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.

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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.

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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 $[^{-}O_2\dot{N}Ph–X–CO_2Co^{III}(NH_3)_5]^{+}$ 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 $[^{-}O_2\dot{N}Ph–X–CO_2Co^{III}(NH_3)_5]^{+}$ and identify the possible intramolecular electron-transfer pathways around and through the bridging group X.

Experimental Section

Complexes of the form $[O_2NPh–X–CO_2Co^{III}(NH_3)_5](ClO_4)_2$, 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 ($k = (1–2) \times 10^9\ M^{-1}\ s^{-1}$) with $\cdot CO_2^{-}$ to produce the reduced complexes (reaction 1) which

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

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 $[^{-}O_2\dot{N}Ph–X–CO_2Co^{III}(NH_3)_5]^{+}$ 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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$$[^{-}O_2\dot{N}Ph\text{-}X\text{-}CO_2Co^{III}(NH_3)_5]^+ \xrightarrow{k_{et}} [O_2NPh\text{-}X\text{-}CO_2Co^{II}(NH_3)_5]^+ \quad (2)$$

$$[O_2NPh\text{-}X\text{-}CO_2Co^{II}(NH_3)_5]^+ \xrightarrow{H^+} Co^{2+}(aq) + 5NH_4^+ + O_2NPh\text{-}X\text{-}CO_2^- \quad (3)$$

Values of k_{et} for the ortho, meta, and para isomers of nitrobenzoato complexes are given in Table I. Reduction potentials of these nitro radicals, when uncoordinated, have been previously determined by electron-transfer reaction with duroquinone.[15] The potentials vary little and are in the range -0.396 V for the para isomer to -0.433 V for the meta analogue. The dissimilar isomeric trend and the $>10^3$-fold variation in the observed k_{et} values for the complexed radical anions implicate a significant intrinsic (i.e., nonthermodynamic) component in the intramolecular electron-transfer process. That the redox potentials of the ortho, meta, and para isomers of dinitrobenzene and dinitrobenzoate free radicals are only 0.05–0.14 V less reducing than the nitrobenzoate analogues[15] provides a basis for generalization. Given the *same* donor, lead-in, and acceptor groups for the intramolecular electron-transfer process of all the complexes reported in Table I, it is unlikely that the 10^5-fold variation in the observed k_{et} values derives solely from an overall driving force difference dependent only on the bridging group. This group can, however, clearly change the approach to, and nature of, the transition state.

The k_{et} trend observed for the nitrobenzoatao series ($o > p > m$) was previously explained[15] in terms of the significant electron spin density distribution at or adjacent to the lead-in group; the spin density is a maximum at the positions ortho and para to the nitro radical and negligible in the meta position. In the ortho case, direct nitro radical overlap with carboxylate and/or metal orbitals probably facilitates the transfer process. Undoubtedly, introduction of a CH_2 group greatly reduces the spin density at the lead-in carboxylate. However, close examination of Ealing CPK molecular model structures shows that the ortho overlap is also possible in the nitrophenylacetato case and that for the para isomer a configuration is possible in which the carboxylate group overlaps the ring carbon para to the nitro radical. Such overlap is eliminated in the more rigidly protruding *trans*-cinnamato series of complexes. The rate data do suggest, however, that the olefinic linkage may provide an effective means of delocalizing the spin density through the extended π system for the ortho and para isomers. In contrast, the meta derivative has no extended π conjugation, negligible spin density adjacent to the ethylenic linkage, and ostensibly no nitro radical–carboxylate nor –metal orbital overlap configurational possibilities. Consequently, the observed value of $k_{et} = 3.1\ s^{-1}$ for *m*-cinnamato may represent an unassisted transfer of an electron through the ligand bridging system.

