Infrared spectroscopy was used for further confirmation of azido coordination. The asymmetric N–N stretching frequency, expected between 2000 and 2100 cm^{-1}, cannot be used, since selenocyanate would exhibit a C–N stretch in the same region. However, the symmetric N–N stretching frequency is expected between 1240 and 1280 cm^{-1},[17,18] with no counterpart in the selenocyanate or bipyridine spectrum. A band was observed at 1246 cm^{-1}, which would appear to be the ν_5(N–N–N) mode.

The selenocyanate reaction in particular, and $[Ru(bpy)_3]^{2+}$ photosubstitution reactions in general, appears to merit additional investigation aimed at unraveling both mechanistic and overall stoichiometric details of the process.

Registry No. $[Ru(bpy)_3]Cl_2$, 14323-66-9; $[Ru(bpy)_3]I_2$, 23792-07-6; $[Ru(bpy)_3](NO_2)_2$, 71031-49-7; $[Ru(bpy)_3](mal)$, 71000-88-9; $[Ru(bpy)_3](N_3)_2$, 71000-89-0; $[Ru(bpy)_3](CN)_2$, 71050-17-4; $[Ru(bpy)_3](SeCN)_2$, 71031-52-2; $[Ru(bpy)_3](IO_3)_2$, 71000-90-3; $Ru(bpy)_2I_2$, 71048-70-9; $Ru(bpy)_2(NO_2)_2$, 29241-01-8; $Ru(bpy)_2(N_3)_2$, 55124-48-6; $Ru(bpy)_2(mal)$, 71000-91-4; $Ru(bpy)_2(CN)_2$, 20506-36-9.

References and Notes

(1) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, **16**, 544 (1962).
(2) N. R. Davies and T. L. Mullins, *Aust. J. Chem.*, **20**, 657 (1967).
(3) N. R. Davies and T. L. Mullins, *Aust. J. Chem.*, **21**, 915 (1968).
(4) G. M. Bryant, J. E. Fergusson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
(5) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).
(6) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **98**, 1884 (1976).
(7) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, **16**, 42 (1963).
(8) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, **19**, 2229 (1966).
(9) R. Charonnat, *Ann. Chim. (Paris)*, **16**, 5 (1931).
(10) C. F. Liu, N. C. Liu, and J. C. Bailar, *Inorg. Chem.*, **3**, 1197 (1964).
(11) E. C. Johnson, B. P. Sullivan, D. J. Salmon, S. A. Adeyemi, and T. J. Meyer, *Inorg. Chem.*, **17**, 2211 (1978).
(12) J. N. Demas, T. F. Turner, and G. A. Crosby, *Inorg. Chem.*, **8**, 674 (1969).
(13) A. A. Schilt, *J. Am. Chem. Soc.*, **85**, 904 (1963).
(14) P. E. Hoggard and G. B. Porter, *J. Am. Chem. Soc.*, **100**, 1457 (1978).
(15) W. M. Wallace and P. E. Hoggard, submitted for publication.
(16) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).
(17) W. Beck, W. P. Fehlhammer, P. Pöllman, E. Schuierer, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967).
(18) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley-Interscience, New York, 1970.

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The $[Co(NH_3)_5(O_2C^-\cdot)]^{2+}$ Coordinated Ligand-Radical Complex[1]

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One of the first coordinated ligand-radical species to be proposed in electron-transfer reactions was $[Co(NH_3)_5(O_2C^-\cdot)]^{2+}$ which was postulated by Candlin and Halpern[2] as an intermediate in the MnO_4^- oxidation of $Co(NH_3)_5O_2CH^{2+}$ in aqueous solution. They interpreted their observations in terms of intramolecular electron transfer in the coordinated $\cdot CO_2^-$ complex to form Co^{2+} (aq) and CO_2 in competition with reaction with MnO_4^- to form $Co(NH_3)_5OH_2^{3+}$ and CO_2. The ratio of the rate constants of these reactions was evaluated but their absolute values were not determined.

