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Study of Cyanoaquonitrosyl Complexes of Chromium. VI.* Study of the $NO(H_2O)_4Cr{-}NC{-}Hg^{3+}$ Formation Kinetics and of the $NO(H_2O)_4Cr{-}NC^+$ Isomerization

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It has been found from a kinetic and spectrophotometric study that the formation of $NO(H_2O)_4Cr{-}NC{-}Hg^{3+}$ *involves two steps: 1) rapid equilibrium association of* $NO(H_2O)_4Cr{-}CN^+$ *with* Hg^{2+} *(the equilibrium constant* $K = (7.2 \pm 0.8) \times 10^2$ M^{-1} *for 278 K, an ionic strength of 1*M *and* $[H^+] = 0.1$ M*); 2) the rate-determining step, independent of* $[Hg^{2+}]$*, with a rate constant of* $k = 6.0 \times 10^{-2}$ s^{-1} *for 278 K, an ionic strength of 1* M *and* $[H^+] = 0.1$ M*. The spectrophotometric measurements extrapolated to the instant of mixing of the reactants verify the formation of the associate and enable the calculation of the equilibrium constant in good agreement with the value obtained kinetically, as well as the construction of the intermediate visible spectrum.*

It has been found that the rate of the $NO(H_2O)_4Cr{-}NC^+$ *isomerization to the more stable* $NO(H_2O)_4Cr{-}CN^+$ *is pH-dependent, as the isomerization rate constant for the reactant protonated form,* k_p*, is given by* $k_p < 0.05\, k_n$*, where* $k_n = (26 \pm 2) \times 10^{-2}$ s^{-1} *is the isomerization rate constant for the unprotonated form at 293.16 K and an ionic strength of 1* M*. The equilibrium constant for this protonation is* $Q_p = [NO(H_2O)_4Cr{-}NCH^{2+}]/[NO(H_2O)_4Cr{-}NC^+][H^+] = 45 \pm 4$ M^{-1} *for the above conditions. The* $NO(H_2O)_4Cr{-}NC^+$ *visible spectrum was also obtained.*

The two reactions studied are discussed from the point of view of the common mechanistic features and are compared with analogous reactions of cyanochromium(III) complexes that do not contain the NO ligand.

Introduction

In the previous papers of this series [1–3], the stoichiometry of the complexes of Ag^+ and Hg^{2+} with $NC{-}Cr(H_2O)_4NO^+$ and their formation equilibrium constants were described. Detailed information on the electrode redox reactions of these substances was further given. The properties of these polynuclear complexes and their chemical and electrochemical reactivity indicate that the cyanide is the bridge ligand between Hg and Cr, the stable form containing the Hg–CN–Cr arrangement. Therefore, bond isomerization of the cyanide ligand must occur during the formation of these polynuclear complexes [1–3].

The present paper deals with the kinetics and mechanism of the Hg^{2+} reaction with $NO(H_2O)_4Cr{-}CN^+$ and of the $NO(H_2O)_4Cr{-}NC^+$ isomerization, with the emphasis placed on the relationships between the two reactions.

Experimental

Chemicals

The preparation and purification of $NO(H_2O)_4Cr{-}CN^+$ and of its adducts with Hg^{2+} have been described elsewhere [2]. The other chemicals used were of the R.G. purity and were not further purified.

Kinetic Measurements

It follows from the potentiometric measurements [2] that $NO(H_2O)_4Cr{-}CN^+$ reacts with Hg^{2+} at a molar ratio of 1:2, if $[Hg^{2+}]$ is small compared with $[NO(H_2O)_4CrCN^+]$ (Eqs. (1) and (2)). With higher $[Hg^{2+}]$ a 1:1 product is formed (Eq. (1)).

$$Hg^{2+} + NO(H_2O)_4Cr{-}CN^+ \rightleftharpoons NO(H_2O)_4Cr{-}NCHg^{3+} \qquad (1)$$

$$NO(H_2O)_4Cr{-}NCHg^{3+} + NO(H_2O)_4Cr{-}CN^+ \rightleftharpoons \{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+} \qquad (2)$$

The kinetics of these reactions were followed by evaluating

1) the time-dependence of the reacting solution absorbance,

2) the time-changes in the limiting diffusion current of Hg(II) at a potential at which no Cr-containing component is reduced (*e.g.* –0.5 V *vs.* SCE) [3]; Hg(II) is bound into the complex with a lower diffusion coefficient than that of Hg^{2+} aq ion;

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*Part V in this series is ref. [1].

