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Oxidation of Azidopentaamminecobalt(III) Ion by Hydroxyl Radicals

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Oxidation of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ with hydroxyl radical ($k = 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) has been observed to yield a surprisingly stable coordinated radical, presumed to be $[\text{Co}(\text{NH}_3)_5\text{NNOH}]^{2+}$ which decays by a first-order intramolecular redox process ($k = 60 \pm 10 \text{ s}^{-1}$ at 25 °C) to give Co(II), N_2 , and N_2O as products. N_2O appears to arise from dimerization of NOH to $\text{H}_2\text{N}_2\text{O}_2$ which decomposes in acidic solution to N_2O and H_2O .

Introduction

Studies of the oxidation of coordinated ligands such as N_3^- by the thermodynamically powerful oxidants Np(VII) , Ag(II) , and Co(III) have shown some complex rate properties.⁴ Features of these reactions include induction periods, irreproducibility of the rates, and evidence for consecutive processes. The results point to the formation of some relatively long-lived radical intermediates which were not observed directly. The present pulse radiolysis investigation was undertaken in order to study the reaction of the coordinated azide ligand with a powerful oxidant, the OH radical, over short time intervals, in the hope of observing the formation and decay of coordinated radical intermediates.

Experimental Section

$[\text{Co}(\text{NH}_3)_5(^{14}\text{N}_3)](\text{ClO}_4)_2$ was prepared from chloride salt (5 g) with use of HClO_4 (6 M) or through the diacetate salt with use of $\text{Ag}(\text{CH}_3\text{CO}_2)$ (2.1 g) in water (10 mL). In the latter instance, the mixture was filtered, and then the complex was precipitated as the perchlorate salt by addition of HClO_4 (12 M, 5 mL). The complex was thrice recrystallized, in the dark, from acidified (pH 3, Vycor HClO_4) triple-distilled water by the addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (puriss).

$[\text{Co}(^{15}\text{NH}_3)_5(^{14}\text{N}_3)](\text{ClO}_4)_2$ (containing approximately 10% of NH_3 as $^{15}\text{NH}_3$) was prepared by the same method using appropriately ^{15}N -enriched NH_4Cl .

$[\text{Co}(\text{NH}_3)_5(^{15}\text{N}^{14}\text{N}^{14}\text{N})](\text{ClO}_4)_2$, $[\text{Co}(\text{NH}_3)_5(^{14}\text{N}^{14}\text{N}^{15}\text{N})](\text{ClO}_4)_2$ was synthesized by reacting $[\text{Co}(\text{NH}_3)_5(\text{Me}_2\text{SO})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Na}(^{15}\text{N}^{14}\text{N}^{14}\text{N})$ (approximately 12% of the terminal atoms were ^{15}N) in dimethyl sulfoxide (Me_2SO) at 70 °C for 20 min. The azide complex was thrice triturated with ether and then with ethanol/ether (1:1), collected, and washed with ethanol and ether. It was recrystallized as above. The ^{15}N content of the complex was determined by reacting a helium-purged solution of the complex (0.5 g) in HClO_4 (0.1 M, 5 mL) with NaNO_2 (0.5 g) and sampling the evolved gases with an evacuated Urey tube. The ^{15}N content in the N_2 (6.00 atom %) and N_2O (6.35 atom %) were determined with a VG Micromass 602D mass spectrometer operated in the scanning mode at 36 eV and 200 μA emission current. m/e 28, 29, 32, 44, and 45 peaks were individually attenuated by adjusting the gain on the minor beam amplifier.

