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Reduction of the Tetraaquo(ethylenediamine)cobalt(III) Ion by Bromide and Hydrogen Peroxide in Acid Solution

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We have recently reported on the preparation of the tetraaquo(ethylenediamine)cobalt(III) ion and its substitution reaction with chloride.[2] Comparison of the properties of this compound to those of the closely related diammineaquocobalt(III) should provide the basis for understanding the controlling factors in substitution reactions in the lower members of the series $Co(NH_3)_n(H_2O)_{6-n}{}^{3+}$. We report here the kinetics of the reduction of $Co(en)(H_2O)_4{}^{3+}$ by H_2O_2 and Br^-, compare the results to the similar diammine system,[3,4] and comment on the likelihood of the involvement of superoxide and $Br_2{}^-\cdot$ intermediates in the reaction.[3,4]

Kinetic Studies

The $Co(en)(H_2O)_4{}^{3+}$ used in the kinetic studies was generated from solid $KCo(en)(CO_3)_2 \cdot H_2O$ in perchloric acid solution as described previously.[2] The extinction coefficients were checked at 510 and 373 nm to establish the purity of the complex. The initial Co(III) concentrations used in the kinetic studies ranged primarily from 0.8×10^{-2} to 1.2×10^{-2} M (Table I). The reaction solutions were made by combining the requisite amounts of stock $NaClO_4$ solution, stock $HClO_4$ solution, and $KCo(en)(CO_3)_2 \cdot H_2O$ and then initiating the reaction by adding the requisite amount of stock H_2O_2 solution (standardized by Ce(IV) titrations) or stock NaBr solution. The ionic strength of the reactions was maintained at 2.0 M.

Reagent grade $NaClO_4$ was used to make the stock $NaClO_4$ solutions. Occasionally a stock solution was contaminated by a small amount (less than 1%) of Cl^-. This generated the monochloro complex in the reaction solution.[17] When this occurred the stock solution was discarded and remade with Cl^--free $NaClO_4$. The kinetics reactions were repeated if the monochloro species had been more than 10% of the tetraaquo complex concentration in the reaction solution. Rate constants for the Cl^--containing and non-Cl^--containing reaction solutions were the same within experimental error.

The reduction of the Co(III) complex was followed spectrophotometrically with a Guilford 2000 spectrophotometer with a thermostated cell compartment. Zero time for a reaction was taken 5 min after a cell containing the reaction solution was placed in the cell compartment. The reduction by peroxide was followed at 373 nm and the reduction by Br^- at 510 nm. Due to the interference of the absorption of the $Br_3{}^-$ ion, 373 nm could not be used for the Br^- reaction. In both cases the reaction continued until no Co(III) complex could be detected spectrophotometrically. The pseudo-first-order rate constants are given in Table I. The rates increase with increasing Br^- and H_2O_2 concentrations and decrease with increasing H^+ concentration. The Br^- reaction was observed at 25.0 ± 0.2 °C and the H_2O_2 reaction at 35.0 ± 0.2 °C. Values of k_{obsd} were obtained from a nonlinear least-squares program for first-order kinetics. A plot of $[H^+]k_{obsd}$ vs. Br^- has a slope of $(0.26 \pm 0.03) \times 10^{-4}$ s^{-1} and an intercept of $(0.28 \pm 0.25) \times 10^{-5}$ M s^{-1}. For the H_2O_2 reaction a similar plot has a slope of $(0.87 \pm 0.06) \times 10^{-4}$ s^{-1} and an intercept of $0.40 \pm 0.16 \times 10^{-5}$ M s^{-1}. For the Br^- reaction a plot of k_{obsd} vs. $1/[H^+]$ has a slope of $(0.25 \pm 0.01) \times 10^{-4}$ M^{-1} s^{-1} and an intercept of $(0.21 \pm 0.04) \times 10^{-4}$ s^{-1}. For the H_2O_2 reaction a similar plot has a slope of $(0.40 \pm 0.06) \times 10^{-4}$ M^{-1} s^{-1} and an intercept of $(0.04 \pm 0.29) \times 10^{-4}$ s^{-1}.