TABLE I. Pseudo-First Order Rate Constants for the Reaction of $NO(H_2O)_4Cr–CN^+$ with Hg^{2+} at ionic strength 1.00 M (ClO_4^-, H^+, Na^+, Hg^{2+}); $[NO(H_2O)_4–CN^+]_0 \leq 0.1\ [Hg^{2+}]_0$.

$[Hg^{2+}]$ mM	$[H^+]$ M	T K	$10^2 \times k^a_{obs}$ s^{-1}	$[Hg^{2+}]$ mM	$[H^+]$ M	T K	$10^2 \times k^a_{obs}$ s^{-1}
300	0.1	278	6.14	40	0.5	278	5.78
300	0.1	278	5.92	40	0.5	278	5.72
100	0.1	278	5.82	40	0.5	278	5.82
40	0.1	278	5.75	40	0.5	278	5.82
27	0.1	278	5.78	2.5	0.5	278	3.73
23	0.1	278	5.62	2.5	0.5	278	3.79
20	0.1	278	5.68	2.5	0.5	278	3.72
10	0.1	278	5.37	2.5	0.5	278	3.69
10	0.1	278	5.23	40	0.02	278	5.75
5	0.1	278	4.74	40	0.02	278	5.72
5	0.1	278	4.67	40	0.02	278	5.82
2.5	0.1	278	3.91	40	0.02	278	5.65
2.5	0.1	278	3.83	2.5	0.02	278	3.79
2.5	0.1	278	3.78	2.5	0.02	278	3.85
2.0	0.1	278	3.62	2.5	0.02	278	3.82
2.0	0.1	278	3.54	2.5	0.02	278	3.70
2.0	0.1	278	3.47	25	0.1	279	5.76
1.25	0.1	278	2.91	25	0.1	280	6.61
1.25	0.1	278	2.88	25	0.1	282	7.51
1.25	0.1	278	2.83	25	0.1	284	9.06
1.0	0.1	278	2.58	25	0.1	287	11.44
1.0	0.1	278	2.47	25	0.1	289	13.62

[a] $k_{obs} = -d\ln[NO(H_2O)_4Cr–CN^+]/dt$.

3) the time-changes in the limiting diffusion current of $NO(H_2O)_4Cr–NC^+$ [3]; this procedure was chiefly used in the study of the Cr–N isomerization to the Cr–C isomer.

The two polarographic procedures, 2) and 3), are less suitable because of a high excess of Hg(II) required, as small variations of the current have to be followed superimposed on a high constant value (the method was used mainly in ref. [4]). In the study of the $NO(H_2O)_4Cr–NC^+$ isomerization the excess of Hg(II) is not large and procedure 3) is advantageous. The relatively rapid changes of the mean diffusion current were monitored with a dropping mercury indicator electrode connected to a device for controlling the drop-time (about 1 s) with maintainment of a low mercury flow-rate (1.6 mg s^{-1} at a mercury column height of 64 cm). The measurement was carried out with an OH-102 polarograph and an OH-991 test-rapid adaptor (Metrimpex, Hungary).

Most of the results given in this paper were obtained by using procedure 1) (the necessary excess of colourless Hg(II) does not interfere here). The rate constant measured was independent of the wavelength; most measurements were carried out at 370 nm on a Specord UV–VIS recording spectrophotometer (Zeiss, Jena, GDR).

Results

Kinetics of the $HgCNCr(H_2O)_4NO^{3+}$ Complex Formation

Excess Hg^{2+} was present in all experiments, so that a single complex, $HgCNCr(H_2O)_4NO^{3+}$, was practically present. The large Hg^{2+} excess (10 times the concentration of the chromium complex) simultaneously ensured the conditions for pseudomonomolecular formation of $HgCNCr(H_2O)_4NO^{3+}$. As the rate of reaction (1) attained too large values for classical recording of the absorbance with the instrument specified in the experimental part at laboratory temperature, most dependences had to be measured at a decreased temperature. The rate constants measured, defined as $-d\ln[NO(H_2O)_4CrCN^+]/dt$, are given in Table I for various reactant concentrations, $[H^+]$ and temperatures.

It should be pointed out that the overall rate constants obtained include, in addition to the reaction studied, other parallel reactions undergone by $NO(H_2O)_4CrCN^+$ in the given medium.