Kinetics. The pulse radiolysis facility at the Australian Atomic Energy Commission Research Establishment utilized for this work consisted of a 1-MeV Van de Graaff electron accelerator which delivered electron pulses (3.4- μs duration) through a thin wall (0.30–0.4 nm) of a Suprasil cell with an optical path length of 1 cm. By remote operation of a peristaltic pump, the solution was changed in the cell, and each irradiated volume received only one pulse of fast electrons corresponding to ca. $3 \times 10^{-6} \text{ M}$ of OH radicals. The optical transmissions of a beam of light passing through the cell before, during, and after the pulse were monitored with use of a Bausch and Lomb

monochromator and an 1P28 photomultiplier tube. The transmission change was processed by a Biomation 610B analogue digital converter and storage facility unit linked to a PDP11/03 minicomputer. The software program has been described.⁶ A signal-averaging program allowed several traces to be averaged (usually 10), in order to improve the signal:noise ratio. A linear least-squares program calculated both first- and second-order rate constants for the reaction of the transient and displayed the results on the visual display unit so that the fit of the data could be evaluated.

Aqueous solutions 10^{-2} – 10^{-3} M in complex were prepared in triple-distilled water (pH 6.4), in dilute HClO_4 (pH 3.6) or in 0.01 M $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ buffer solutions (pH 6.8). Solutions were protected from all extraneous light and, immediately before irradiation, were purged for 30 min with N_2O . Photodegradation of the solution in the cell was minimized by a shutter in front of the xenon light source (450 W). The shutter was opened just prior to the electron pulse, and a Perspex filter protected the solution from ultraviolet light. For a 10^{-3} M solution of complex in dilute HClO_4 solution, typical absorbance increases for the transient over the parent ion in the range 350–630 nm were as follows: 627 nm, 0; 587 nm, 0.007; 532 nm, 0.009; 500 nm, 0.011; 477 nm, 0.012; 464 nm, 0.010; 441 nm, 0.014; 400 nm, 0.009; 351 nm, 0.004. The reaction kinetics were therefore determined at 440 nm, the position of maximum absorbance change.

Additional experiments were carried out on aqueous solutions of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)](\text{ClO}_4)_2$ (10^{-3} M) purged with N_2O under conditions where the OH radical was efficiently scavenged by *tert*-butyl alcohol (8 mL/100 mL of solution). On irradiation, no transient absorption was observed in the region 410–480 nm.

Tracer Experiments. After N_2O was shown to be a product of the reaction, helium was used instead of N_2O to purge the reaction solution when the gaseous products of the reaction were required to be analyzed. Under these conditions both OH radicals and hydrated electrons reacted with $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$. The apparatus consisted of a glass gas line which allowed the initial solution, the receiving flask, and the irradiation cell to be effectively purged with He prior to the irradiation experiment. Immediately before irradiation was begun, the He purge of the receiving flask was stopped, but the flask was maintained under a positive He pressure. Solutions of the complex (10^{-3} M , 400 mL, pH 6.0 or 3.6), protected from all light, were passed through the irradiation cell (25 mL/min), irradiated with a train of electron pulses (50/s), and collected in the receiving flask under positive He pressure, which contained 1 M HClO_4 sufficient to bring the resultant solution to 0.1 M HClO_4 . The receiving flask was then transferred to a vacuum line bearing an evacuated Urey tube, the line was evacuated ($2 \times 10^{-4} \text{ atm}$), and the gases present above the solution were sampled. The reaction vessel was then stirred and sampled again.

Gas samples from irradiated solutions of the unenriched complex and NaN_3^- , and from irradiated water were analyzed with use of an AEI-MS 902 high-resolution mass spectrometer. Identification of N_2 (mass 28.0061), N_2O (mass 44.0011), and NO (mass 29.9980 \pm 0.0003) as products of irradiation of the $[\text{Co}(\text{NH}_3)_5(\text{N}_3)](\text{ClO}_4)_2$ solutions was established unequivocally by this high-resolution technique.

