text{O})\text{Cr}{<}^{\text{CN}}_{\text{CN}}] + \text{Hg}^{2+} \rightarrow$$

$$\rightarrow \textit{cis-}[\text{NO(en)}(\text{H}_2\text{O})\text{Cr}{<}^{\text{CN}}_{\text{CN}}{>}\text{Hg}]^{2+} \qquad (A)$$

$$\downarrow \qquad\qquad (B)$$

$$\textit{cis-}[\text{NO(en)}(\text{H}_2\text{O})\text{Cr}{<}^{\text{NC}}_{\text{NC}}{>}\text{Hg}]^{2+} \leftarrow$$

$$\leftarrow \textit{cis-}[\text{NO(en)}(\text{H}_2\text{O})\text{Cr}{<}^{\text{NC}}_{\text{NC}}{>}\text{Hg}]^{2+} \qquad (C)$$

For the *trans*-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ the proposed scheme is as follows

$$2\ \textit{trans-}[\text{Cr(NH}_3)_4(\text{CN})_2]^+ + \text{Hg}^{2+} \rightarrow$$

$$\rightarrow [\{\textit{trans-}(\text{CN})\text{Cr(NH}_3)_4(\text{CN})\}_2\text{Hg}]^{4+} \qquad (D)$$

$$\downarrow \qquad\qquad (E)$$

$$[\{\textit{trans-}(\text{CN})\text{Cr(NH}_3)_4(\text{NC})\}_2\text{Hg}]^{4+} \leftarrow$$

$$\leftarrow [\textit{trans-}(\text{CN})\text{Cr(NH}_3)_4(\text{CN})\text{Hg-}$$
$$(\text{CN})(\text{NH}_3)_4\text{Cr(CN)}]^{4+} \qquad (F)$$

This indicated a significant difference in the adducts formation.

The advantage of polarography is that each substance occurring in the reaction mixture (reactants, intermediates, products) represents itself in a polarographic wave with the distinctly separated half-wave potential. Though in comparison with the studied reactions of dicyano complexes with Hg^{2+} their proton-catalyzed aquation reactions are relatively slow, the aquation products may occur in the solution. Moreover, as it will be discussed later, they may be present in solution also as the products of the decomposition reactions of oligomer adducts. As an example of the proton-catalyzed aquation the scheme for hydrolysis of *cis*-[Cr(en)(H$_2$O)(NO)(CN)$_2$] is given

$$\textit{cis-}[\text{Cr(en)}(\text{H}_2\text{O})(\text{NO})(\text{CN})_2] + \text{H}_3\text{O}^+ \rightarrow$$

$$\rightarrow \textit{cis-}[\text{Cr(en)}(\text{H}_2\text{O})_2(\text{NO})(\text{CN})]^+ + \text{HCN} \qquad (G)$$

$$\downarrow$$

$$\textit{cis-}[\text{Cr(en)}(\text{H}_2\text{O})_3(\text{NO})]^{2+} + \text{HCN} \qquad (H)$$

Polarographic properties of all involved species were investigated first. It was found that in above-described medium *cis*-[Cr(en)(H$_2$O)(NO)(CN)$_2$] and its aquation reaction products *cis*-[Cr(en)(H$_2$O)$_2$(NO)(CN)]$^+$ and *cis*-[Cr(en)(H$_2$O)$_3$(NO)]$^{2+}$ are reduced in the diffusion-controlled irreversible polarographic waves with the half-wave potentials given in Table 1 (No. *1, 4, 6*). The half-wave potentials of the polarographic waves found for *cis*-[Cr(H$_2$O)$_3$(NO)(CN)$_2$], *cis*-[Cr(H$_2$O)$_4$(NO)(CN)]$^+$, *cis*-[Cr(H$_2$O)$_5$(NO)]$^{2+}$ are given in Table 2 (No. *1, 4, 6*), for *cis*-[Cr(en)$_2$(CN)$_2$]$^+$, *cis*-[Cr(en)$_2$(H$_2$O)(CN)]$^{2+}$, *cis*-[Cr(en)$_2$(H$_2$O)$_2$]$^{3+}$ in Table 3 (No. *1, 4, 6*), and for *trans*-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$, *trans*-[Cr(NH$_3$)$_4$(H$_2$O)(NC)]$^{2+}$, *trans*-[Cr(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ in Table 4 (No. *1, 4, 6*).