First of all it must be taken into consideration that the Cr-containing reactant occurs in two isomeric forms in solution,

$$NO(H_2O)_4CrCN^+ \underset{}{\overset{k_i}{\rightleftharpoons}} NO(H_2O)_4CrNC^+ \qquad (3)$$

(equilibrium constant Q_i)

Only the Cr–CN form is a reactant for the reaction studied; the Cr–NC form reacts very rapidly to give a product identical with that of the main (studied) reaction [1],

$$NO(H_2O)_4Cr\text{–}NC + Hg^{2+} \rightleftharpoons NO(H_2O)_4Cr\text{–}NCHg^{3+} \qquad (4)$$

(very fast)

The decrease in the Cr–CN reactant concentration owing to slow equilibrium (3) can be neglected under the given experimental conditions. The Cr-containing ractant is stored in a stock solution at $[H^+] = 10^{-3}\,M$, where equilibrium (3) is strongly shifted to the left [1]. A parallel reaction sequence (Eqs. (3) and (4)) is connected with reaction (3). The extent of the effect of reaction (3) is given by the k_i value, which can be calculated from the known value of Q_i [1] and the rate constant for the spontaneous isomerization at the given $[H^+]$. The k_i value never exceeds $3 \times 10^{-4}\ s^{-1}$, from which it follows that this reaction path is negligible, as it does not amount to more than 1–2% of the total reaction under the conditions of the kinetic measurements performed.

Another competitive reaction path is the acid hydrolysis of $NO(H_2O)_4Cr\text{–}CN^+$,

$$NO(H_2O)_4Cr\text{–}CN^+ + H^+ \rightleftharpoons NO(H_2O)_4Cr\text{–}CNH^{2+}\ (fast) \qquad (5)$$

(equilibrium constant K_5)

$$NO(H_2O)_4Cr\text{–}CNH^{2+} + H_2O \xrightarrow{k_5} (H_2O)_5CrNO^{2+} + HCN \qquad (6)$$

However, in solutions with $[H^+] \leqslant 0.5$ this reaction path does not represent more than 3% of the total reaction of $NO(H_2O)_4CrCN^+$ [2, 5].

It can be seen from Table I that the rate constant measured at constant $[H^+]$ and temperature increases with increasing $[Hg^{2+}]$ in the region of low $[Hg^{2+}]$ values and approaches a constant value for larger $[Hg^{2+}]$. This dependence can be explained by the existence of an equilibrium step preceding the rate-determining step,

$$NO(H_2O)_4Cr\text{–}CN^+ + Hg^{2+} \overset{K}{\rightleftharpoons} A \qquad (7)$$

$$A \xrightarrow{k} NO(H_2O)_4Cr\text{–}NCHg^{3+} \qquad (8)$$

Scheme (7, 8) obeys the rate law given by

$$-\frac{d[NO(H_2O)_4Cr\text{–}CN^+]}{dt} = \frac{kK[Hg^{2+}]}{1 + K[Hg^{2+}]}[NO(H_2O)_4Cr\text{–}CN^+] \qquad (9)$$

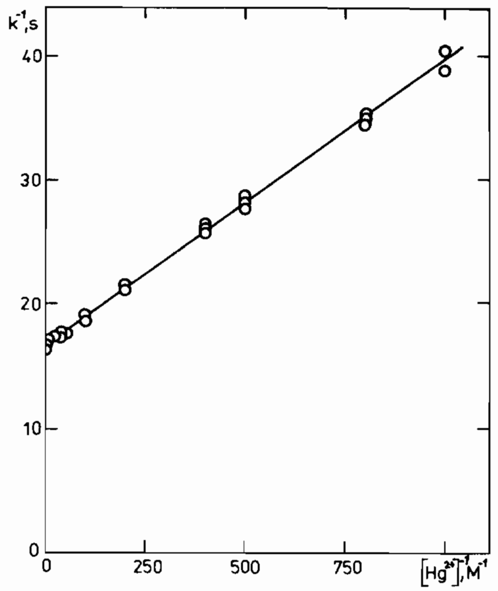


Figure 1. Plot of kinetic data for $[H^+] = 0.1\,M$ at 278 K and ionic strength 1 M (ClO_4^-, Na^+, H^+, Hg^{2+}) in coordinates according to equation 10.

from which the relationship for the rate constant measured follows,

$$k_{obs} = \frac{kK[Hg^{2+}]}{1 + K[Hg^{2+}]} \qquad (10)$$

It follows from Eq. (10) that k_{obs}^{-1} is a linear function of $[Hg^{2+}]^{-1}$. The values from Table I, corresponding to $[H^+] = 0.1\,M$ and a temperature of 278 K, were plotted in these coordinates in Fig. 1. The linear dependence verifies the validity of scheme (7, 8). It also follows from Eq. (10) that the intercept of the k_{obs}^{-1} *vs.* $[Hg^{2+}]^{-1}$ linear dependence with the k_{obs}^{-1}-axis has the value, k^{-1}, and the slope the value, $(kK)^{-1}$. Hence the dependences plotted according to Fig. 1 enable the calculation of the equilibrium constant of reaction (7) and the rate constant of reaction (8). The values thus obtained for various values of $[H^+]$ are given in Table II.

