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Study of Cyanoaquonitrosyl Complexes of Chromium. III.[a] Formation of Adducts of $Cr(CN)(H_2O)_4NO^+$ with Ag^+ and Hg^{2+} and Their Decomposition

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The paper describes the conditions for the preparation of $Cr(CN)(H_2O)_4NO^+$*, its isolation in solution and its identification on the basis of the analysis of the components, spectrophotometric and elctrochemical properties and the kinetics of acid hydrolysis. The reactions of* $Cr(CN)(H_2O)_4NO^+$ *with* Ag^+ *and* Hg^{2+} *ions were studied from the point of view of the stoichiometry and equilibrium. The products of these reactions were characterized by the electronic absorption spectra and sorption on ion-exchangers. On the basis of the product properties, the course of the reactions and of analogous reactions, the structures characterized by groups Cr–N–C–Hg and Cr–N–C–Ag were proposed.*

The kinetics of the decomposition reactions of the $Cr(CN)(H_2O)_4NO^+$ *adducts with* Ag^+ *and* Hg^{2+}*, giving* $Cr(H_2O)_5NO^{2+}$ *and* $Hg(CN)_2$*, are described and the factors affecting them are discussed.*

Introduction

In the previous papers in this series [1, 2], the properties of the intermediate in the two-step hydrolysis of $Cr(CN)_2(H_2O)_3NO$ in strongly acidic media were described and the kinetics of its formation and decomposition were studied. On the basis of the stoichiometry of the hydrolysis reaction, the intermediate composition was found to be $Cr(CN)(H_2O)_4NO^+$.

The kinetic data obtained [2] were used for the preparation of the hydrolysis intermediate, its identification and investigation of its hydrolytic reaction and the reactions with Ag^+ and Hg^{2+} ions.

Experimental

Reagents

$[Cr(CN)(H_2O)_4NO]ClO_4$ was prepared in solution by acid hydrolysis of $Cr(CN)_5NO^{3-}$, determining the acid concentration and the duration of the hydrolysis (specified in the following procedure) by optimization on the basis of kinetic data [2]. A typical procedure involves dissolution of 0.6949 g $K_3Cr(CN)_5NO$ (2 mmol) in 50 ml of 0.2*M* $HClO_4$. The solution was allowed to stand for 30 min at room temperature and the reaction products (in addition to the substance to be prepared the solution contains predominantly $Cr(CN)_2(H_2O)_3NO$ and $Cr(H_2O)_5NO^{2+}$) were then separated on a strongly acidic cation-exchanger column (Dowex 50 W in the Na^+ cycle). The solution was diluted to twice the original volume and applied to the column. The column was washed with about 100 ml of 0.01*M* $NaClO_4$ (pH = 3), to elute the uncharged reaction products (*e.g.* $Cr(CN)_2(H_2O)_3NO$) and anions (*e.g.* CN^-). Product $Cr(CN)(H_2O)_4NO^+$ that formed a green band on the column was eluted by 0.4*M* $NaClO_4$ of pH = 3; $Cr(H_2O)_5NO^{2+}$ is not eluted by this solution. The stock solution (about 5–10 m*M*) was stored at pH 3 and the ionic strength of 0.4*M* $NaClO_4$, frozen at a temperature of about –70 °C. In this state the solution was stable for a long time. For exact measurements the solutions were, after melting, freed of small amounts of $Cr(H_2O)_5NO^{2+}$ by passing through a short cation-exchanger column ($Cr(H_2O)_5NO^{2+}$ is sorbed on Dowex 50 W).

Chromium was determined spectrophotometrically in the stock solution of $Cr(CN)(H_2O)_4NO^+$, after oxidation of the complex to chromate by hydrogen peroxide in an alkaline medium; this method was employed for the determination of the complex concentration in the stock solutions. Cyanide was determined polarographically after hydrolysis of the complex in 3*M* HCl and adjustment of the medium composition from the anodic wave of the formation of the CN^- complex with Hg^{2+}. This procedure indicated 97% of the theoretical amount of CN^- in the sample; consequently the molar ratio of chromium to cyanide is 1:1. When a $Cr(CN)(H_2O)_4NO^+$ solution in 1*M* $HClO_4$ was freed of HCN by three hour's passage of nitrogen, the visible absorption spectrum of the resultant solution was in excellent agreement with that of $Cr(H_2O)_5NO^{2+}$ [3, 4]. This

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[a] Part II in this series is ref. [1].