As for the reaction stoichiometry, the polarographic experiments were in full agreement with the above-described potentiometric observations. All studied *cis*-dicyano complexes revealed much similar polarographic behaviour. Polarography was applied to investigate the course of reactions of complexes with Hg^{2+} on the basis of the time development of the polarographic waves. Polarograms were taken in different times, *i.e.* in different stages of the reaction. In the case of *cis*-[Cr(en)(H$_2$O)(NO)(CN)$_2$] an addition of Hg(ClO$_4$)$_2$ to the complex solution led to the decrease of the polarographic wave of the original complex with the half-wave potential -1.1 V *vs.* SCE (Fig. 1) and to the formation of more positive polarographic waves. The decrease of the original wave and increase of a new one at -0.70 V *vs.* SCE was also gradual with amounts of Hg(ClO$_4$)$_2$ added to the complex solution up to the mole ratio of the complex to Hg^{2+} = 1:1 which supported the proposal of the reaction stoichiometry based on potentiometric investigation.

Curves *a, b, c* in Fig. 1 indicate changes in the presence of individual substances in the course of the reaction. Shortly (1 min) after Hg(ClO$_4$)$_2$ was added (curve *b*) the dominant became the wave with the half-

Table 1. Half-Wave Potentials of the Polarographic Irreversible Reduction Waves of the Species Occurring in the Course of the Reaction of cis-$[Cr(en)(H_2O)(NO)(CN)_2]$ with $Hg(ClO_4)_2$. $[H^+] = 0.001$ mol dm^{-3}. Ionic Strength 1 mol dm^{-3} (ClO_4^-, Na$^+$, H$^+$, Hg^{2+}). $T = 298$ K

	Parent species	Electroactive species	$E_{1/2}$ $vs.$ SCE/V
1		cis-$[Cr(en)(H_2O)(NO)(CN)_2]$	−1.10
2	cis-$[Cr(en)(H_2O)(NO)(CN)(NC)Hg]^{2+}$	cis-$[Cr(en)(H_2O)(NO)(CN)(NC)]$	−0.89
3	cis-$[Cr(en)(H_2O)(NO)(NC)_2Hg]^{2+}$	cis-$[Cr(en)(H_2O)(NO)(NC)_2]$	−0.70
4		cis-$[Cr(en)(H_2O)_2(NO)(CN)]^+$	−1.20
5	cis-$[Cr(en)(H_2O)_2(NO)(NC)Hg(CN)]^{2+}$	cis-$[Cr(en)(H_2O)_2(NO)(NC)]^+$	−0.92
6		cis-$[Cr(en)(H_2O)_3(NO)]^{2+}$	−0.96

Table 2. Half-Wave Potentials of the Polarographic Irreversible Reduction Waves of the Species Occurring in the Course of the Reaction of cis-$[Cr(H_2O)_3(NO)(CN)_2]$ with $Hg(ClO_4)_2$. $[H^+] = 0.001$ mol dm^{-3}. Ionic Strength 1 mol dm^{-3} (ClO_4^-, Na$^+$, H$^+$, Hg^{2+}). $T = 298$ K

	Parent species	Electroactive species	$E_{1/2}$ $vs.$ SCE/V
1		cis-$[Cr(H_2O)_3(NO)(CN)_2]$	−1.12
2	cis-$[Cr(H_2O)_3(NO)(CN)(NC)Hg]^{2+}$	cis-$[Cr(H_2O)_3(NO)(CN)(NC)]$	−0.90
3	cis-$[Cr(H_2O)_3(NO)(NC)_2Hg]^{2+}$	cis-$[Cr(H_2O)_3(NO)(NC)_2]$	−0.66
4		cis-$[Cr(H_2O)_4(NO)(CN)]^+$	−1.21
5	cis-$[Cr(H_2O)_4(NO)(NC)Hg(CN)]^{2+}$	cis-$[NO(H_2O)_4Cr(NC)]^+$	−0.98
6		cis-$[Cr(H_2O)_5(NO)]^{2+}$	−0.95

