Reduction of Cobalt(III) Complexes by Intramolecular Electron Transfer from Bound Free Radicals. A Pulse Radiolytic Study

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The specific rates of reduction of $[Co(NH_3)_6]^{3+}$ by a series of nitrobenzoate and nitrogen heteroaromatic anion radicals are reported. The rates of intramolecular electron transfer from the same anion radicals to a central cobalt(III) bound to them *via* a carboxylate group are reported, as well as for some pyrazine carboxylate anion radicals bound to the cobalt *via* the carboxylate and the N^1 atom. The factors affecting the rate of intramolecular electron-transfer processes are discussed in detail.

INTEREST is growing in the measurement of the rate of electron transfer through extended double bond systems.[1] This is due to (*a*) the 'simplicity' of these reactions which makes them of interest to theoretical chemists, (*b*) the hope of producing one-dimensional electric conductors, and (*c*) their being model systems for one of the elementary steps in inner-sphere redox reactions.

Studies in this field in solution have focused on two major approaches; the first being study of the properties of mixed-valence complexes and the second, the study of the rate of intramolecular electron-transfer reactions of the type (1) where the precursor complex $[M_a^{n+}LM_b^{m+}]$ is

$$[M_a^{n+}LM_b^{m+}] \xrightarrow{k_1} M_a^{(n-1)+} + [LM_b^{(m+1)+}] \quad (1)$$

stable enough so that it can be synthesized *in situ* [2] and k_1 can be directly measured. When L is an organic ligand with an extended double-bond system, reaction (1) can follow two mechanisms. The 'resonance mechanism' involves transfer of the electron from M_b to M_a directly without forming an intermediate in which it is located on the ligand.[1] For the 'chemical mechanism' [3] reaction (1) can be rewritten as (2) and (3). Thus for systems

$$[M_a^{n+}LM_b^{m+}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [M_a^{n+}L^{\bullet-}M_b^{(m+1)+}] \quad (2)$$

$$[M_a^{n+}L^{\bullet-}M_b^{(m+1)+}] \xrightarrow{k_3} M_a^{(n-1)+} + [LM_b^{(m+1)+}] \quad (3)$$

which follow the chemical mechanism,[1,2] $k_1 = K_2k_3$ and no direct measurement of the rates of the individual steps is possible.

Recently, Hoffman and co-workers [4] showed that powerful reducing free radicals ($R^{\bullet}$) react with penta-amminecobalt(III) *p*-nitrobenzoate *via* the reaction sequence (4) and (5) ($k_4 = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k_5 = 2.6 \times 10^3$ s^{-1}).

$$R^{\bullet} + [(NH_3)_5Co^{III}(p\text{-}O_2CC_6H_4NO_2)]^{2+} \xrightarrow{k_4} R^+ + [(NH_3)_5Co^{III}(p\text{-}O_2CC_6H_4NO_2^{\bullet-})]^+ \quad (4)$$

$$[(NH_3)_5Co^{III}(p\text{-}O_2CC_6H_4NO_2^{\bullet-}])^+ \xrightarrow{k_5} [(NH_3)_5Co^{II}(p\text{-}O_2CC_6H_4NO_2)]^+ \quad (5)$$

Some of the radicals $R^{\bullet}$, *i.e.* e$^-$(aq) reduce both the Co^{III} centre and the ligand [4] so that only a partial yield of $[(NH_3)_5Co^{III}(p\text{-}O_2CC_6H_4NO_2^{\bullet-})]^+$ is obtained. Others, however, *i.e.* $CO_2^{\bullet-}$ and $(CH_3)_2\dot{C}OH$ reduce preferentially the ligand [5] due to the kinetic barriers in the reduction of Co^{III}.[6] Reaction (5) is a model reaction to reaction (3) and thus provides a first measurement of the rate of this elementary step in the 'chemical mechanism'.

Since the first report by Hoffman and co-workers [4] several similar studies have been reported.[7-9] However, all the systems studied were of nitrobenzoate radical anions bound to the cobalt(III) *via* the carboxylate group.† The role of the carboxylate group in the electron-transfer process caused some controversy and has been discussed elsewhere in detail,[4,7,13] the conclusion being that the carboxylate seems to hinder the electron-transfer reaction.

It seemed of interest to extend the study of intramolecular electron transfer (i.e.t.) reactions by (*a*) measuring the rate of i.e.t. from anion radicals other than nitrobenzoate to cobalt(III) *via* a carboxylate group, (*b*) measuring the rate of i.e.t. from the same anion radicals to cobalt(III) *via* other ligating groups, and (*c*) studying the effect of non-participating ligands of the cobalt(III) on the rate of i.e.t. Some results in this direction are reported here.

EXPERIMENTAL

Materials.—The complexes $[Co(NH_3)_5(O_2CC_4H_3N_2)][ClO_4]_2$ ($O_2CC_4H_3N_2$ = pyrazinecarboxylate), $[Co(NH_3)_4(O_2CC_4H_3N_2)][ClO_4]_2$, $[Co(en)_2(O_2CC_4H_3N_2)][ClO_4]_2$ (en = ethylenediamine), $[Co_2(OH)_2(NH_3)_6(4\text{-}O_2CC_4H_3N_2)][ClO_4]_3$, $[Co_2(OH)_2(NH_3)_6(5\text{-}O_2CC_4H_3N_2)][ClO_4]_3$ (4- and 5-$O_2CC_4H_3N_2$ = pyrimidine-4- and -5-carboxylate), and $[Co_2(OH)_2(NH_3)_6(2\text{-}O_2CC_5H_4NMe)][ClO_4]_3$ (2-$O_2CC_5H_4NMe$ = 1-methylpyridinium-2-carboxylate) were prepared according to procedures described in the literature.[14]

All other chemicals used were of analytical grade and were used without further purification. Deionized water, using a Milli-Q-Millipore set-up, with a resistance $\geqslant 10^7$ Ω cm^{-1} was used throughout this study. The pH was adjusted with $HClO_4$ and NaOH. Nitrous oxide was purified from

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† The reaction $[(NH_3)_5Co^{III}\text{–}O(O{=})C^{\bullet-}] \longrightarrow [Co(NH_3)_5]^{2+} + CO_2$ was reported to be too fast to be measured [10] and an intramolecular electron transfer in $[(NH_3)_5Co^{III}\text{–}NC_5H_4\text{–}OH]$ was reported;[11,12] however, see ref. 13.

dioxygen traces by bubbling through a train of washing bottles containing VSO_4 in dilute H_2SO_4 over zinc amalgam, followed by a washing bottle containing pure water.