Because of the efficient reactions of OH radicals and H atoms with HCO_2H ($k = 1.5 \times 10^8$ and 1.1×10^6 M^{-1} s^{-1})[3,4] and HCO_2^- ($k = 2.0 \times 10^9$ and 5.0×10^7 M^{-1} s^{-1})[3,4] to form $\cdot CO_2^-$, we reasoned that OH and H should react with $Co(NH_3)_5O_2CH^{2+}$ via H abstraction to form $[Co(NH_3)_5(O_2C^-\cdot)]^{2+}$. In this way we could test whether or not $[Co(NH_3)_5(O_2C^-\cdot)]^{2+}$ engages in intramolecular electron transfer, evaluate the rate constants for the various processes, and provide insight into the mechanism of induced electron transfer in which an oxidizing agent causes the reduction of the metal center.[5]

Experimental Section

$[Co(NH_3)_5O_2CH](ClO_4)_2$ was prepared according to the method of Sebera and Taube;[6] the spectral characteristics of the compound were identical with those reported in the literature.

Pulse radiolyses with optical absorption detection were conducted by using the apparatus at the U.S. Army Natick Research and Development Command;[7] pulse radiolyses with kinetic conductivity detection were performed at the Radiation Laboratory of the University of Notre Dame.[8] Continuous radiolyses were conducted at Boston University in ^{60}Co γ-ray sources (dose rates $\sim 3.5 \times 10^{16}$ and $\sim 7.0 \times 10^{17}$ eV mL^{-1} min^{-1}); the Fricke dosimeter[9] was used to evaluate the exact radiation dose received by the solutions.

The solutions were purged of air by saturation with N_2O (2.5×10^{-2} M); alternatively, the solutions were saturated with O_2 (1.3×10^{-3} M). Reagent grade chemicals and Millipore water were used to prepare the solutions. Kitson's method[10] was used for the analysis of Co^{2+}(aq). UV–vis spectra were determined with a Cary 118 spectrophotometer.

Results and Discussion

The radiolysis of water and aqueous solutions proceeds according to the overall reaction $H_2O \rightsquigarrow e_{aq}^-$ (2.8), OH (2.8), H (0.55) where the numbers in parentheses represent the *G* values (number of radicals formed/100 eV of energy absorbed) of the species. N_2O, H^+, and O_2 are effective scavengers for e_{aq}^-;[11] H and $\cdot CO_2^-$ also react with O_2.[4]

$$e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^- \quad (k = 8.7 \times 10^9\ M^{-1}\ s^{-1})$$

$$e_{aq}^- + H^+ \rightarrow H \quad (k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1})$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad (k = 2.0 \times 10^{10}\ M^{-1}\ s^{-1})$$

$$H + O_2 \rightarrow HO_2 \quad (k = 2.0 \times 10^{10}\ M^{-1}\ s^{-1})$$

$$HO_2 \rightleftarrows H^+ + O_2 \quad (pK_a = 4.8)^{12}$$

$$\cdot CO_2^- + O_2 \rightarrow CO_2 + O_2^- \quad (k = 1.5 \times 10^9\ M^{-1}\ s^{-1})^{13}$$

The pulse radiolysis (optical absorption) of buffered N_2O-saturated solutions of 5.0×10^{-4} M $Co(NH_3)_5O_2CH^{2+}$ (pH 1–7) reveals pseudo-first-order bleaching of the substrate absorbance in the microsecond time frame corresponding to a second-order disappearance with $k \sim 2 \times 10^9$ M^{-1} s^{-1}; no other transient or permanent absorbances are observed.[14] Continuous radiolysis under the same conditions produces Co^{2+}(aq) in quantitative yield ($G = 6.1 \pm 0.3$) independent of pH, radiation dose, [substrate], and [phosphate buffer]; the absorption spectra of the radiolyzed solutions show loss of substrate stoichiometric with the formation of Co^{2+}(aq). The pulse radiolysis (kinetic conductivity) of 5.0×10^{-4} M $Co(NH_3)_5O_2CH^{2+}$ at pH 4.3 reveals that the full yield of Co(III) is generated within 2 μs as evidenced by the uptake of H^+ from the release of NH_3. In fact, the results are very similar to those obtained for the reaction of e_{aq}^- with $Co(NH_3)_5Cl^{2+}$.[15] The release of two ammonias, and presumably the nonammonia ligand, occurs with $t_{1/2} < 2$ μs; the fourth, fifth, and sixth ligands are released with $t_{1/2} = 8$, 80, and 500 μs, respectively.

