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A pulse radiolysis study of the rate of ligand dissociation from mixed ligand cobalt(II) complexes

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The reduction and subsequent reactions of the series of mixed ligand cobalt(III) complex cations, [Co(bipy)$_3$]$^{3+}$, [Co(phen)$_3$]$^{3+}$, [Co(en)$_3$]$^{3+}$, [Co(en)$_2$(bipy)]$^{3+}$, [Co(en)$_2$(phen)]$^{3+}$, [Co(en)$_2$(5-NO$_2$-phen)]$^{3+}$, [Co(en)$_2$(DPPZ)]$^{3+}$, [Co(bipy)$_2$(NH$_3$)$_2$]$^{3+}$, [Co(bipy)(NH$_3$)$_4$]$^{3+}$, [Co(phen)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$]$^{3+}$ and [Co(phen)(NH$_3$)$_4$]$^{3+}$, (where bipy is 2,2′-bipyridine, phen is 1,10-phenanthroline, en is ethylenediamine, 5-NO$_2$-phen is 5-nitro-1,10-phenanthroline and DPPZ is dipyrido[3,2-*a*:2′,3′-*c*]phenazine) have been studied using pulse radiolysis. The crystal structures of the mixed ligand complexes [Co(bipy)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$, [Co(bipy)(NH$_3$)$_4$]Cl$_{0.5}$(ClO$_4$)$_{2.5}$, [Co(phen)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ and [Co(phen)(NH$_3$)$_4$](ClO$_4$)$_3$, have been determined. The mechanism of reduction of the cobalt(III) centre by e$^-_{\mathrm{aq}}$ has been found to vary depending upon the nature of the ligands present in the complex. When an aromatic ligand is present the formation of a coordinated ligand radical is observed. This decays *via* intramolecular electron transfer to produce the cobalt(II) complex. The rate constants for the intramolecular electron transfer processes are of the order of 10^3–10^4 s^{-1}. The rates of ligand dissociation of bidentate ligands from the resulting cobalt(II) complexes have been determined. The relative rates of the dissociation of the first ligand from the complexes is found to be dependent upon the identity of the ligand and is related to the ligand structure. For the dissociation of the same ligand from related complexes, the electronic structure of the complex becomes a factor.

Introduction

One of the striking properties of cobalt is its relative inertness to ligand substitution in the 3+ oxidation state as compared to the 2+ oxidation state. Data on the kinetics and mechanism of ligand substitution of cobalt(III) complexes is plentiful. In contrast, however, equivalent data on cobalt(II) complexes is scarce. The hexa(aqua)cobalt(II) cation has been studied in detail, and aquation rate constants have been determined for a limited number of simple cobalt complexes containing monodentate ligands, such as [Co(NH$_3$)$_6$]$^{2+}$. However, the rate of ligand dissociation from cobalt(II) is in general too rapid to measure using normal laboratory techniques. Indeed, even using techniques such as pulse radiolysis, in which the cobalt(II) analogue is able to be rapidly produced from the stable cobalt(III) precursor complex using reducing radicals, it has been found that the rate of dissociation of the first monodentate ligand may be too rapid to measure.[1,2] Due to this, studies have generally focussed on the mechanism and rate of polydentate ligand dissociation from cobalt(II), although Cohen *et al*[3,4] and Simic *et al*[5–7] have carried out a detailed pulse radiolytic investigation of cobalt(III) complexes containing a mono- or di-nitrobenzoato ligand. These investigations have largely been concerned with the mechanism of the reduction of cobalt(III) to cobalt(II) using reducing radicals.

Systematic investigations of complexes containing polydentate amine ligands such as ethylenediamine, diethylenetriamine and triethylenetetramine have been conducted for binary and mixed ammine/halide systems.[1,8] In addition to these studies tris-cobalt(II) complexes of acetylacetonate,[9] glycinate,[10] 2,2′-bipyridine and 1,10-phenanthroline[11,12] have been investigated as well as a mixed ligand complex containing derivatives of ethylenediamine and acetylacetonate.[13] This work has led to some understanding of structural and coulombic factors affecting the rate of ligand substitution of different ligands bound to cobalt(II). There is, however, a paucity of information on the substitution kinetics of mixed ligand complexes. To this end, we have chosen to examine a series of related mixed ligand cobalt complexes and to compare their kinetic behaviour with that of the corresponding tris- coordinated complexes. These studies are also germane to our work in progress on the use of functionalised analogues of the dipyrido[3,2-*a*: 2′,3′-*c*]phenazine moiety as acceptor units in bridged donor–acceptor complexes. We report here the results of our pulse radiolytic studies on a series of related cobalt complexes containing nitrogen donor ligands, in particular the bidentate amine ethylenediamine, the bidentate imines 2,2′-bipyridine, 1,10-phenanthroline, dipyridophenazine as well as the monodentate ligand ammonia. Processes occurring in solution were measured using UV-visible spectroscopy.

We have also fully characterised the complexes [Co(bipy)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$, [Co(bipy)(NH$_3$)$_4$]Cl$_{0.5}$(ClO$_4$)$_{2.5}$, [Co(phen)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ and [Co(phen)(NH$_3$)$_4$](ClO$_4$)$_3$ by single crystal X-ray diffraction so that, when complemented by data from the literature, structural information is available on the full set of complexes examined by pulse radiolysis with the exception of [Co(en)$_2$(5-NO$_2$-phen)]$^{3+}$. The results of this work are also described in this report.

Experimental

Materials

All reagents used were of AR grade. [Co(bipy)$_3$](ClO$_4$)$_3$·3H$_2$O, [Co(phen)$_3$](ClO$_4$)$_3$·2H$_2$O, [Co(en)$_3$]Cl$_3$, [Co(en)$_2$(bipy)]Br(ClO$_4$)$_2$, [Co(en)$_2$(phen)]Br$_3$, [Co(en)$_2$(5-NO$_2$-phen)]Br$_3$, [Co(en)$_2$(DPPZ)](ClO$_4$)$_3$·1/2H$_2$O, [Co(bipy)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$, [Co(bipy)(NH$_3$)$_4$](ClO$_4$)$_3$, [Co(phen)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$ and [Co(phen)(NH$_3$)$_4$](ClO$_4$)$_3$, were prepared and purified as described in the literature.[14–20] All reagents used were of AR grade. Complexes were characterised using NMR and UV-visible spectrophotometry. UV-visible spectra of aqueous solutions were measured using a Hewlett-Packard 8452A Diode Array Spectrophotometer or a Perkin-Elmer Lambda2 Spectrophotometer. For radiation measurements, solutions of concentration 2 × 10^{-4}–3 × 10^{-5} M were prepared using ultrapure water from a Millipore system and the pH adjusted if required using KOH (BDH Chemicals). N_2 gas (BOC), KOH and *tert*-butyl alcohol (AJAX) were used as received.

Crystallography

Crystal data. $[Co(bipy)_2(NH_3)_2](ClO_4)_3$: empirical formula $C_{20}H_{22}Cl_3CoN_6O_{12}$, M = 703.72, monoclinic, space group $P2_1/c$ (no. 14), a = 11.793(3), b = 13.978(3), c = 17.462(4) Å, β = 108.69(2)°, V = 2726.7(11) Å^3, $F(000)$ = 1432, Z = 4, D_c = 1.714 g cm^{-3}, μ = 9.97 cm^{-1}, Mo-Kα radiation (graphite monochromatised) λ = 0.71073 Å, T = 293(1) K.

