alized as reflecting differences in the degree of ion-pairing and salting-out effects.[12]

Registry No. PNAH, 35756-49-1; $Fe(CN)_6^{3-}$, 13408-62-3; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Cs^+, 18459-37-5; Et_4N^+, 66-40-0.

Supplementary Material Available: A listing of k_{obsd} at various concentrations of alkali-metal and tetraethylammonium chlorides (1 page). Ordering information is given on any current masthead page.

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(11) J. H. Gordon, "The Organic Chemistry of Electrolyte Solutions", Wiley, New York, 1975, Chapters 1 and 3.
(12) The authors wish to thank a reviewer for suggesting the possibility.

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Syntheses and Properties of Pentaamminecobalt(III) Complexes Containing *N*-Methyl-, *N*,*N*-Dimethyl-, and *N*,*N'*-Dimethylethylenediamine and (2-Aminoethyl)trimethylammonium Ion

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Received March 26, 1980

In a recent article, it was concluded that an intense absorption in the ultraviolet region observed for $[Co(NH_3)_5(en)]^{3+}$ was a charge-transfer band due to the intramolecular hydrogen bonding between a free amino group and an NH proton on the cobalt(III) center:[1] There are two possible modes of hydrogen bonding as shown in Chart I. In this work, pentaamminecobalt(III) complexes containing the following analogues of ethylenediamine were synthesized and their pK_a values were determined: $CH_3NHCH_2CH_2NH_2$ (meen), $(CH_3)_2NCH_2CH_2NH_2$ (*asym*-dimeen), $CH_3NHCH_2CH_2NHCH_3$ (*sym*-dimeen), and $(CH_3)_3NCH_2CH_2NH_2^+$ (tmen$^+$). The spectral features of these complexes are discussed in terms of the hydrogen bonding as mentioned above.

Experimental Section

A. Materials. The ligands meen, *asym*-dimeen, and *sym*-dimeen were obtained from Tokyo Kasei Co. (The diamines will hereafter be referred to as N-N.) The ligand tmenBr·$HClO_4$ was prepared according to the literature.[2]

B. Preparation of Complexes. The complexes $[Co(NH_3)_5(N-N-H)](ClO_4)_4$ and $[Co(NH_3)_5(tmen)](ClO_4)_4$ were prepared in a way similar to that which has been reported for the preparation of $[Co(NH_3)_5(enH)](ClO_4)_4$.[3] The analytical data for the complexes prepared in this work are given in Table I.[4]

Caution! Although no explosions were encountered in the present study, perchlorate salts should be handled with appropriate precautions.

Products of the Reaction of $[Co(H_2O)(NH_3)_5]X_3$ (X = ClO_4^- or BF_4^-) with N-N. N-N = meen. Equimolar amounts (0.01 mol each) of $[Co(H_2O)(NH_3)_5]X_3$ and meen were added to 250 mL of dimethyl sulfoxide (Me_2SO). The solution was kept at 85 °C for 15 min. The resulting solution was neutralized with HCl and diluted to 1 L with water. This was poured into a column (3 × 25 cm) of SP-Sephadex C-25 (SPC). The column showed three bands: red at the bottom, yellow in the middle, and yellowish orange at the top. The first and second species were eluted together with a 0.4 M KBr solution and were characterized as a mixture of $[Co(H_2O)(NH_3)_5]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(meen)]^{3+}$, $[Co(NH_3)_2(meen)_2]^{3+}$, and $[Co(meen)_3]^{3+}$.[5] The yellowish orange species was eluted with a 0.6 M KBr solution. The eluate was reloaded on an SPC column. After the column was washed with a 0.3 M HCl solution, the adsorbed species was eluted with a 1 M $LiClO_4$ solution of pH 2.5 (adjusted with $HClO_4$). The eluate was evaporated to dryness. The remaining solid $LiClO_4·3H_2O$ was washed out with ethanol. Crystals of $[Co(NH_3)_5(meenH)](ClO_4)_4$ remained; yield 0.4 g.