Preparation of Complexes.—*μ-(Pyrazinecarboxylato)-bis-[hydroxo(1,4,7-triazacyclononane)cobalt(III)] perchlorate.* $[Co_2(\mu\text{-}OH)_3(tacn)_2][ClO_4]_3$ [14d] (1.5 g) (tacn = 1,4,7-triazacyclononane) and pyrazinecarboxylic acid (0.5 g) were dissolved in 1 mol dm^{-3} perchloric acid (50 cm^3). The solution was heated to 60 °C for 20 min during which time the solution became red. The solution was allowed to stand for 12 h in the refrigerator. Red crystals were filtered off, washed with ethanol and diethyl ether, and air-dried (yield *ca.* 1.3 g). Under these conditions the protonated tetraperchlorate is obtained.

μ-p-Nitrobenzoato-bis[hydroxo(1,4,7-triazacyclononane)-cobalt(III)] triperchlorate. *p*-Nitrobenzoic acid (0.7 g) was dissolved in 0.2 mol dm^{-3} perchloric acid (100 cm^3) at 80 °C. To this solution, $[Co_2(\mu\text{-}OH)_3(tacn)_2][ClO_4]_3$ (2 g) was added with stirring (10 min). The solution was filtered from unreacted $HO_2CC_6H_4NO_2$-*p*. Upon cooling of the solution to 0 °C, red crystals precipitated which were filtered off, washed with ethanol and diethyl ether, and air-dried (yield *ca.* 1.1 g).

In order to simplify the definition of the complexes the following abbreviations are used: $R^1 = Co^{III}(NH_3)_5$, $R^2 = (H_3N)_3Co^{III}(\mu\text{-}OH)_2Co^{III}(NH_3)_3$, and $R^3 = (tacn)Co^{III}(\mu\text{-}OH)_2Co^{III}(tacn)$. For R^2 and R^3 the carboxylate group of the organic ligand co-ordinates to the two Co^{III} centres *via* the oxygen atoms.

Irradiations.—The pulse radiolytic experiments were carried out using 0.05—1.5-μs, 5-MeV, 200-mA pulses from the electron linear accelerator at the Hebrew University of Jerusalem. The dose per pulse was 150—3 000 rad.* The experimental set-up and the methods used for evaluating the results have been described elsewhere in detail.[15]

Kinetics.—Solutions were saturated with N_2O or Ar before irradiations. The kinetics of formation or bleaching of absorbance were followed. Pseudo-first- or -second-order rates were calculated when a plot of a good first order or second order was linear for at least three half-lives. All experiments were carried out at room temperature (22 ± 2 °C).

Production of Reducing Reagents.†—The radiolysis of water by ionizing radiation can be described by the equation (6).

$$H_2O \xrightarrow{\gamma,\, e^-} e^-(aq),\ OH,\ H,\ H_2O_2,\ H_2, H_3O^+ \quad (6)$$

The yields of the products are: $G[e^-(aq)] = 2.65$, $G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.75$ (where the G value is the number of product molecules formed by the absorption of 100 eV in the solution). Somewhat higher yields are expected in concentrated solutions.[16] The products are homogeneously distributed within less than 10^{-7} s after the absorption of the radiation.

(*a*) *Reactions with* $e^-(aq)$. In 0.1 mol dm^{-3} t-butyl alcohol, Ar saturated solutions reaction (7) occurs, and as the

$$OH + (CH_3)_3COH \longrightarrow \dot{C}H_2C(CH_3)_2(OH) \quad k = 5.2 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \quad (7)$$

$CH_2C(CH_3)_2(OH)$ radical is a weak reducing agent which does not react with Co^{III}-ammine complexes,[17] the main reactive species remaining in solution within less than 1 μs after the pulse is the hydrated electron.

(*b*) *Production of* $(CH_3)_2\dot{C}OH$ *or* $CO_2^{\bullet -}$ *radicals.* In 0.1 mol dm^{-3} propan-2-ol or 0.1 mol dm^{-3} sodium formate, N_2O-saturated solutions (*ca.* 2×10^{-2} mol dm^{-3}) reactions (8)—(11) occur. Thus the only reactive species within less than 1 μs after the pulse are the $(CH_3)_2\dot{C}OH$ or the $CO_2^{\bullet -}$ radicals (depending on the organic solute added).

$$e^-(aq) + N_2O \xrightarrow{H_3O^+} N_2 + OH \quad k_8 = 8.7 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \quad (8)$$

$$e^-(aq) + H_3O^+ \longrightarrow H + H_2O \quad k_9 = 2.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \quad (9)$$

$$(CH_3)_2CHOH + OH/H \longrightarrow (CH_3)_2\dot{C}OH + H_2O/H_2 \ddagger \quad k_{OH} = 2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1},\ k_H = 7.5 \times 10^7\ dm^3\ mol^{-1}\ s^{-1} \quad (10a,b)$$

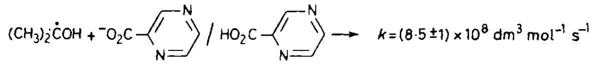
$$HCO_2^- + OH/H \longrightarrow CO_2^{\bullet -} + H_2O/H_2 \quad k_{OH} = 3.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1},\ k_H = 1.8 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \quad (11a,b)$$