Table 3. Half-Wave Potentials of the Polarographic Irreversible Reduction Waves of the Species Occurring in the Course of the Reaction of cis-$[Cr(en)_2(CN)_2]^+$ with $Hg(ClO_4)_2$. $[H^+] = 0.001$ mol dm^{-3}. Ionic Strength 1 mol dm^{-3} (ClO_4^-, Na$^+$, H$^+$, Hg^{2+}). $T = 298$ K

	Parent species	Electroactive species	$E_{1/2}$ $vs.$ SCE/V
1		cis-$[Cr(en)_2(CN)_2]^+$	−1.11
2	cis-$[Cr(en)_2(CN)(NC)Hg]^{3+}$	cis-$[Cr(en)_2(CN)(NC)]^+$	−0.86
3	cis-$[Cr(en)_2(NC)_2Hg]^{3+}$	cis-$[Cr(en)_2(NC)_2]^+$	−0.64
4		cis-$[Cr(H_2O)(en)_2(CN)]^{2+}$	−0.96
5	cis-$[Cr(H_2O)(en)_2(NC)Hg(CN)]^{3+}$	cis-$[(en)_2(H_2O)Cr(NC)]^{2+}$	−0.75
6		cis-$[Cr(H_2O)_2(en)_2]^{3+}$	−0.81

Table 4. Half-Wave Potentials of the Polarographic Irreversible Reduction Waves of the Species Occurring in the Course of the Reaction of $trans$-$[Cr(NH_3)_4(CN)_2]^+$ with $Hg(ClO_4)_2$. $[H^+] = 0.001$ mol dm^{-3}. Ionic Strength 1 mol dm^{-3} (ClO_4^-, Na$^+$, H$^+$, Hg^{2+}). $T = 298$ K

	Parent species	Electroactive species	$E_{1/2}$ $vs.$ SCE/V
1		$trans$-$[Cr(NH_3)_4(CN)_2]^+$	−1.15
2	$trans$-$[Cr(NH_3)_4(CN)(NC)Hg]^{3+}$	$trans$-$[Cr(NH_3)_4(CN)(NC)]^+$	−0.80
3	$trans$-$[Hg(CN)Cr(NH_3)_4(NC)Hg]^{5+}$	$trans$-$[Cr(NH_3)_4(NC)_2]^+$	−0.65
4		$trans$-$[Cr(NH_3)_4(H_2O)(CN)]^{2+}$	−0.98
5	$trans$-$[(NH_3)_4(H_2O)Cr(NC)Hg(CN)]^{2+}$	$trans$-$[Cr(NH_3)_4(H_2O)(NC)]^{2+}$	−0.74
6		$trans$-$[Cr(NH_3)_4(H_2O)_2]^{3+}$	−0.82

wave potential −0.89 V $vs.$ SCE. Lately (10 min) after the Hg^{2+} addition (curve c) the dominant became the wave with the half-wave potential −0.70 V $vs.$ SCE. Its height, however, never reached the height of the wave of the original complex. It can be explained by the fact that the adducts formed in the course of reactions (A—C) are analyzed on the basis of their polarographic waves of Cr component reduction.