The results demonstrate that the reaction of OH radicals and H atoms with $Co(NH_3)_5O_2CH^{2+}$ leads quantitatively to Co^{2+}(aq) and that the primary intermediate from the radical interaction has a lifetime toward the generation of Co(II) of ≤ 2 μs. The sequence of events given in eq 1–7 can be written

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$$\mathrm{Co^{III}(NH_3)_5O_2CH^{2+} + OH \rightarrow [Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} + H_2O} \quad (1)$$

$$\mathrm{Co^{III}(NH_3)_5O_2CH^{2+} + H \rightarrow [Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} + H_2} \quad (2)$$

$$\mathrm{[Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+} \rightarrow [Co^{II}(NH_3)_5O_2C]^{2+}\ (low\ spin)} \quad (3)$$

$$\mathrm{[Co^{II}(NH_3)_5O_2C]^{2+}\ (low\ spin) \rightarrow [Co^{II}(NH_3)_5O_2C]^{2+}\ (high\ spin)} \quad (4)$$

$$\mathrm{[Co^{II}(NH_3)_5O_2C]^{2+}\ (high\ spin) \rightarrow Co^{II}(NH_3)_3{}^{2+} + CO_2 + 2NH_3} \quad (5)$$

$$\mathrm{Co^{II}(NH_3)_3{}^{2+} \xrightarrow{t_{1/2}\,=\,8\ \mu s} Co^{II}(NH_3)_2{}^{2+} \xrightarrow{t_{1/2}\,=\,80\ \mu s} Co^{II}(NH_3)^{2+} \xrightarrow{t_{1/2}\,=\,500\ \mu s} Co^{2+}(aq)} \quad (6)$$

$$\mathrm{NH_3 + H_3O^+ \rightarrow NH_4{}^+ + H_2O} \quad (7)$$

with $k_1 \sim 2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 \sim 10^7\ \mathrm{M^{-1}\ s^{-1}}$,[16] $k_4 > 10^6\ \mathrm{s^{-1}}$,[17] $k_5 \geq 10^6\ \mathrm{s^{-1}}$, and $k_7 = 4.3 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$.[18] We estimate $k_3 \geq 10^6\ \mathrm{s^{-1}}$, with the lifetime of $\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$ toward intramolecular electron transfer $\leq 10^{-6}$ s. This conclusion is very resonable in light of what we know about the powerful reducing ability of $\mathrm{\cdot CO_2{}^-}$ toward Co(III) complexes[19] and the lifetimes of ligand radicals coordinated to Co(III) centers.[20]

In continuously radiolyzed $\mathrm{O_2}$-saturated solution containing 5.0×10^{-4} M $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ and 0.5 M $\mathrm{NaHCO_2}$ at pH 6, $G(\mathrm{Co^{2+}(aq)}) = 1.3$ which corresponds entirely to the direct reaction of $\mathrm{e_{aq}{}^-}$, which escape scavenging by $\mathrm{O_2}$, with the complex with $k_8 \sim 5 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$; $\mathrm{\cdot CO_2{}^-}$ reacts preferentially with $\mathrm{O_2}$ than with $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ ($k \sim 1 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$).[19] This result establishes that

$$\mathrm{Co(NH_3)_5O_2CH^{2+} + e_{aq}{}^- \rightarrow Co^{2+}(aq) + 5NH_3 + {}^-O_2CH} \quad (8)$$

$\mathrm{O_2{}^-}$ radicals do not reduce $\mathrm{Co(NH_3)_5O_2CH^{2+}}$. With this result, we can interpret the $G(\mathrm{Co^{2+}(aq)})$ values obtained for the continuous radiolysis of $\mathrm{O_2}$-saturated solutions containing 5.0×10^{-4} M $\mathrm{Co(NH_3)_5O_2CH^{2+}}$; $G(\mathrm{Co^{2+}(aq)}) = 2.8$, 3.1, and 3.8 at pH 1.0, 3.1, and 6.8, respectively. The results are in complete accord with reactions 1, 2, and 8 leading to $\mathrm{Co^{2+}(aq)}$ and with $\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$ not being quenched by $\mathrm{O_2}$ in competition with reaction 3. If reaction 9 occurred to any

$$\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+} + O_2 \rightarrow [Co(NH_3)_5O_2C]^{3+} + O_2{}^-} \quad (9)$$

significant extent, a diminution in the yield of $\mathrm{Co^{2+}(aq)}$ and the formation of $\mathrm{Co(NH_3)_5OH_2{}^{3+}}$ would be expected; these effects were not observed. It can be concluded that k_9 has a value of $\sim 10^9\ \mathrm{M^{-1}\ s^{-1}}$ as an upper limit.