TABLE I. Comparison of Spectrophotometric, Voltammetric and Kinetic Properties of Isolated $Cr(CN)(H_2O)_4NO^+$ and the Intermediate of Acid Hydrolysis of $Cr(CN)_2(H_2O)_3NO$.[a]

Property	Intermediate	$Cr(CN)(H_2O)_4NO^+$
$\lambda_{max}(\epsilon_{max})$	303 nm (194 M^{-1} cm^{-1}) 370 nm (211 M^{-1} cm^{-1}) 450 nm (120 M^{-1} cm^{-1}) 610 nm (37.0 M^{-1} cm^{-1}) [2]	303 nm (197 M^{-1} cm^{-1}) 369 nm (217.0 M^{-1} cm^{-1}) 445 nm (123 M^{-1} cm^{-1}) 610 nm (37.5 M^{-1} cm^{-1})
E_p[b]	1.120 V *vs.* SCE	1.123 V *vs.* SCE
$E_{p/2}$	1.045 V *vs.* SCE	1.049 V *vs.* SCE
i_p/c	7.4×10^{-2} A M^{-1} [2]	7.5×10^{-2} A M^{-1}
K_p[c]	5.8 ± 0.6 M^{-1}	5.5 ± 0.3 M^{-1}
k_p	$(1.45 \pm 0.14) \times 10^{-3}$ s^{-1} [2]	$(1.38 \pm 0.1) \times 10^{-3}$ s^{-1}

[a] Data concerning the intermediate are taken from [1]; properties of $Cr(CN)(H_2O)_4NO^+$, this paper. [b] 25 °C, ionic strength 1 M (ClO_4^-, Na^+, H^+), paraphine impregnated graphite disc electrode; electrode area 0.247 cm^2; scan rate 1.25×10^{-2} V s^{-1}; c, analytical concentration of the complex. [c] Rate law of acid hydrolysis of $Cr(CN)(H_2O)_4NO^+$ (valid in both cases) $k_{obs} = k_pK_p[H^+]/(1 + K_p[H^+])$; 25 °C, ionic strength 2 M (ClO_4^-, Na^+, H^+).

solution (which contained 2.5 mmol. Cr) was simultaneously analyzed for nitrogen. To a sample in a strongly acidic solution was added pulverized zinc, the solution was heated until the original red–brown colour disappeared and then cooled. An excess of NaOH was added and the NH_3 liberated was distilled with water vapour into a flask containing a standard H_2SO_4 solution. The back-titration verified the 1:1 ratio of chromium to the non-cyanide nitrogen (the analytical results were 4% higher than the theoretical value). The other chemicals used were of *p.a.* purity and were not purified further.

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.

Voltammetric (and polarographic) measurements were carried out on an OH-102 polarograph (Radelkis, Budapest). The dropping mercury electrode had a mercury flow-rate of 1.65 mg s^{-1} and a drop time of 4.3 s (at a mercury reservoir height of 64 cm and in a short circuit with a saturated calomel electrode).

Results and Discussion

$Cr(CN)(H_2O)_4NO^+$

The solution prepared by the procedure described in the experimental part was found identical with the intermediate of acid hydrolysis of $Cr(CN)_2(H_2O)_3NO$ on comparison of the absorption spectra (the maximum wavelengths and the molar absorption coefficients), the voltammetric properties (peak potential E_p, half-peak potential $E_{p/2}$ and peak current i_p) and the kinetics of acid hydrolysis (protonation equilibrium constant K_p and rate constant for the substitution of the protonated form, k_p). Table I shows that the corresponding parameters agree well.