These are growing on the Hg(II) complex reduction current background. The actual electroactive species for characterization of oligonuclear adducts (parent species) are therefore corresponding chromium complexes formed at the electrode surface. The polarographic wave with the half-wave potential −0.70 V $vs.$ SCE is lower because after reduction Hg(II) bound in adducts released less stable isomers which sponta-
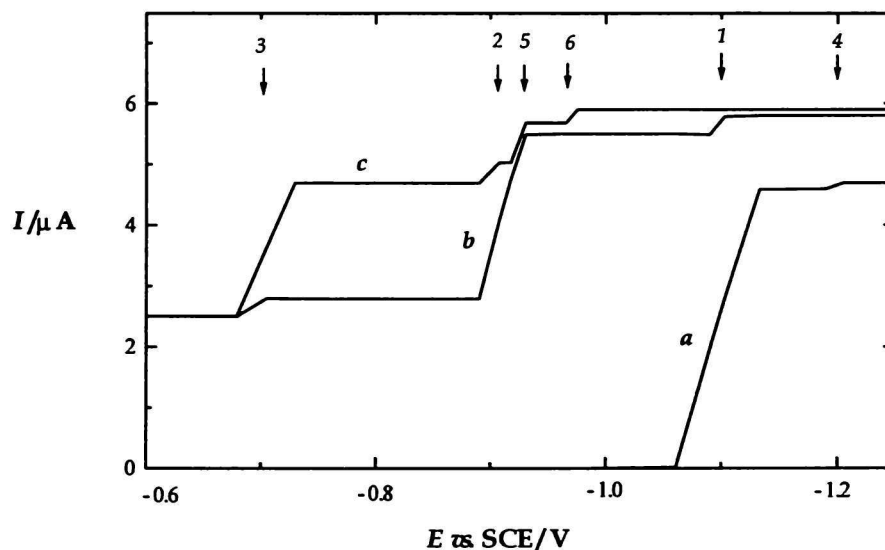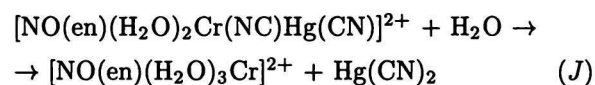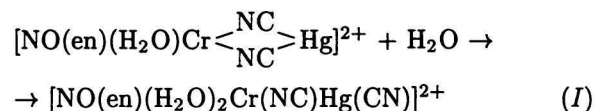
Fig. 1. Schematic presentation of the polarographic behaviour of aqueous 0.001 mol dm^{-3} cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$] in 0.001 mol dm^{-3} HClO$_4$. Ionic strength $\mu = 1.0$ mol dm^{-3} (ClO$_4^-$, Na$^+$, H$_3$O$^+$, Hg^{2+}), $T = 298$ K. Waves: a) before Hg(ClO$_4$)$_2$ addition; b) 1 min after addition of 0.0005 mol dm^{-3} Hg(ClO$_4$)$_2$; c) 90 min after Hg(ClO$_4$)$_2$ addition. 1. cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$]; 2. cis-[Cr(en)(H$_2$O)(NO)(CN)(NC)]; 3. cis-[Cr(en)(H$_2$O)(NO)(NC)$_2$]; 4. cis-[NO(en)(H$_2$O)$_2$Cr(CN)]$^+$; 5. cis-[NO(en)(H$_2$O)$_2$Cr(NC)]$^+$; 6. cis-[Cr(en)(H$_2$O)$_3$(NO)]$^{2+}$.

neously isomerize to stable ones during the polarization of the working electrode to the more negative potentials of the reduction of the chromium component. In lowering of the wave height also the fact that the bigger molecule of adduct with lower diffusion coefficient is reduced plays a role. Also proton-catalyzed aquation reaction of all involved complexes may occur which is leading to the decrease of this wave. The height of the polarographic wave at -0.70 V vs. SCE in much longer time of reaction (90 min) started to decrease due to the adduct decomposition. The wave at -0.70 V vs. SCE is lowering on behalf of the increase of waves at -1.20 V vs. SCE, -0.92 V vs. SCE, and -0.95 V vs. SCE (for assignment see Table 1). All complexes which may be present in solution in the course of cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$] reaction with Hg^{2+} cations are listed in Table 1.