Chart I

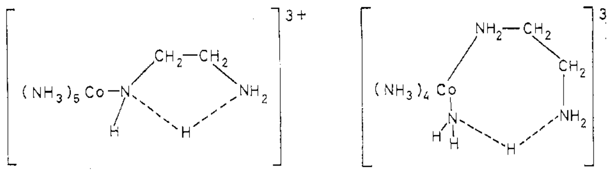

Table II. pK_a Values of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$, HN-NH^{2+}, and Htmen^{2+} at 25 °C[a]

compd	pK_{a1}	pK_a	pK_{a2}
$[Co(NH_3)_5(enH)]^{4+}$ [b]		7.52 ± 0.03	
$[Co(NH_3)_5(meenH)]^{4+}$		7.88 ± 0.03	
$[Co(NH_3)_5$-(*asym*-dimeenH)$]^{4+}$		7.24 ± 0.03	
H_2en^{2+} [b]	7.15 ± 0.03		9.87 ± 0.04
H_2meen^{2+}	7.40 ± 0.03		10.21 ± 0.04
H_2(*asym*-dimeen)$^{2+}$	6.81 ± 0.03		9.85 ± 0.04
H_2(*sym*-dimeen)$^{2+}$	7.17 ± 0.03		10.07 ± 0.04
Htmen^{2+} [c]		7.1	

[a] At I = 0.1 (NaCl), unless otherwise indicated. [b] From ref 1. [c] From ref 2; at I = 0.007 ($NaClO_4$).

N-N = *asym*-dimeen and *sym*-dimeen. Equimolar amounts (0.01 mol each) of $[Co(H_2O)(NH_3)_5]X_3$ and *asym*- or *sym*-dimeen were added to 1 L of Me_2SO. The solution was treated in the way described for the meen system. Four bands were observed on an SPC column. The lowest and the second species were identified as Co^{2+} and $[Co(H_2O)(NH_3)_5]^{3+}$, respectively. The third band was found to contain $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_4(dimeen)]^{3+}$.[6] The fourth species was eluted with a 0.6 M KBr solution. The eluate from the *asym*-dimeen system was reloaded on an SPC column. The adsorbed species was treated in the way described for the isolation of $[Co(NH_3)_5(meenH)](ClO_4)_4$. Orange crystals of $[Co(NH_3)_5$(*asym*-dimeenH)$](ClO_4)_4·0.2HClO_4·2H_2O$ were obtained; yield 0.23 g. Although the solid sample from the fourth eluate of the *sym*-dimeen was not isolated because of the very low yield, the species was concluded to be $[Co(NH_3)_5$(*sym*-dimeenH)$]^{4+}$ from the flow rate on the SPC column[7] and the electronic spectrum.

N-N = tmen$^+$. To 200 mL of Me_2SO solution containing 0.01 mol of $[Co(H_2O)(NH_3)_5](BF_4)_3$ were added 3.6 mmol of tmenBr·$HClO_4$, 0.5 g of active carbon, and 3 mL of triethylamine. The solution was kept at 85 °C for 15 min. After removal of the active carbon by filtration, the solution was treated in the way described for the meen system. The SPC column showed five bands: Co^{2+}, $[CoBr(NH_3)_5]^{2+}$, $[Co(H_2O)(NH_3)_5]^{3+}$, $[Co(NH_3)_6]^{3+}$, and $[Co(NH_3)_5(tmen)]^{4+}$ from the bottom to the top of the column. After the former four species had been eluted out, the uppermost species was eluted with a 1 M NaCl solution. This eluate was treated in the way described for the isolation of $[Co(NH_3)_5(meenH)](ClO_4)_4$. Crystals of $[Co(NH_3)_5(tmen)](ClO_4)_4$ were obtained; yield 0.06 g.

