ACID HYDROLYSIS OF THE DIAQUACYANOETHYLENEDIAMINE-NITROSYLCHROMIUM CATION AND ITS REACTIONS WITH MERCURY(II) AND SILVER(I) IONS

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Preparation of the $[Cr(H_2O)_2CN\ (en)\ NO]^+$ ion in solution by acid hydrolysis of $[CrH_2O(CN)_2\ (en)\ NO]$ including its ion exchange separation is described. The polarographic properties of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ as well as the kinetics of its acid hydrolysis were studied. Reactions of this complex with Hg(II) and Ag(I) were investigated and binuclear and trinuclear adducts were found to form. Linkage isomerization of the bridging cyanide in such adducts is deduced from their electrochemical properties. The spontaneous isomerization of the unstable isomer with the Cr–NC bond to the stable isomer with the Cr–CN bond was followed after its liberation by a competitive complexation of Hg(II) with excess iodide. The kinetics of decomposition of the adducts with Hg(II) was measured to examine the influence of H^+ and Hg(II) concentrations.

Our previous papers were concerned with the chromium monocyano complexes $[Cr(H_2O)_4CN(NO)]^+$ (refs[1 – 4]) and $[Cr(H_2O)CN\ (en)_2]^{2+}$ (ref.[5]), examined mainly by voltammetric methods. Attention was also paid to their reactions with Hg(II) and Ag(I). This paper deals with the acid hydrolysis of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ and its complexation with the two heavy metal ions studied by the polarographic, potentiometric and spectrophotometric techniques.

EXPERIMENTAL

Reagents

Analytical grade reagents and triply distilled water were used. $[CrH_2O(CN)_2\ (en)\ NO]$ was synthesized following ref.[6]. $[Cr(H_2O)_2CN\ (en)\ NO]^+$ was prepared by acid hydrolysis of $[CrH_2O(CN)_2\ (en)\ NO]$ and isolated in solution by the conventional cation-exchange technique. The optimum H^+ concentration in solution and time of acid hydrolysis were determined based on a kinetic investigation. In a typical experiment, 0.536 g (2 mmol) of $[CrH_2O(CN)_2\ (en)\ NO]$ were dissolved in 50 ml of 0.2 M $HClO_4$. The solution was allowed to stand for 30 min at 25 °C and after dilution to twice the initial volume, passed through a column of a strongly acidic cation-exchanger (Dowex 50W in the Na^+ cycle). The column was then washed with approximately 100 ml of 0.01 M $NaClO_4$ to elute the uncharged Cr reaction products (e.g. $[CrH_2O(CN)_2\ (en)\ NO]$) and anions (e.g. CN^-) which can be present. The $[Cr(H_2O)_2CN\ (en)\ NO]^+$ ion prepared was eluted with 0.4 M $NaClO_4$ at pH 3; no $[Cr(H_2O)_3(en)NO]^{2+}$, which is another acid hydrolysis product that might be present, was eluted with this solution. The stock solution of $[Cr(H_2O)_2CN(en)NO]^+$ (about 5 mmol dm^{-3}) was stored at pH 3 and 0.4 M $NaClO_4$, frozen at about −70 °C. In such conditions the solution was stable for a minimum of 30 days. For very precise measurements, the stock solution, after melting, was freed from small amounts of $[Cr(H_2O)_3(en)NO]^{2+}$ by passing it through a short cation-exchanger column. The visible absorption spectrum of $[Cr(H_2O)_2CN(en)NO]^+$ exhibits three absorption bands at 369, 450 and 606 nm (molar absorptivities 187, 104 and 29.3 $dm^3 mol^{-1} cm^{-1}$, respectively).

$[Cr(H_2O)_3(en)NO]^{2+}$ was eluted from the cation exchanger column with 1 M $NaClO_4$ at pH 3. Its visible absorption spectrum displays absorption bands at 394, 454 and 565 nm (86.5, 118 and 24.5 $dm^3 mol^{-1} cm^{-1}$, respectively).

Apparatus

Polarographic measurements were carried out on a PA 4 polarograph (Labora, Praha). The mercury flow rate of the dropping mercury electrode was 1.65 mg s^{-1}, drop time 4.3 s in 1 M NaCl at a mercury reservoir height of 64 cm and in a short circuit with a saturated calomel electrode (SCE).