Polarographic behaviour and the time development of the other two studied cis-dicyano complexes cis-[Cr(en)$_2$(CN)$_2$]$^+$ and cis-[Cr(H$_2$O)$_3$(NO)-(CN)$_2$] much resembled those described for cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$]. The half-wave potentials of all complexes present in the reacting solution in the course of reaction of cis-[Cr(en)$_2$(CN)$_2$]$^+$ with Hg are given in Table 2. The values found in the study of reaction of cis-[Cr(H$_2$O)$_3$(NO)(CN)$_2$] with Hg^{2+} needed for polarographic characterization of the reacting species are summarized in Table 3. The analysis of data given in these tables allows to conclude that the difference in half-wave potentials of the polarographic waves of all studied original cis-dicyano complexes and waves dominant in short time after Hg(ClO$_4$)$_2$ was added to their solutions (ca. 10 min) was approxi-

mately the same, ca. 400 mV. This allows to propose that the processes of the oligonuclear adducts formation in these reactions are similar. On the basis of the time development of the polarographic waves and the difference in the half-wave potentials it can be proposed that in these adducts Hg^{2+} ions-assisted stepwise linkage isomerization of the Cr—CN bonds to the less stable Cr—NC isomers takes place as demonstrated for the case of cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$] in the reaction schemes (A—C).

In the final oligonuclear adducts both bridging cyano groups are bonded to Cr atom through N atom and to Hg atom through C atom. The formation of adducts is followed by their slow proton-catalyzed reaction

$$[NO(en)(H_2O)Cr \mathord{<}^{NC}_{NC} \mathord{>} Hg]^{2+} + H_2O \rightarrow$$

$$\rightarrow [NO(en)(H_2O)_2Cr(NC)Hg(CN)]^{2+} \qquad (I)$$

$$[NO(en)(H_2O)_2Cr(NC)Hg(CN)]^{2+} + H_2O \rightarrow$$

$$\rightarrow [NO(en)(H_2O)_3Cr]^{2+} + Hg(CN)_2 \qquad (J)$$

The assignment of the polarographic waves based on the time development of the polarographic waves was confirmed by the spontaneous isomerization of the released less stable (Cr—NC) isomers. It can be demonstrated on the case of the cis-[Cr(en)(H$_2$O)-(NO)(CN)$_2$] adducts with Hg^{2+} cations. Since the stability constant of [HgI$_4$]$^{2-}$ is higher than that of [NO(en)(H$_2$O)Cr(NC)$_2$Hg]$^{2+}$ or its decomposition product [NO(en)(H$_2$O)$_2$Cr(NC)Hg(CN)]$^{2+}$ the reactions (K) and (L) are shifted to the right.
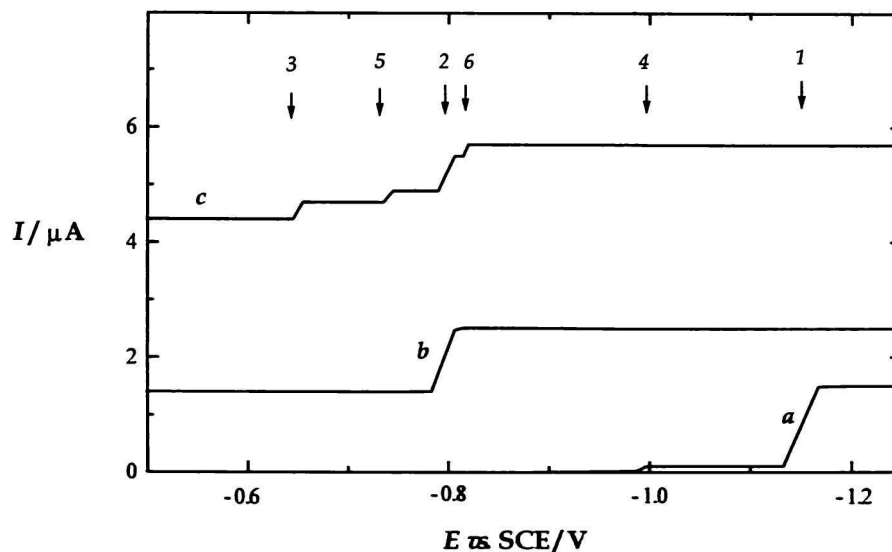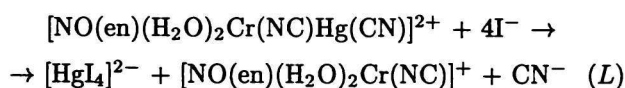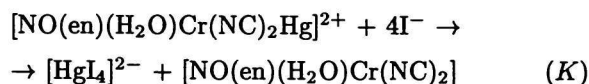
Fig. 2. Schematic presentation of the polarographic behaviour of aqueous 0.001 mol dm^{-3} trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ in 0.001 mol dm^{-3} HClO$_4$. Ionic strength μ = 1.0 mol dm^{-3} (ClO$_4^-$, Na$^+$, H$_3$O$^+$, Hg^{2+}), T = 298 K. Waves: a) before Hg(ClO$_4$)$_2$ addition; b) 30 min after addition of 0.0005 mol dm^{-3} Hg(ClO$_4$)$_2$; c) 30 min after addition of 0.002 mol dm^{-3} Hg(ClO$_4$)$_2$. 1. trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$; 2. trans-[Cr(NH$_3$)$_4$(CN)(NC)]$^+$; 3. trans-[Cr(NH$_3$)$_4$(NC)$_2$]$^+$; 4. trans-[Cr(NH$_3$)$_4$(H$_2$O)(CN)]$^{2+}$; 5. trans-[Cr(NH$_3$)$_4$(H$_2$O)(NC)]$^{2+}$; 6. trans-[Cr(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$.