C. Determination of pK_a Values and Measurements of Electronic Spectra. For determining the pK_a values, pH titrations were made with a standard sodium hydroxide or hydrochloric acid solution as described previously.[1] The measurements of electronic spectra were made with a Union-Giken SM-401 spectrophotometer, also reported previously.[1]

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(1) Ogino, H. *Inorg. Chem.* **1980**, *19*, 1619.
(2) Lin, C.-T.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402.
(3) Ogino, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2459.
(4) Supplementary material.
(5) These species were separated as follows: The concentration of the eluate gave solid $[Co(NH_3)_6]Br_3$. The filtrate was reloaded on an SPC column. Four bands appeared by elution with 0.01–0.025 M $Na_4P_2O_7$ solutions. The order of the elution was $[Co(H_2O)(NH_3)_5]^{3+}$, $[Co(meen)_3]^{3+}$, $[Co(NH_3)_4(meen)]^{3+}$, and $[Co(NH_3)_2(meen)_2]^{3+}$.
(6) The concentration of the eluate gave solid $[Co(NH_3)_6]Br_3$. The filtrate was reloaded on an SPC column. The adsorbed species was eluted with a 0.5 M HCl solution. The concentration of the eluate gave solid $[Co(NH_3)_4(dimeen)]Cl_3·nH_2O$.
(7) Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1836.

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Table III. Electronic Absorption Spectra of the Complexes Prepared in This Work and the Related Complexes

complex	medium	abs max,[a] nm (ϵ, M^{-1} cm^{-1})
$[Co(NH_3)_5(enH)](ClO_4)_4$ [b]	1.0×10^{-2} M $HClO_4$	480 (63), 343 (52)
$[Co(NH_3)_5(en)]^{3+}$ [b,c]	6.53×10^{-6} M OH^-	480 (67), 340 (61)
$[Co(NH_3)_5(meenH)](ClO_4)_4$	1.0×10^{-2} M $HClO_4$	482 (63), 343 (51)
$[Co(NH_3)_5(meen)]^{3+}$ [c]	5.0×10^{-3} M NaOH	482 (66), 343 sh (80), 270 sh (775)
$[Co(NH_3)_5($*asym*-dimeenH$)](ClO_4)_4 \cdot 0.2HClO_4 \cdot 2H_2O$	1.0×10^{-2} M $HClO_4$	484 (64), 343 (52)
$[Co(NH_3)_5($*asym*-dimeen$)]^{3+}$ [c]	5.0×10^{-3} M NaOH	484 (80), 343 sh (110), 270 sh (780)
$[Co(NH_3)_5($*sym*-dimeenH$)]^{4+}$ [d]	H_2O	512 (113)
$[Co(NH_3)_5(tmen)](ClO_4)_4$	1.0×10^{-2} M $HClO_4$	482 (68), 343 (61)
$[Co(NH_3)_5(tmen)](ClO_4)_4$	5.0×10^{-3} M NaOH	482 (73), 343 (70)
$[Co(NH_3)_4(meen)]Cl_3 \cdot H_2O$	H_2O	480 (74), 344 (64)
$[Co(NH_3)_2(meen)_2]I_3$	H_2O	484 (94), 344 (185), 226 (63 000)
$[Co(meen)_3](ClO_4)_3$ [e]	H_2O	492 (115), 351 (102), 231 (23 000)
$[Co(NH_3)_4($*asym*-dimeen$)]Cl_3 \cdot 3H_2O$	H_2O	494 (78), 349 (59), ca. 235 sh (12 000), 209 (19 000)
$[Co(NH_3)_4($*asym*-dimeen$)]Cl_3 \cdot 1.5H_2O$ [f]	H_2O	491 (76), 345 (69), ca. 236 (ca. 13 000), 209 (17 000)
$[Co(NH_3)_4($*sym*-dimeen$)]Cl_3 \cdot H_2O$	H_2O	484 (72), 348 (63), 217 (22 000)

[a] sh = shoulder. [b] From ref 1. [c] Counterion = ClO_4^-. [d] Counterion = Cl^-. [e] Ogino, H.; Kawasaki, K., unpublished data. [f] Akamatsu, K.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2586.