$[Co(bipy)(NH_3)_4](ClO_4)_{2.5}Cl_{0.5}\cdot 1.5H_2O$: empirical formula $C_{10}H_{20}Cl_3CoN_6O_{11.50}$, M = 573.60, orthorhombic, space group $Pcca$ (no. 54), a = 18.499(3), b = 32.113(5), c = 14.620(3) Å, V = 8685(3) Å^3, $F(000)$ = 4672, Z = 16, D_c = 1.755 g cm^{-3}, μ = 12.3 cm^{-1}, Mo-Kα radiation (graphite monochromatised) λ = 0.71073 Å, T = 293(1) K.

$[Co(phen)_2(NH_3)_2](ClO_4)_3\cdot H_2O$: empirical formula $C_{24}H_{24}Cl_3CoN_6O_{13}$, M = 769.77, monoclinic, space group $P2_1/c$ (no. 14), a = 14.199(5), b = 14.569(2), c = 14.467(6) Å, β = 91.477(19)°, V = 2991.7(17) Å^3, $F(000)$ = 1568, Z = 4, D_c = 1.709 g cm^{-3}, μ = 9.19 cm^{-1}, Mo-Kα (graphite monochromatised) λ = 0.71073 Å, T = 293(1) K.

$[Co(phen)(NH_3)_4](ClO_4)_3$: empirical formula $C_{12}H_{20}Cl_3CoN_6O_{12}$, M = 605.62, monoclinic, space group $P2_1/c$ (no. 14), a = 10.551(4), b = 28.226(4), c = 15.1401(12) Å, β = 90.838(17)°, V = 4508.4(19) Å^3, $F(000)$ = 2464, Z = 8, D_c = 1.784 g cm^{-3}, μ = 11.89 cm^{-1}, Mo-Kα (graphite monochromatised) λ = 0.71073 Å, T = 293(1) K.

Single X-ray quality crystals of $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ were grown by the slow evaporation of aqueous solutions of the complexes. The data for $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, were collected from a yellow prism of approximate dimensions 0.12 × 0.14 × 0.22 mm and for $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ from an orange prism of approximate dimensions 0.24 × 0.36 × 0.36 mm in sealed capillary tubes in the presence of mother liquor. Data for $[Co(phen)(NH_3)_4](ClO_4)_3$ were collected from an orange prism of approximate dimensions 0.13 × 0.19 × 0.25 mm. Single X-ray quality crystals of $[Co(phen)_2(NH_3)_2](ClO_4)_3$ were grown by the slow diffusion of ethanol into an aqueous solution of the complex and data was collected from an orange plate of approximate dimensions 0.10 × 0.11 × 0.14 mm in a sealed capillary tube in the presence of mother liquor.

Details of the data collection refer to $[Co(bipy)_2(NH_3)_2](ClO_4)_3$. The corresponding details for $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}\cdot 1.5H_2O$, $[Co(phen)_2(NH_3)_2](ClO_4)_3\cdot H_2O$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ respectively, are given in parentheses. Accurate unit cell parameters were calculated using a least-squares procedure from the setting angles of 25 reflections. Intensity data were collected on an Enraf-Nonius CAD4-MachS single crystal X-ray diffractometer. The ω (ω, ω–2θ, ω) scan method and graphite monochromatised Mo-Kα radiation, λ = 0.71073 Å, were used. During collection three intensity control reflections were monitored every 7200 (9600, 9600, 7200) s of X-ray exposure time. These showed no deterioration in intensity for $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ but for $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ a deterioration of 35% was observed during the data collection; for this complex the data were corrected in order to account for this variation. A total of 7049 (10050, 8299, 8367) reflections were measured, $2 \le 2\theta \le 27°$ ($2 \le 2\theta \le 25°$, $2 \le 2\theta \le 27.5°$, $2 \le 2\theta \le 25°$), of which 5930 (7680, 6883, 7912) were unique (R_{int} = 0.0218 (0.0565, 0.0354, 0.0136)) and 4083 (4202, 3471, 5929) considered observed ($I \ge 2\sigma(I)$). Corrections were applied for Lorentz and polarization effects as well as for absorption, the corrections for $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ being evaluated by Gaussian integration[21] whilst that for $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ was evaluated using empirical methods.[22] The maximum and minimum transmission factors were 0.8272 and 0.7517 (0.7275 and 0.3502; 0.8740 and 0.7767; 0.7792 and 0.6370).

The structures of $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ were solved using a combination of Patterson, direct methods and difference synthesis[23,24] whilst the structure of $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ was solved by a combination of direct methods and difference synthesis.[23,24] For all complexes the perchlorate anions were found to be disordered and they were included in the refinement in up to two orientations. For $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ these were constrained to geometrical estimates. The structures were refined using a full-matrix least-squares procedure based on F^2. Hydrogen atoms were located from the difference map and were constrained to geometrical estimates. Final refinement was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms and isotropic for the hydrogen atoms. A weighting scheme of type $[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where a = 0.1146 and b = 1.797 (0.1768 and 60.027, 0.672 and 0.000, 0.0797 and 7.4637) was used where $P = (\max(F_o^2,0) + 2F_c^2)/3$. At convergence, R ($I \ge 2\sigma(I)$) = 0.0650 (0.0990, 0.0651, 0.0549), wR (all data) = 0.1928 (0.3455, 0.1521, 0.1507), and S = 1.035 (1.092, 0.959, 1.048), where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2)^{1/2}$. Maximum and minimum residual peak heights were 1.228 and −0.773 (1.018 and −0.932; 0.524 and −0.415; 1.363 and −0.902) e Å^{-3} respectively and were located close to the perchlorate anions.

The atomic scattering factors were those incorporated in the SHELXL-97 program system.[24] Fig. 1 was prepared from the output of ORTEP3 for Windows.[25] Selected bond lengths and angles for complexes $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ are given in Table 1. Material deposited includes hydrogen atom coordinates, complete geometry, displacement parameters and a listing of the observed and calculated structure factors.

CCDC reference numbers 169187–169190.

See http://www.rsc.org/suppdata/dt/b1/b107392n/ for crystallographic data in CIF or other electronic format.

Radiation techniques

This work was carried out at the ARPANSA (Australian Radiation Protection and Nuclear Safety Agency) laboratories using a 20 MW linear accelerator (Linac) delivering a train of 6–20 MeV electron pulses with a pulse repetition rate of 50 Hz. The pulse duration typically used was 400–700 ns. The electron beam was focussed into a quartz flow cell with an optical path length of 10 mm containing a solution of the complex being studied. The monitoring light source employed was an Osram XBO 450W xenon arc lamp, coupled to a Bausch & Lomb monochromator with a grating of 1200 grooves mm^{-1}. Data was captured and digitised on a CompuScope 250 data acquisition card interfaced to a PC. The transmission/time data was fitted to single or double exponential functions using IGOR Pro version 3.12 (Wavemetrics). All rate constants reported are the average of at least 12 different scans at no less than 3 different wavelengths and have an estimated error of 20%.