An OP-205 potentiometer (Radelkis, Budapest) was used for potentiometric measurements. A hanging mercury drop electrode (HMDE) served as the working electrode in potentiometric titrations with Hg^{2+}, and an Ag-wire, in titrations with Ag^+. A saturated calomel electrode (SCE) with a salt bridge containing 1 M $NaNO_3$ was employed as the reference electrode.

Spectrophotometric measurements were carried out on a Specord UV-VIS (Zeiss, Jena) instrument. The cells were thermostatted for the kinetic measurements.

RESULTS AND DISCUSSION

Electroanalytical Properties and Acid Hydrolysis of $[Cr(H_2O)_2CN(en)NO]^+$

Dissolved in a weakly acidic solution at $c(H^+) = 0.01$ mol dm^{-3} and ionic strength 1 mol dm^{-3} (ClO_4^-, Na^+, H^+), the complex ion $[Cr(H_2O)_2CN(en)NO]^+$ is reduced in polarographic conditions giving rise to a diffusion controlled irreversible wave whose limiting current corresponds to the exchange of 3 electrons and whose half wave potential is $E = -1.20$ V vs SCE (using the dropping mercury electrode specified in the Experimental). In the same experimental conditions, $[Cr(H_2O)_3(en)NO]^{2+}$ is reduced to give a diffusion controlled irreversible wave whose limiting current corresponds to the exchange of 3 electrons and whose half wave potential is −0.95 V vs SCE[7].

The polarographic limiting diffusion current of $[Cr(H_2O)_2CN(en)NO]^+$ was used to monitor the concentration of the complex during the kinetic study of its acid hydrolysis.

$$[Cr(H_2O)_2CN(en)NO]^+ + H_3O^+ \longrightarrow [Cr(H_2O)_3(en)NO]^{2+} + HCN \quad (A)$$

The rate of reaction (*A*) was also studied spectrophotometrically by examining the time change of absorbance at 369 nm. The kinetics obeyed the monomolecular rate law. The rate constants for various H^+ concentrations obtained by the two techniques are summarized in Table I; they are in a reasonable agreement within the experimental errors.

As Table I demonstrates, the rate constants are linearly dependent on the H^+ concentration over the entire range of acidities of 0.01 – 0.3 mol dm^{-3}. The intercept of this linear dependence does not differ statistically significantly from zero. This acid-independent reaction path is insignificant, the cyanide release proceeding predominantly by the acid catalyzed pathway.

Stoichiometry of the Reaction of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ *with* Hg^{2+} *and* Ag^+ *Ions*

The reaction of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ with the two heavy metal ions is accompanied by changes in its visible spectrum. This is illustrated in Fig. 1 for various Hg^{2+} to $[Cr(H_2O)_2CN\ (en)\ NO]^+$ molar ratios. The spectral changes are most pronounced up to the molar ratio *c*(Hg) : *c*(Cr) = 0.5. This indicates that the stoichiometry of the reaction is 1 Hg to 2 Cr.

The spectra in Fig. 1 were recorded several minutes after the addition of Hg^{2+}. After that time, no other spectral changes occur at comparable rates. The slow change in the spectrum of the Hg(II) adduct is ascribed to its decomposition reaction (vide infra). The visible spectrum which contains three bands at 387, 448 and 598 nm (molar absorptivities 125, 129 and 22.5 $dm^3\ mol^{-1}\ cm^{-1}$, respectively), can be ascribed to the trinuclear adduct of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ with Hg(II).

$$2\,[Cr(H_2O)_2CN\,(en)\,NO]^+ + Hg^{2+} \rightleftharpoons [Hg\{CNCr(H_2O)_2\,(en)\,NO\}_2]^{4+} \qquad (B)$$

Potentiometric and amperometric titrations were also used to identify the stoichiometry in the reactions of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ with Hg^{2+} and Ag^+. In the titration with Hg(II), each point on the titration curve was taken in a separate experiment using a solution with a different titrant to titrand molar ratio. This way of performing titrations enables the potential or current to be read at the optimum time with a minimum error arising from the relatively slow formation and subsequent decomposition of the adduct. For the titration with Ag(I) the solution of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ did not have