(*c*) *Production of* $Ni^+(aq)$ *or* $Cd^+(aq)$ *cations.* In 0.1 mol dm^{-3} t-butyl alcohol, containing 10^{-2} mol dm^{-3} $NiSO_4$ or $CdSO_4$ Ar-saturated solutions, reactions (12) occur, as well as reaction (7). As the $\dot{C}H_2C(CH_3)_2OH$ radicals are weak reducing agents the only reducing species within less than 1 μs after the pulse are $Ni^+(aq)$ or $Cd^+(aq)$ cations (depending on the inorganic solute added).§

$$e^-(aq) + Ni^{2+}(aq)/Cd^{2+}(aq) \longrightarrow Ni^+(aq)/Cd^+(aq) \quad k_{Ni} = 2.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}, k_{Cd} = 5.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \quad (12)$$

RESULTS

Irradiation of Solutions of the Free Ligands.—The pyrazinecarboxylate radical, $^-O_2C\dot{C}_4H_3N_2$, was prepared by irradiation of N_2O-saturated, 1 mol dm^{-3} propan-2-ol solutions which also contained 10^{-4}—10^{-2} mol dm^{-3} pyrazinecarboxylate in the pH range 1—5.5. Formation of a transient absorbing in the range 300—750 nm was observed, the formation being pseudo-first order in the pyrazinecarboxylate concentration (see below). The spectrum of the intermediate formed is plotted in Figure 1(*a*). The disappearance of the transient obeyed a second-order rate law.



m-Nitrobenzoate radicals *m*-$^-O_2CC_6H_4NO_2^{\bullet -}$ were produced by reduction of the nitro-group by $(CH_3)_2\dot{C}OH$ radicals at pH 6. At pH 1 the radical produced is in the acidic form, *m*-$HO_2CC_6H_4\dot{N}O_2H$. These radicals absorb in the range 300—500 nm and disappear *via* a second-order process.

Pyrimidine-4-carboxylate radicals were produced *via* reduction of 8×10^{-4} mol dm^{-3} solutions of the free ligand

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* Throughout this paper: 1 rad = 10^{-2} J kg^{-1}.

† Specific reaction rates were taken from M. Bambenck and A. B. Ross, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 1975, vol 43; M. Anbar, Farhataziz, and A. B. Ross, *ibid.*, 1975, vol. 51; Farhataziz and A. B. Ross, *ibid.*, 1977, vol. 59.

‡ In the reaction of OH radicals with $(CH_3)_2CHOH$,[18] *ca.* 14% of $\dot{C}H_2CH(OH)CH_3$ is formed; however these radicals are weak reducing agents, like $\dot{C}H_2C(CH_3)_2OH$, and they do not intervene in the reactions.

§ These low-valent cations are known [19] to react with $\dot{C}H_2C(CH_3)_2(OH)$ radicals to yield M^{II}–$CH_2C(CH_3)_2(OH)$ but these are second-order reactions and in the presence of high enough concentrations of the oxidants, the reduction of the latter by $M^+(aq)$ can be studied.

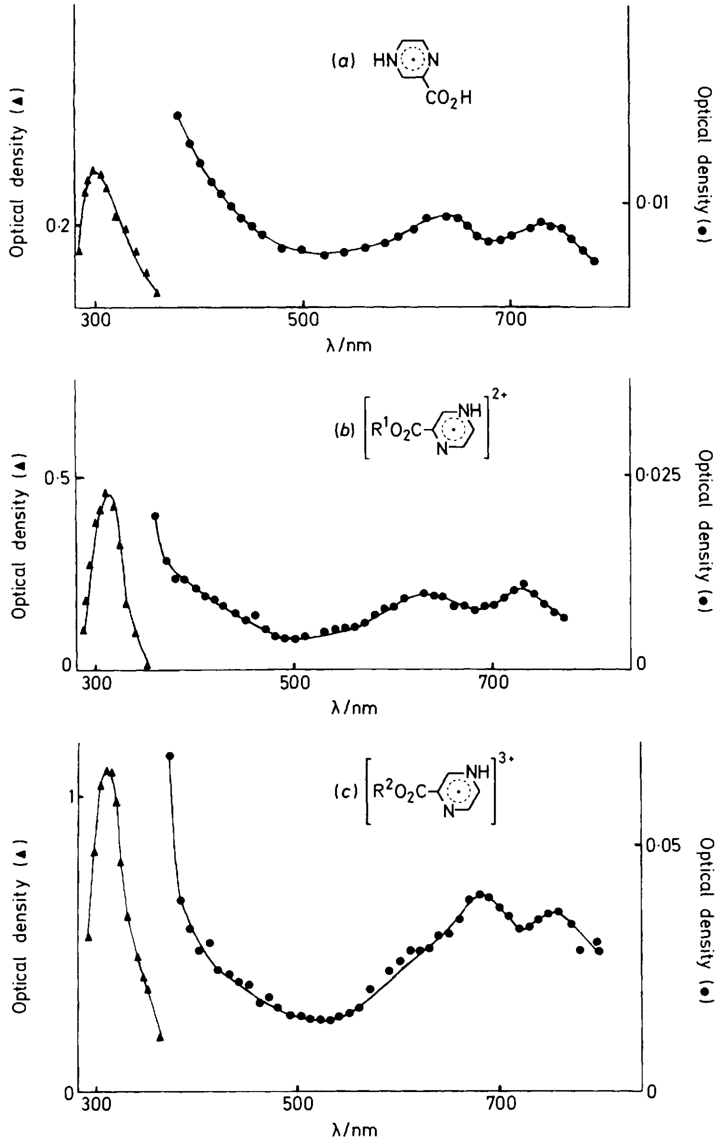
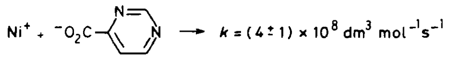
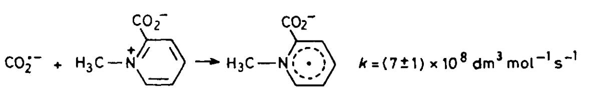


FIGURE 1 Absorption spectra of the free radical intermediates. Ar saturated solutions containing 1 mol dm^{-3} propan-2-ol at pH1.0: (*a*) 2 × 10^{-4} mol dm^{-3} (●), with 2 × 10^{-5} mol dm^{-3} $HO_2CC_4H_3N_2$ (▲); (*b*) 3 × 10^{-4} mol dm^{-3} (●), with 2 × 10^{-5} mol dm^{-3} $[R^1(O_2CC_4H_3N_2)]^{2+}$ (▲); (*c*) 3 × 10^{-4} mol dm^{-3} (●), with 2 × 10^{-5} mol dm^{-3} $[R^2(O_2CC_4H_3N_2)]^{3+}$ (▲)

by Ni^+ [this reducing agent was chosen as $CO_2^{\bullet-}$ and $(CH_3)_2\dot{C}OH$ radicals react too slowly with pyrimidine-4-carboxylate]; the rate of the reaction was determined by following the disappearance of the monovalent nickel [16] (see below). The free radical thus formed absorbs in the region 300—600 nm.