$$[NO(en)(H_2O)Cr(NC)_2Hg]^{2+} + 4I^- \rightarrow$$
$$\rightarrow [HgI_4]^{2-} + [NO(en)(H_2O)Cr(NC)_2] \qquad (K)$$

$$[NO(en)(H_2O)_2Cr(NC)Hg(CN)]^{2+} + 4I^- \rightarrow$$
$$\rightarrow [HgI_4]^{2-} + [NO(en)(H_2O)_2Cr(NC)]^+ + CN^- \quad (L)$$

The released less stable linkage isomers undergo fast-step isomerization reactions to the more stable ones

$$[NO(en)(H_2O)Cr(NC)_2] \rightarrow$$
$$\rightarrow [NO(en)(H_2O)Cr(CN)(NC)] \rightarrow$$
$$\rightarrow [NO(en)(H_2O)Cr(CN)_2] \qquad (M)$$
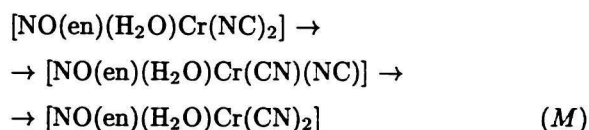
The same holds for the decomposition product [NO(en)(H$_2$O)$_2$Cr(NC)]$^+$

$$[NO(en)(H_2O)_2Cr(NC)]^+ \rightarrow$$
$$\rightarrow [NO(en)(H_2O)_2Cr(CN)]^+ \qquad (N)$$
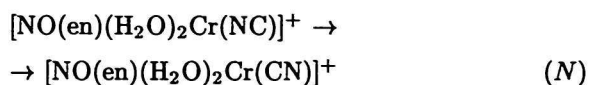
The reactions (K) and (L) followed by the reactions (M) and (N) proved the assignment of polarographic waves with half-wave potentials -0.70 V vs. SCE to cis-[NO(en)(H$_2$O)Cr(NC)$_2$], -0.89 V vs. SCE to cis-[NO(en)(H$_2$O)Cr(CN)(NC)], and -0.92 V vs. SCE to cis-[NO(en)(H$_2$O)$_2$Cr(NC)]$^+$, respectively. Addition of excess KI to the reacting solution leads to the full recovery of corresponding stable isomers polarographic waves with half-wave potentials -1.10 V vs. SCE for original complex cis-[Cr(en)(H$_2$O)(NO)(CN)$_2$] and -1.20 V vs. SCE for its first-step aquation product cis-[Cr(en)(H$_2$O)$_2$(NO)(CN)]$^+$.

