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Study of Cyanoaquonitrosyl Complexes of Chromium. V[a]. Electrochemical Properties of the Cyanide Bond Isomers of $NO(H_2O)_4CrCN^+$ and of Their Complexes with Silver(I) and a Study of Their Equilibria

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The equilibrium of the CN bond isomers of $NO(H_2O)_4Cr(CN)^+$ was studied polarographically using the fast formation of the $NO(H_2O)_4Cr{-}NC^+$ complex with Hg^{2+}. The isomerization equilibrium constant, $Q_i = [NO(H_2O)_4Cr{-}CN^+]/[NO(H_2O)_4Cr{-}NC^+] = (2.6 \pm 0.1) \times 10^2$, and the deprotonation equilibrium constant, $K_a = [NO(H_2O)_4Cr{-}NC^+][H^+]/[NO(H_2O)_4Cr{-}NCH^{2+}] = (2.5 \pm 0.2) \times 10^{-2}$ M, (both values at 25 °C and an ionic strength of 1 M), obtained from these measurements are in a good agreement with the values obtained by other methods. The electrochemical reactions of $\{NO(H_2O)_4CrNC\}_2Ag^{3+}$ were described and explained from the viewpoint of the stochiometry and the mechanism of the formation reaction. The schemes proposed are based on voltammetric and coulometric measurements. From an analysis of the polarographic limiting diffusion current for the reduction of complexes Ag(I), the value of the equilibrium constant, $Q = [NO(H_2O)_4Cr{-}NCAg^{2+}]^2/[Ag^+][\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+}] = (0.12 \pm 0.08)$, was obtained for 25 °C and an ionic strength of 1 M.

Introduction

Voltammetric methods have yielded valuable information on the composition [2] and the chemical equilibria [1] of the cyanide bond isomers of $NO(H_2O)_4Cr(CN)^+$ with Hg^{2+} and on the kinetics and mechanism of some of their chemical reactions [3]. The obtainment of this information was always preceded by a detailed study of the electrochemical reactions of the complexes in equilibrium or during a chemical reaction. The complexes of $NO(H_2O)_4CrCN^+$ with Ag^+ were also studied potentiometrically and amperometrically [2], to determine their composition (the stoichiometry of their formation reactions) and the stability constants.

In the present paper, the formation reactions of the $NO(H_2O)_4CrCN^+$ complexes with Ag^+ are studied voltammetrically, chiefly on a Hg electrode. Polarography was used for the study of the bond isomerization equilibrium of $NO(H_2O)_4CrCN^+$. The electrochemical reactions in equilibria of the given complexes were studied. The Hg electrode often affects the redox processes in these measurements and thus does not play its usual role of an indifferent electrode.

Experimental

Linear-sweep voltammetric measurements were carried out using a carbon rod (spectral grade, SU-type, Elektrokarbon, Topol'cany, Czechoslovakia) impregnated with paraffin *in vacuo* as the working electrode. The paraffin layer on the sides of the electrode was renewed daily. The working surface of the electrode was prepared by cleaning the cylinder base with ultra-fine sand paper followed by polishing on a filter paper. The effective working area of the electrode was determined by voltammetric methods using *o*-dianisidine in 1 *M* H_2SO_4 as a model substance [2]. The tip of the Luggin capillary of the reference electrode was placed close to the working electrode in such a manner that the axis of either of them was on a circle in the middle of which the auxiliary platinum electrode was located. All measurements were performed at the scan rate 4.63×10^{-2} V s^{-1} at the electrode with the electrode area A = 0.251 cm^2.

Instruments used for voltammetric as well as for coulommetric measurements are specified in [1]. Characteristics of applied dropping mercury electrode preparation and measurement procedures are also described in [1]. The formation of adduct of $NO(H_2O)_4CrCN^+$ with Ag^+ is complete shortly after addition of heavy metal ion. Moreover the aquation of the Ag(I) adduct is relatively very slow (much slower aquation rate than in the case of Hg(II) adduct). Therefore it was unnecessary ro prepare a separate solution for each measurement as was done in the case of Hg(II) adduct [1].