Rate constants k_{obs} given in Table I for various temperatures at a constant $[H^+] = 0.1\,M$ can be considered practically equal to the k values (a high concentration of Hg^{2+}). The activation energy for reaction (8) was calculated from them, $\Delta H^{\neq} = 13.7$ kcal/mol for $[H^+] = 0.1\,M$ and an ionic strength of 1 M (ClO_4^-, Na^+, H^+, Hg^{2+}).

Formation and Properties of Intermediate A

Equilibrium (7) can be studied more deeply by extrapolating the absorbance time-dependences to the

TABLE II. Equilibrium and Rate Constants for Reactions (7) and (8), resp. Ionic Strength I = 1 M (ClO_4^-, H^+, Na^+ Hg^{2+}).

$[H^+]$ M	T K	K M^{-1}	k s^{-1}	Number of Kinetic Runs
0.02	278	$(7.1 \pm 0.8) \times 10^2$	5.9×10^{-2}	8
0.10	278	$(7.2 \pm 0.8) \times 10^2$	6.0×10^{-2}	22
0.50	278	$(6.6 \pm 0.8) \times 10^2$	6.05×10^{-2}	8

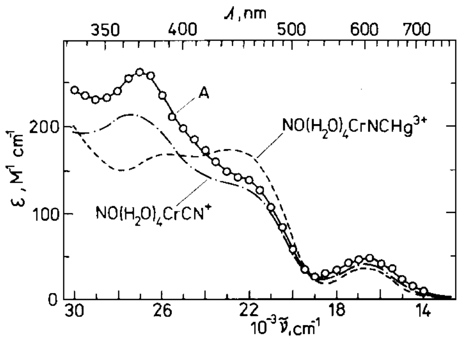


Figure 2. Absorption spectra of reactant, $NO(H_2O)_4CrCN^+$, intermediate, A, and product $NO(H_2O)_4CrNCHg^{3+}$ of reaction (7) and (8). Experimental points of the spectrum A were obtained by extrapolation to the time of mixing the reactant with Hg^{2+}; 278K; $[H^+]$ = 0.1 M; I = 1 M (ClO_4^-, H^+, Na^+, Hg^{2+}).

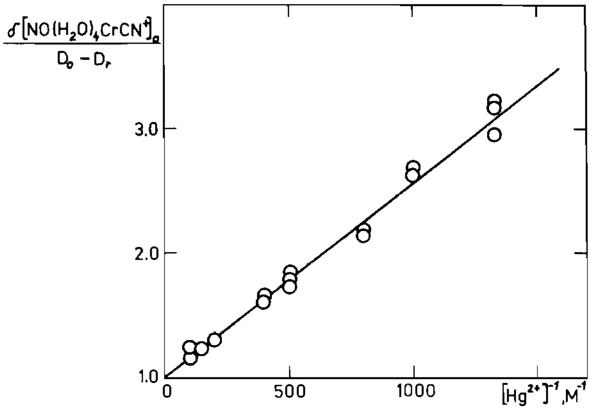


Figure 3. Determination of equilibrium constant of reaction (7) by evaluation of zero time absorbance of reaction mixture, according to equation (11).

instant of mixing the reactants – Hg^{2+} and $NO(H_2O)_4Cr–CN^+$. Preliminary experiments have shown that the extrapolated absorbance value, D_o, differs from the absorbance value corresponding to the same $NO(H_2O)_4Cr–CN^+$ concentration at the given wavelength (Hg^{2+} does not absorb in the spectral range studied). In accordance with the proposed interpretation of the kinetic data, these deviations can be explained by the existence of a further substance (A), formed by an equilibrium reaction and posessing different spectral properties from those of reactant $NO(H_2O)_4CrCN^+$ and product $NO(H_2O)_4CrNCHg^{3+}$. From the above interpretation it follows that at a high Hg^{2+} concentration (the rate constant is independent of $[Hg^{2+}]$) the Cr-containing reactant is virtually quantitatively converted into intermerdiate A.

