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A Stoichiometric Investigation of the Reaction of Nitrosylpentaamminechromium(2+) with Ethylenediaminetetraacetatoaquachromate(II)

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Synopsis. The reaction of $Cr(NH_3)_5NO^{2+}$ with $Cr^{II}(edta)(H_2O)^{2-}$ gives four chromium products: $Cr^{III}(edta)(H_2O)^-$, $Cr(NH_3)_6^{3+}$, a reddish-violet species which is considered to be a chromium dimer with a +2 charge, and a trace amount of $Cr(H_2O)(NH_3)_5^{3+}$.

Recently, Armor *et al.* studied the reaction of $Cr(NH_3)_5NO^{2+}$ with $Cr(H_2O)_6^{2+}$ (Cr^{2+}) and observed at least five different chromium(III) products.[1] In this work, the products of the reaction of $Cr(NH_3)_5NO^{2+}$ with ethylenediaminetetraacetatoaquachromate(II) ($Cr^{II}(edta)(H_2O)^{2-}$) are examined, and the results compared with those obtained by Armor *et al.*

Experimental

Materials. The $[Cr(NH_3)_5NO](ClO_4)_2$ complex was prepared by the method of Mori *et al.*[2] The solutions of Cr^{2+} and $Cr^{II}(edta)(H_2O)^{2-}$ were prepared as has been reported previously.[3]

Identification and Analyses of Products. The reaction of $Cr(NH_3)_5NO^{2+}$ with $Cr^{II}(edta)(H_2O)^{2-}$ was carried out in an acetate-buffer solution under a nitrogen atmosphere. The reaction was completed within 5 s under the present experimental conditions. The complex ions, $Cr(NH_3)_5NO^{2+}$, were always treated with more than four equivalents of $Cr^{II}(edta)(H_2O)^{2-}$. After the solution of the reaction mixture had been exposed to air, it was diluted with five times as much water and then poured into an SP-Sephadex C-25 column. The species which passed through the column without any affinity to the resin was identified as $Cr^{III}(edta)(H_2O)^-$ from the measurement of the visible and ultraviolet absorption spectra. After the column had then been washed with water, the adsorbed species on the column were eluted with an 0.2 M $NaClO_4$–0.1 M $HClO_4$ solution. Three distinct bands were observed—reddish-violet, reddish-orange (trace amount), and yellow from the bottom to the top of the column. The eluate from the lowest band was concentrated with a rotary evaporator below 40 °C. Reddish-violet crystals were thus deposited. However, the attempted isolation of crystals sufficiently pure to be subjected to elemental analyses has not yet been successful because of the highly hygroscopic nature of this compound. From the flow rate on the Sephadex column, this species was estimated to have a +2 charge. The visible absorption spectrum shows two maxima, at 566 nm (ε=17) and 406 nm (ε=19).[4] The reddish-orange and yellow bands were eluted out with an 0.5 M $NaClO_4$–0.1 M $HClO_4$ solution. The reddish-orange species was characterized as $Cr(H_2O)(NH_3)_5^{3+}$ from the measurement of the visible absorption spectra. When the yellow eluate was concentrated with a rotary evaporator, yellow crystals were deposited. They were identified as $[Cr(NH_3)_6](ClO_4)_3$ from the measurement of the infrared, visible, and ultraviolet absorption spectra. The chromium content of each fraction was determined spectrophotometrically as CrO_4^{2-} after oxidation with an alkaline hydrogen-peroxide solution. The visible and ultraviolet absorption spectra were recorded with a Hitachi EPS-3 spectrophotometer.

Results and Discussion

The quantitative product distribution was determined at 25 °C with a solution (total volume, 4.00 ml) with an ionic strength of 0.3 ($NaClO_4$) and a pH of 4.3 which had initially contained 3.68×10^{-3} M $Cr(NH_3)_5NO^{2+}$, 1.83×10^{-2} M $Cr^{II}(edta)(H_2O)^{2-}$, 6.7×10^{-3} M EDTA, and an acetate buffer with 0.125 M acetate. For the separation of the chromium products, a Sephadex column 1.4 cm in diameter and 5 cm in height was used; into it the reaction mixture was poured. From the chromium content of each product separated, the concentrations of $Cr(NH_3)_6^{3+}$, the reddish-violet species, and $Cr^{III}(edta)(H_2O)^-$ were determined to be 2.59×10^{-3} M, 2.21×10^{-3} M, and 1.64×10^{-2} M respectively. The following stoichiometry can be assigned to the formation of $Cr(NH_3)_6^{3+}$:

$$Cr(NH_3)_5NO^{2+} + 4Cr^{II}(edta)(H_2O)^{2-} + 5H^+ \longrightarrow Cr(NH_3)_6^{3+} + 4Cr^{III}(edta)(H_2O)^- + H_2O \quad (1)$$