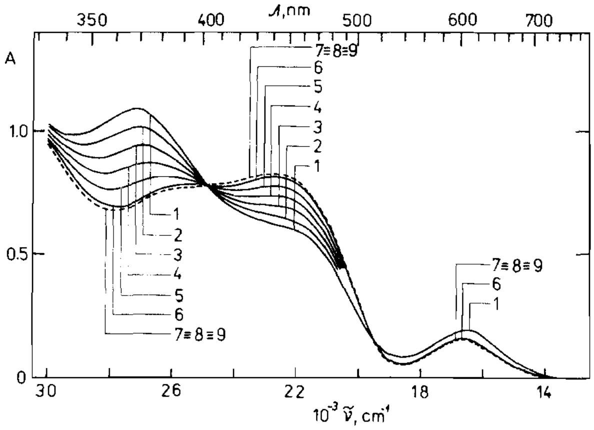

Figure 1. Absorption spectra of reacted solutions of $Cr(CN)(H_2O)_4NO^+$ with Hg^{2+}; 25 °C, ionic strength 1M (ClO_4^-, Na^+, H^+, Hg^+); $[H^+] = 0.01M$; light path length 5 cm; recording time 2.2 min; initial concentration of $[Cr(CN)(H_2O)_4NO^+]$ = 1 mM; initial concentration Hg^{2+}: 0 mM-curve 1, 0.1 mM - curve 2, 0.2 mM - curve 3, 0.3 mM - curve 4, 0.4 mM - curve 5, 0.5 mM - curve 6, 0.75 mM - curve 7, 1.0 mM - curve 8, 10 mM - curve 9.

The only product of acid hydrolysis of the prepared complex containing Cr was $Cr(H_2O)_5NO^{2+}$. The charge of $Cr(CN)(H_2O)_4NO^+$ was determined from the velocity of the movement of its band on the cation-exchanger column (Dowex 50 W).

Stoichiometry of the $Cr(CN)(H_2O)_4NO^+$ Reaction with Hg^{2+} and Ag^+

$Cr(CN)(H_2O)_4NO^+$ reacts with ions of heavy metals and these reactions are accompanied by changes in the visible spectra. This is illustrated in Fig. 1 for additions of Hg^{2+} to a $Cr(CN)(H_2O)_4NO^+$ solution. It can be seen from the figure that pronounced spectral changes take place up to a molar ratio of [Hg]/[Cr] = 0.5 (curves 1–6) and then the spectrum changes only little (curves 7–9). These changes in the spectrum indicate the stoichiometry of the reaction.

From the analogy with the described reactions of $Cr(CN)(H_2O)_5^{2+}$ [5, 6], $Co(NH_3)_5CN^{2+}$ [7] and $Cr(H_2O)_5NCS^{2+}$ [8] with Hg^{2+}, the following scheme can be proposed for the reaction studied,

$$2NO(H_2O)_4Cr\text{-}CN^+ + Hg^{2+} \rightleftharpoons \{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+} \qquad (1)$$

The reaction with Ag^+ is analogous,

$$2\,NO(H_2O)_4Cr\text{-}CN^+ + Ag^+ \rightleftharpoons \{NO(H_2O)_4Cr\text{-}NC\}_2Ag^{3+} \qquad (2)$$

In this case association of two ions of the same polarity is facilitated by the fact that one of the reactants contains a bidentate ligand in which there is a donor atom with the character of a strong base and a donor atom with the character of a weak base, capable of simultaneous interaction with both metal ions with the characters of a strong and a weak Lewis acid. Such an interaction is responsible for the relatively high stability of the highly positively charged ion, $CrNCSHg^{4+}$ [8]. The high stability of cyanide complexes is caused by strong Hg–C interaction that necessitates bond isomerization of the more stable Cr–CN isomer to the less stable Cr–NC isomer, connected with the formation of adduct 1.

Reaction 1 is slow, evidently because of the necessary Hg^{2+}-assisted bond isomerization and the spectrum (Fig. 1) can only be recorded several minutes after addition of Hg^{2+}. However, after stabilization of the spectrum no other changes occur at rates comparable with the stabilization rate.

A very slow change in the spectrum of the polynuclear complex does not significantly affect the stabilization and is ascribed to the following reaction on the basis of the analysis of the products,

$$\{NO(H_2O)_4Cr\text{-}NC\}_2Hg^{4+} + 2\,H_2O \longrightarrow Hg(CN)_2 + 2Cr(H_2O)_5NO^{2+} \qquad (3)$$

Hence the visible spectrum containing three bands with maxima described by the following wavelengths and molar absorption coefficients, 392 nm (157 M^{-1} cm^{-1}), 445 nm (163 M^{-1} cm^{-1}), and 603 nm (32.5 M^{-1} cm^{-1}), can be ascribed to the trinuclear adduct on the right-hand side of eq. 1.