The extrapolated values, D_o, determined for various wavelengths and for a high $[Hg^{2+}]$ ($[Hg^{2+}] > 0.03$ M) can thus be used for the construction of the intermediate A spectrum. This spectrum is given in Fig. 2, together with the absorption spectra of $NO(H_2O)_4CrCN^+$ and $NO(H_2O)_4CrNCHg^{3+}$. The spectrum of intermediate A exhibits three absorption maxima at 372 nm ($\epsilon = 264\, M^{-1}\, cm^{-1}$), 445 nm ($\epsilon = 144\, M^{-1}\, cm^{-1}$) and 610 nm ($\epsilon = 48\, M^{-1}\, cm^{-1}$).

If the Hg^{2+} concentration is lower, $NO(H_2O)_4CrCN^+$ and A are present in solution in equilibrium at comparable concentrations and the absorbance extrapolated to the time of mixing the Cr-containing reactant with Hg^{2+} is given by the sum of the absorbances of the two equilibrium substances. From this absorbance balance, the following equation is obtained,

$$\frac{\delta x [NO(H_2O)_4CrCN^+]_o}{D_o - D_r} = \frac{1}{K}[Hg^{2+}]^{-1} + 1 \qquad (11)$$

where $\delta = l(\epsilon_A - \epsilon_r)$

l is the optical path length

ϵ_A is the molar absorption coefficient of A

ϵ_r is the molar absorption coefficient of $NO(H_2O)_4CrCN^+$

$[NO(H_2O)_4CrCN^+]_o$ is the initial total concentration of the Cr-containing reactant, whose absorbance equals D_r.

Eq. (11) is an equation of a straight line, with a known value of the intercept on the coordinate. If the extrapolated absorbance values, D_o, for various $[NO(H_2O)_4CrCN^+]_o$ and $[Hg^{2+}]$ are plotted as the dependence of the coordinate equalling the left-hand side of Eq. (11) on $[Hg^{2+}]^{-1}$, a linear dependence verifies the validity of the proposed interpretation with preceding equilibrium (7, 8) and from the slope the equilibrium constant, K, can be calculated.

It can be seen in Fig. 3 that the D_o values measured obey a linear dependence according to Eq. (11).

TABLE III. Rate Constants k_s of Isomerisation Reaction at Ionic Strength I = 1 *M* (ClO_4^-, I^-, H^+, Na^+, HgI_4^{2-}) and $C_N^o = 2.4 \times 10^{-4}$ *M*[a].

$[H^+]$, *M*	T, K	$10^2 \times k_s$, s^{-1}	$[H^+]$, *M*	T, K	$10^2 \times k_s$, s^{-1}
0.4	293	1.5	0.0075	293	19.4
0.3	293	1.58	0.005	293	21.2
0.2	293	2.17	0.5	278	0.21
0.2	293	2.6	0.5	283	0.38
0.1	293	4.6	0.5	288	0.78
0.1	293	5.0	0.5	293	1.4
0.075	293	5.6	0.5	298	2.6
0.05	293	8.2	0.005	274	3.85
0.04	293	9.1	0.005	278	5.2
0.025	293	11.5	0.005	283	9.2
0.02	293	14.1	0.005	288	13.5
0.01	293	18.5	0.005	298	34.5

[a] c_N^o denotes the initial concentration of Cr–N isomer in both protonated and unprotonated forms.

The equilibrium constant thus calculated equals K = (6.0 ± 1.2) × 10^2 M^{-1} for T = 278 K, an ionic strength of 1 *M* (ClO_4^-, H^+, Na^+, Hg^{2+}) and $[H^+]$ = 0.1 *M*. This value can be compared with the equilibrium constant obtained from the kinetic measurement (Table II). The agreement with the constant for $[H^+]$ = 0.1 *M* can be considered good, in view of the poor precision of the determination.

Isomerization of $NO(H_2O)_4Cr{-}NC^+$

The overall stability constant of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ [1] has a value substantially lower than that of HgI_2 [6]. Hence the reaction,

$$\{NO(H_2O)_4CrNC\}_2Hg^{4+} + 2I^- \rightleftharpoons HgI_2 + 2NO(H_2O)_4CrNC^+ \qquad (12)$$

can be used to generate the unstable bond isomer, $NO(H_2O)_4CrNC^+$ and to study its isomerization.

The kinetics of the isomerization of the unstable isomer forming $NO(H_2O)_4CrCN^+$ were monitored as the change in the polarographic limiting current by the procedure described more closely in the experimental part. The formal kinetic equations for the first-order reactions conformed with the current time-dependences. The first-order rate constants measured are given in Table III.