The concentration of chromium in the reddish-violet species is equal to $2\times([Cr(NH_3)_5NO^{2+}]-[Cr(NH_3)_6^{3+}])$. Therefore, the reddish-violet species is considered to be a chromium dimer having a +2 charge:

$$Cr(NH_3)_5NO^{2+} + Cr^{II}(edta)(H_2O)^{2-} \longrightarrow \text{reddish-violet species}^{2+} \quad (2)$$

The product distribution revealed that 70% of the $Cr(NH_3)_5NO^{2+}$ was converted to $Cr(NH_3)_6^{3+}$ and the rest, to the reddish-violet species. The formation of $Cr(NH_3)_6^{3+}$ from $Cr(NH_3)_5NO^{2+}$ is chemical evidence that the nitrosyl group in $Cr(NH_3)_5NO^{2+}$ is a nitrogen-bonded ligand.

The chromium products of the reaction of $Cr(NH_3)_5NO^{2+}$ with Cr^{2+} were found to be $Cr(H_2O)_6^{3+}$, $Cr(H_2O)(NH_3)_5^{3+}$, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, and two polymeric products which may be represented by the formula $(NH_3)_5Cr\text{-}X\text{-}Cr(H_2O)_4Y^{n+}$, X=$OH^-$ or NH_2OH, Y=H_2O or NH_2OH.[1] These products are quite different from the products observed in the present reaction. According to the results obtained by Armor *et al.*[1], 1 mol of $Cr(NH_3)_5NO^{2+}$ reacts with 2 mol of Cr^{2+} to give 1 mol of NH_2OH. On the other hand, at least 70% of the nitrosyl group in $Cr(NH_3)_5NO^{2+}$ is reduced to NH_3 by $Cr^{II}(edta)(H_2O)^{2-}$ reduction. Therefore, the kind of ligand coordinated to the chromium (II)ions dramatically changes the products of the reactions of $Cr(NH_3)_5NO^{2+}$ with chromium(II). A similar observation was also made of the reduction of NO_3^-. The reaction of NO_3^- with Cr^{2+} gives $Cr(H_2O)_5NO^{2+}$ [5], and the further reaction with Cr^{2+} yields NH_2OH.[6] The reaction of NO_3^- with $Cr^{II}(edta)(H_2O)^{2-}$ gives NH_4^+.[7,8] The difference between the reaction with Cr^{2+} and that with $Cr^{II}(edta)(H_2O)^{2-}$ may primarily come from the difference in their reduction potentials.[9] It is also apparent that the nature of the central metal ion inherently coordinated to the nitrosyl group controls the extent of the reduction of the nitrosyl group, because it is known that $Ru(NH_3)_5NO^{3+}$ reacts with Cr^{2+} to give $Ru(NH_3)_6^{2+}$.[10]

The absorption spectra of $Cr(NH_3)_5NO^{2+}$ change slowly in $NaClO_4$–$HClO_4$ media. It seems worthwhile to present some observations on these spectral changes (at 25 °C and at an ionic strength of 1.0 ($NaClO_4$–$HClO_4$)). When the hydrogen-ion concentration is higher than 0.2 M, absorbances over the whole range of the visible region decrease with the time. The rate of this change increases with an increase in the concentrations of hydrogen ions. For example, the rate constants of this process, as estimated by the Guggenheim method,[11] are $6.5\times10^{-4}\ s^{-1}$ at $[H^+]=0.313$ M and $8.4\times10^{-4}\ s^{-1}$ at $[H^+]=0.783$ M. When the hydrogen-ion concentration falls below 0.1 M, the reaction mentioned above can be neglected and another reaction occurs. The initial stage of the spectral changes shows isosbestic points at 351 nm and 430 nm. The rate constant of this process was determined to be $7.1\times10^{-5}\ s^{-1}$ at $[H^+]=0.0940$ M. Then, the isosbestic points collapse and the spectra change in a complicated manner, suggesting the occurrence of some consecutive reactions. The spectrum which was obtained after heating the solution on a boiling water bath shows absorption bands at 390 nm (shoulder, $\varepsilon=94$), 447 nm ($\varepsilon=116$), and 566 nm ($\varepsilon=31$). This spectrum coincides satisfactorily with that of $Cr(H_2O)_5NO^{2+}$ reported by Griffith.[12] Therefore, the spectral changes at $[H^+]<0.1$ M may correspond to the following reaction:

$$Cr(NH_3)_5NO^{2+} + nH_3O^+ \longrightarrow Cr(H_2O)_n(NH_3)_{5-n}NO^{2+} + nNH_4^+ \quad (3)$$

where $1\leq n\leq 5$.

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