Results and Discussion

In $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ containing asymmetric N-N, viz., meen or *asym*-dimeen, linkage isomerism is possible. One is coordination to the $[Co(NH_3)_5]^{3+}$ moiety with the primary amino group of N-N. The other is coordination with the secondary amino group for the meen or with the tertiary amino group for the *asym*-dimeen. However, the N-N is apparently coordinated to the $[Co(NH_3)_5]^{3+}$ moiety through the primary amino group, because the primary amino group is more able to coordinate with cobalt(III) than the secondary amino group and the tertiary amino group has no tendency to coordinate with cobalt(III).[8] This is supported by the facts that $[Co(NH_3)_5($*sym*-dimeenH$)]^{4+}$ was obtained in very low yield, in which *sym*-dimeen has only secondary amino groups,[9] and that the heating of the Me_2SO solution containing $[Co(H_2O)(NH_3)_5]^{3+}$ under the presence of triethylamine did not give any $[Co(NH_3)_5(\text{triethylamine})]^{3+}$ (see Experimental Section). The pK_a values shown in Table II also suggest that the primary amino groups in meen and *asym*-dimeen are coordinated to $[Co(NH_3)_5]^{3+}$ moieties. If the meen and *asym*-dimeen are coordinated to $[Co(NH_3)_5]^{3+}$ moieties through *N*-methyl- and *N*,*N*-dimethylamino groups, respectively, the pK_a values of $[Co(NH_3)_5(enH)]^{4+}$, $[Co(NH_3)_5(meenH)]^{4+}$, and $[Co(NH_3)_5($*asym*-dimeenH$)]^{4+}$ would be very similar to one another, because each complex has a common $-CH_2CH_2NH_3^+$ group. However, this is not the case, and the data indicate the decreasing order of the pK_a values of the coordinated diamines to be meen > en > *asym*-dimeen. This order agrees with the known order for the pK_a values of free aliphatic amines, e.g., 10.73 for $(CH_3)_2NH$, 10.66 for CH_3NH_2, and 9.75 for $(CH_3)_3N$.[10] The data in Table II indicate the order $pK_{a1} < pK_{complex} << pK_{a2}$; a similar order was found previously.[1]

The numerical data for the absorption spectra of the complexes are summarized in Table III. Figure 1 shows a comparison of the spectra of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ and $[Co(NH_3)_5(tmen)]^{4+}$ in 0.01 M $HClO_4$ solutions with those of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ and $[Co(NH_3)_5(tmen)]^{4+}$ in 5.0×10^{-3} M NaOH solutions. Increased absorbance in the ultraviolet region as observed for $[Co(NH_3)_5(en)]^{3+}$ [1] appears for $[Co(NH_3)_5(meen)]^{3+}$ and for $[Co(NH_3)_5($*asym*-dimeen$)]^{3+}$, respectively. The maximum values of the ratios of the absorption coefficient of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ (ϵ_B) to that of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ (ϵ_A) are 120 at 36.0×10^3 cm^{-1} for the en system, 189 at 35.6×10^3 cm^{-1} for the meen system, and 164 at 35.7×10^3 cm^{-1} for the *asym*-dimeen system, respectively. The increased absorbance for $[Co(NH_3)_5(N\text{-}N)]^{3+}$ indicates the appearance of a charge-transfer band due to the intramolecular hydrogen bonding as shown in Chart I. In $[Co(NH_3)_5(tmen)]^{4+}$, such hydrogen bonding cannot be formed because the free end of the $tmen^+$ is the quaternary nitrogen atom. As $[Co(NH_3)_5(tmen)]^{4+}$ has higher charge by 1 unit than $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$, it would be expected that the deprotonation from the former complex occurs more easily than from the latter complex. However, the pH titration curve of $[Co(NH_3)_5(tmen)]^{4+}$ did not show the existence of any dissociable proton up to at least pH 11.6. The ratio of the absorption coefficient of $[Co(NH_3)_5(tmen)]^{4+}$ in a 5.0×10^{-3} M NaOH solution to that in a 0.01 M $HClO_4$