The total dose per pulse was determined before each series of experiments by measuring the change in absorbance of an aqueous solution (N_2O-saturated) of potassium thiocyanate. The dose received was calculated using ε (480 nm) $(CNS)_2^-$ = 7600 M^{-1} cm^{-1}.[26] The dose per pulse was varied by a factor of 20 by either varying the gun current on the linac or the duration of the pulse received. Doses of between 3.2 and 64 Gy/pulse were used (corresponding to a concentration of between 1 × 10^{-6} and 2 × 10^{-5} M e^-_{aq}). Samples were prepared immediately prior to use and dissolved oxygen was removed by purging

Table 1 Selected bond lengths (Å) and angles (°) for the complexes $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$, and $[Co(phen)(NH_3)_4](ClO_4)_3$

$[Co(bipy)_2(NH_3)_2](ClO_4)_3$		$[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$		$[Co(phen)_2(NH_3)_2](ClO_4)_3$		$[Co(phen)(NH_3)_4](ClO_4)_3$	
Co–N(1)″	1.939(4)	Co–N(1)	1.938(10)	Co–N(10′)	1.944(4)	Co–N(5)	1.952(4)
Co–N(1)	1.943(4)	Co–N(1′)	1.938(10)	Co–N(3)	1.946(4)	Co–N(10)	1.952(4)
Co–N(1′)″	1.944(4)	Co–N(3)	1.942(10)	Co–N(1)	1.946(4)	Co–N(1)	1.962(4)
Co–N(3)	1.951(4)	Co–N(5)	1.949(9)	Co–N(10)	1.946(4)	Co–N(3)	1.962(4)
Co–N(1′)	1.953(4)	Co–N(2)	1.974(10)	Co–N(1′)	1.948(4)	Co–N(2)	1.964(4)
Co–N(4)	1.957(4)	Co–N(4)	1.977(10)	Co–N(2)	1.955(4)	Co–N(4)	1.964(4)
		Co″–N(1)″	1.943(9)			Co′–N(3)′	1.955(4)
		Co″–N(1′)″	1.953(9)			Co′–N(10)′	1.957(4)
		Co″–N(2)″	1.957(9)			Co′–N(5)′	1.958(4)
		Co″–N(5)″	1.967(9)			Co′–N(2)′	1.962(4)
		Co″–N(4)″	1.968(10)			Co′–N(1)′	1.964(4)
		Co″–N(3)″	1.982(10)			Co′–N(4)′	1.969(4)

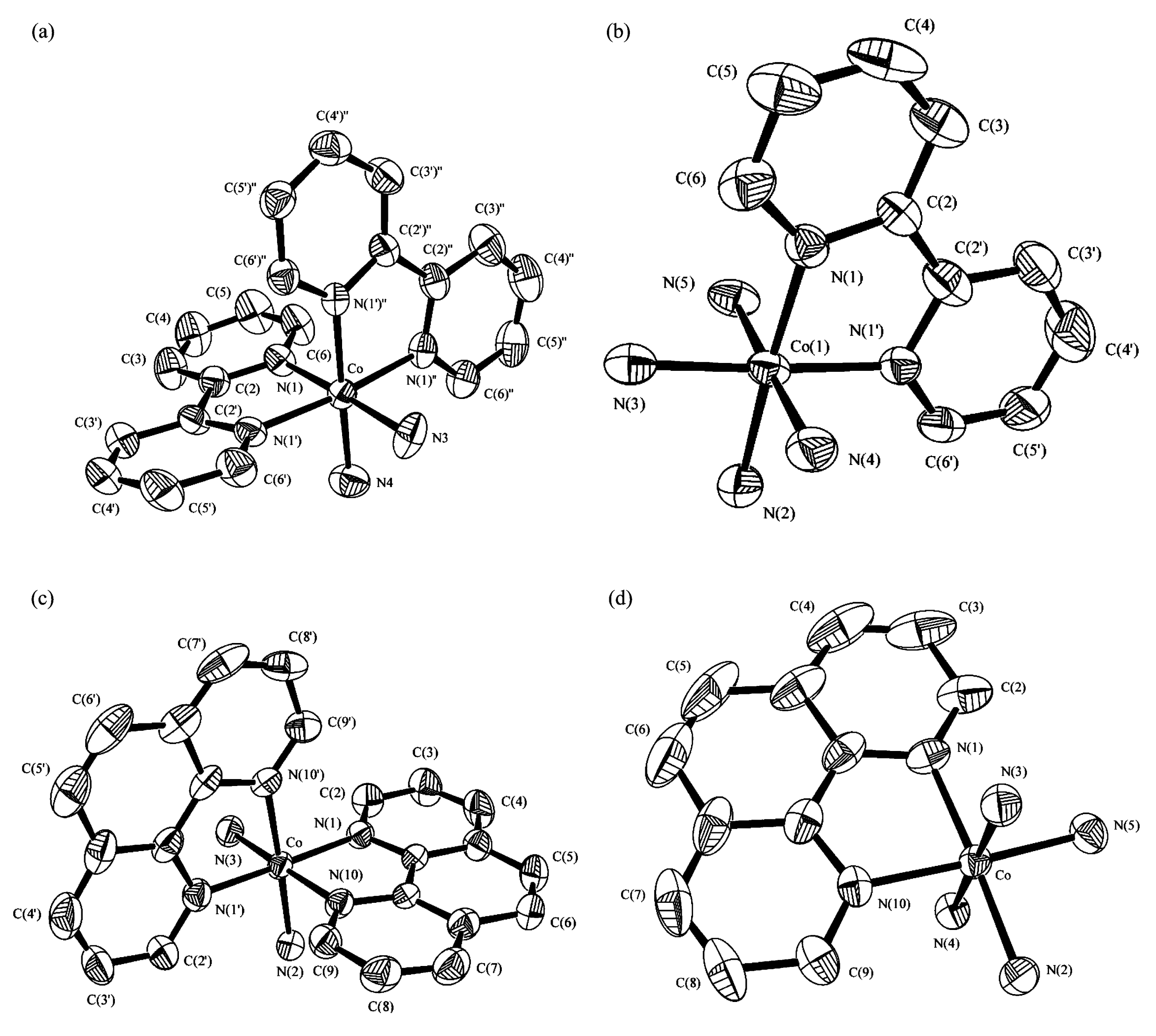

Fig. 1 Structures of the (a) $[Co(bipy)_2(NH_3)_2]^{3+}$, (b) $[Co(bipy)(NH_3)_4]^{3+}$, (c) $[Co(phen)_2(NH_3)_2]^{3+}$ and (d) $[Co(phen)(NH_3)_4]^{3+}$ cations. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted.

with N_2 gas for at least 15 min. During irradiation samples were exposed to as little UV light as possible to avoid photodecomposition, although no evidence of this occurring was found within the time frames monitored. Measurements were carried out at pH 7 and 25 °C unless otherwise noted.

Results

Crystal structures

Selected bond lengths and angles for complexes $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ are given in Table 1. Fig. 1 shows the structures of the cations $[Co(bipy)_2(NH_3)_2]^{3+}$, $[Co(bipy)(NH_3)_4]^{3+}$, $[Co(phen)_2(NH_3)_2]^{3+}$ and $[Co(phen)(NH_3)_4]^{3+}$.

Pulse radiolysis

The radiolysis of an aqueous solution generates the reactive species e^-_{aq}, $OH^\bullet$ and H atoms according to the following equation

$$H_2O \rightsquigarrow e^-_{aq}\,(2.8) + OH^\bullet\,(2.8) + H^\bullet\,(0.55) \qquad (1)$$

where the numbers in parentheses represent the G values (number of molecules produced per 100 eV of energy absorbed) of the species.[26] The production of the reactive species and their diffusion into the bulk solution is complete within 10^{-8} s,[26,27] hence the kinetics of subsequent radiation induced reactions are homogeneous. In our experiments, OH$^\bullet$ and H$^\bullet$ were scavenged using *tert*-butyl alcohol (0.1 M), which reacts with OH$^\bullet$ and H$^\bullet$ atoms to form *tert*-butyl alcohol radicals.[8] The *tert*-butyl alcohol radicals are unreactive towards cobalt complexes and the hydrated electron.[1,8] The rate of reaction of e^-_{aq} with cobalt(III) complexes is diffusion controlled, $k \sim 2.5 \times 10^{10}$–$8.5 \times 10^{10}$ M^{-1} s^{-1} and is complete within the time of the pulse at the concentrations employed.[5,7,10,12,28–33] For all complexes investigated the kinetic data were found to be independent of both radiation dose and complex concentration.