The rate constant depends on $[H^+]$ in the region of the acid–base equilibrium of $NO(H_2O)_4Cr{-}NC^+$ (protonation). On this fact is based the proposed explanation of this dependence. The overall spontaneous isomerization can be considered as the sum of the reactions of the two equilibrium forms,

$$\begin{tikzcd}
NO(H_2O)_4Cr{-}NC^+ + H^+ \arrow[r, shift left, "Q_p"] \arrow[d, "k_n"] & NO(H_2O)_4CrNCH^{2+} \arrow[l, shift left] \arrow[d, "k_p"] \\
NO(H_2O)_4Cr{-}CN^+ + H^+ \arrow[r, shift left] & NO(H_2O)_4CrCNH^{2+} \arrow[l, shift left]
\end{tikzcd} \qquad (13)$$

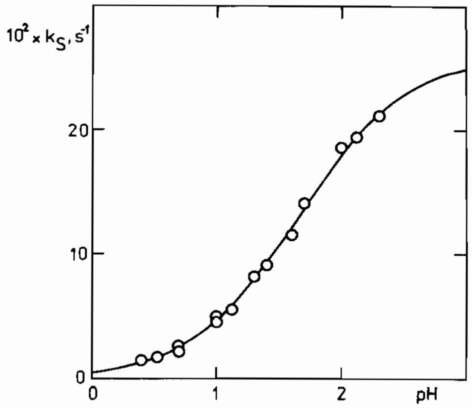


Figure 4. pH dependence of the isomerisation rate constant k_s: 293.16 K, ionic strength 1 *M*. The curve is calculated according to eq. (14) for $k_n = 26 \times 10^{-2}$ s^{-1}; $k_p = 0$ s^{-1}; $Q_p = 45 \pm 4$ M^{-1}.

Reaction scheme (13) leads to the following expression for the measured rate constant,

$$k_s = \frac{d\ln c_N}{dt} = \frac{k_n + k_pQ_p[H^+]}{1 + Q_p[H^+]} \qquad (14)$$

where c_N = $[NO(H_2O)_4Cr{-}NC^+]$ + $[NO(H_2O)_4Cr{-}NCH^{2+}]$.

The values, $k_n = (26 \pm 2) \times 10^{-2}$ s^{-1}; $k_p < 0.05$ k_n and $Q_p = (45 \pm 4)$ M^{-1}, were calculated by the least squares method from the experimental data (Table III) for 293 K and I = 1 *M*, employing Eq. (14). The k_s = f(pH) curve, representing Eq. (14) for the above values of k_n and Q_p and for $k_p = 0$ s^{-1}, is given in Fig. 4; the experimental data are shown as the points in the figure.

As the Cr–N isomer is present virtually completely in the form $NO(H_2O)_4CrNCH^{2+}$ at $[H^+]$ = 0.4 *M* and its non-protonated form predominates at $[H^+]$ = 0.005 *M*, it is possible to determine the isomerization

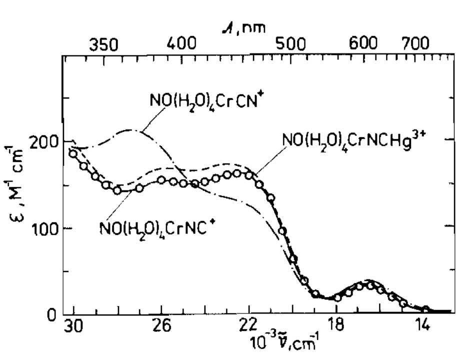


Figure 5. Absorption spectrum of $NO(H_2O)_4CrNC^+$ in the solution of ionic strength 1 *M* (ClO_4^-, H^+, Na^+), $[H^+] = 0.01$ *M*, 20 °C. Experimental points of the spectrum were obtained by extrapolation to the time of mixing $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ with 100-fold molar excess of HCN. Spectra of $NO(H_2O)_4CrCN^+$ and $NO(H_2O)_4CrNCHg^{2+}$ taken under the same conditions are given for comparison.

activation energy for the two forms from the temperature dependences at these $[H^+]$ values; $\Delta H_p^{\neq} = 20.8$ kcal mol^{-1} and $\Delta H_n^{\neq} = 14.6$ kcal mol^{-1} (for unit ionic strength).

In addition to the electrochemical monitoring of the isomerization rate, attempts were made to follow the isomerization by recording time-changes of the absorbance. As the optical measurements were limited in the visible region by HgI_4^{2-} absorption and by the contemporary turbidity formation, a large excess of HCN was used for the displacement of $NO(H_2O)_4Cr–NC^+$ from $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$; to ensure a shift of the displacement equilibrium toward $NO(H_2O)_4Cr–NC^+$. When the experiments were carried out at a decreased temperature (5 °C), the half-time of the absorbance time-change was about 1 min.