Homarine radicals, 2-$^-O_2C\dot{C}_5H_4NCH_3$, were produced *via* the reduction of the free ligand by $CO_2^{\bullet-}$ radicals. This radical absorbs in the range 300—600 nm and disappears *via* a second-order mechanism.

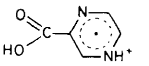
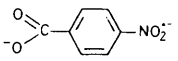
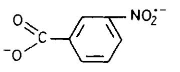
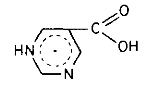
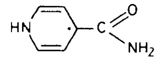
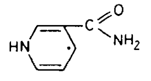
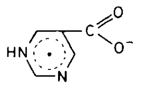
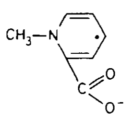


Reduction of Cobalt(III) *Complexes*.—The specific rates of reduction of hexa-amminecobalt(III) by the free ligand radicals were measured by following the disappearance of the absorption of the free ligand radicals in the presence of the complex and correcting (when needed) for the disappearance of the radical in the absence of additives. Usually, the kinetics of disappearance changed upon adding the complex, from a second-order rate law to pseudo-first-order {in $[Co(NH_3)_6]^{3+}$} when reduction of the complex occurred. The results are summarized in Table 1.

When solutions containing (1—5) × 10^{-4} mol dm^{-3} $[R^3(p\text{-}O_2CC_6H_4NO_2)]^{2+}$ or $[R^3(O_2CC_4H_3N_2)]^{3+}$ and 1 mol dm^{-3} propan-2-ol (at pH 1 or pH *ca*. 5) saturated with Ar or N_2O, respectively, were irradiated, formation of a transient with an absorption spectrum in the range 300—600 nm was observed. The rate of formation of the absorption obeyed a pseudo-first-order rate law: $(CH_3)_2\dot{C}OH + [R^3(p\text{-}O_2CC_6H_4NO_2)]^{2+} \longrightarrow$, $k = (1 \pm 0.1) \times 10^9$ and $(7 \pm 1) \times 10^9$

TABLE 1

Rates of reduction of $[Co(NH_3)_6]^{3+}$ by some heterocyclic free radicals ($R^•$)

Radical ($R^•$)	$E_{\frac{1}{2}}^0$ [a]/V	k/dm³ mol⁻¹ s⁻¹	pK_a
	−0.02 [a]	4.0 × 10⁴	10.5 [d]
	−0.396 [b]	1.2 × 10⁵	2.8
	−0.433 [c]	≤3 × 10⁴	3.0
	−0.80 [d,e]	3 × 10⁶	7.6 [d]
	−0.80 [f]	7.5 × 10⁶ [f]	1.9 [g]
	−0.95 [f]	1.1 × 10⁸ [f]	1.1 [g]
	−0.8 [h]	7.4 × 10⁷	
	−0.9 [h]	1.9 × 10⁸	

[a] Redox potential for the couples $R^•/R^+$ *versus* n.h.e. [b] From ref. 20, calculated for $[H^+] = 0.2$ mol dm⁻³. [c] From ref. 21. [d] pK for the loss of the second proton, *i.e.* that bound to the nitrogen atom, from ref. 22. [e] The redox potential given is the only one which we found in the literature. It should be noted that this is a so-called ' kinetic redox potential ' and its validity has been questioned by many authors. [f] From ref. 23. [g] From ref. 24, pK for the addition of a proton to the amide group. [h] Polarographic half-wave potential; unpublished results of M. Nutkovich.

dm³ mol⁻¹ s⁻¹ at pH 1 and 5 respectively; and $(CH_3)_2\dot{C}OH$ + $[R^3(O_2CC_4H_3N_2)]^{3+}$, $k = (2.2 \pm 0.2) \times 10^9$ and $(3.5 \pm 0.4) \times 10^8$ dm³ mol⁻¹ s⁻¹ at pH 1 and 5, respectively. In both cases the disappearance of the absorption obeyed a first-order rate law and was independent of wavelength and complex concentration. However, the rate was pH-dependent (as shown in Figure 2) for $[R^3(O_2CC_4H_3N_2)]^{3+}$.

Upon irradiation of N_2O-saturated solution containing 1 mol dm⁻³ propan-2-ol and (1—5) × 10⁻⁴ mol dm⁻³ of $[R^2(4\text{-}O_2CC_4H_3N_2)]^{3+}$ or $[R^2(5\text{-}O_2CC_4H_3N_2)]^{3+}$ at pH 5, no reaction of $(CH_3)_2\dot{C}OH$ radicals with the binuclear complex is observed and the bleaching of the absorption of the i-propyl alcohol radicals obeys a second-order rate law due to disproportionation. However, on acidification to pH 0.7 * the bleaching is faster and the kinetics change to pseudo-first-order: $(CH_3)_2\dot{C}OH + [R^2(5\text{-}O_2CC_4H_3N_2)]^{4+} \longrightarrow$, $k = (1.3 \pm 0.2) \times 10^8$ dm³ mol⁻¹ s⁻¹; and $(CH_3)_2\dot{C}OH + [R^2(4\text{-}O_2CC_4H_3N_2)]^{4+}$, $k = (3.6 \pm 0.4) \times 10^8$ dm³ mol⁻¹ s⁻¹ were determined at pH 0.7. When Ni⁺ is used as the reducing agent (see above) the rates observed are 2.7 × 10⁸ and ≤ 1 × 10⁷ dm³ mol⁻¹ s⁻¹ at pH 4.0 for the pyrimidine-4- and -5-carboxylate complexes respectively. No transients other than $(CH_3)_2\dot{C}OH$ or Ni⁺(aq) respectively were observed in these systems.