The plots of absorbance vs time obtained upon radiolysis were for all complexes of the same general form. Representative plots for $[Co(en)_2(bipy)](ClO_4)_2Br$ are shown in Fig. 2. Over different timescales a number of processes were observed. The first of these is due to the reaction of e^-_{aq} with the cobalt(III) complex, and is complete within the time of the electron pulse (Fig. 2(a)). The magnitude of the absorbance change is dependent upon the complex and wavelength (at some wavelengths an emission spike is observed due to Cerenkov radiation). Following reaction of e^-_{aq} with the cobalt complex a number of decays are observed corresponding to electronic re-organisation within the complex and ligand dissociation. Within the time period from the initial reaction to 1 ms following reaction a fast decay occurs (Fig. 2(b)). For all complexes, with the exception of $[Co(en)_3]^{3+}$ and $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{3+}$, this process has kinetics which are best fitted to two first order processes. For $[Co(en)_2(bipy)](ClO_4)_2Br$, $[Co(en)_2(phen)]Br_3$, $[Co(en)_2(DPPZ)](ClO_4)_3$ and $[Co(phen)_2(NH_3)_2](ClO_4)_3$ these processes can be measured separately in wavelength regions where only one of these decays is present, with the other decay showing negligible absorbance change. The complexes $[Co(bipy)(NH_3)_4](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$ display regions in which the absorbance changes of the two decays are in opposite directions. For $[Co(en)_3]^{3+}$ and $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{3+}$ the decay consists of only one first order process within this time regime.

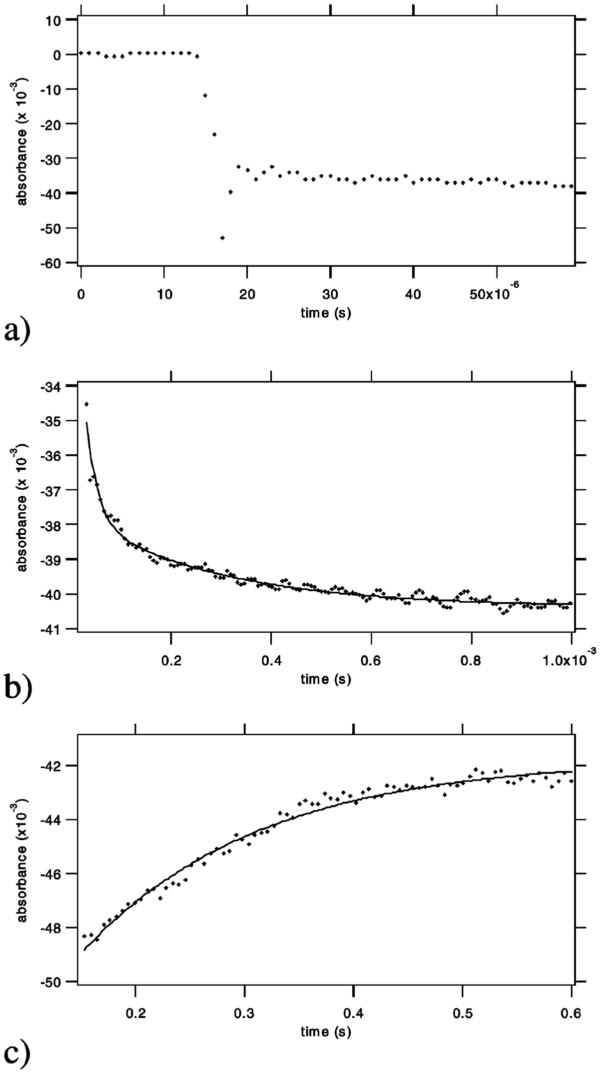

Fig. 2 The individual components of kinetic processes occurring during a typical scan for $[Co(en)_2(bipy)](ClO_4)_3$ (concentration 3.0×10^{-5} M, at T = 24 °C, pH 7.4) at 315 nm, radiation dose 4.5 Gy. Experiments were carried out at sample intervals of 1 µs for (a) and (b) and 100 µs (c), each graph represents the average of four separate experiments.

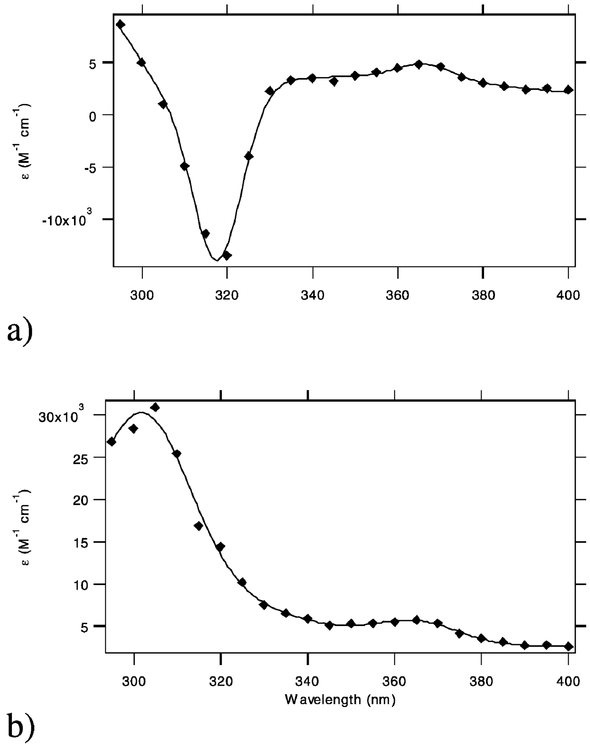

Fig. 3 Differential absorbance and spectrum due to the initial transient formed upon reaction of $[Co(bipy)_3]^{3+}$, with e^-_{aq} (concentration 3.0×10^{-5} M, T = 22.0 °C, pH 7.1).

Fig. 3(a) shows the change in absorbance directly following the electron pulse and this data can be used to produce the spectrum of the initial species (Fig. 3(b)). For the complex $[Co(bipy)_3]^{3+}$ the absorption spectrum of the initial transient formed upon reduction has a peak at 365 nm and a more intense peak at 305 nm. The absorption spectrum of the free, uncomplexed 2,2′-bipyridine radical also displays the previously reported[34–36] peak at 365 nm. It has been shown for aromatic ligands such as those here[12,36–39] that the spectrum of a coordinated radical is similiar to that of the free, uncomplexed species. Hence one of the species formed initially is likely to be a Co(III) centre containing a coordinated aromatic bipyridine radical. The peak at 365 nm disappears totally during the initial decay processes. The initial transients of the other complexes containing aromatic ligands also display broad peaks in the wavelength region 340–400 nm as expected for the corresponding radical (2,2′-bipyridine,[34–36] 1,10-phenanthroline,[35] 5-nitro-1,10-phenanthroline (this work) and dipyridophenazine[40]). The initial product formed upon reaction of $[Co(en)_3]^{3+}$ with e^-_{aq} absorbs only in the 270–330 nm region. Therefore, for all complexes studied one of the initial transients formed is assigned as

Table 2 Rate constants and half lives for intramolecular electron transfer processes