The comparison of the bands in the visible spectra of the adduct and of $Cr(CN)(H_2O)_4NO^+$ [1] shows the changes caused by the bond isomerization of CN combined with coordination of a heavy metal ion. The first adduct band (counted from lower energies to higher) is slightly shifted to higher energies (16.4×10^3 cm^{-1} → 16.6×10^3 cm^{-1}), the second has practically the same energy (22.5×10^3 cm^{-1}) and the third is strongly shifted to lower energies (27.1×10^3 cm^{-1} → 25.5×10^3 cm^{-1}). These changes can be explained on the basis of the orbital energy diagram calculated by Manoharan and Gray [9] for complexes of the $[M(CN)_5NO]$ type. This diagram has further been modified [10] and used also for interpretation of the spectra of cyanoaquonitrosyl complexes of chromium. The energy level in the diagram increases in the order, $6e < 2b_2 < 7e < 3b_1$ (only the energy levels required for assignment of the three absorption bands in the visible spectrum are considered). The first band of $Cr(CN)(H_2O)_4NO^+$ is ascribed to the $6e \rightarrow 2b_2$ transition, the second to the $6e \rightarrow 7e$ transition and the third to the $2b_2 \rightarrow 3b_1$ transition. The bond isomerization accompanying the formation of the adduct causes a decrease in two components of the ligand field strength, namely, that following from the ligand–central atom σ-interaction and that following from the central atom → ligand π-interaction. The N-bonded cyanide ion has a larger π-acceptor and a smaller σ-donor ability [11] than the C-bonded ion. This increased π-acceptor ability of the ligand results in an increase in the energy of the 6e, $2b_2$ and 7e levels, whereas the energy of the $3b_1$ level remains unchanged. A change in the σ-bond affects, on the other hand, predominantly the $3b_1$ level by decreasing its energy (however, the change in the $3b_1$ level is substantially smaller than the changes in the 6e, $2b_2$ and 7e energies due to the change in the π-acceptor ability). The decrease in the $3b_1$ energy level and the increase in the $2b_2$ energy level gives rise to the pronounced shift of the third band to lower energies. The changes in the energies of the 6e, $2b_2$ and 7e levels due to bond isomerization are roughly equal, as follows from the independence of the first and second band energies of the isomerization.

The stoichiometry of the reaction of $Cr(CN)(H_2O)_4NO^+$ with Hg^{2+} and Ag^+ was also examined by potentiometric titration of $Cr(CN)(H_2O)_4NO^+$ with heavy metal ions.

Typical titration curves are given in Fig. 2. Similar to the spectrophotometric experiments, the potential stabilization required a certain time after each addition of the heavy metal ion. To avoid the effect of the above slow reaction, 3, each point on 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. 3 is much slower with Ag(I), this

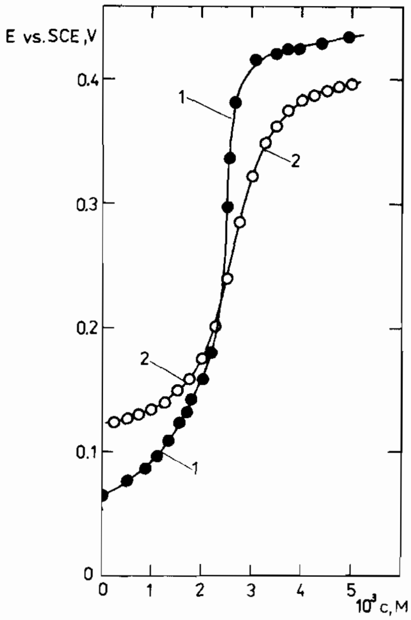

Figure 2. Potentiometric titrations of $Cr(CN)(H_2O)_4NO^+$ with Hg^{2+} and Ag^+; curve 1 - 0.5 m*M* $Cr(CN)(H_2O)_4NO^+$, ionic strength 1*M* (ClO_4^-, Na^+, H^+), $[H^+] = 0.01M$ - titrated with Hg^{2+} (concentration given in abscissa); curve 2 - 0.5 m*M* $Cr(CN)(H_2O)_4NO^+$, ionic strength 1*M* (ClO_4^-, Na^+, H^+), $[H^+] = 0.01M$ - titrated with Ag^+ (concentration given in abcissa).