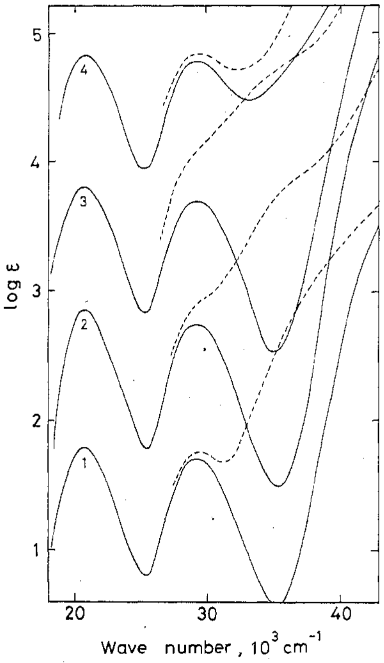

Figure 1. Spectra of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ and $[Co(NH_3)_5(tmen)]^{4+}$ in 1.0×10^{-2} M $HClO_4$ solution (solid line) and $[Co(NH_3)_5(N\text{-}N)]^{3+}$ and $[Co(NH_3)_5(tmen)]^{4+}$ in 5.0×10^{-3} M NaOH solution (broken line). Curves 1, 2, 3, and 4 correspond to the complexes containing en, meen, *asym*-dimeen, and $tmen^+$, respectively. Curves 2, 3, and 4 are shifted upward by 1, 2, and 3 log ϵ units, respectively.

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(9) In this connection, we have obtained the following results: In Me_2SO solvent, $[Co(H_2O)(NH_3)_5]X_3$ reacted with various linear and branched primary aliphatic amines to give $[Co(NH_3)_5(\text{primary amine})]^{3+}$ in good yield. Although a similar reaction occurred with $(CH_3)_2NH$ to give $[Co(NH_3)_5((CH_3)_2NH)]^{3+}$, the yield was much lower than that of $[Co(NH_3)_5(\text{primary amine})]^{3+}$ in accordance with the expectation that a secondary amine has a lower tendency to coordinate with cobalt(III).

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solution reaches a maximum at 38 × 10^3 cm^{-1}, but its value is only 5, which is comparable in magnitude to the corresponding values of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$.[1] Therefore, the increased absorbance of $[Co(NH_3)_5(tmen)]^{4+}$ in the ultraviolet region is due to the ion-pair formation between the complex and hydroxide ion.

Acknowledgment. The authors wish to thank the Kurata Foundation for a grant to H.O.

Registry No. $[Co(NH_3)_5(meenH)](ClO_4)_4$, 74482-87-4; $[Co(NH_3)_5(meen)](ClO_4)_3$, 74482-86-3; $[Co(NH_3)_5($*asym*-dimeenH$)](ClO_4)_4$, 74482-90-9; $[Co(NH_3)_5($*asym*-dimeen$)](ClO_4)_3$, 74482-89-6; $[Co(NH_3)_5($*sym*-dimeenH$)]Cl_4$, 74482-91-0; $[Co(NH_3)_5(tmen)](ClO_4)_4$, 74482-93-2; $[Co(NH_3)_4($*sym*-dimeen$)]Cl_3$, 74482-94-3; $[Co(NH_3)_4(meen)]Cl_3$, 74523-72-1; $[Co(NH_3)_2(meen)_2]I_3$, 74482-95-4; $[Co(meen)_3](ClO_4)_3$, 74498-46-7; $[Co(NH_3)_4($*asym*-dimeen$)]Cl_3$, 68448-00-0; H_2meen^{2+}, 38685-41-5; $H_2($*asym*-dimeen$)^{2+}$, 38685-42-6; $H_2($*sym*-dimeen$)^{2+}$, 38685-36-8.

Supplementary Material Available: Table I, listing analytical data for the complexes (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Alteration of Intramolecular Electron-Transfer Rates by Bridging Groups[1]

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Over the past several years, we have developed[3-5] a strategy for the study of intramolecular electron-transfer dynamics in coordination complexes in which the formation of coordinated ligand radicals of the form M^{III}–$L^-\cdot$ permits a direct examination of the nature of ligand structure and lead-in group in the mediation of electron transfer. Other strategies[6-14] involve binuclear systems of the form M^{III}–L–M^{II} where the oxidant and reductant are bound to a bridging ligand in which the functional groups and their isomeric configurations are varied. These strategies all focus on the dependence of the intramolecular electron-transfer rate constant, k_{et}, on the electronic coupling between the redox sites.