Complex	First decay $k_{et}(1)/s^{-1}$	Second decay $k_{et}(2)/s^{-1}$
$[Co(bipy)_3]^{3+}$	$4.4 \pm 0.6 \times 10^4$	$9.6 \pm 0.7 \times 10^3$
$[Co(phen)_3]^{3+}$	$4.0 \pm 0.1 \times 10^4$	$9.1 \pm 0.1 \times 10^3$
$[Co(en)_3]^{3+}$		$7.4 \pm 0.1 \times 10^3$
$[Co(en)_2(bipy)]^{3+}$	$4.3 \pm 0.4 \times 10^4$	$4.3 \pm 0.3 \times 10^3$
$[Co(en)_2(phen)]^{3+}$	$3.2 \pm 0.1 \times 10^4$	$2.3 \pm 0.1 \times 10^3$
$[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{3+}$	$2.7 \pm 0.1 \times 10^4$	
$[Co(en)_2(DPPZ)]^{3+}$	$2.6 \pm 0.3 \times 10^4$	$3.3 \pm 0.6 \times 10^3$
$[Co(bipy)_2(NH_3)_2]^{3+}$	$3.9 \pm 0.6 \times 10^4$	$2.7 \pm 0.2 \times 10^3$
$[Co(bipy)(NH_3)_4]^{3+}$	$7.2 \pm 1.9 \times 10^4$	$4.3 \pm 0.5 \times 10^3$
$[Co(phen)_2(NH_3)_2]^{3+}$	$3.8 \pm 1.0 \times 10^4$	$2.4 \pm 0.5 \times 10^3$
$[Co(phen)(NH_3)_4]^{3+}$	$2.6 \pm 0.2 \times 10^4$	$2.3 \pm 0.2 \times 10^3$

a cobalt(III) centre containing a coordinated ligand radical. We propose that this species then decays *via* intramolecular electron transfer to form the cobalt(II) species. This is supported by the similarity of the spectra at the completion of this decay and those of independently prepared solutions of the appropriate Co(II) tris-complex ($[Co(N\text{–}N)_3]^{2+}$) (Fig. 4).

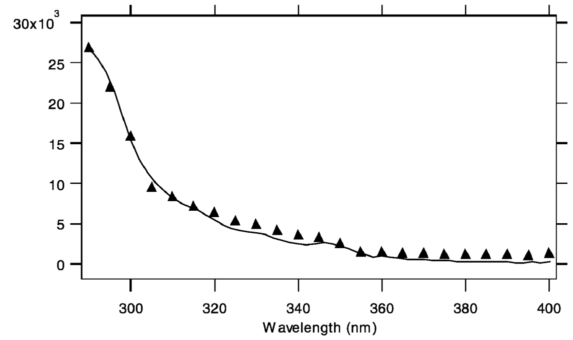

Fig. 4 Spectrum of the second transient formed upon pulse radiolysis of $[Co(phen)_3](ClO_4)_3$, (▲) (concentration 3.0×10^{-5} M, at $T = 22.0$ °C, pH 7.1) and the spectrum of an independently prepared solution of $[Co(phen)_3]^{2+}$ (—).

For the complexes studied the rates of intramolecular electron transfer to form cobalt(II), $k_{et}(1)$ and $k_{et}(2)$, are consistently in the range of 10^3–10^5 s^{-1} and are reported in Table 2.

All further decays were found to be first order (Fig. 2(c)) and correspond to ligand loss from the labile cobalt(II) complex. For all complexes the final spectra obtained were the same as those of stoichiometric solutions of cobalt(II) and containing the appropriate ligands. Controlled electrolytic Co(III)/Co(II) reduction of all complexes was also carried out. The spectra taken during the reduction were of the same form as that obtained from the stoichiometric solutions and from pulse radiolysis (Fig. 5).

Due to the high equilibrium constants for the coordination of successive bipyridine and phenanthroline ligands in the complexes $[Co(bipy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ full aquation of the resultant cobalt(II) ion does not occur. In these cases the final products exist in solution as equilibrium mixtures of the mono- and bis-bipyridine/phenanthroline cobalt(II) species. For $[Co(bipy)_3]^{2+}$ the loss of two bipyridine ligands was observed, however the rate constant for the loss of the second could not be determined due to the slow nature of the decay. For $[Co(phen)_3]^{2+}$ the loss of only the first phenanthroline ligand was observed consistent with both its higher equilibrium constant for coordination to cobalt(II) and slower rate of dissociation.

For the mixed ligand complexes $[Co(en)_2(bipy)]^{2+}$, $[Co(en)_2(phen)]^{2+}$, $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{2+}$ and $[Co(en)_2(DPPZ)]^{2+}$ the first ligand to dissociate is assigned as the ethylenediamine ligand. The assignment is based upon the similarity between the observed rate constants and the rate constants found for the loss of the first ethylenediamine ligand from $[Co(en)_3]^{2+}$ (Table 3), combined with the typically small changes in the UV spectra due to the dissociation of the ethylenediamine ligand compared to the larger changes seen for the aromatic ligands. This conclusion is also consistent with the equilibrium constant for the binding of ethylenediamine to a cobalt(II) centre being lower than that of the diimines. Dissociation of all three bidentate ligands was observed for $[Co(en)_2(bipy)]^{2+}$ and $[Co(en)_2(DPPZ)]^{2+}$. For $[Co(en)_2(phen)]^{2+}$ and $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{2+}$ the absorbance change upon dissociation of the second ethylenediamine ligand was too small to allow accurate and reliable determination of its dissociation rate.

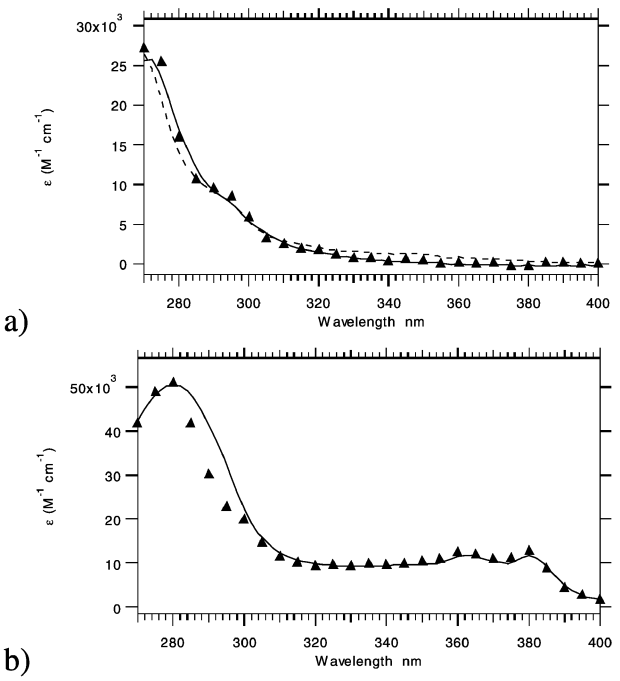

Fig. 5 (a) UV-visible spectrum obtained following the controlled potential electrolysis of $[Co(en)_2(phen)]Br_3$ (—), pulse radiolysis permanent product of $[Co(en)_2(phen)]Br_3$ (▲) ($c = 3.0 \times 10^{-5}$ M, $T = 23$ °C, pH = 7.1) and spectrum of a solution of cobalt(II) containing two equivalents of ethylenediamine and one equivalent of 1,10-phenanthroline (---). (b) UV-visible spectrum obtained following the controlled potential electrolysis of $[Co(en)_2(DPPZ)](ClO_4)_3$ (—) and the pulse radiolysis permanent product of $[Co(en)_2(DPPZ)](ClO_4)_3$ (▲) ($c = 3.0 \times 10^{-5}$ M, $T = 25$ °C, pH = 7.1).