procedure was unnecessary in titrations with Ag^+. The molar ratios corresponding to the inflection points on the potentiometric titration curves (Fig. 2) indicate the formation of trinuclear complexes.

The stoichiometry of the reaction of $Cr(CN)(H_2O)_4NO^+$ with the above heavy metal ions was further studied by amperometric titration. The indicator electrode potential was selected so that 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. Fig. 3 shows that the current increases linearly with increasing concentration of the heavy metal ion up to a molar ratio of the heavy metal ion to $Cr(CN)(H_2O)_4NO^+$ equal to 0.5. The proportionality coefficient of this linear dependence is the Ilkovič constant* for the given trinuclear adduct. On a further increase in $[Hg^{2+}]$ and $[Ag^+]$, the following reactions take place,

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

or

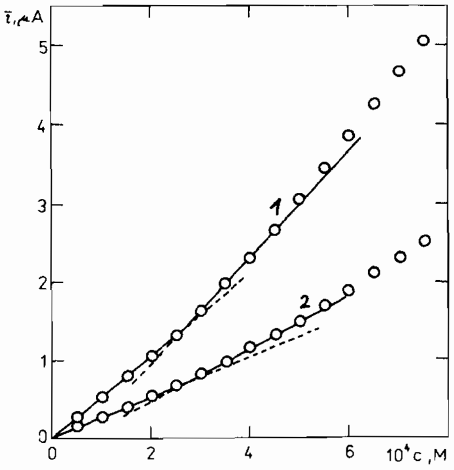

Figure 3. Amperometric titration of 0.5 m*M* $Cr(CN)(H_2O)_4NO^+$ with Hg^{2+} (curve 1) and Ag^+ (curve 2). Concentration of heavy metal ion indicated in abcissa.

$$\{NO(H_2O)_4CrNC\}_2Ag^{3+} + Ag^+ \rightleftharpoons 2\ NO(H_2O)_4CrNCAg^{2+} \qquad (5)$$

or Hg^{2+} or Ag^+ are concentrated, causing a sharper current increase with increasing heavy metal ion concentration at molar ratios higher than 0.5 (Fig. 3). A higher value of the diffusion coefficient for the product of reaction 4 and for Hg^{2+}, compared with that for $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ (and analogously for silver) that follows from the shape of the curves in Fig. 3, is in agreement with the expected situation. The position of the breaks on the titration curves also supports the assumption that trinuclear adducts are formed.

The effect of reaction 3 on the amperometric titrations was avoided in the same way as in the potentiometric titration.

The stoichiometry of the adduct formation was also indirectly studied by the determination of the adduct charge. The complex is deposited on the Dowex 50-WX4 cation-exchanger from the reacted solution containing 2 m*M* $Cr(CN)(H_2O)_4NO^+$ and 1 m*M* Hg^{2+} (an ionic strength of 0.1 *M*). The green band of the complex is not eluted by 0.8*M* $NaClO_4$ with pH 2 adjusted by $HClO_4$ ($Cr(H_2O)_5NO^{2+}$ is readily eluted from the cation-exchanger by this solution), but moves slowly through the column with 2*M* $NaClO_4$. The velocity of the band movement is lower than in the elution of $Cr(H_2O)_6^{3+}$ with 2*M* $NaClO_4$.

This experiment suggests that the positive charge of the complex is probably higher than 3+, which supports the composition given by eq. 1.

Stability of Binuclear and Trinuclear Adducts

The potentiometric titration was used for the calculation of the equilibrium constants for the adduct

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See J. Heyrovský and J. Kůta, "Principles of Polarography", Publ. House of the Czechoslov. Acad. of Sci., Prague 1965, p. 84.