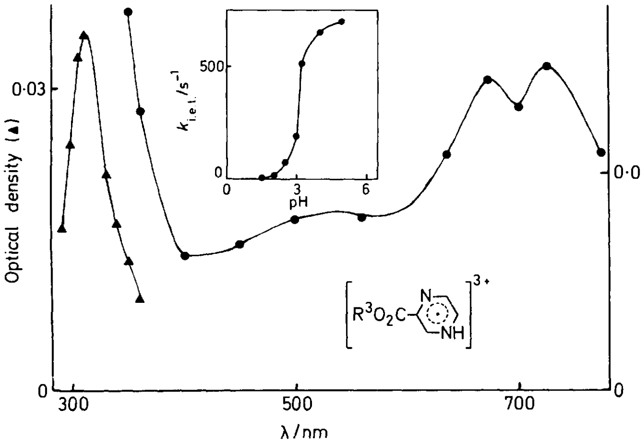
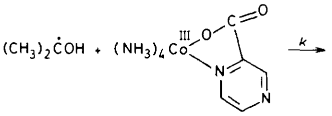


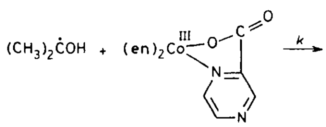
FIGURE 2 Absorption spectrum of the indicated free radical intermediate in Ar-saturated solution at pH 1.25 containing 5 × 10⁻⁶ mol dm⁻³ of the complex $[R^3(O_2CC_4H_3N_2)]^{3+}$; optical path = 4 cm (▲) and 12.5 cm (●). Insert: pH-dependence of the first-order disappearance of the intermediate

When N_2O-saturated solutions containing 1 mol dm⁻³ propan-2-ol and $[Co(NH_3)_4(O_2CC_4H_3N_2)]^{2+}$ (1 × 10⁻⁴—4 × 10⁻⁴ mol dm⁻³) at pH 6.7—5.1 were irradiated, a pseudo-first-order bleaching of the absorption band of the complex was observed. This bleaching is due to the reaction of the $(CH_3)_2\dot{C}OH$ radicals with the complex. The rate of this reaction is slightly pH dependent, k (see below) = (9 ± 2) × 10⁸ and (4.5 ± 0.5) × 10⁸ dm³ mol⁻¹ s⁻¹ at pH 5.1 and 0.7 respectively. No intermediate other than $(CH_3)_2\dot{C}OH$ was observed in these experiments.



Upon irradiation of N_2O-saturated solutions containing 0.1 mol dm⁻³ propan-2-ol or 0.1 mol dm⁻³ sodium formate at pH 5.5 and (0.5—5) × 10⁻⁴ mol dm⁻³ of the complex $[Co^{III}(en)_2(O_2CC_4H_3N_2)]^{2+}$, formation of a transient absorption (Figure 3), independent of the reducing radical [Cd⁺(aq) was used also] is observed; the rate of formation of the absorption obeys a pseudo-first-order rate law (see below): $k = (3 \pm 0.4) \times 10^9$ dm³ mol⁻¹ s⁻¹ at pH 5.5.†

This transient absorption disappears, at pH 1 or 5.5, in a first-order process, the rate of which is independent of wavelength, organic solute, complex concentration, and pulse intensity, $k = (5 \pm 0.5) \times 10^4$ and $(1.0 \pm 0.1) \times 10^5$ s⁻¹ at pH 5.5 and 1 respectively.



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* At this pH the charges on the complexes are probably increased.

† At acidic pH and with $CO_2^{•-}$ as the reducing radical the reaction was not measurable ($k \geqslant 5 \times 10^9$ dm³ mol⁻¹ s⁻¹), under the experimental conditions.

In Tables 2 and 3 are summarized the intramolecular electron-transfer (i.e.t.) reaction rates from the bound ligand radicals to the Co^{III} centre measured for the different ligand radicals by following the disappearance of the absorption due to the bound free radical.

DISCUSSION

Identification of the Reduced Intermediates.—The only reducing agent remaining in the solution within less than 1 μs from the end of the pulse is the one chosen [$e^-(aq)$; $(CH_3)_2\dot{C}OH$, $CO_2^{\bullet -}$, $Ni^+(aq)$, or $Cd^+(aq)$] (see above).

The reducing agent $R^{\bullet}$ can react in a solution containing $Co^{III}L$ * *via* three main reaction pathways (13)—(15).

$$2\,R^{\bullet} \longrightarrow RR \text{ or } R^+ + R^- \qquad (13)$$

$$R^{\bullet} + Co^{III}L \longrightarrow Co^{III}L^{\bullet -} + R^+ \qquad (14)$$

$$R^{\bullet} + Co^{III}L \longrightarrow Co^{II}L + R^+ \qquad (15)$$

In order to clarify which type of reaction occurred, reaction (13) in the absence of the complex, and reduction of the free ligand were also studied. The spectrum of $L^{\bullet -}$ was compared to that of the intermediate formed in the presence of the complex (if reduction occurs). When the same spectra were obtained for solutions containing the free ligand and the complex, the intermediate observed in the latter solution is identified as $Co^{III}L^{\bullet -}$.

The effect of ligating the free radical to the central cobalt(III) on the absorption spectrum depends clearly on the overlap of the orbitals of the central metal ion with those of the ligand and more specifically with that occupied by the unpaired electron. For all the nitroaromatic radicals studied so far, bound *via* a carboxylate to the cobalt(III), there were only minor changes in the spectrum (either $\lambda_{max.}$ or $\varepsilon_{max.}$) of the bound as compared to that of the free ligand radicals.[4,7] Similarly, we find also for the heteroaromatic radicals that ligation through carboxylate to Co^{III} causes only minor changes in the spectra observed.