For the mixed ligand complexes containing ammonia, $[Co(bipy)_2(NH_3)_2]^{2+}$, $[Co(bipy)(NH_3)_4]^{2+}$, $[Co(phen)_2(NH_3)_2]^{2+}$ and $[Co(phen)(NH_3)_4]^{2+}$ the dissociation of the first monodentate ligand was too fast to be determined. For these complexes the rate determining step was the reduction of cobalt(III) to cobalt(II) rather than ligand dissociation. Following reduction either one or two first order decays due to ligand dissociation were observed. For $[Co(bipy)(NH_3)_4]^{3+}$, marginally faster intramolecular electron transfer rates as well as two subsequent first order decays with rate constants of 10 s^{-1} and 0.85 s^{-1} were seen. The origin of the slower of the processes is uncertain. The complexes $[Co(phen)_2(NH_3)_2]^{3+}$ and $[Co(phen)(NH_3)_4]^{3+}$ both displayed very slow decays with small absorbance changes following reduction of cobalt(III). Due to the length and small amplitude of these decays the rate constants could not be determined with any certainty.

Discussion

Description of crystal structures

In order to examine any connection between the structures and kinetics of ligand dissociation from the complexes, crystal

Table 3 Rate constants for ligand loss from cobalt(II)

Complex	k_{L1}/s^{-1}	k_{L2}/s^{-1}	k_{L3}/s^{-1}
$[Co(bipy)_3]^{2+}$	2.6 ± 0.2		
$[Co(phen)_3]^{2+}$	0.81 ± 0.2		
$[Co(en)_3]^{2+}$	(3.8 ± 0.9) × 10^2	50[a]	14[a]
$[Co(en)_2(bipy)]^{2+}$	(3.1 ± 0.1) × 10^2	5.8 ± 0.3	0.76 ± 0.19
$[Co(en)_2(phen)]^{2+}$	(2.7 ± 0.9) × 10^2		0.81 ± 0.2
$[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{2+}$	(4.8 ± 0.4) × 10^2		~0.4
$[Co(en)_2(DPPZ)]^{2+}$	(1.1 ± 0.2) × 10^2	4.5 ± 0.2	~0.37
$[Co(bipy)_2(NH_3)_2]^{2+}$	5.9 ± 1.6	0.65 ± 0.5	
$[Co(bipy)(NH_3)_4]^{2+}$	10 ± 4.0	0.85 ± 0.07	
$[Co(phen)_2(NH_3)_2]^{2+}$	—		
$[Co(phen)(NH_3)_4]^{2+}$	—		

[a] Ref. 8.

structures for each were required. The crystal structures of $[Co(bipy)_3]^{3+}$, $[Co(phen)_3]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(en)_2(bipy)]^{3+}$, $[Co(en)_2(phen)]^{3+}$ and $[Co(en)_2(DPPZ)]^{3+}$ have been reported previously,[19,41–43] however, no information concerning the structure of cobalt(III) complexes containing ammonia and aromatic ligands is available. We have determined the single crystal X-ray structures of $[Co(bipy)_2(NH_3)_2](ClO_4)_3$, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$, $[Co(phen)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)(NH_3)_4](ClO_4)_3$.

In each of the structures, the Co–N bond distances (1.94–1.97 Å range) are typical of those found for other cobalt-nitrogen complexes.[19,41–43] Bidentate ligand bite angles impose a slight distortion on the octahedral geometry of the cobalt(III) ion. In all four complexes the phenanthroline ligands are slightly distorted in a bowl shaped manner and bipyridine in an S-shaped manner along the length of the ligand in a manner similar to that observed for the related mixed ligand complexes $[Co(en)_2(bipy)]Br(ClO_4)_2$ and $[Co(en)_2(phen)]Br_3$.[19] In the complexes containing two aromatic ligands, $[Co(bipy)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)_2(NH_3)_2](ClO_4)_3$ one of the aromatic ligands is distorted more from planarity than the other. The cobalt atom lies out of the plane of the aromatic ligand to varying degrees. It is of interest to note that both complexes containing only one aromatic ligand, $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ and $[Co(phen)(NH_3)_4](ClO_4)_3$, crystallise with a larger number of asymmetric units within the unit cell than the complexes $[Co(bipy)_2(NH_3)_2](ClO_4)_3$ and $[Co(phen)_2(NH_3)_2](ClO_4)_3$. The crystal of complex $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$ was isolated from a reaction mixture containing both a large amount of LiCl and $LiClO_4$, and the crystal was analysed as a mixed salt with the composition $[Co(bipy)(NH_3)_4]Cl_{0.5}(ClO_4)_{2.5}$. Recrystallisation of this from an aqueous solution of $LiClO_4$ is likely to produce the pure perchlorate salt as reported,[20] however, crystals suitable for structure determination were not obtained.

In all structures extensive hydrogen bonding is observed between the perchlorate anions and ammonia ligands.

Pulse radiolysis

Although all groups that have investigated the complex $[Co(bipy)_3]^{3+}$ report the final product of the reaction as a partially aquated Co(II) species, two very different rate constants for the first order decay of the reaction product formed immediately after the electron pulse have been reported. Waltz and Pearson[28] and Baxendale and Fiti[44] observed a broad, weak transient with a λ_{max} at approximately 620 nm that decayed with an observed rate constant around 10^4 s^{-1}. Both groups observed that the kinetics of this decay was not purely first order and predicted the involvement of another process in aqueous solution. Simic *et al.*,[12] however, did not observe this first transient, but rather a transient with an intense λ_{max} at 290 nm which decayed with $k = 3.4 \pm 0.4$ s^{-1} to the final product. A decay with a similar rate constant was also reported following the chemical reduction of tris(2,2′-bipyridine)cobalt(III).[45] Our results for $[Co(bipy)_3]^{3+}$ appear to reconcile the literature reports as both of the reported transients and decays (a fast initial decay comprised of two first order components and a slower decay) have been observed and the rate constants of both have been determined within the one experiment.

Whilst neither Waltz and Pearson[28] or Baxendale and Fiti[44] extended their studies below 400 nm, the fact that their transient displayed a broad peak at approximately 620 nm, as does the free bipyridine radical indicates their initial transient is the same transient we observe immediately following the reaction of the complex with e^-_{aq}. This transient then decays via two first order processes to form the cobalt(II) complex. The cobalt(II) species thus formed then decays via first order kinetics with a rate constant in good agreement with that found by Simic *et al.*[12] This decay is due to the dissociation of the first bipyridine ligand.

The broadness and low absorbance of the aromatic radical ligand peaks observed at $\lambda > 340$ nm (when compared to the absorbances observed for the free ligand radical under the same radiolysis conditions) indicate that the formation of the coordinated ligand radical is not quantitative. Hence we propose that reduction of the cobalt(III) centre to cobalt(II) can also occur by direct reaction of the metal centre with e^-_{aq} without the formation of a coordinated radical ligand. This type of competition has also been observed in the nitrobenzoato cobalt system[7] leading to the proposal that, due to the very strongly reducing nature of e^-_{aq}, an initial excited state of higher energy is formed upon reaction of e^-_{aq} with the complex. Following this, the electron may be transferred to either metal centered orbitals to directly reduce cobalt(III) or the ligand localised π^* orbitals. The intramolecular electron transfer from the ligand π^* orbitals to the metal centered orbitals also results in the production of the reduced metal species.[7] The resultant short lifetime of the coordinated ligand radical may explain the observed lack of reaction between the complex $[Co(bipy)_3]^{3+}$ following radiolysis with O_2 or *p*-benzoquinone.[12] Moreover, the observation of only one fast decay process for the intramolecular electron transfer of the complex $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{3+}$ is the result of a significant change in the electronic properties of the ligand. To be consistent with the other aromatic based systems, it must be postulated that the decay of the initial excited state of $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{3+}$ formed is either too rapid to be observed ($>10^7$ s^{-1}) by the detection system or that it is this step that is the rate determining step with a subsequent fast step occurring.