According to the mechanism of Candlin and Halpern,[2] reaction 3 would be in competition with reaction 10 with k_{10}/k_3

$$\mathrm{[Co(NH_3)_5(O_2C^{-}\cdot)]^{2+} + MnO_4{}^- \xrightarrow{H_2O} Co(NH_3)_5OH_2{}^{3+} + CO_2 + MnO_4{}^{2-}} \quad (10)$$

$= 3 \times 10^2\ \mathrm{M^{-1}}$. From our estimate of k_3, a value of $k_{10} \geq 3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ is obtained. However, the possibility remains that reaction of $\mathrm{MnO_4{}^-}$ with $\mathrm{Co(NH_3)_5O_2CH^{2+}}$ occurs via attachment.[21]

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Registry No. $\mathrm{[Co^{III}(NH_3)_5(O_2C^{-}\cdot)]^{2+}}$, 71214-99-8.

References and Notes

(1) Research supported by the National Science Foundation through Grant No. CHE76-21050.
(2) J. P. Candlin and J. Halpern, *J. Am. Chem. Soc.*, **85**, 2518 (1963).
(3) Farhataziz and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 59** (1975).
(4) M. Anbar, Farhataziz, and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 51** (1975).
(5) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, 1970.
(6) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).
(7) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73**, 4207 (1969).
(8) J. Lilie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).
(9) M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", The M.I.T. Press, Cambridge, Mass., 1969.
(10) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
(11) M. Anbar, M. Bambenek, and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 43** (1973).
(12) B. H. J. Bielski and J. M. Gebicki, *Adv. Radiat. Chem.*, **2**, 177 (1970).
(13) M. Simic in "Fast Processes in Radiation Chemistry and Biology", G. E. Adams, E. M. Fielden, and B. D. Michael, Ed., Wiley, London, 1975.
(14) At pH ≥7 in unbuffered solution, absorbance changes due to the formation and nucleation of hydrous oxides of Co(II) are observed occurring in the second-to-minute time frame.
(15) J. Lilie, N. Shinohara, and M. G. Simic, *J. Am. Chem. Soc.*, **98**, 6516 (1976).
(16) E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76**, 2402 (1972).
(17) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975, Chapter 3.
(18) M. Eigen, *Angew. Chem.*, **75**, 489 (1963).
(19) M. Z. Hoffman and M. Simic, *Inorg. Chem.*, **12**, 2471 (1973).
(20) M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *J. Am. Chem. Soc.*, **99**, 2166, (1977).
(21) Reference 5, p 92.

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Temperature-Dependent Optical Spectra of Manganese Acetate: Intratrimer Exchange

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The magnetic structure of manganous acetate tetrahydrate $[\mathrm{Mn(OAc)_2}]$ has been the subject of study for over 15 years. The quasi-two-dimensional lattice configuration, in which the intraplanar exchange field is about 8000 G and the interplane exchange field is some 1000 G, had been recognized early in the history of these studies.[1-4] Furthermore, the strength of these exchange fields is nearly independent of temperature in the liquid helium to room-temperature range.[5] However, a rather interesting structural feature was revealed in the neutron diffraction and X-ray crystallographic studies of Burlet et al.[6,7] Within the layered structure the Mn(II) ions are grouped into linear trimers. The coupling within the trimer is antiferromagnetic as is the coupling between planes, while the intertrimer exchange coupling is ferromagnetic. As noted above, the latter two interactions have been measured, but the strength of the former exchange interaction can only be qualitatively determined from shifts in the low-temperature EPR resonance field which are observed at temperatures below 30 K[3] and from a slight curvature in the $1/\chi$ vs. T plot in the powder susceptibility measurements.[1]

Two earlier optical studies have been concerned with $\mathrm{Mn(OAc)_2}$. Mehra and Venkateswarlu[8] (MV) have studied the spectrum in the 3000–6000 Å region at 300 and 77 K. There is little doubt but that their classification scheme of the major spectral features is correct. The two lowest energy bands above the $^6\mathrm{A}_1$ ground state labeled A and B by MV are assigned as the transition to the $^4\mathrm{T}_1(\mathrm{G})$ and $^4\mathrm{T}_2(\mathrm{G})$ states. The next band (C) is relatively sharp with some narrow features already present at 77 K and is assigned as the transition to $^4\mathrm{A}_1(\mathrm{G})$ and $^4\mathrm{E}(\mathrm{G})$. It is this spectral region which was studied in detail by Tsujikawa at low temperatures (down to 1.3 K)