TABLE II. Equilibrium Constants of Adducts of $Cr(CN)(H_2O)_4NO^+$ with Ag^+ or Hg^{2+}; 25 °C, Ionic Strength 1 M (ClO_4^-, Na^+, H^+), $[H^+] = 0.01$ M.

Reaction	Equilibrium Constant	Reaction	Equilibrium Constant
1	$K_1 = (2.3 \pm 0.5) \times 10^{16}$ M^{-2}	6	$K_6 = (6 \pm 2) \times 10^3$ M^{-1}
2	$K_2 = (4.3 \pm 0.5) \times 10^8$ M^{-2}	7	$K_7 = (7 \pm 3) \times 10^4$ M^{-1}
4	$K_4 = (6.7 \pm 0.2)$	8	$K_8 = (4 \pm 1) \times 10^8$ M^{-1}
5	$K_5 = (8 \pm 4) \times 10^{-2}$	9	$K_9 = (6 \pm 2) \times 10^7$ M^{-1}

TABLE III. Rate Constants for the Aquation of Adducts of $Cr(CN)(H_2O)_4NO^+$ with Hg^{2+} for Different Hg^{2+} and H^+ Concentrations; 20 °C, Ionic Strength 1 M (ClO_4^-, Na^+, H^+, Hg^{2+}); Initial Adduct Concentration 1 mM.

$[H^+]$, M	$[Hg^{2+}]$, M	$10^4 \times k_a$, s^{-1}	$[H^+]$, M	$[Hg^{2+}]$, M	$10^4 \times k_a$, s^{-1}
5×10^{-1}	10^{-3}	1.94 ± 0.15	5×10^{-2}	3×10^{-3}	2.01 ± 0.15
5×10^{-2}	10^{-3}	2.03 ± 0.15	5×10^{-2}	5×10^{-3}	1.94 ± 0.15
5×10^{-3}	10^{-3}	1.88 ± 0.15	5×10^{-2}	1×10^{-2}	1.91 ± 0.15
5×10^{-2}	5×10^{-4}	1.95 ± 0.15	5×10^{-2}	2×10^{-2}	2.00 ± 0.15
5×10^{-2}	7×10^{-4}	2.02 ± 0.15	5×10^{-2}	3×10^{-2}	1.89 ± 0.15
5×10^{-2}	8×10^{-4}	1.96 ± 0.15	5×10^{-2}	5×10^{-2}	1.98 ± 0.15
5×10^{-2}	2×10^{-3}	1.89 ± 0.15	5×10^{-2}	1×10^{-1}	1.97 ± 0.15

formation, employing the common procedure described in ref. [12]. From the equilibrium constants for reactions 1, 2, 4 and 5, the equilibrium constants of the following reactions can readily be calculated:

$$Cr(CN)(H_2O)_4NO^+ + Ag^+ \rightleftharpoons NO(H_2O)_4CrNCAg^{2+} \quad (6)$$

$$Cr(CN)(H_2O)_4NO^+ + NO(H_2O)_4CrNCAg^{2+} \rightleftharpoons \{NO(H_2O)_4CrNO\}_2Ag^{3+} \quad (7)$$

$$Cr(CN)(H_2O)_4NO^+ + Hg^{2+} \rightleftharpoons NO(H_2O)_4CrNCHg^{3+} \quad (8)$$

$$Cr(CN)(H_2O)_4NO^+ + NO(H_2O)_4CrNCHg^{3+} \rightleftharpoons \{NO(H_2O)_4CrNC\}_2Hg^{4+} \quad (9)$$

The results are summarized in Table II.

It can be seen from the table that the stability constants of the Hg adducts are higher than those of the Ag adducts. From this it follows that the Coulomb interaction of the components cannot play a decisive role in their formation. This is also verified when the stability constants are compared with those for the cyanide chromium complex without nitrosyl – $Cr(H_2O)_5CN^{2+}$ [7]; the latter constants for Hg^{2+} are somewhat lower and those with Ag^+ somewhat higher than the corresponding values for the nitrosyl complexes. The stability constants for the Hg complexes are in both cases higher than those for the Ag complexes, which indicates that the bond of the heavy metal ion to the bridging CN ligand plays a substantial role (probably the Hg–C or Ag–C σ-bond).