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

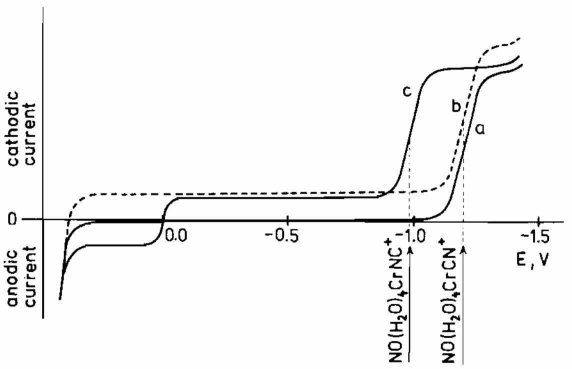

Figure 1. Schematic representation of polarographic behaviour of $\{NO(H_2O)_4CrNC\}_2Ag^{3+}$, *a*, polarographic wave of $NO(H_2O)_4Cr{-}CN^+$; *b*, sum of polarographic wave *a* and Ag^+ added in half molar amount of $NO(H_2O)_4Cr{-}CN^+$; *c*, polarographic waves of reacted solution described under *b* (2 minutes after mixing).

Results

Polarographic Investigation of the Formation of a Polynuclear Complex of $NO(H_2O)_4CrCN^+$ with Ag^+

It has been found that the spectrophotometric study of the formation of a polynuclear complex of $NO(H_2O)_4CrCN^+$ with Ag^+ encounters some difficulties, owing to the formation of a fine (often imperceptible) turbidity, which, unremoved, distorts the visible absorption spectrum. The turbidity is apparently formed from HCN present in $NO(H_2O)_4$-$CrCN^+$ solutions, which cannot be removed even by prolonged passage of nitrogen and ion-exchanger separation. It is possible that these small amounts of HCN that do not substantially affect the amount of the main component are formed by the hydrolysis of the latter.

Whereas the turbidity slowly disappears on addition of small amounts of Ag^+ (the reaction of Ag^+ with the main component), the disappearance is slowed down or stopped when larger amounts of Ag^+ are added.

Polarographic monitoring of the formation of the Ag^+ complex is especially advantageous from this point of view, as the fine turbidity does not interfere in the measurement.

If Ag^+ is added to a weakly acidic solution of $NO(H_2O)_4CrCN^+$*, non-additive changes in the polarographic currents occur (Figs. 1 and 2). Addition of Ag^+ and the formation of a polynuclear complex leads to a decrease in the polarographic wave of $NO(H_2O)_4CrCN^+$ and an increase in a new wave with a half-wave potential of -0.94_7 *V vs.* SCE ($[H^+] = 0.01$ *M*; ionic strength, 1 *M* ClO_4^-, Na^+, H^+). The decrease in the original wave and the increase in the new wave continue until the amount of Ag^+ equal to one half of the molar amount of $NO(H_2O)_4$-$CrCN^+$ is added; then the original wave practically disappears and the new wave attains its maximum height independent of further additions of Ag^+, equal to about 89% of the height of the original wave. In a more positive region (around 0 V *vs.* SCE), an anodic–cathodic wave with equal anodic and cathodic parts appears and increases (Fig. 1). The increase of its both parts ends on addition of the Ag^+ amount equal to one half of the molar amount of $NO(H_2O)_4$-$CrCN^+$ (Fig. 2). On further additions the cathodic part increases at the expense of the anodic part and finally only a cathodic wave appears on addition of an Ag^+ amount approximately equal to the molar amount of $NO(H_2O)_4CrCN^+$.