Discussion

The slopes for a plot of $k_{obsd}[H^+]$ vs. [R] for $Co(H_2O)_6{}^{3+}$, $Co(NH_3)_2(H_2O)_4{}^{3+}$, and $Co(en)(H_2O)_4{}^{3+}$ reacting with Cl^-, Br^-, and H_2O_2 are compared in Table II. For $Co(H_2O)_6{}^{3+}$ the substitution with Cl^- is more rapid than the reduction, and the $Co(H_2O)_5Cl^{2+}$ ion can be observed as a transient intermediate.[18] With Br^- and H_2O_2 no intermediate is observed. In all three cases there is good evidence that the slope of the $k_{obsd}[H^+]$ vs. [R] plot is equal to k_1K_a, and the similarity of the rate parameters for the Br^- and H_2O_2 to those for Cl^- supports the proposal that the Br^- and H_2O_2 reductions of $Co(H_2O)_6{}^{3+}$ take place by a substitution-controlled mechanism.[5]

Table I. Observed Rate Constants for the Reaction of $Co(en)(H_2O)_4{}^{3+}$ with $H_2O_2{}^a$ or Br^- ^{b} in $HClO_4{}^h$

reagent	concn^c	$[H^+]^c$	$10^4k_{obsd}{}^d$
H_2O_2	0.101^e	0.20	0.60 ± 0.40
	0.099	0.20	0.70 ± 0.10
	0.202	0.20	1.11 ± 0.03
	0.198	0.20	1.04 ± 0.05
	0.403	0.20	1.80 ± 0.10
	0.504	0.20	2.50 ± 0.30
	0.498	0.10	3.90 ± 0.30
	0.498	0.40	0.60 ± 0.30
	0.496	0.80	0.40 ± 0.20
	0.498^f	0.80	0.80 ± 0.40
Br^-	1.00^g	0.17	1.59 ± 0.04
	0.75	0.17	1.29 ± 0.04
	0.50	0.17	0.99 ± 0.02
	0.25	0.17	0.50 ± 0.02
	1.00	0.08	3.30 ± 0.20
	1.00	0.35	0.91 ± 0.05
	1.00	0.87	0.52 ± 0.02

^{a} 35.0 ± 0.2 °C. ^{b} 25.0 ± 0.2 °C. ^{c} Units are M. ^{d} Units are s^{-1}. ^{e} 0.8×10^{-2} M Co(III). ^{f} 2.0×10^{-3} M Co(III). ^{g} 1.2×10^{-2} M Co(III). ^{h} $\mu = 2.0$ M.

Table II. Comparison of the $k_{obsd}[H^+]$ vs. [R] Slope for Substitution on or Reduction of Several Co(III) Species by Cl^-, Br^-, and H_2O_2

	$k_1K_a{}^a$			
species	Cl^-	Br^-	H_2O_2	ref
$Co(H_2O)_6{}^{3+}$	24.6^{b,d}	30.4^{c,d}	23.0^{c,d}	5,18
$Co(NH_3)_2(H_2O)_4{}^{3+}$ ^{i}	1.5^{b,e}	1.7^{c,e}	3.9^{c,f}	3,4
$Co(en)(H_2O)_4{}^{3+i}$	0.26^{b,g}	0.26^{c,g}	0.87^{c,h}	2, this work

^{a} Units s^{-1}. ^{b} Substitution. ^{c} Reduction. ^{d} At 25 °C. ^{e} At 28 °C. ^{f} At 38 °C. ^{g} At 26 °C. ^{h} At 35 °C. ^{i} Values × 10^4.

Chloride does not reduce either $Co(NH_3)_2(H_2O)_4{}^{3+}$ or $Co(en)(H_2O)_4{}^{3+}$, thus one can easily measure the true rate of substitution in both of these cases.[2,3] In both of these cases the rate of reduction by Br^- and H_2O_2 is quite similar to the rate of anation by Cl^-, strongly suggesting that the reduction is substitution controlled, as in the $Co(H_2O)_6{}^{3+}$ case.