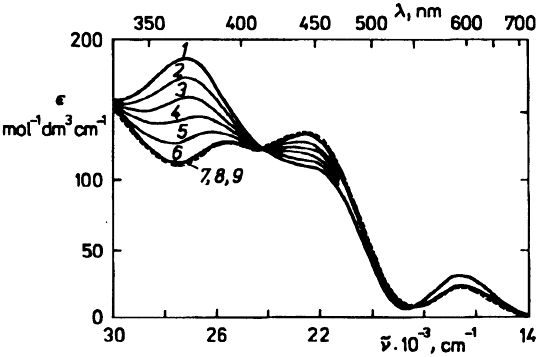

FIG. 1
Absorption spectra of reacted solutions of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ (1 mmol dm^{-3}) with Hg^{2+}. I = 1 mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+}). T = 298 K. Initial concentration of Hg^{2+} (mmol dm^{-3}): *1* 0.0; *2* 0.1; *3* 0.2; *4* 0.3; *5* 0.4; *6* 0.5; *7* 0.75; *8* 1.0; *9* 3.0

to be changed since the decomposition of the Ag adduct is much slower. The inflexion points on the potentiometric titration curves at molar ratios $c(\mathrm{Cr}) : c(\mathrm{Hg})$ (or $c(\mathrm{Ag})$) ≈ 0.5 indicate that trinuclear adducts are formed.

The amperometric titrations are based on the appreciable difference between the diffusion coefficients of the free and bonded Hg(II) and Ag(I) ions. The limiting currents were followed at $E = -0.5$ V vs SCE, at which all forms of the heavy metal ions are reduced. The breaks on the amperometric titration curves at molar ratios of $c(\mathrm{Cr}) : c(\mathrm{Hg})$ (or $c(\mathrm{Ag})$) = 0.5 also bear out the formation of trinuclear adducts.

Based on the results of the spectrophotometric, potentiometric and amperometric titrations and in analogy with the reactions of the similar monocyano complex studied previously[1,5] it can be concluded that the formation of adducts with Hg(II) proceeds according to Eq. (*B*). Reaction with Ag(Cl) is analogous.

$$2\,[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+ + \mathrm{Ag}^+ \rightleftharpoons [\mathrm{Ag\{CNCr(H_2O)_2\,(en)\,NO\}_2}]^{3+} \qquad (C)$$

Polarographic Investigation of the Reaction of $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ with Hg^{2+} and Ag^+

Addition of Hg^{2+} to the solution of $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ brings about decrease of its polarographic wave and formation of a new wave with $E_{1/2} = -0.92$ V vs SCE (Fig. 2). From the differences between the potentials of the initial wave and the new wave appearing during the formation of the Hg(II) adduct with $[\mathrm{Cr(H_2O)_5CN}]^{2+}$ (ref.[8]), $[\mathrm{Cr(H_2O)_4CN(NO)}]^+$ (ref.[3]) and $[\mathrm{Cr(H_2O)CN\,(en)_2}]^{2+}$ (ref.[5]) it is inferred that the

TABLE I

Pseudo-first order rate constants of $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ reaction with $\mathrm{H_3O^+}$ (Eq. (*A*)). $T = 298$ K, $I = 1$ mol dm^{-3} ($\mathrm{ClO_4^-}$, $\mathrm{H^+}$, $\mathrm{Na^+}$)

$[\mathrm{H^+}]$, mol dm^{-3}	Spectrophotometry[a] $k \cdot 10^5$, s^{-1}	Polarography[a] $k \cdot 10^5$, s^{-1}
0.01	0.22 ± 0.02	0.20 ± 0.02
0.03	0.41 ± 0.04	0.40 ± 0.03
0.06	0.72 ± 0.05	0.75 ± 0.06
0.10	1.25 ± 0.10	1.30 ± 0.12
0.30	3.75 ± 0.35	3.90 ± 0.35
k_0, s^{-1}	(3.80 ± 9.80) . 10^{-7}	(2.10 ± 7.80) . 10^{-7}
k_a, *dm*^{3} mol^{-1} s^{-1}	(1.23 ± 0.06) . 10^{-4}	(1.29 ± 0.05) . 10^{-4}

[a] Values $k = k_0 + k_a\,[\mathrm{H^+}]$ are averages of 3 measurements.

process involves formation of the trinuclear adduct (Eq. (*B*)) combined with linkage isomerization of the cyanide bridging group. The new polarographic wave is attributed to the 3-electron reduction of $[\mathrm{Cr(H_2O)_2NC\,(en)\,NO}]^+$ which is formed at the electrode sur- face by the cathodic reduction of Hg(II) bonded in the parent trinuclear adduct (Fig. 2, curve *b*).