The absorption spectrum of the initial species formed upon reaction with e^-_{aq} is hence a composite of cobalt(II) complexes produced by direct reduction of the cobalt(III) centre and cobalt(III) centres. The proportion of cobalt(III) that is directly reduced to cobalt(II) depends upon the both the number and nature of ligands present. Reduction of complexes containing the ligand 2,2-bipyridine proceeds with a smaller proportion of cobalt(III) being directly reduced than those containing 1,10-phenanthroline, as do complexes containing a lower number of aromatic ligands. In the less sterically crowded ligand systems the metal orbitals are more directly accessible.

The rate constants observed for the intramolecular electron transfer from radical mono- or di-nitrobenzoato ligands to cobalt(III) may be as low as 10^2 s^{-1}.[3–6] It has been suggested that the linking carboxylate group of the nitrobenzoato ligand acts to inhibit the electron transfer to varying degrees depending upon the position/s of substitution of the nitro- group on the benzene ring.[7] We observe that the rates of intramolecular electron transfer for the present complexes are all relatively rapid and vary little throughout the series. This is consistent with the experimental results obtained for the nitrobenzoato complexes in that the metal bonding of the 2,2′-bipyridine, 1,10-phenanthroline and dipyridophenazine is not expected to be vastly different for each of these aromatic ligands.[40,46–49] Furthermore, the modulation of the electronic structure of 1,10-phenanthroline by the addition of a strongly electron withdrawing nitro-group would be expected to change the kinetics of the intramolecular electron transfer. This change is observed with the kinetics of decay best fitting two first order processes for complexes containing 1,10-phenanthroline, whereas the introduction of the nitro-group to the ligand in the 5 position as 5-nitro-1,10-phenanthroline leads to the decay kinetics following only one first order process.

For the complexes containing at least one 2,2′-bipyridine, 1,10-phenanthroline or dipyridophenazine ligand, the observation that the processes occurring within the first millisecond follow biphasic kinetics, and where the rate constants for the first and second processes do not vary significantly throughout the series, is surprising and difficult to rationalise.

For complexes containing only 2,2′-bipyridine and the mixed ligand complexes containing ethylenediamine, it might be possible that the first decay is a simple intramolecular electron transfer from a coordinated aromatic ligand radical to cobalt(III) whilst the second process observed is the dissociation of one end of the bidentate ethylenediamine or 2,2′-bipyridine ligand from the now labile metal ion.[8] This, however, does not seem reasonable for the complexes $[Co(phen)_3]^{2+}$, $[Co(phen)_2(NH_3)_2]^{2+}$ and $[Co(phen)(NH_3)_4]^{2+}$ where the rigidity of the 1,10-phenanthroline ligand is generally accepted as precluding a monodentate intermediate species. In addition, it seems unlikely that the rate of dissociation of one end of the structurally different ligands ethylenediamine and 2,2′-bipyridine would be so similar (Table 2).

A model which seems more consistent to us is one in which an initial excited state, formed upon reaction of e^-_{aq} with the complex, decays *via* intramolecular electron transfer to directly reduce cobalt(III) or forms a metastable coordinated ligand radical. Intramolecular electron transfer from the coordinated ligand radical to the cobalt(III) centre then quantitatively forms cobalt(II). These two intramolecular electron transfer steps would result in the observation of biphasic kinetics, with rate constants $k_{et}(1)$ and $k_{et}(2)$, leading to the reduction of the cobalt(III) centre. For complexes containing ammonia ligands, we should note that the loss of the ammonia would be strongly coupled to the reduction step, based upon the report that loss of the first three ammonia ligands from the complex $[Co(NH_3)_6]^{2+}$ occurs in less than 2 μs.[2]

This proposal may be integrated with that of Lilie *et al.*[1,8] for the dissociation of bidentate ligands. The initial transient of $[Co(en)_3]^{3+}$, the only complex not containing an aromatic ligand, is observed by us to decay *via* one simple first order process with a rate constant of 7.4×10^3 s^{-1}. This is only a factor of two different from the extrapolated value of 1.5×10^4 s^{-1} obtained by Lilie *et al.*[8] for ethylenediamine, where under his conditions monodentate ligand formation leads immediately to ligand loss. Our proposal would suggest that monodentate ligand formation for ethylenediamine is limited by the rate of metal ion reduction ($k = 7.4 \times 10^3$ s^{-1} in our experiments). For complexes in which the first ligand to dissociate is aromatic and more sterically hindered, the reduction of the cobalt(III) centre would not be expected to be the rate determining step for monodentate ligand formation and ligand dissociation is observed to take place in longer time regimes.

Table 4 Energies of d–d band transitions for complexes $[Co(en)_2(bipy)]Br(ClO_4)_2$, $[Co(en)_2(phen)]Br_3$ and $[Co(en)_2(DPPZ)](ClO_4)_3$

Complex	$^1A_{1g} \longrightarrow {}^1T_{2g}$/cm^{-1}	$^1A_{1g} \longrightarrow {}^1T_{1g}$/cm^{-1}
$[Co(en)_2(bipy)]Br(ClO_4)_2$	22438	21072
$[Co(en)_2(phen)]Br_3$	22732	21152
$[Co(en)_2(DPPZ)](ClO_4)_3$	22864	21285

Whilst the explanation offered accounts for the observed biphasic kinetic behaviour and data, we must regard it as conjecture; at this stage we only seek to report the results of our pulse radiolysis studies. Further insights into the details of the mechanism (in particular the nature of any excited state) may be afforded by molecular orbital calculations designed to establish the accessible energy levels in the complexes, but these are beyond the scope of the present study.

Studies of ligand dissociation from cobalt(II) complexes formed by reduction of the corresponding cobalt(III) species have focussed primarily on the mechanism of dissociation. Polydentate ligands have been found to dissociate via a "peeling off" or "unzipping" of the ligand from the metal centre following the scission of the first cobalt(II)–ligand bond and subsequent protonation of the free, uncoordinated heteroatom.[1,8,9] As the reformation of the chelate ring and protonation of the heteroatom are in competition it thus follows that the rate of ligand detachment is pH dependent in the absence of steric effects.[12,45] The kinetics of these ligand detachments have been rationalised in terms of the rigidity and charge of the ligand, where the more flexible ligands dissociate more rapidly than rigid ligands due to their ability to rotate away from the metal ion and prevent reformation of the chelate ring. This effect is seen in our results where for the tris-complexes, in accordance with its greater flexibility, ethylenediamine dissociates more rapidly than 2,2′bipyridine which in turn is more labile than 1,10-phenanthroline. The rates reported for dissociation of ethylenediamine and 2,2′bipyridine from their respective tris-cobalt(II) complexes, $[Co(bipy)_3]^{2+}$ and $[Co(phen)_3]^{2+}$, agree within experimental error with those previously reported.[1,8,12]

As the first ligand to dissociate from the complexes $[Co(en)_3]^{2+}$, $[Co(en)_2(bipy)]^{2+}$, $[Co(en)_2(phen)]^{2+}$, $[Co(en)_2(5\text{-}NO_2\text{-}phen)]^{2+}$ and $[Co(en)_2(DPPZ)]^{2+}$ is ethylenediamine, these complexes may be used to probe the effect of the other ligands on the rate of the ethylenediamine dissociation. The ligands employed throughout this work are all strong σ-donors. Although 2,2′-bipyridine, 1,10-phenanthroline and dipyridophenazine differ in the extent of their π system, their σ-donor orbitals are remarkably similar.[40,46,48] In contrast the nitro-group in 5-nitro-1,10-phenanthroline exerts its electron withdrawing effect through the σ-bonding orbitals[50] and might be expected to behave differently from the other diimines in this context. The aromatic ligands are also π acceptor ligands. The electronic spectra place the aromatic ligands bipyridine, phenanthroline and dipyridophenazine very close together in the spectrochemical series (Table 4), but in the order:

2,2′-bipyridine < 1,10-phenanthroline < dipyrido[3,2-*a*:2′,3′-*c*]phenazine

The difference between the ligand field splittings produced as a result of the coordination of the different aromatic ligands is small, being of the order of less than 1000 cm^{-1}. With no π-acceptor properties it is known that ethylenediamine lies below these diimines in the series. It is observed that the rate of ethylenediamine dissociation from the reduced complex, k_{L1}, decreases slightly in the order $[Co(en)_3]^{2+} > [Co(en)_2(bipy)]^{2+} > [Co(en)_2(phen)]^{2+} > [Co(en)_2(DPPZ)]^{2+}$; this order correlates with extension of the π system of the aromatic ligand.