The ^{15}N enrichment in the N_2 and N_2O products of irradiation of solutions of $[\text{Co}(^{15}\text{NH}_3)_5(^{14}\text{N}_3)](\text{ClO}_4)_2$ with 10 atom % $^{15}\text{NH}_3$ and $[\text{Co}(^{14}\text{NH}_3)_5(^{14}\text{N}^{14}\text{N}^{15}\text{N})](\text{ClO}_4)_2$, $[\text{Co}(^{14}\text{NH}_3)_5(^{15}\text{N}^{14}\text{N}^{14}\text{N})](\text{ClO}_4)_2$ ($^{15}\text{N}^{14}\text{N}^{14}\text{N}$ -labeled terminally with 12.35% ^{15}N) were determined with a VG Micromass spectrometer operated in the scanning mode (36 eV, 200 μA emission current), by measuring

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the heights of the relevant mass peaks, determining their ratios with respect to internal oxygen as standard, correcting for the result from a blank solution, and then determining the relative abundances of the masses 29/28 ($^{15}\text{N}^{14}\text{N}^{14}\text{N}_2$) and 45/44 ($^{15}\text{N}^{14}\text{NO}^{14}\text{N}_2\text{O}$).

Product Analysis. Solutions of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)](\text{ClO}_4)_2$ (0.2 g in 200 mL H_2O at pH 6.0 or 3.6 with Vycor HClO_4) purged with N_2O were irradiated by a train of pulses and collected as in the tracer experiments. The cations were sorbed on a DOWEX (H^+ 50W \times 2, 200–400 mesh, 7×1 cm) ion-exchange column. Elution with 0.5 M NH_4NCS gave 0.10 \pm 0.01 mM or $\text{Co}(\text{II})$ and with 1 M NaClO_4 (pH 3 with HClO_4) gave 0.44 ± 0.01 mM of the unreacted azido complex.

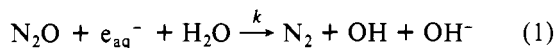
Ferrous sulfate dosimetry was used to measure the radiation doses delivered to the solution by the train of pulses. The G value for the combined OH, H, and e_{aq}^- reactions was 4.7.

Solutions of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)](\text{ClO}_4)_2$ in N_2O saturated water irradiated with ^{60}Co γ rays for 1.5 h (60 krad/h), analyzed in the same fashion, gave similar results except that small amounts of Co_2O_3 and/or polymeric complexes (10%) were also sorbed on the columns.

Competition Studies. Mixtures of solutions of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)](\text{ClO}_4)_2$ (1.14×10^{-2} M) and KNCS (10^{-2} M) in triple-distilled water were prepared. The solutions were purged with N_2O and irradiated, and the absorbance changes at 480 nm due to the formation of the radical $(\text{NCS})_2^{\cdot-}$ were measured. The solution compositions and the absorbance changes which resulted on irradiation are as follows (concentrations in 10^{-3} M followed by reciprocal absorbance): Co, 10.9, NCS^- , 0.48, 34.5; Co, 10.3, NCS^- , 1.01, 19.8; Co, 9.68, NCS^- , 1.53, 15.3; Co, 8.71, NCS^- , 2.53, 12.1; NCS^- , 2.0, 6.25; NCS^- , 0.2, 7.6; Co, 11.4, 143.

Results and Discussion

The pulse radiolysis technique provides a powerful tool for the investigation of rapid redox reactions. On receiving a pulse of fast electrons, water is dissociated into two main reactive species, the OH radical ($G = 2.7$) which is a powerful oxidant ($E^\circ \geq 2$ V) and the hydrated electron ($G = 2.7$) which is a powerful reductant ($E^\circ = 2.8$ V).⁸ The former is effectively quenched by radical scavengers such as *tert*-butyl alcohol added to the solution, while the latter is scavenged by N_2O , with the formation of an equivalent amount of OH radical (eq 1). The rapid formation of the OH radical in solution, coupled



$$k = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ \text{C}$$

with the use of a rapid-response spectrophotometric system, allows the detection and characterization of the initial species produced on OH capture and their subsequent decay.