The latter observations indicate that there is at most a weak interaction between the central cobalt(III) and the conjugated double-bond system of the organic ligand.

Rates of the Intramolecular Electron-transfer Reactions.—(*a*) *Effect of the redox potential of the free radical.* The electron-transfer process from the bound ligand radical to the metal centre is a reduction process of the Co^{III} ion. Thus if the ligand radical $L^{\bullet -}$ is a stronger reducing agent the reaction should be faster. Indeed this was found for the reduction of $[Co(NH_3)_6]^{3+}$ by the non-bound free radicals, Table 1 (the only exception being *m*- *versus p*-nitrobenzoate anion radical, see below). When the radical is co-ordinated to the cobalt(III) there is also a correlation between the rate of i.e.t. and the redox potential. Along the series of the binuclear hexaaminecobalt(III)-bound radicals homarine, pyrimidine-4-carboxylate, 4-nitrobenzoate, and pyrazine-2-carboxylate radicals for which the corresponding reduction potentials are −0.9, −0.8, −0.4, and −0.02 V *versus* n.h.e. (normal hydrogen electrode) the rate of i.e.t. is $\geqslant 1 \times 10^5$, $\geqslant 3 \times 10^4$, 2×10^3, and 9×10^2 s^{-1} respectively, Tables 2 and 3. Similarly, we note that the rate of i.e.t. for the acidic form of the free radicals (LH) is always slower than that of the basic form ($L^{\bullet -}$), in accord with the redox potential of the two forms.

TABLE 2

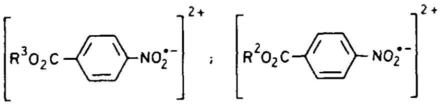
Specific rates of intramolecular electron-transfer reactions of some carboxylate-bound nitroaromatic radicals

$CoL^{\bullet -}$	$k_{i.e.t.}/s^{-1}$
$[R^1(p\text{-}O_2CC_6H_4\dot{N}O_2H)]^{2+}$	$\leqslant 1$ [a]
$[R^1(p\text{-}O_2CC_6H_4NO_2^{\bullet -})]^{+}$	2.6×10^3 [b]
$[R^1(m\text{-}O_2CC_6H_4NO_2^{\bullet -})]^{+}$	$\leqslant 10^2$
$[R^1(o\text{-}O_2CC_6H_4NO_2^{\bullet -})]^{+}$	4×10^5 [b]
$[R^2(p\text{-}O_2CC_6H_4\dot{N}O_2H)]^{3+}$	*ca.* 2 [c]
$[R^2(p\text{-}O_2CC_6H_4NO_2^{\bullet -})]^{2+}$	2×10^3 [c]
$[R^3(p\text{-}O_2CC_6H_4\dot{N}O_2H)]^{3+}$	$\leqslant 10^2$
$[R^3(p\text{-}O_2CC_6H_4NO_2^{\bullet -})]^{2+}$	*ca.* 30

[a] Taken from ref. 5. [b] Taken from ref. 4. [c] Taken from ref. 7.

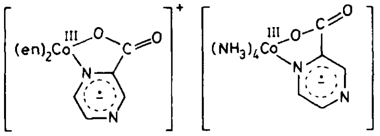
(*b*) *Effect of non-participating ligands.* It is known[6] that substitution of ammonia ligands of Co^{III} complexes with bidentate or tridentate amine ligands lowers the oxidation potential of the complex. Thus it is expected that such a substitution would lower the rate of i.e.t. from a given bound radical to the central cobalt(III). Indeed, for the pair (i), the rate of i.e.t. is 30 s^{-1} in the

(i)



tridentate tacn complex and 2×10^3 s^{-1} for the bis(triammine) complexes. Similarly, for the pair (ii) the

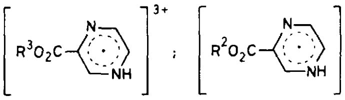
(ii)



rates are 5×10^4 and $>3 \times 10^4$ s^{-1} respectively. We could obtain only a lower limit for the tetra-ammine complex, but the value is most probably in accord with the expectation from the known trend of change in the redox potential.

However, this is not the case for the third pair (iii),

(iii)



where the rate of i.e.t. is practically unaffected by changing the tridentate tacn ligand by three ammines (6×10^2 and 1×10^3 s^{-1} respectively). This observation indicates that the redox potential is not the only parameter which affects the i.e.t. rate. The reason for this observation might be that in the pyrazine there is a high probability of finding the unpaired electron on the N^1 atom in an orbital which might overlap with one of the

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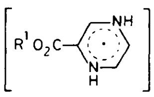
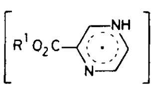
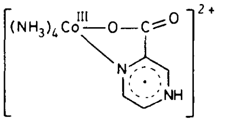
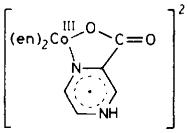
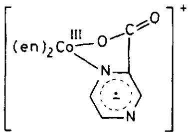
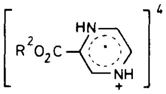
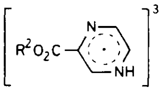
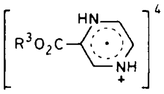
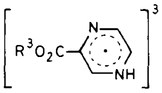
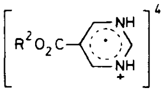
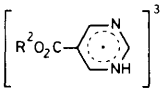
* $Co^{III}L$ can be $Co^{III}(NH_3)_5L$, $Co^{III}(NH_3)_4L$, or $Co^{III}{}_2L$ binuclear complexes.

nitrogens bound to the cobalt or the carboxylate oxygen atom.