Very similar to the polarographic behaviour depicted in Fig. 1 were polarograms taken in the case of other two cis-dicyano complexes cis-[Cr(H$_2$O)$_3$(NO)(CN)$_2$] and cis-[Cr(en)$_2$(CN)$_2$]$^+$. It allows to propose also for these cis-dicyano complexes reaction schemes analogous to the schemes $(A$—$C)$. Double CN-bridged (six-memberred ring) complexes were also reported by Anson in [12] for cis-[Cr(H$_2$O)$_3$(NO)(CN)$_2$] and by Heatherington in [13] for cis-[Cr(en)$_2$(CN)$_2$]$^+$ on the basis of spectral measurements.

The situation was quite different in case of trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ complex. The potentiometric determination of the reaction stoichiometry indicated the formation of the reaction product different from the case of cis-dicyano complexes. The inflection point of the titration curve was observed at the mole ratio trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ to Hg(ClO$_4$)$_2$ equal to 2:1. No significant change of indicating electrode potential was observed at 1:1 mole ratio of trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ to Hg(ClO$_4$)$_2$ in the potentiometric titration allowing to propose any significant role of the second cyanide in the adduct formation. The polarographic study provided more information. Schematic polarograms are shown in Fig. 2. The additions of Hg(ClO$_4$)$_2$ to trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ led to the gradual decrease of its polarographic wave with half-wave potential -1.15 V vs. SCE and increase of a new one with half-wave potential -0.80 V vs. SCE up to the mole ratio of trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ to Hg(ClO$_4$)$_2$ equal to 2:1. This observation could be explained by the reaction schemes $(D$—$F)$.

As it can be seen from Fig. 2, in the presence of excess of Hg(ClO$_4$)$_2$ compared to trans-[Cr(NH$_3$)$_4$(CN)$_2$]$^+$ (2:1), the polarographic wave ob-

served at -0.80 V $vs.$ SCE characteristic of $trans$-$[Cr(NH_3)_4(CN)(NC)]^+$ was still dominant. The height of polarographic wave at -0.65 V $vs.$ SCE corresponding to the reduction of $trans$-$[Cr(NH_3)_4(NC)_2]^+$ (with both cyanides linked to Cr atom through N atom) indicates that this trinuclear complex is present in a very low concentration in reaction mixture. This height by far does not reach the height of the original wave of $trans$-$[Cr(NH_3)_4(CN)_2]^+$. This fact allows to conclude that formation of trinuclear adduct with two Hg^{2+} ions is not effective

$$trans\text{-}[Cr(NH_3)_4(CN)_2]^+ + 2Hg^{2+} \rightarrow$$

$$\rightarrow [Hg(CN)Cr(NH_3)_4(NC)Hg]^{5+} \qquad (O)$$
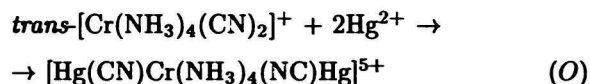
Polarographic behaviour thus proved nonexistence of the CN-double bridged binuclear (Cr, Hg) complex. In the case of $trans$-dicyano complex the double CN-bridged complex containing one Cr and one Hg atom obviously cannot be expected. As in case of cis-complexes the formation of adducts of $trans$-$[Cr(NH_3)_4(CN)_2]^+$ with Hg^{2+} cations is also followed by adducts aquation and so some other substances may be present in the solution. The polarographic waves shown in Fig. 2 with half-wave potentials -1.0 V $vs.$ SCE and -0.75 V $vs.$ SCE belong to $trans$-$[Cr(NH_3)_4(H_2O)(NC)]^{2+}$ and $trans$-$[Cr(NH_3)_4(H_2O)_2]^{3+}$, respectively. The assignment was also based on time dependence of the polarographic waves and the experiments with iodide addition to the reacting solution in different time from the beginning of the reaction.

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