The reaction between $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ and OH resulted in the rapid formation of a transient species with a visible spectrum similar to that of the parent ion but more intensely absorbing. Since the intensity of the first ligand field band of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ is uncommonly large for substituted cobalt(III) pentaammine ions ($\epsilon_{519}^{\text{max}} = 272 \text{ M}^{-1} \text{ cm}^{-1}$ whereas usually $\epsilon^{\text{max}} = 50 \pm 10 \text{ M}^{-1} \text{ cm}^{-1}$), the spectrum of the transient can be viewed as related to that of the azido ion but modified by reaction with the OH radical. We presume that the attack is at the azide ligand and that the reaction produces either the neutral $\cdot\text{N}_3$ radical or the $\cdot\text{NNNOH}^-$ radical ion. The former would arise by electron transfer from the bound azide to OH and the latter by addition of OH to the azide moiety. The latter path is a major reaction path of OH radicals with many organic molecules.

The rate of formation of the oxidized azido complex was too rapid to measure directly with the instrumentation available (limited by the minimum pulse width of 3.4 μs), but it was evaluated by a competition experiment. Both NCS^-

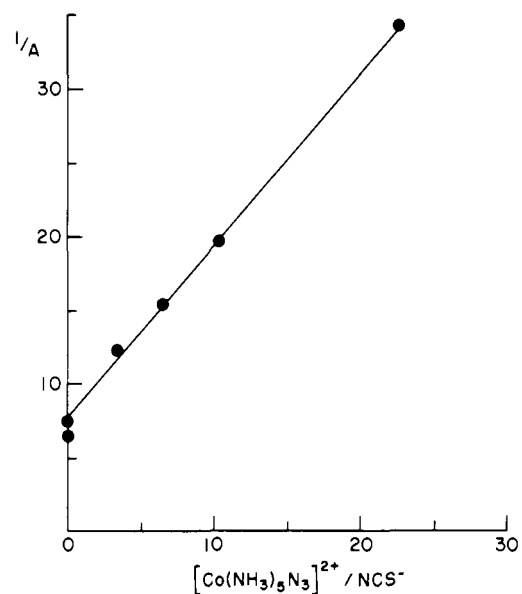


Figure 1. Plot of reciprocal absorbance ($1/A$) against the ratio $(\text{NH}_3)_5\text{CoN}_3^{2+}/\text{KNCS}$ for the competition reaction of the two species with OH radical at 25°C (see Experimental Section).

and the complex compete in reducing OH. The former reacts rapidly with OH ($k = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C) to form the highly absorbing $(\text{NCS})_2^{\cdot-}$ radical ion.⁹ The results of the competition experiment are presented in Figure 1. From these results one calculates that $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ was oxidized by OH with a rate constant of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C .

Once formed, the oxidized azido complex was surprisingly stable, decaying with a first-order rate constant of $60 \pm 10 \text{ s}^{-1}$ at 25°C which was independent of the initial $\text{Co}(\text{III})$ concentration, pH, and the radiation dose rate. In the presence of 0.01 M $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ buffer (pH 6.8), the observed rate constant was considerably larger, $8.0 (\pm 1.0) \times 10^2 \text{ s}^{-1}$, and the G values were considerably smaller. These results imply that under these experimental constraints a different species is the predominant reactant with OH.

Decomposition of the oxidized $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ ion in N_2O saturated solutions yields $\text{Co}(\text{II})$ quantitatively and N_2 as the only detectable products above the background. The solubility of N_2 precluded its quantitative measurement, but tracer studies determined its origin. The N_2 recovered from the reaction of an equimolar mixture of $[\text{Co}(\text{NH}_3)_5(^{15}\text{N}^{14}\text{N}^{14}\text{N})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(^{14}\text{N}^{14}\text{N}^{15}\text{N})]^{2+}$ (labeled terminally with 8.35% ^{15}N) with OH was found to contain 4.0 atom % ^{15}N (natural abundance ^{15}N is 0.7 atom %). This isotopic content is diluted by an equivalent amount of unlabeled N_2 arising from the reaction in eq 1. The amount of the label in the N_2 arising from the reaction of OH with the complex is therefore almost double that observed.