The conclusion that the redox potential of the couple L/L$^{\bullet-}$ is one of the major factors affecting the rate of i.e.t. is in agreement with earlier conclusions, based on solvent effects on the rate of i.e.t., and with the suggestion that i.e.t. through carboxylate can be considered as an 'intramolecular outer-sphere electron transfer process'.[7]

TABLE 3

Specific rates of intramolecular electron transfer from heteroaromatic radicals to a central cobalt(III)

CoL$^{\bullet-}$	$k_{\text{i.e.t.}}/\text{s}^{-1}$
	$\leqslant 1$
	90
	$\geqslant 3 \times 10^4$ *
	1×10^5
	5×10^4
	$\leqslant 0.1$
	9×10^2
	$\leqslant 0.1$
	6×10^2
	$\geqslant 3 \times 10^4$ *
	$\geqslant 3 \times 10^4$ *

* Only a lower limit of the rate constant is given when no bound free radical intermediate was observed. The rate given is that of the disappearance of the reducing free radical in the presence of the highest Co$^{\text{III}}$ complex concentration. The rate of reduction of the complexes by these radicals is much higher than that of $[Co(NH_3)_6]^{3+}$, thus indicating that the reduction proceeds *via* the reduced heteroaromatic ligand.

However it should be pointed out that although the redox potential of the reducing radical and the nature of the lead-in group seem to be the major factors affecting the rate of the i.e.t., other factors contribute also. Thus although the redox potential of the couples p-$^{-}O_2CC_6H_4NO_2^{\bullet-}$/$p$-$^{-}O_2CC_6H_4NO_2$ and m-$^{-}O_2CC_6H_4NO_2^{\bullet-}$/$m$-$^{-}O_2CC_6H_4NO_2$ are similar, m-$^{-}O_2CC_6H_4NO_2^{\bullet-}$ is a considerably less reactive reductant in the intramolecular electron-transfer reactions and the outer-sphere process, Tables 1 and 2. This difference seems to stem from the different resonance configurations of the two isomers. Thus the probability of finding the unpaired electron on the carbon α to the carboxylate is smaller in the *meta isomer.* For the i.e.t. this means that the electron is further away from the cobalt(III) centre and the reaction is slower. If the outer-sphere process involves the formation of an ion pair in which the carboxylate has a high probability of approaching the $[Co(NH_3)_6]^{3+}$, a similar result is expected.

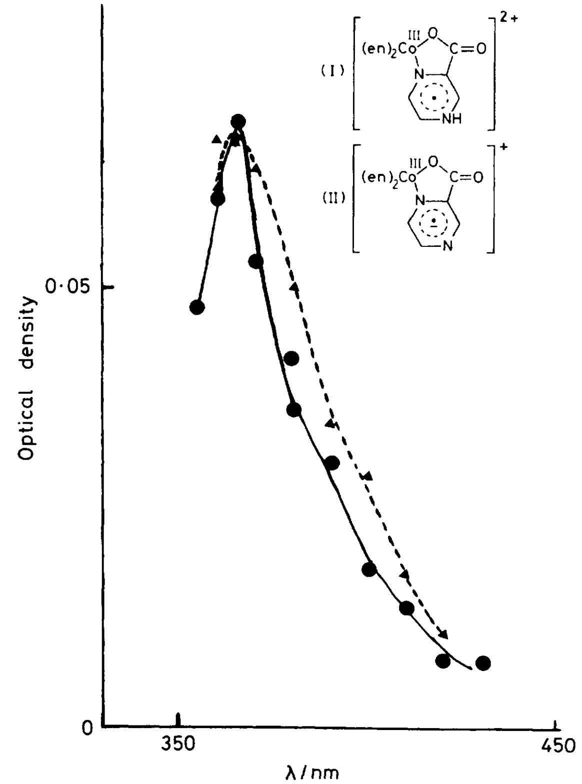
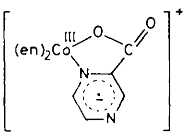
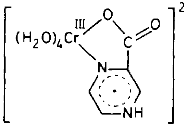


FIGURE 3 Absorption spectrum of $[Co^{III}(en)_2(O_2CC_4H_3N_2)]^{2+}$: pH 1 and Ar-saturated (●), transient (I); pH 6 and N_2O-saturated (▲), transient (II). The solution contained 6×10^{-4} mol dm^{-3} of the complex and 0.1 mol dm^{-3} propan-2-ol

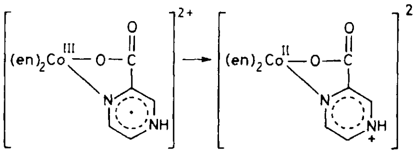
Intramolecular Electron Transfer from Free Radicals bound to the Cobalt(III) via *one of the Nitrogen Atoms of Pyrazine.*—Only in one case, *i.e.* for the ethylenediamine derivative (below) where an additional nitrogen atom of the heteroaromatic ring is co-ordinated to the central



cobalt(III), does the spectrum (Figure 3) differ considerably from that of the non-bound free radical, both in $\lambda_{max.}$ and $\varepsilon_{max.}$. Thus when the nitrogen atom of the heteraromatic ring serves as the lead-in group there is a strong interaction between the molecular orbitals of the ligand and those of the central Co^{III} moiety. Similarly, it was reported by Dunne and Hurst [25] for the same radical bonded through the same two atoms to Cr^{3+} (below) that $\lambda_{max.} = 548$ nm compared to 370 nm in the

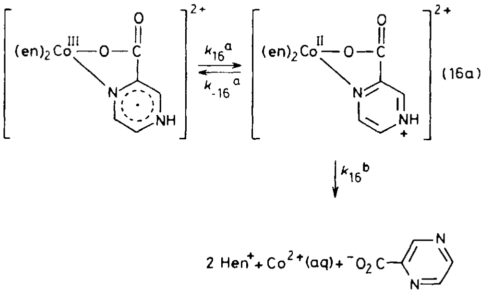


Co^{III}-bound system and 320 nm in the unbound ligand radical. This result indicates, as expected, that when overlap between metal orbitals and the highest occupied molecular orbital of the free radical exists, the absorption spectrum strongly depends on the nature of the central metal cation. It is of interest to note that, as expected, the rate of i.e.t. from the pyrazine radical is considerably higher when it is bound also through the nitrogen atom. This result indicates that the latter is much better than carboxylate as a lead-in group for i.e.t. reactions to a cobalt(III) centre. It should be noted that due to the very small free-energy gain in reaction (16) and due to the fact that the cobalt(II) formed is



(16)

chelated to the heteroaromatic ligand, it is plausible that reaction (16) is an equilibrium reaction and should be rewritten as (16a); then $k_{obs.} = 1 \times 10^5 = K_{16}{}^{a} \cdot k_{16}{}^{b}$.