Table I. Intramolecular Electron Transfer Rates for $[^-O_2\dot{N}Ph\text{–}X\text{–}CO_2Co^{III}(NH_3)_5]^+$ Coordinated Ligand Radical Systems at pH 7[a]

X (isomer)	k_{et}, s^{-1}	X (isomer)	k_{et}, s^{-1}
– (*o*)	4.0 × 10^5 [b]	CH=CH (*o*)	1.7 × 10^3
– (*m*)	1.5 × 10^2 [b]	CH=CH (*m*)	3.1
– (*p*)	2.6 × 10^3 [b]	CH=CH (*p*)	4.8 × 10^2
CH_2 (*o*)	3.5 × 10^4	$CH_2CH_2CH_2$ (*p*)	1.5 × 10^2
CH_2 (*m*)	1.0 × 10^2	$CONHCH_2$ (*p*)	5.8
CH_2 (*p*)	3.9 × 10^2	$CONHCH_2CONHCH_2$ (*p*)	1.5 × 10^3

[a] N_2O-saturated solutions containing 0.2 M $NaHCO_2$; 22 °C. [b] Reference 4.

In particular, we have shown[3,4] that k_{et} can be measured directly for $[^-O_2\dot{N}PhCO_2Co^{III}(NH_3)_5]^+$ complexes which are formed by the interaction of radiation-generated reducing radicals with the (nitrobenzoato)pentaamminecobalt(III) substrates; the unpaired electron in the reduced species is localized predominantly on the nitro group. The reduced species can be detected easily and characterized by fast-kinetics optical absorption spectroscopy (pulse radiolysis; time resolution <1 μs). The values of k_{et} have been found to be dependent upon the number and isomeric position of the nitro groups and appear to depend on the electron spin density at or adjacent to the lead-in carboxylate group.[15] In this paper we report the values of k_{et} for reduced complexes of the form $[^-O_2\dot{N}Ph\text{–}X\text{–}CO_2Co^{III}(NH_3)_5]^+$ and identify the possible intramolecular electron-transfer pathways around and through the bridging group X.

Experimental Section

Complexes of the form $[O_2NPh\text{–}X\text{–}CO_2Co^{III}(NH_3)_5](ClO_4)_2$, where X = CH_2 (*o*, *m*, and *p*), CH=CH (*o*, *m*, and *p*), $CH_2CH_2CH_2$ (*p*), $CONHCH_2$ (*p*), and $CONHCH_2CONHCH_2$ (*p*), were prepared and recrystallized by the general literature method.[16] Elemental analyses (Co, C, H, N) were satisfactory, indicating the presence of negligible quantities of the free ligands.

The radiation chemical techniques (pulse and continuous) and the analytical methods have been described previously.[4] Radiolyses were conducted in N_2O-saturated aqueous solutions containing ≤5 × 10^{-4} M complex and 0.2 M $NaHCO_2$ at pH 7 (phosphate buffer). Under these conditions, e_{aq}^-, OH, and H are removed and the only reducing species is $\cdot CO_2^-$. Rate constants determined by pulse radiolysis were obtained at 22 °C with a precision of 10–15%.

Results and Discussion

The complexes react rapidly ($k = (1\text{–}2) \times 10^9\ M^{-1}\ s^{-1}$) with $\cdot CO_2^-$ to produce the reduced complexes (reaction 1) which

$$[O_2NPh\text{–}X\text{–}CO_2Co^{III}(NH_3)_5]^{2+} + \cdot CO_2^- \rightarrow [^-O_2\dot{N}Ph\text{–}X\text{–}CO_2Co^{III}(NH_3)_5]^+ + CO_2 \quad (1)$$

exhibit intense absorption bands (ϵ_{max} 10^3–10^4 $M^{-1}\ cm^{-1}$) in the 300-nm region characteristic of $PhNO_2^-$ intermediates.[4,15,17] The first-order decay kinetics of these bands are independent of [substrate] and radiation dose. The final product of the reaction of $\cdot CO_2^-$ with the Co^{III} complexes is Co^{2+}(aq) in quantitative yield ($G(Co^{2+}(aq)) = 6.2 \pm 0.4$).

The first-order decay of $[^-O_2\dot{N}Ph\text{–}X\text{–}CO_2Co^{III}(NH_3)_5]^+$ is attributed to reaction 2; ligand labilization of the Co^{II} species leads rapidly (μs time scale) and irreversibly to Co^{2+}(aq) (reaction 3).[18]

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(2) (a) Boston University. (b) U.S. Army Natick Research and Development Command. Address correspondence to M.G.S. at the National Bureau of Standards, Washington D.C. 20234.

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