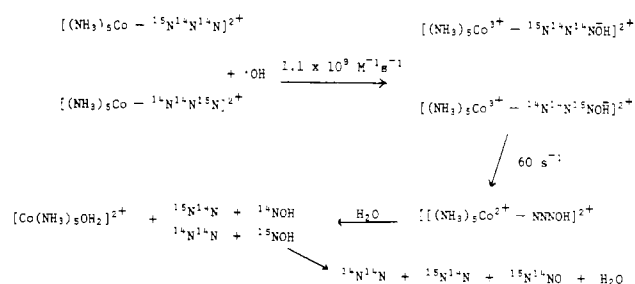
Since a product of the oxidation of $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ by OH was N_2O , it was necessary to conduct further ^{15}N tracer experiments in solutions purged with He rather than N_2O . Under these conditions both the OH radical and the hydrated electron react with the complex. The latter leads to reduction of $\text{Co}(\text{III})$ to $\text{Co}(\text{II})$ presumably without affecting the bound N_3^- ($k = 6.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 25°C).⁹ However, the cobalt(II) azido product (ca. 10^{-6} M) should not affect the reaction of the OH radical with the residual $\text{Co}(\text{III})$ complex (ca. 10^{-3} M) since its concentration is so small. Even if the cobalt(II) azido complex dissociated N_3^- , it would not influence the tracer measurements despite the fact that the products detected in the reaction of N_3^- with OH (10^{-3} M, pH 6,

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Scheme I



HClO₄) in a He purged solution were N₂ and N₂O. In this last respect our results are at variance with those of Hayon and Simic¹⁰ who claim N₂ as the sole product of this reaction at pH 9. However, they conducted their experiments in a medium saturated with N₂O, and naturally this molecule would not have been observed as a product. The other difference between the two experiments is the pH, but in both instances N₃⁻ is the most abundant species and not HN₃.

The gaseous products of the irradiation of [Co(NH₃)₅-(¹⁴N¹⁴N¹⁵N)]²⁺ and [Co(NH₃)₅(¹⁵N¹⁴N¹⁴N)]²⁺ (containing ¹⁵N¹⁴N¹⁴N⁻ with 12.35% ¹⁵N, He-purged solutions) were identified as N₂ (containing 6.18 atom % of ¹⁵N), N₂O (containing 10.88 atom % of ¹⁵N), and an amount of NO. NO presumably arose from decomposition of N₂O in the mass spectrometer. The high enrichment in the N₂O produced implies that it has arisen from two N-containing fragments both labeled.

The reaction of [Co(¹⁵NH₃)₅(¹⁴N₃)]²⁺ (10 atom % ¹⁵NH₃) with the OH radical in He-purged solution yielded small amounts of ¹⁴N¹⁵N (1.9 atom %) and ¹⁵N¹⁴NO (2.1 atom %). Since these gases were not substantially enriched above those produced by unenriched complex [N₂, 0.80 atom %; N₂O, 0.76 atom % (i.e., natural abundance)] oxidation of coordinated NH plays only a minor role if any in the reaction. The small yields of the gaseous products make the isotopic ratio difficult to measure accurately when the difference from natural abundance and instrumental background is not great. These enrichments therefore may reflect the errors more than the relative isotopic abundances.