Decomposition of the $Cr(CN)(H_2O)_4NO^+$ adducts with Hg^{2+}

As already mentioned, the $Cr(CN)(H_2O)_4NO^+$ adducts with Hg^{2+} undergo the relatively slow reaction in which $Cr(H_2O)_5NO^{2+}$ and $Hg(CN)_2$ or $Hg(CN)^+$ are formed. This reaction is expressed by eq. 3 for the trinuclear adduct; for the binuclear adduct it can be formulated as follows,

$$NO(H_2O)_4CrNCHg^{3+} + H_2O \longrightarrow Cr(H_2O)_5NO^{2+} + HgCN^+ \quad (10)$$

A product of this reaction, $Cr(H_2O)_5NO^{2+}$, was identified from the absorption spectrum of the reacted solution and from analysis on a cation-exchanger column. Reactions 3 and 10 were studied using the time-changes of the absorbance at 430 nm. It has been found that the reaction obeys the first-order kinetics,

$$-d[\text{adduct}]/dt = d[Cr(H_2O)_5NO^{2+}]/dt = k_a[\text{adduct}] = k_a[Cr(CN)(H_2O)_4NO^+] \quad (11)$$

The last equality is valid because the high value of constant K_1 ensures virtually quantitative conversion of $Cr(CN)(H_2O)_4NO^+$ into an adduct (1:2 or

1:1) for molar concentrations [Hg] $\geqq$ 0.5 [Cr(CN)-$(H_2O)_4NO^+$]. As these are slow reactions, the rate constants were obtained from the slopes of the Guggenheim dependences and the common kinetic evaluation using the known absorbance of the solution after reaction was carried out only in certain selected kinetic experiments. The values obtained by the two procedures agreed well.

The rate constants are given in Table III for various concentrations of mercury and hydrogen ions. It can be seen from the table that the rate constant of aquation, k_a, is independent of the hydrogen ion concentration for [Hg^{2+}] > 0.5 [$Cr(CN)(H_2O)_4NO^+$]. The adduct formation prevents acid catalyzed aquation of $Cr(CN)(H_2O)_4NO^+$ described in the first part of this work as a reaction parallel with the studied reaction 3 or 10. The concentration of this substance in the reacting solution is very low at the above concentration ratio, [Hg^{2+}]/[$Cr(CN)(H_2O)_4$-NO^+]. The independent adduct aquation rate indicates that protonation of the bridging CN group is energetically unfavourable (substantially more difficult than protonation of the CN in Cr(CN)-$(H_2O)_4NO^+$). This is caused by the high positive charge on the adduct, but also by the unfavourable electronic structure.

The rate constant does not change even with a variation in [Hg^{2+}] over a wide range of 0.1M > Hg > 0.0005M (with 1 mM of $Cr(CN)(H_2O)_4NO^+$). From its constancy at [Hg^{2+}] > 5 mM it can be concluded that the decomposition rate of the binuclear adduct is independent of the presence of excess Hg^{2+}. It can be assumed from stability constants K_8 and K_9 that in a concentration range of 5 mM > [Hg^{2+}] > 0.5 mM (1 mM $Cr(CN)(H_2O)_4NO^+$) the bi- and trinuclear complexes are present in the solution in comparable concentrations. Hence the aquation in this Hg^{2+} concentration range must be considered as the sum of parallel aquation of the bi- and trinuclear adducts. The constancy of the rate constant (within experimental error, Table III) indicates that dissociation of $Cr(H_2O)_5NO^{2+}$ from the bi- and trinuclear complex proceeds at the same rates. As these are chemically analogous reactions of two ions differing in their charges, it should be concluded that the decomposition rate is not determined by Coulomb interactions.

The study of the decomposition of the adducts with Ag^+ using spectral measurements is complicated by the formation of AgCN turbidity. Orientative experiments based on polarographic monitoring have shown that the rate of decomposition of the Ag^+ adducts is substantially (more than 10 times) lower than that for Hg^{2+}. The same order of the aquation rate constants was found in ref. [12] for the Cr(CN)-$(H_2O)_5^{2+}$ adducts with Hg^{2+} and Ag^+.

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