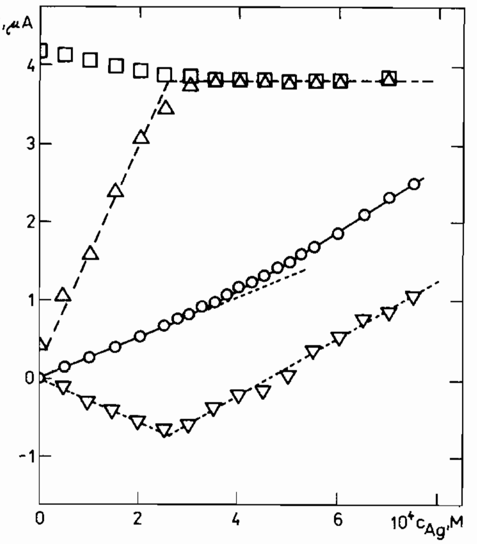

Figure 2. Dependence of polarographic limiting current on the concentration of added Ag^+; concentration of added $NO(H_2O)_4CrCN^+$ 5×10^{-4} *M*; 25 °C; ionic strength 1 *M*; $[H^+] = 0.01$ *M*; current measured at +0.2 V *vs.* SCE, ▽; at −0.5 V *vs.* SCE, ○; △, difference of currents at −1.1 V and −0.5 V *vs.* SCE; □, difference of current at −1.32 V and −0.5 V *vs.* SCE.

The total height of the wave remains, however, practically constant. On further addition of Ag^+ the waves remain virtually unchanged, but shift somewhat toward cathodic currents, as the reduction current increases immediately from the potential of the anodic Hg dissolution. The limiting currents of all the waves described are diffusion-controlled.

Voltammetric Measurements on a Graphite Electrode

Some experiments were also carried out on a graphite electrode with a linear time-change of the potential. A stationary disk electrode was employed.

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*$NO(H_2O)_4CrCN^+$ yields a diffusion-controlled cathodic wave in solutions with $[H^+] = 0.01$ *M* and ionic strength, 1 *M* (ClO_4^-, Na^+, H^+), corresponding to the three-electron reduction of the complex ion, with $E_{1/2} = -1.21_4$ V *vs.* SCE [4].

TABLE I. Anodic Polarographic Currents Corresponding to the Complex Formation of Equilibrium $NO(H_2O)_4Cr{-}NC^+$ with Hg^{2+}; Temperature 25 °C, Ionic Strength 1 *M* (ClO_4^-, Na^+, H^+); Analytical Concentration (including both isomeric Forms): 9.42×10^{-3} *M*.

$[H^+]$, *M*	$\bar{I}_a$, μA^a	$[H^+]$, *M*	$\bar{I}_a$, μA^a	$[H^+]$, *M*	$\bar{I}_a$, μA^a
0.001	0.12	0.025	0.23	0.100	0.67
0.005	0.13	0.050	0.34	0.200	0.78
0.010	0.16	0.075	0.46	0.300	0.85

[a] Parameters of dropping mercury electrode used for current measurement are given in the experimental section.

This electrode was unsuitable for a systematic study because of a narrow potential range (the small hydrogen overvoltage did not permit the study of the reduction of the Cr components) and because of considerably slower electrode reactions compared with mercury electrodes. The most important result is the finding that an anodic current did not appear at potentials more negative than +0.3V *vs.* SCE with any amount of Ag^+ added to the solution containing $NO(H_2O)_4CrCN^+$.

Coulometric Measurements on a Mercury Electrode

Electrolysis was carried out in solutions containing Ag^+ in the amount equal to one half that of $NO(H_2O)_4CrCN^+$.

At a working electrode potential of –0.5V *vs.* SCE, the total charge measured during the electrochemical reduction corresponded to addition of 1.05 ± 0.05 electrons per Ag^+ ion. After completion of the electrolysis, only a single polarographic wave appeared, corresponding to the reduction of $NO(H_2O)_4CrCN^+$.

At a working electrode potential of –1.05 V *vs.* SCE, the electrolysis was more complicated. The total charge was determined from the time variation of the current and the charge passed and amounted to the addition of 6.7 ± 0.2 electrons per complexed Ag(I); in the final stages of the electrolysis, the number of exchanged electrons calculated was even higher.

The electrolysis at a potential of +0.25 V *vs.* SCE was quite irregular and a precipitate was formed on the surface of the Hg electrode.