The formation of the linkage isomer with Cr–NC–Hg bonds was also confirmed by an experiment in which a large excess of iodide was added to the solution of the adduct. Since the stability constant of $\mathrm{HgI_2}$ is much higher than that of $[\mathrm{Hg\{(CN)Cr(H_2O)_2\,(en)\,NO\}_2}]^{4+}$, the equilibrium of the reaction

$$[\mathrm{Hg\{(CN)Cr(H_2O)_2\,(en)\,NO\}_2}]^{4+} + 2\,\mathrm{I}^- \rightleftharpoons \mathrm{HgI_2} + 2\,[\mathrm{Cr(H_2O)_2NC\,(en)\,NO}]^+ \quad (D)$$

is shifted to the right and this reaction can be used for generation of the unstable linkage isomer in the solution bulk. The less stable Cr–NC isomer released isomerizes spontaneously to the more stable Cr–CN form.

$$[\mathrm{Cr(H_2O)_2NC\,(en)\,NO}]^+ \overset{k_s}{\rightleftharpoons} [\mathrm{Cr(H_2O)_2\,(en)\,NO}]^+ \qquad (E)$$

Addition of KI to the solution of $[\mathrm{Hg\{(CN)Cr(H_2O)_2\,(en)\,NO\}_2}]^{4+}$ led to changes in the polarograms. The wave corresponding to the reduction of the $[\mathrm{Cr(H_2O)_2NC\,(en)\,NO}]^+$ initially bonded in the adduct disappeared while a polarographic wave of $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ appeared, giving evidence of a complete transformation of $[\mathrm{Hg\{(CN)Cr(H_2O)_2\,(en)\,NO\}_2}]^{4+}$ to $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ via reactions (*D*) and (*E*).

An attempt was made to determine the rate of the spontaneous isomerization (Eq. (*E*)) by measuring the decrease in the limiting diffusion current at the potential of the plateau of the polarographic wave due to the unstable isomer, but since the spontaneous

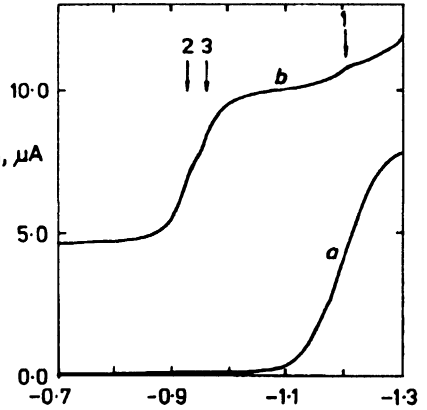

FIG. 2

Polarographic behaviour of the reacting solution of $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$ (1 mmol $\mathrm{dm^{-3}}$) with $\mathrm{Hg^{2+}}$ (0.5 mmol $\mathrm{dm^{-3}}$). $[\mathrm{H^+}] = 0.01$ mol $\mathrm{dm^{-3}}$; $I = 1$ mol $\mathrm{dm^{-3}}$ ($\mathrm{ClO_4^-}$, $\mathrm{Na^+}$, $\mathrm{H^+}$, $\mathrm{Hg^{2+}}$); $T = 298$ K; curves: *a* before $\mathrm{Hg^{2+}}$ addition; *b* 50 min after $\mathrm{Hg^{2+}}$ addition. Polarographic waves: 1 $[\mathrm{Cr(H_2O)_2CN\,(en)\,NO}]^+$; 2 $[\mathrm{Cr(H_2O)_2NC\,(en)\,NO}]^+$; 3 $[\mathrm{Cr(H_2O)_3\,en\,NO}]^{2+}$

isomerization is a fast process, polarography did not allow its rate constant to be quantitatively evaluated.

Addition of Ag^+ to the solution of $[Cr(H_2O)_2CN\ (en)\ NO]^+$ resulted in a similar polaro- graphic behaviour. Formation of $[Ag\{(CN)Cr(H_2O)_2\ (en)\ NO\}_2]^{3+}$ gives rise to a polaro- graphic wave with $E_{1/2} = -0.92$ V vs SCE, which is identical with that observed in the case of the Hg(II) adduct.