The rates of reduction reported here are much slower than those observed for the reduction of $Co(NH_3)_2(H_2O)_4{}^{3+}$ by several reducing agents where the reduction is not substitution controlled on the Co(III) center.[6] On the basis of qualitative I^- results previously reported,[2] we believe the same would be true for $Co(en)(H_2O)_4{}^{3+}$. On the basis of the marked $1/H^+$ dependence of k_{obsd}, it appears that the major path for substitution, and thus reduction, in all cases compared ($Co(H_2O)_6{}^{3+}$, $Co(NH_3)_2(H_2O)_4{}^{3+}$, $Co(en)(H_2O)_4{}^{3+}$) is through the hydroxyaquo species.

On the basis of our results we have proposed the following general mechanism (eq 1–3) for the substitution-controlled reduction of $Co(en)(H_2O)_4{}^{3+}$, where R = Br^- or H_2O_2 and R_2 = Br_2 or O_2, ignoring the contribution of the tetraaquo species

$$Co(en)(H_2O)_4{}^{3+} \rightleftarrows Co(en)(H_2O)_3(OH)^{2+} + H^+ \quad K_a$$

$$Co(en)(H_2O)_3(OH)^{2+} + R \xrightarrow{k_1} Co(en)(H_2O)_2(OH)(R)^{n+} + H_2O \quad (1)$$

$$Co(en)(H_2O)_2(OH)(R)^{n+} \xrightarrow{k_2} Co(II) + R\cdot + \text{other products} \quad (2)$$

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$$\left.\begin{array}{r}\mathrm{Co(en)(H_2O)_3(OH)^{2+}} + \mathrm{R}\cdot \xrightarrow{k_3} \\ \text{or} \\ \mathrm{Co(en)(H_2O)_4{}^{3+}} + \mathrm{R}\cdot \xrightarrow{k_3}\end{array}\right] \rightarrow \mathrm{Co(II)} + \mathrm{R_2} + \text{other products} \qquad (3)$$

because it is small. The steady-state approximation was applied to the R· and $Co(en)(H_2O)_2(OH)(R)^{n+}$ concentrations, assuming all steps after k_1 to be fast, and $-d[Co(en)(H_2O)_4{}^{3+}]/dt = (2k_1K_a/[H^+])[Co(en)(H_2O)_4{}^{3+}][R]$, with $k_{obsd} = 2k_1K_a[R]/[H^+]$.

Another possibility for the disappearance of the radical would be its disproportionation. For superoxide this reaction is

$$2HO_2\cdot \xrightarrow{k_4} H_2O_2 + O_2 \qquad (4)$$

and for Br·

$$Br\cdot + Br^- \rightarrow Br_2{}^-\cdot$$

$$2Br_2{}^-\cdot \xrightarrow{k_4} Br_3{}^- + Br^- \qquad (5)$$

This would eliminate reaction 3 if k_4 is large enough. Stoichiometrically the importance of eq 3 and 4 or 5 would not be distinguishable.

For the reaction of $Co(NH_3)_2(H_2O)_4{}^{3+}$ with H_2O_2, reaction 4 has been ignored in mechanistic considerations.[4] We have attempted to qualitatively measure the importance of reactions 3 and 4. R· for the H_2O_2 reaction would be $HO_2\cdot$ (the protonated superoxide ion). The pK_a of this species has been reported as 4.8[7] and k_4 has been determined to be ca. 10^6 M^{-1} s^{-1}.[8] It is possible that some $H_2O_2{}^+$ was present in our reaction solutions,[9] but this does not change the estimate of k_4.[8] $HO_2\cdot$ has been reported not to reduce Co(III) complexes in several cases.[10–13] To look very qualitatively at the reaction of $HO_2\cdot$ with $Co(en)(H_2O)_4{}^{3+}$ we took a rapidly stirring solution at 25 °C that was 0.4 M in $HClO_4$ and 9×10^{-3} M in $Co(en)(H_2O)_4{}^{3+}$ and added about 7-mg amounts of solid KO_2 to the solution four times. The visible spectrum was scanned on a Cary 14 spectrophotometer before and after the addition of all of the KO_2 with no change in the spectrum, within experimental error, although approximately a 4 molar excess of KO_2 had been added to the solution. Within 0.01 s after the addition of the KO_2, the $HO_2\cdot$ would be about 10^{-4} M. The steady-state concentration of $HO_2\cdot$ would be less than 10^{-10} M; $[R\cdot] = (k_1/k_3)(K_a/[H^+])[R]$ if $k_3 > k_4$. Since there is no detectable reaction at 10^{-4} M $HO_2\cdot$, this would argue that $k_3 < k_4$ and probably $<10^{-2}$ M^{-1} s^{-1}. Consequently, nearly all of the $HO_2\cdot$ generated in solution would react with itself and not the $Co(en)(H_2O)_4{}^{3+}$.