Polarographic Study of the $\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+} + Ag^+ \rightleftharpoons 2\ NO(H_2O)_4Cr{-}NC{-}Ag^{2+}$ *Equilibrium*

From the current measured at –0.5 V *vs.* SCE in dependence on the amount of Ag^+ added, the equilibrium constant of the above reaction can be obtained. The evaluation is based on the various values of the diffusion coefficients for the Ag(I) components participating in the equilibrium. The experimental data summarized in Table I were evaluated by the procedure proposed and verified in ref. [1]. The value, Q = (0.12 ± 0.08), was obtained for 25 °C, an ionic strength of 1 *M* (ClO_4^-, Na^+, H^+) and $[H^+] = 0.01$ *M*. Considering the poor precision of the determination of Q, the agreement with the value obtained for this equilibrium from potentiometric measurements can be considered satisfactory.

Polarographic Investigation of the $NO(H_2O)_4CrCN^+$*–*$NO(H_2O)_4CrNC^+$ *Equilibrium*

The equilibrium constant of the reaction of $NO(H_2O)_4CrCN^+$ with Hg^{2+} in a ratio of 2:1 equals 2.3×10^{16} M^{-2} [2]. The formation of a Hg^{2+} complex with such a high equilibrium constant should give rise to an anodic polarographic wave controlled by the $NO(H_2O)_4CrCN^+$ "ligand" diffusion toward the dropping mercury electrode. No such wave with a limiting diffusion current comparable with the cathodic wave of the "ligand" reduction was found. This is apparently caused by a low rate of the complex formation, so that the equilibrium cannot be established under the polarographic conditions.

However, during the study of relatively concentrated solutions of monocyanotetraquonitrosyl complex of chromium an anodic wave appeared around 0 V *vs.* SCE with the limiting current 200–300 times lower than would correspond to the formation of the Hg^{2+} complex with $NO(H_2O)_4CrCN^+$. The limiting current of this anodic wave is diffusion-controlled and depends on the hydrogen ion concentration (see Table I). The overall stability constant of the 2:1 complex of $NO(H_2O)_4CrCN^+$ with Hg^{2+} ($K' = [\{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+}]/[NO(H_2O)_4Cr{-}CN^+]^2[Hg^{2+}] = 2.3 \times 10^{16}\ M^{-2}$ [2]) is related to the equilibrium constant calculated from the half-wave potential of the reversible reduction of $\{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+}$ ($K = [\{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+}]/[NO(H_2O)_4Cr{-}NC^+]^2[Hg^{2+}] = 1.43 \times 10^{21}\ M^{-2}$ [1]) by the equation,

$$K = K'Q_i^2 \tag{1}$$

where $Q_i = [NO(H_2O)_4CrCN^+]/[NO(H_2O)_4CrNC^+] \doteq 250$ [1].

Hence the solution of chromium monocyanotetraquonitrosyl contains about 0.4% $NO(H_2O)_4CrNC^+$ under the conditions of the measurement of K and K′ (25 °C, ionic strength 1 *M*). The stability constant for this "ligand" with Hg^{2+} is sufficiently high for the complex formation giving rise to an anodic polarographic wave in the SCE potential region and

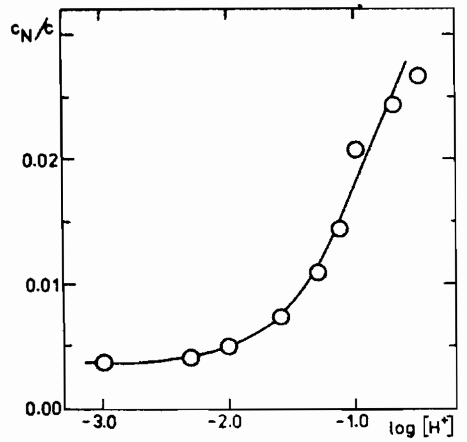

Figure 3. Dependence of the molar fraction of equilibrium Cr–N isomeric forms on log hydrogen ion concentration; 25 °C; ionic strength 1 *M* (ClO_4^-, Na^+, H^+); analytical concentration (including both isomeric forms): 9.42×10^{-3} *M*.

since the $NO(H_2O)_4CrNC^+$ reaction with Hg^{2+} is very fast, there are no kinetic obstacles to the formation of this anodic wave.