This slow change permitted a very precise extrapolation of the absorbance to the instant of mixing $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ with excess HCN. The absorbances thus obtained at various wavelengths differed from the absorbances corresponding to $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ at the given concentration (HCN does not absorb radiation in this spectral region) and the spectrum of $NO(H_2O)_4CrNC^+$ could be constructed from them. The extrapolated absorbance values are independent of $[H^+]$ within experimental error; hence, the protonated and unprotonated Cr–N isomer forms have identical absorption spectra. The spectrum of the Cr–N isomer, together with the spectra of $NO(H_2O)_4CrCN^+$ and $NO(H_2O)_4CrNCHg^{3+}$, is depicted in Fig. 5.

Discussion

A comparison of the contributions from the parallel reactions of the $NO(H_2O)_4Cr–NCHg^{3+}$ formation from $NO(H_2O)_4Cr–CN^+$ and Hg^{2+} has shown that the reaction studied follows scheme (7)–(8) to at least 95%, *i.e.* intermediate A is formed, which can be characterized by its absorption spectrum. The intermediate formation is a very rapid reaction, very probably connected with substitution of the H_2O in the Hg^{2+} coordination sphere. Since $Cr(H_2O)_5NO^{2+}$ exhibits no interaction with Hg^{2+}, it seems probable that only the CN ligand participates in the substitution, the orbitals localized predominantly on C or N being used for the formation of a bond to Hg^{2+}. From this two structures can be proposed for intermediate A, characterized by arrangements $Hg–\overset{N}{C}–Cr$ and Hg–N–C–Cr. The decision between these two possibilities could be made on the basis of the vibrational spectra of CN.

Two analogous adduct structures have been proposed for other interactions of Hg^{2+} with a Cr-containing complex containing bidentate ligand CN [7] and SCN [8]. The formation constant for the adduct of the cyanochromium(III) complex with Hg^{2+} [7] is 27 M^{-1}, whereas that for intermediate A with the above structure is more than 20 times larger. A possible explanation of this large value is a smaller value of the Coulomb repulsion of the components, as the adduct described in ref. [7] carries the charge 4+ and adduct A the charge 3+.

In accordance with the proposed structure of intermediate A, reaction (8) is the bond isomerization in which the Cr–C bond is broken and the Cr–N bond simultaneously formed. The rate constant of this reaction is independent of $[H^+]$, but that of the similar process described in ref. [7] ($CrCN^{2+} + Hg^{2+}$) is a linear function of $1/[H^+]$. The rate constant dependence has been explained by an acceleration of the process owing to the presence of an OH^- group in the *trans* position to CN. It can thus be formulated on the basis of the assumption of two parallel reaction paths by

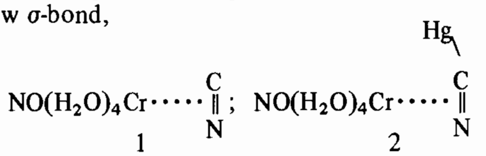
$$k = k_{H_2O} + k_{OH} K_H [H^+]^{-1} \qquad (15)$$

where k_{H_2O} is the rate constant for the acid form (H_2O *trans* to CN^-), k_{OH} is that for the basic form (OH^- *trans* to CN^-) and K_H is the protonation equlibrium constant for the basic form.

The very low value of the proportionality coefficient with $[H^+]^{-1}$ in Eq. (15) for the conversion of A into $NO(H_2O)_4CrNCHg^{3+}$, compared with 0.010 mol l^{-1} s^{-1} for the $CrCN^{2+}$ reaction with Hg^{2+} [7], can be explained by a lower K_H value for complex A with charge 3+ compared with the K_H value of the proposed $CrCNHg^{4+}$ intermediate (the K_H values may differ by several orders of magnitude [11]). Another cause may be the presence of the NO ligand *cis* to CN, which favours deprotonation on another place than the *trans* position with respect to CN, which is advantageous for acceleration of reaction (8). Naturally, the possibility that the k_{OH}/k_{H_2O} values are different in the two cases also cannot be excluded.