A similar argument can be made concerning the likelihood of Br· reacting with either $Co(NH_3)(H_2O)_4{}^{3+}$[3] or $Co(en)(H_2O)_4{}^{3+}$.[3] The reaction of $Br\cdot + Br^- \rightarrow Br_2{}^-\cdot$ is very rapid, $k \approx 10^{10}$ M^{-1} s^{-1}, $K \approx 10^7$ M^{-1}, and the disproportionation $2Br_2{}^-\cdot \rightarrow Br_3{}^- + Br^-$ is also rapid, $k \approx 3.3 \times 10^9$ M^{-1} s^{-1}.[14–16] For the reduction of Co(III) to compete, it would have to be quite rapid.

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Registry No. $Co(en)(H_2O)_4{}^{3+}$, 67426-09-9; H_2O_2, 7722-84-1; Br^-, 24959-67-9.

References and Notes

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Synthesis and Structure of Complexes of Lanthanide Nitrates and Isonicotinic Acid Hydrazide, $Ln(NO_3)_3\cdot 3INH\cdot 3H_2O$[1]

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The transition-metal complexes of isonicotinohydrazide (INH) have been a subject of occasional studies[3] for a number of years since the report[4] that INH has antitubercular properties. Recently Dutt and Sen Gupta have reported[5] the preparation of rare-earth complexes of INH of the formulas $Ln(ClO_4)_3\cdot 5INH$ and $Ln(ClO_4)_3\cdot 3INH\cdot H_2O$. From spectroscopic studies, they conclude that the INH bonds to the lanthanide(III) ion only by the heterocyclic nitrogen. Other lanthanide complexes of INH perchlorates[6] and chlorides[7] have been reported. There is no definitive evidence for the coordination of INH in any of these complexes.

In this paper, we report the synthesis and characterization of complexes of composition $Ln(NO_3)_3\cdot 3INH\cdot 3H_2O$ and the single-crystal X-ray structure for the samarium compound. In contrast to the presumed structures previously reported, the ligand INH acts as a bidentate ligand with the heterocyclic nitrogen uncoordinated to the metal ion.

Experimental Section

The hydrated lanthanide nitrate was dissolved in a minimum amount of absolute ethanol and treated with a saturated acetonitrile–INH solution. The precipitate was filtered, washed with small portions of acetonitrile, and dried in vacuo over anhydrous calcium chloride.

Lanthanide ions were titrated with EDTA,[8] and carbon, hydrogen, and nitrogen were determined by microanalytical procedures (Midwest Microlab Ltd.); the results, summarized in Table I, are in excellent agreement with the proposed stoichiometry. The compounds are very soluble in water, methanol, and ethanol, slightly soluble in acetonitrile, and practically insoluble in nitromethane, chloroform, carbon tetrachloride, and benzene. Conductance measurements, at 25.00 ± 0.02 °C, of millimolar solutions in methanol, using a conductivity bridge composed of a Leeds and Northrup 4760 resistance box, a 2370 AC pointer galvanometer, and a cell with $K_c = 0.1070_8$ cm^{-1}, are in accordance with a 1:1 electrolyte behavior,[9] probably due to methanol's dissociative properties. The infrared spectra were recorded in a Perkin-Elmer 457 spectrophotometer in Nujol mulls between KBr plates.

The spectra lines (in cm^{-1}) for the metal complexes are as follows: ν_{CO}, 1654–1660; δ_{NH_2}, 1615–1620; $\delta_{NH} + \nu_{CN}$, 1549–1551; ν_{CN}, 1418–1422; $\delta_{NH} + \nu_{CN}$, 1339–1343; CH (in plane), 1220–1222,

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