Therefore, it is proposed to assign the anodic wave measured to the formation of the complex of the N-isomer of $NO(H_2O)_4Cr{-}NC^+$ present in equilibrium with Hg^{2+}. The anodic current observed is directly proportional to the total concentration of the Cr–N form ($\bar{i} = \mathcal{K}.c$). The Ilkovič coefficient, $\mathcal{K}$, should equal 1/3 of that for the reduction of $NO(H_2O)_4CrCN^+$, assuming that the diffusion coefficients of the two bond isomers are the same.

Coefficient 1/3 follows from the number of electrons exchanged, which is 3 for the reduction and 1 for the anodic process of $NO(H_2O)_4Cr{-}NC^+$ (the 2:1 complex is exclusively formed). It follows from the dissociation constant of $NO(H_2O)_4Cr{-}NCH^{2+}$ ($K_a = [NO(H_2O)_4Cr{-}NC^+][H^+]/[NO(H_2O)_4Cr{-}NCH^{2+}] = 2.75 \times 10^{-2}$ *M* [1]) that in the region of the hydrogen ion concentrations studied (0.001 to 0.300 *M*) both the non-protonated and the protonated forms of the Cr–N bond isomer must be considered, $c_N = [NO(H_2O)_4CrNC^+] + [NO(H_2O)_4CrNCH^{2+}]$. The analytical concentration, c, further involves the more stable isomer, $NO(H_2O)_4CrCN^+$. Using the definition relationships for Q_i and K_a, the following ratio can be expressed,

$$\frac{c_N}{c} = \frac{K_a + [H^+]}{K_a(1 + Q_i) + [H^+]} = \frac{K_a + [H^+]}{K_aQ_i + [H^+]} \qquad (2)$$

The second equality is valid for high values of Q_i, which can be expected for the equilibrium studied. According to Eq. (2), ratio c_N/c is independent of $[H^+]$ and equals $1/Q_i$ for $[H^+] \ll K_a$. At higher $[H^+]$ values the c_N/c would vary linearly with varying $[H^+]$ with a slope of $1/K_aQ_i$ and for $[H^+] \gg K_aQ_i$ it would attain unity.

The $[H^+]$ range is here limited by alkaline hydrolysis of the complex from below and by protonation of $NO(H_2O)_4CrCN^+$ from above, followed by loss of the cyanide [2]. Fig. 3 depicts the dependence of c_N/c (calculated from the limiting current of the anodic wave) on log $[H^+]$. The experimental points are best fitted by the curve calculated from Eq. (2) with the values, $K_a = (2.5 \pm 0.2) \times 10^{-2}$ *M* and $Q_i = (2.6 \pm 0.1) \times 10^2$ (for 25 °C and ionic strength 1 *M*). Both the values are in good agreement with the values obtained from the half-wave potential of the reversible reduction of $\{NO(H_2O)_4CrNC\}_2Hg^{4+}$ [1] and from the potentiometric titration of $NO(H_2O)_4CrCN^+$ with Hg^{2+} [2].

Discussion

Polarographic investigation of the formation of the $NO(H_2O)_4CrCN^+$ complexes with Ag^+ has shown that the molar amount of Ag^+ equal to one half that of $NO(H_2O)_4CrCN^+$ suffices for complete complexation. This result agrees with the results of the potentiometric and spectrophotometric investigation of the reaction described in ref. [2].

$$2\,NO(H_2O)_4CrCN^+ + Ag^+ \rightleftharpoons \{NO(H_2O)_4CrNC\}_2Ag^{3+} \qquad (3)$$

Reaction (3) is, in contrast to the analogous reaction of Hg^{2+}, completed shortly after mixing of the reactants and consequently cannot be monitored without special devices (*e.g.* the stopped-flow technique). One of the facts that supported the assumption of bond isomerization accompanying reaction (3) was the slowness of the reaction with Hg(II). This argument is not unambiguous with Ag^+ and here the mechanism of the electrochemical reduction becomes the most important argument for verification of the bond isomerization. If the cathodic process in the more positive potential region is ascribed, in agreement with the results of the coulometric measurements, to the reduction of the complexed Ag(I),

$$\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+} + e \Rightarrow Ag + 2\,NO(H_2O)_4Cr{-}NC^+ \qquad (4)$$

then the absence of the polarographic wave of $NO(H_2O)_4Cr{-}CN^+$ in the polarographic picture of the trinuclear complex (Fig. 1) indicates the absence of this substance among the primary products of the electrode reduction, (4). On the other hand, the occurrence of a polarographic wave about 250 mV more positive than the $NO(H_2O)_4CrCN^+$ wave indicates that a less stable (more easily reducible) isomer is present, similar to the Hg(II) complex [1].