(16a)

Thus it is plausible that the i.e.t. reaction ($k_{16}{}^{a}$) is even faster than that observed.

Finally, let us note that our results seem to indicate that measurement of i.e.t. from a reduced radical ligated to the cation is plausible only if (*a*) there is a kinetic barrier for the reduction of the central cation which enables preferential reduction of the ligand; (*b*) the free-energy gain in the i.e.t. process is not too large, otherwise the reduction of the ligand is the rate-determining step; and (*c*) the group binding the ligand to the central cation does not provide for a good overlap of the lowest unoccupied orbital of the central cation and the orbital of the unpaired electron in the free radical ligand. The larger the free-energy gain in the i.e.t. is, the less overlap through the lead-in group is required.

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REFERENCES

[1] (*a*) H. Taube, ' Electronic Transfer Reactions of Complex Ions in Solution,' Academic Press, New York, 1970; (*b*) A. Haim, *Acc. Chem. Res.*, 1975, **8**, 264.

[2] (*a*) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, 1971, **93**, 7347; (*b*) S. S. Isied and H. Taube, *ibid.*, 1973, **95**, 8198; (*c*) J. K. Hurst and R. M. Lane, *ibid.*, 1973, **95**, 1703; (*d*) R. D. Cannon and J. Gardiner, *Inorg. Chem.*, 1974, **13**, 390; (*e*) H. Fisher, D. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, 1976, **98**, 5512; (*f*) J. Iow and A. Haim, *ibid.*, 1976, **98**, 1172; (*g*) A. L. Oliviera, H. E. Toma, and E. Giesbrecht, *Inorg. Chim. Acta*, 1977, **22**, 269; (*h*) H. Spiecker and K. Wieghardt, *Inorg. Chem.*, 1977, **16**, 1290; (*i*) K. Rieder and H. Taube, *J. Am. Chem. Soc.*, 1977, **99**, 7981; (*j*) H. Bertram and K. Wieghardt, *Angew. Chem.*, 1978, **90**, 218; (*k*) J. M. Malin, D. A. Ryan, and T. V. O'Halloran, *J. Am. Chem. Soc.*, 1978, **100**, 2097.

[3] H. Taube and E. S. Gould, *Acc. Chem. Res.*, 1969, **2**, 321.

[4] (*a*) M. Z. Hoffman and M. G. Simic, *J. Am. Chem. Soc.*, 1972, **94**, 1757; (*b*) M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *ibid.*, 1977, **99**, 2166; (*c*) M. Z. Hoffman and M. G. Simic, *Proc. Int. Conf. Coord. Chem. Toronto*, 1972, 501; (*d*) K. D. Whitburn, M. Z. Hoffman, M. G. Simic, and N. Brezniak, *Inorg. Chem.*, 1980, **19**, 3180.

[5] H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1975, 2477.

[6] F. Basolo and R. G. Pearson, ' Mechanism of Inorganic Reactions,' Wiley, New York, 1968.

[7] K. Wieghardt, H. Cohen, and D. Meyerstein, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 388.

[8] J. V. Beitz, J. R. Miller, H. Cohen, K. Wieghardt, and D. Meyerstein, *Inorg. Chem.*, 1980, **19**, 966.

[9] K. Wieghardt, H. Cohen, and D. Meyerstein, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 608.

[10] N. V. Brezniak and M. Z. Hoffman, *Inorg. Chem.*, 1979, **18**, 2935.

[11] M. Z. Hoffman, N. V. Brezniak, M. A. Jamieson, R. Sriram, D. W. Kimmel, and M. G. Simic, *Inorg. Chem.*, 1978, **18**, 2749.

[12] M. Z. Hoffman and D. W. Kimmel, *J. Chem. Soc., Chem. Commun.*, 1975, 549.

[13] H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1976, 1976.

[14] (*a*) H. Bertram, E. Balsing, H. Spiecker, and K. Wieghardt, *Inorg. Chem.*, 1978, **17**, 221; (*b*) E. S. Gould, *J. Am. Chem. Soc.*, 1965, **87**, 4730; (*c*) H. E. Toma, *J. Inorg. Nucl. Chem.*, 1975, **37**, 785; (*d*) K. Wieghardt, W. Schmidt, B. Nubes, and J. Weiss, *Chem. Ber.*, 1979, **112**, 2220.

[15] (*a*) D. Meyerstein and W. A. Mulac, *Inorg. Chem.*, 1970, **9**, 1762; (*b*) H. Cohen and D. Meyerstein, *ibid.*, 1974, **13**, 2434.

[16] M. S. Matheson and L. M. Dorfman, ' Pulse Radiolysis,' MIT Press, Cambridge, Massachusetts, 1969.

[17] H. Cohen and D. Meyerstein, *J. Am. Chem. Soc.*, 1972, **92**, 6944.

[18] K. D. Asmus, H. Hockal, and A. Henglein, *J. Phys. Chem.*, 1973, **77**, 1218.

[19] (*a*) M. Kelm, J. Lilie, and A. Henglein, *J. Chem. Soc., Faraday Trans. 1*, 1975, 1132; (*b*) M. Kelm, J. Lilie, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1974, **78**, 882.

[20] J. S. Paton, Y. M. Wu, T. Y. Fanchian, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, 1978, **17**, 326.

[21] P. Neta., M. G. Simic, and M. Z. Hoffman, *J. Phys. Chem.*, 1976, **80**, 2018.

[22] R. N. Moorthy and E. Hayon, *J. Phys. Chem.*, 1974, **78**, 2615.

[23] H. Cohen and D. Meyerstein, *Isr. J. Chem.*, 1974, **12**, 1049.

[24] E. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, 1974, **96**, 6169.

[25] T. G. Dunne and J. K. Hurst, *Inorg. Chem.*, 1980, **19**, 1152.