Table I also includes values of k_{et} for *p*-nitrophenylcarboxylate complexes having bridging groups varying in both length and flexibility. Examinations of the molecular models show that among the multitude of possible configurations, a *common* positional arrangement arises for X = CH_2, $CH_2CH_2CH_2$, and $CONHCH_2CONHCH_2$: proximity of a carboxylate oxygen to within ~1 Å of the para carbon of the aromatic ring (based on van der Waals radii). This configuration may be further enhanced by H-bonding interaction of the nitro oxygens with the ammonia hydrogens of the $Co(NH_3)_5$ moiety. Thus, despite the long-chain character of the bridging units, electron density can be directed to the lead-in group by effectively bypassing through-chain mediation. The degree of favorable π-orbital vertical overlap is most nearly attained for the dipeptide ligand structure; this complex exhibits a k_{et} value larger than that of the two alkyl chain analogues. The more rigid monopeptide complex has *no* configuration that allows such orbital overlap. The further absence of direct configurational interaction at the metal or lead-in group and resonance delocalization through the bridging unit is consistent with the k_{et} value for X = $CONHCH_2$, again reflecting an unassisted through-chain electron transfer.

A pattern of mechanisms of intramolecular electron transfer emerges from the rate data and configurational considerations. The passage of electron density from the donor to the acceptor site can occur either through the bridging unit or via a path that effectively bypasses it. π bonding within the bridge may facilitate through-chain transfer because of favorable extended π conjugation between the donor and lead-in sites. In the absence of such resonance assistance, the through-chain rate of transfer is markedly decreased. Consistent with the similarity of the two lowest observed k_{et} values must be the dominance of fundamental rate-determining parameters: Franck–Condon barriers, acceptor/lead-in orbital symmetry matching, and overall driving force. Indeed, the considerable lower intramolecular rates of similarly accepting binuclear complexes may reflect lower overall thermodynamic drives in those cases.[6]

A favorable disposition of the donor to the acceptor or lead-in site may well create a more facile path of electron transfer than is offered by the through-chain alternative. We propose the most effective configurations to be those that allow orbital overlap between the nitro group and the metal center, the nitro group and the coordinated carboxylate, and the para ring carbon and the carboxylate. In addition, there is the possibility of electron transfer without direct orbital overlap; an outer-sphere transfer mechanism of related phenomena has been previously proposed.[19] Apart from the obvious relevance of these results to the "chemical" mechanism of electron transfer,[20] the coordinated ligand radical species serve as models for even more complex intramolecular electron transfer. In the case of electron transfer in large biomolecules, the contributions of "through-chain" and "bypass" transfer must be assessed.

Registry No. $[^{-}O_2\dot{N}Ph\text{-}o\text{-}CH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-07-0; $[^{-}O_2\dot{N}Ph\text{-}m\text{-}CH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-08-1; $[^{-}O_2\dot{N}Ph\text{-}p\text{-}CH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-09-2; $[^{-}O_2\dot{N}Ph\text{-}o\text{-}CH{=}CHCO_2Co^{III}(NH_3)_5]^+$, 74298-10-5; $[^{-}O_2\dot{N}Ph\text{-}m\text{-}CH{=}CHCO_2Co^{III}(NH_3)_5]^+$, 74298-11-6; $[^{-}O_2\dot{N}Ph\text{-}p\text{-}CH{=}CHCO_2Co^{III}(NH_3)_5]^+$, 74298-12-7; $[^{-}O_2\dot{N}Ph\text{-}p\text{-}CH_2CH_2CH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-13-8; $[^{-}O_2\dot{N}Ph\text{-}p\text{-}CONHCH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-14-9; $[^{-}O_2\dot{N}Ph\text{-}p\text{-}CONHCH_2CONHCH_2CO_2Co^{III}(NH_3)_5]^+$, 74298-15-0.

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Substitution Lability of Chromium(III) Complexes with Ground-State Distortion

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The substitution inertness of the d^3 chromium(III) ion in aquo-ligand environments has already been established.[1] However, there are some exceptions in aquo(ethylenedi-

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