The assignment of this more positive wave with $E_{1/2} = -0.94_7$ V *vs.* SCE to the electrochemical reduction of the less stable bond isomer, $NO(H_2O)_4Cr{-}$

NC^+, is also supported by the result of the coulometric electrolysis at a potential of −0.5 V *vs.* SCE, in which $NO(H_2O)_4CrCN^+$ was identified polarographically and spectrophotometrically as the only product after the one-electron reduction. The primary product, $NO(H_2O)_4Cr{-}NC^+$, observed polarographically, isomerized to the more stable $NO(H_2O)_4CrCN^+$ during the duration of the coulometric experiment (15–20 min).

The polarographic limiting diffusion current corresponding to the reduction of $NO(H_2O)_4CrNC^+$ was about 11% lower than that corresponding to $NO(H_2O)_4CrCN^+$ at the same molar concentration of Cr. This decrease can be ascribed to a lower value of the diffusion coefficient of $\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+}$, in the form of which the $NO(H_2O)_4CrNC^+$ is transported by diffusion toward the indicator electrode. If then the reduction scheme for $NO(H_2O)_4Cr{-}NC^+$ is the same as that for $NO(H_2O)_4Cr{-}CN^+$ [4], the number of electrons required for the reduction of the $\{NO(H_2O)_4CrNC\}_2Ag^{3+}$ ion must be seven. The coulometrically obtained value, 6.7 ± 0.2, permits the formulation of the overall reduction equation,

$$\{NO(H_2O)_4CrNC\}_2Ag^{3+} + 7e + 2H_2O + 8H^+ \Rightarrow Ag + 2Cr(H_2O)_6^{2+} + 2HCN + 2NH_2OH \qquad (5)$$

The increase in the number of electrons exchanged described for the coulometric reduction at −1.05 V is evidently caused by reoxidation of Cr(II) by water or hydroxylamine.

The relatively complex polarographic behaviour of the trinuclear complex of Ag(I) in the more positive region (around the SCE potential) can be explained by a displacement reaction of the heavy metal ion in the trinuclear complex,

$$\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+} + Hg^{2+} \rightleftharpoons \{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+} + Ag^+ \qquad (6)$$

The comparison of the equilibrium constants of the formation of the Ag^+ and Hg^{2+} trinuclear complexes [2] shows that equilibrium (6) will be strongly shifted to the right. As it is connected with a substitution on central ions with the d^{10} electronic configuration, it can be expected to be very rapid. In the vicinity of the indicator Hg electrode the displacement reaction, (6), will be accompanied by an anodic current at potentials more negative than the Ag^+/Ag formal potential, the magnitude of the current being given by the difference between the current of the two-electron oxidation of the electrode material (Hg) and that of the one-electron reduction of Ag^+. The decrease in the anodic current and the increase in the cathodic current at a potential of about 0 V *vs.* SCE are connected with the reduction of the trinuclear complexes themselves. The active role of the electrode material in the formation of the anodic current is also indicated by the experiments on the carbon electrode, where no anodic current appears in this potential region.

The anodic–cathodic wave steps growing on completion of the formation of $\{NO(H_2O)_4Cr{-}NC\}_2Ag^{3+}$. Further addition of Ag^+ to the solution results in concentration of Ag^+ because of the poorly effective formation of the binuclear complex (the low value of the equilibrium constant – see above) and the cathodic current of Ag^+ shifts the anodic–cathodic wave to the region of cathodic currents.

The described anodic current of $NO(H_2O)_4Cr{-}NC^+$ which appears in equilibrium solutions is also connected with the electroactive electrode material. Mercury is oxidized to Hg^{2+}, which is bound into $\{NO(H_2O)_4Cr{-}NC\}_2Hg^{4+}$ with a high stability constant, forming very stable Hg–C σ-bond. A similar formation of a complex with isocyanocomplex is described in ref. [5].

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