Principal products of the decomposition of the OH-oxidized [Co(NH₃)₅N₃]²⁺ ion were Co(II), N₂, and N₂O although the mass balance for N₂ was not determined. Since [Co(NH₃)₅H₂O]³⁺ was sought and not detected, the decay of the transient species presumably cannot involve dissociation of the coordinated radical to yield a cobalt(III) species and either ·N₃ or ·NNNOH. In addition, the observed first-order rate of decay of the transient does not allow dimerization of two complex fragments as the rate-determining step. An intramolecular electron-transfer reaction is indicated and a proposal which appears to fit the rate law, the limited stoichiometry data, the tracer results, and the general chemistry (Scheme I) follows.

Addition of OH to the coordinated azido ion as shown in Scheme I is in keeping with much of the addition chemistry found for the reactions of OH radicals both with organic molecules and coordinated ligands.¹¹ Moreover the electrophilic OH radical would be expected to attack at the site most distant from the N attached to the electrophilic Co(III) center. Intramolecular electron transfer from radical ligand to metal

ion reduces the Co(III) to Co(II) and generates N₂ and NOH. The latter then rapidly dimerizes to H₂N₂O₂ which decomposes in the acidic solution to N₂O and water.¹²

Scheme I implies that only the azido ion with the label bound to Co(III) leads to label in the N₂ product. Conversely, the terminally labeled azido ion puts label into the N₂O product. This yields one in four of N atoms labeled in N₂ and one in two N atoms labeled in N₂O, and it accounts for the significantly higher labeling observed in the N₂O product over the N₂ product.

The prospect of the OH radical accepting an electron directly from the coordinated azide ion would also be consistent with the powerful reducing capacity of the azide ion (2N₃⁻ → 3N₂ + 2e⁻, E° = 3.4 V).¹³ The N₃ radical bound to the Co(III) center could then undergo the intramolecular electron transfer to generate N₃⁺ which in turn should rapidly capture OH⁻ to yield N₂ and NOH. We have no way to distinguish between the two reaction schemes at present, but the addition reaction appears to be more consistent with the known chemistry of OH reactions.

The spectral decay observed would be consistent with the intramolecular redox process [(NH₃)₅Co^{III}NNNOH]²⁺ → [(NH₃)₅Co^{II}NNNOH]²⁺. The Co(II) intermediate would be expected to absorb at lower wavelengths with a much reduced intensity (ca. 10-fold) if the general analogy between comparable Co(II) and Co(III) complex ions holds.

The neutral NNNOH molecule seems a reasonable intermediate analogous to the halogen azides, and it has been proposed as an intermediate in the reaction between MnO₄⁻ and HN₃.¹⁴ The NOH radical derived from this molecule has also been postulated in the reaction between Sn(II) and NO₃⁻ and NO₂⁻ catalyzed by Mo(VI)¹⁵ as well as in the oxidation of HN₃ by BrO₃⁻.¹⁵ In the latter study, stoichiometric, kinetic, and nitrogen-15 tracer data presented were consistent with the postulate of the existence of HON and its dimerization to H₂N₂O₂. In addition, the rate of formation of H + NO = NOH (k = 1.1 × 10¹⁰ M⁻¹ s⁻¹) has been calculated from radiation studies of aqueous solutions of NO.¹⁷

The stability of the coordinated radical whatever its form (·NNNOH or ·NNN) is striking (t_{1/2} = 10⁻² s). It clearly must be largely delocalized, and it is conceivable that it loses considerable delocalization energy by undergoing electron transfer to the metal ion. Such an effect could accommodate the slow rate. Also, its long lifetime might account for the variable kinetics for Ag(II)(aq), Np(VII)(aq), and Co(III)(aq) oxidations of (NH₃)₅CoN₃²⁺. If this were true, radical scavengers such as O₂ (in variable concentrations) could compete for the long-lived radical. The chain processes in such systems are then unlikely to be reproducible. More experimental work is in progress exploring the factors which influence the stability of such coordinated radicals.

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Registry No. [Co(NH₃)₅(N₃)]²⁺, 14403-83-9; OH·, 3352-57-6; [Co(NH₃)₅NNNOH]²⁺, 78199-02-7.

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