The spectrum of intermediate A is compared with those of $NO(H_2O)_4CrCN^+$ and $NO(H_2O)_4CrNCHg^{3+}$ in Fig. 2. It can be seen that the intermediate spectrum is very similar to that of $NO(H_2O)_4CrCN^+$. Hence the chromophore of the intermediate is not substantially changed compared with that of $NO(H_2O)_4CrCN^+$, except for a small hyperchromic effect caused by the presence of the Hg–N σ-bond. This corresponds to the above concept of the intermediate structure, with the bonding situation at the central Cr virtually unchanged from that in $NO(H_2O)_4Cr\text{-}CN^+$. On the other hand, the CN bond isomerization should be considered as a change in the chromophore structure leading to larger changes in the electronic spectrum. This is demonstrated by comparison of the $NO(H_2O)_4Cr–NC^+$ and $NO(H_2O)_4Cr–CN^+$ spectra. The similarity between the spectra of $NO(H_2O)_4CrNC^+$ and $NO(H_2O)_4CrNCHg^{3+}$ (Fig. 5) is another example of the relatively small influence of the coordinated Hg^{2+} on the electronic spectrum type (here the formation of the Hg–C σ-bond causes again a weak hyperchromic effect).

It follows from this reasoning that reaction (8) is very similar to the isomerization reactions of the chromium tetraaquocyanonitrosyl complex alone. In both reactions the donor atom is changed with preservation of the chromium–ligand bond, the ligand being connected with the metal by a π-bond during the breakage of the original and the formation of the new σ-bond,



$$NO(H_2O)_4Cr\cdots\cdots\overset{C}{\underset{N}{\|}}\;;\quad NO(H_2O)_4Cr\cdots\cdots\overset{\overset{Hg}{\diagdown}}{\overset{C}{\underset{N}{\|}}}$$

1 2

(the proposed structure of the transition state follows from the proposal for analogous reactions of $CrCN^{2+}$ in ref. [7]). The two transition states differ only in the existence of the Hg–C σ-bond, similar to the difference between the initial substances in the two reactions, $NO(H_2O)_4Cr–CN^+$, $NO(H_2O)_4Cr–CNHg^{3+}$, and between the products, $NO(H_2O)_4Cr–NC^+$, $NO(H_2O)_4Cr–NCHg^{3+}$.

The rate constant of reaction (8) is, however, about 2000 times higher than that of the $NO(H_2O)_4CrCN^+$ isomerization to $NO(H_2O)_4CrNC^+$.* For the analogous reactions of $CrCN^{2+}$ described in ref. [7], the ratio of the corresponding rate constants is only about 100.**

The 100 fold acceleration is explained in the paper cited by a decrease in the transition state energy owing to the formation of a sterically uncrowded Hg–C σ-bond. It is still unresolved, why this effect is so much more pronounced with the NO complexes, especially because the effect of the NO coordination on the ratios of the corresponding equilibrium constants is small,

$$\frac{[CrNCHg^{4+}]}{[CrCNHg^{4+}]} : \frac{[CrNC^{2+}]}{[CrCN^{2+}]} = 2.4 \times 10^8$$

$$\frac{[NO(H_2O)_4CrNCHg^{3+}]}{[NO(H_2O)_4CrNCHg^{3+}]} :$$

$$\frac{[NO(H_2O)_4CrNC^+]}{[NO(H_2O)_4CrCN^+]} = 1.67 \times 10^8\,†$$

In other words, the stabilization of the reaction product (the Cr–NC isomer) by the σ-bond with Hg^{2+} is roughly the same for the NO complex as for a complex not containing NO, whereas the acceleration of the process by the bonding to Hg^{2+} is about 20 times larger for the NO complex than for complexes without NO. The effect of the coordination of NO is apparently chiefly manifested in the transition state energy. Structures 1 and 2 have energies more different than the similar structures without NO proposed in ref. [7].

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*The rate constant of reaction (8) was obtained for 293,16 K and I = 1 *M* by extrapolation of the temperature dependence and equals 0.185 s^{-1}. The rate constant of the $NO(H_2O)_4CrCN^+$ isomerization to $NO(H_2O)_4CrNC^+$ is $k_n/Q_i = 9.5 \times 10^{-5}$ s^{-1} for 293.16 K and I = 1 *M*.

**For the calculation of the ratio, the isomerization rate constant $k_i = 2.3 \times 10^{-4}$ s^{-1} was taken, *i.e.* the value ten times lower than that given in ref. [7]. The k_i value was calculated from the isomerization equilibrium constant, 208, given in ref. [9]; this value should be preferred over the estimate given in ref. [10], which was employed for the calculation of k_i in ref. [7]. For the rate constant of the $CrCNHg^{2+}$ reaction to $CrNCHg^{2+}$, the rate constant of the acid form (H_2O *trans* to CN^-) was taken.

†To calculate the ratios, the data from refs. [1], [2], [7], [9] were used, in addition to the results obtained in this paper.

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