Kinetics of Decomposition of $[Hg\{(CN)Cr(H_2O)_2\ (en)\ NO\}_2]^{4+}$

Decomposition of the $[Cr(H_2O)_2CN\ (en)\ NO]^+$ adduct with Hg(II) is a relatively slow process leading to $Hg(CN)_2$.

$$[Hg\{CNCr(H_2O)_2\ (en)\ NO\}_2]^{4+} + 2\ H_2O \xrightarrow{k_6} 2\ [Cr(H_2O)_3\ (en)\ NO]^{2+} + Hg(CN)_2 \quad (F)$$

In our previous paper[5] the adduct decomposition rate for the similar chromium cyano complex $[Hg\{(CN)Cr(H_2O)\ (en)_2\}_2]^{6+}$ was evaluated based on the time change of the differential pulse voltammetry (DPV) peak current of the $[Cr(H_2O)_2\ (en)_2]^{3+}$ product. In the present case, however, the half wave potential of reduction of $[Cr(H_2O)_3\ (en)\ NO]^{2+}$, viz. −0.95 V vs SCE, is too close to the half wave potential of $[Cr(H_2O)_2NC\ (en)\ NO]^+$ (Fig. 2). Therefore the decomposition cannot be followed polarographically, and the time change of the absorption peak of $[Hg\{(CN)Cr(H_2O)_2\ (en)\ NO\}_2]^{4+}$ at 387 nm was employed to examine the rate of the adduct decomposition. In analogy with the reactions of the similar monocyano chromium complexes[1,5,7] with Hg^{2+}, the binuclear adduct can be expected to form at higher $c(Hg) : c(Cr)$ ratios:

$$[Hg\{CNCr(H_2O)_2\ (en)\ NO\}_2]^{4+} + Hg^2 \rightleftharpoons 2\ [Hg\{(CN)Cr(H_2O)_2\ (en)\ NO\}]^{3+} \quad (G)$$

Decomposition of the binuclear complex proceeds according to the equation

$$[Hg\{(CN)Cr(H_2O)_2\ (en)\ NO\}]^{3+} + H_2O \xrightarrow{k_8} [Cr(H_2O)_3\ (en)\ NO]^{2+} + HgCN^+ \quad (H)$$

The decrease in the adduct concentration obeys the monomolecular rate low. The rate constants for various Hg^{2+} and H^+ concentrations are given in Table II.

Table II demonstrates that the rate constant of adduct decomposition k is independent of the hydrogen ion concentration, which indicates that protonation of the bridging CN group is energetically unfavourable and substantially more difficult than the protonation of CN in $[Cr(H_2O)CN\ (en)_2]^{2+}$. This may be due to the high positive charge at the adduct, although the unfavourable electronic structure can play a role as well.

The decomposition rate constant is also independent of the Hg^{2+} concentration across the range of $c(Hg) = 0.005$ to 0.05 mol dm^{-3}. From this it can be deduced that tri- and binuclear adducts decompose at the same rate constants $k_6 = k_8 = k_d$.

Precipitate of AgCN appeared during the decomposition of $[Ag\{(CN)Cr(H_2O)_2(en)NO\}_2]^{3+}$, which complicated the spectrophotometric evaluation of the decomposition rate. The estimated rate constant is about 3 times lower than that for the corresponding Hg(II) adduct.

TABLE II
Rate constants of the decomposition reaction of the $[Cr(H_2O)_2CN(en)NO]^+$ adduct with Hg(II) for various H^+ and Hg^{2+} concentrations. $T = 298$ K, $I = 1$ mol dm^{-3} (ClO_4^-, Na^+, H^+, Hg^{2+})

$[H^+]$, mol dm^{-3}	$[Hg^{2+}]$, mol dm^{-3}	$k_d \cdot 10^4$, s^{-1}
$5 \cdot 10^{-1}$	$0.5 \cdot 10^{-3}$	0.50 ± 0.08
$5 \cdot 10^{-2}$	$0.5 \cdot 10^{-3}$	0.45 ± 0.06
$5 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	0.45 ± 0.04
$5 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$	0.42 ± 0.05
$5 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	0.49 ± 0.06
$5 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$	0.55 ± 0.08

[a] Initial $[Cr(H_2O)_2CN(en)NO]^+$ concentration $1 \cdot 10^{-3}$ mol dm^{-3}, values are averages of 3 measurements.

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