From the X-ray crystal data[19] it is observed that there is no significant variation in the cobalt(III)–ethylenediamine bond length for these complexes implying minimal effect of change in structure of the complexes on the ground state stabilisation of the cobalt(III)–ethylenediamine bond. Assuming this effect carries through to the cobalt(II) complexes, the slight decrease in k_{L1} would appear to be associated with the destabilisation of the transition state by the extension of the diimine aromatic system. For these complexes, however, this effect is small.

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References

1 J. Lilie, N. Shinohara and M. G. Simic, *J. Am. Chem. Soc.*, 1976, **98**, 6516.
2 M. Simic and J. Lilie, *J. Am. Chem. Soc.*, 1974, **96**, 291.
3 J. V. Beitz, J. R. Miller, H. Cohen, K. Weighardt and D. Meyerstein, *Inorg. Chem.*, 1980, **19**, 966.
4 H. Cohen and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1975, 2477.
5 M. Z. Hoffman and M. Simic, *J. Am. Chem. Soc.*, 1972, **92**, 1757.
6 M. Z. Hoffman and M. Simic, *J. Am. Chem. Soc.*, 1970, **92**, 5533.
7 M. G. Simic, M. Z. Hoffman and N. V. Brezniak, *J. Am. Chem. Soc.*, 1977, **99**, 2166.
8 N. Shinohara, J. Lilie and M. G. Simic, *Inorg. Chem.*, 1977, **16**, 2809.
9 D. Meisel, K. H. Schmidt and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 971.
10 N. Shinohara and J. Lilie, *Inorg. Chem.*, 1990, **29**, 3812.
11 M. Z. Hoffman and M. Simic, *J. Chem. Soc., Chem. Commun.*, 1973, 640.
12 M. G. Simic, M. Z. Hoffman, R. P. Cheney and Q. G. Mulazzani, *J. Phys. Chem.*, 1979, **83**, 439.
13 R. F. Anderson, W. A. Denny, D. C. Ware and W. R. Wilson, *Br. J. Cancer*, 1996, **74**(Suppl. 27), S48.
14 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
15 J. I. Sachinidis, R. D. Shalders and P. A. Tregloan, *Inorg. Chem.*, 1996, **35**, 2497.
16 J. B. Work, *Inorg. Synth.*, 1946, **II**, 221.
17 L. S. Dollimore and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, 1973, 933.
18 R. D. Gillard, R. E. E. Hill and R. Maskill, *J. Chem. Soc. A*, 1970, 1447.
19 A. M. Funston, R. W. Gable, D. W. McFadyen and P. A. Tregloan, *Aust. J. Chem.*, 1999, **52**, 817.
20 J. Josephsen and C. E. Schaffer, *Acta. Chem. Scand. Ser. A.*, 1977, **31**, 813.
21 G. M. Sheldrick, SHELXS76: Program for Crystal Structure Solution. Cambridge, England, 1976.
22 N. Walker and D. Stuart, *Acta. Crystallogr., Sect. A*, 1983, **39**, 158.
23 G. M. Sheldrick, *Acta. Crystallogr., Sect A.*, 1990, **46**, 467.
24 G. M. Sheldrick SHELXL-97: Program for the Refinement of Crystal Structures, University of Gottingen, Germany 1997.
25 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
26 Y. Tabata, Y. Ito and S. Tagawa, *CRC Handbook of Radiation Chemistry*, ed. Y. Tabata, Boca Raton, CRC Press, Inc, FL, 1st edn., 1991.
27 E. J. Hart M. Anbar, *The Hydrated Electron*, Wiley-Interscience, New York, 1970.
28 W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.
29 N. Shinohara and J. Lilie, *Inorg. Chem.*, 1979, **18**, 434.
30 A. Szutka, J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 289.
31 M. A. Tait, M. Z. Hoffman and E. Hayon, *Int. J. Radiat. Phys. Chem.*, 1976, **8**, 691.
32 M. Anbar, *Quart. Rev.*, 1968, **22**, 578.
33 M. Kumar, E. Natarajan and P. Neta, *J. Phys. Chem.*, 1994, **98**, 8024.
34 M. Simic and M. Ebert, *Int. J. Radiat. Phys. Chem.*, 1971, **3**, 259.
35 Q. G. Mulazzani, S. Emmi, P. G. Fuochi, M. Venturi, M. Z. Hoffman and M. G. Simic, *J. Phys. Chem.*, 1979, **83**, 1582.
36 M. Z. Hoffman, M. G. Simic, Q. G. Mulazzani, S. Emmi, P. G. Fuochi and M. Venturi, *Radiat. Phys. Chem.*, 1978, **12**, 111.
37 Q. G. Mulazzani, S. Emmi, P. G. Fuochi, M. Z. Hoffman and M. Venturi, *J. Am. Chem. Soc.*, 1978, **100**, 981.
38 R. P. Patel, S. K. Kulshreshtha and H. Mohan, *J. Chem. Soc., Dalton Trans.*, 1993, 1245.
39 R. P. Patel, M. A. Vaidya, H. Mohan and S. K. Kulshreshtha, *Radiat. Phys. Chem.*, 1996, **48**, 41.
40 J. Fees, W. Kaim, M. Moscherosch, W. Matheis, J. Klima, M. Krejcik and S. Zalis, *Inorg. Chem.*, 1993, **32**, 166.
41 K. Yanagi, Y. Ohashi, Y. Kaizu and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 118.
42 E. C. Niederhoffer, A. E. Martell, P. Rudolf and A. Clearfield, *Cryst. Struct. Commun.*, 1982, **11**, 1951.
43 M. Iwata, K. Nakatzu and Y. Saito, *Acta. Crystallogr., Sect. B*, 1969, **25**, 2562.
44 J. H. Baxendale and M. Fiti, *J. Chem. Soc., Dalton Trans.*, 1972, 1995.
45 R. Davies, M. Green and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1972, 1171.
46 J. Fees, M. Ketterle, A. Klein, J. Fiedler and W. Kaim, *J. Chem. Soc., Dalton Trans.*, 1999, 2595.
47 F. Barigelletti, A. Juris, V. Balzani, P. Belser and A. v. Zelewsky, *Inorg. Chem.*, 1987, **26**, 4115.
48 W. Kaim, *J. Am. Chem. Soc.*, 1982, **104**, 3833.
49 J. Reinhold, R. Benedix, H. Zwanziger and H. Hennig, *Z. Phys. Chem. (Leipzig)*, 1980, **216**, 989.
50 K. K. Cloninger and R. W. Callahan, *Inorg. Chem.*, 1982, **20**, 1611.