Reactions of Chromium(III) Complexes of 1,10-Phenanthroline, 2,2'-Bipyridyl, and Oxalate with the Pulse Radiolytically Generated Aquated Electron, Zinc(I), and Cadmium(I)

Geoffrey A. Lawrance *
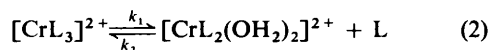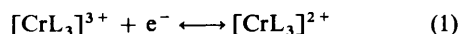*Department of Chemistry, The University of Newcastle, New South Wales 2308, Australia*
David F. Sangster
Division of Chemical Physics, Commonwealth Scientific and Industrial Research Organisation, Lucas Heights Research Laboratories, Private Bag 7, Sutherland 2232, Australia

The chromium(III) ions $[Cr(phen)_3]^{3+}$, $[Cr(bipy)_3]^{3+}$, $[Cr(phen)_2(ox)]^+$, $[Cr(bipy)_2(ox)]^+$, $[Cr(phen)(ox)_2]^-$, and $[Cr(bipy)(ox)_2]^-$ (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridyl, ox = oxalate) react rapidly with the aquated electron to form the chromium(II) analogues. Rate constants for formation of the chromium(II) species are dependent on complex charge, increasing with increasing positive charge, but all greater than 10^{10} dm^3 mol^{-1} s^{-1}. Electronic spectra of the chromium(II) complexes prior to any dissociation were measured. While $[Cr(phen)_3]^{2+}$ and $[Cr(bipy)_3]^{2+}$ decompose only slowly in aqueous solution, all complexes with oxalate ligands decompose rapidly with first-order rate constants $> 8 \times 10^3$ s^{-1}. This behaviour parallels the voltammetric behaviour at a glassy carbon electrode, where only $[Cr(phen)_3]^{3+}$ and $[Cr(bipy)_3]^{3+}$ exhibit any reversible character for the Cr^{III}–Cr^{II} couple. Electron-transfer reactions between the chromium(III) complexes and zinc(I) or cadmium(I), initiated radiolytically, have rate constants near 2×10^9 dm^3 mol^{-1} s^{-1} in all cases, and are probably diffusion controlled.

The chromium(III) complex of 1,2-diaminoethane (en), $[Cr(en)_3]^{3+}$, undergoes an irreversible one-electron reduction in aqueous solution, since rapid ligand exchange forms aquachromium(II) complexes.[1] The oxalate (ox) complex $[Cr(ox)_3]^{3-}$ is also irreversibly reduced.[2] By contrast, chromium(III) complexes of the di-imines 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy), $[Cr(phen)_3]^{3+}$ and $[Cr(bipy)_3]^{3+}$, in water appeared in an earlier study to undergo a series of apparently reversible steps to, nominally, chromium(0),[3] paralleling the chain of reversible one-electron redox processes observed for $[Cr(phen)_3]^{3+}$ in acetonitrile, for example.[4] More recently, detailed studies of the redox chemistry of $[Cr(bipy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$ complexes in aqueous solution identified a series of reactions initiated by dissociation of one di-imine from the chromium(II) complex, which led to the remaining chromium(III) being converted into the $[CrL_2(OH_2)_2]^{3+}$ ion (L = bipy or phen).[5,6]

Following initial reduction [equation (1)], the rate of ligand dissociation [k_1 in equation (2)] is significant in

$$[CrL_3]^{3+} + e^- \longrightarrow [CrL_3]^{2+} \quad (1)$$

$$[CrL_3]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [CrL_2(OH_2)_2]^{2+} + L \quad (2)$$

defining reversibility. When k_1 is large, reversibility of the couple is impaired; clearly this is the case for $[Cr(en)_3]^{2+}$, for example. However, the $[Cr(phen)_3]^{2+}$ and $[Cr(bipy)_3]^{2+}$ ions are sufficiently long-lived to allow determination of their electronic spectra.[7-9] The series of chromium(III)–di-imine complexes from $[CrL_3]^{3+}$ to $[CrL(ox)_2]^-$, where the number of di-imine ligands co-ordinated diminishes stepwise with the introduction of oxalate ligands, offers a system where the variation in stability of the chromium(II) complexes with the number of co-ordinated di-imine ligands may be probed. Replacement of even one di-imine may reduce the lifetime of the chromium(II) complex.

We have investigated this series for L = bipy and phen by pulse radiolysis where a definitive and rapid one-electron

reduction to the chromium(II) complex can be induced, the spectrum of each chromium(II) intermediate can be measured, and both the rate constants for formation and decay of the chromium(II) complex can be determined. These studies have been augmented by voltammetric studies of the series in neutral aqueous solution. Further, the intramolecular electron-transfer reactions of the series of chromium(III) complexes with pulse radiolytically generated zinc(I) and cadmium(I) have been studied.

Experimental

The preparations of the racemic chromium(III) complexes $[Cr(phen)_3][ClO_4]_3$,[10] $[Cr(bipy)_3][ClO_4]_3$,[10] $[Cr(phen)_2(ox)]ClO_4$,[11] $[Cr(bipy)_2(ox)]ClO_4$,[11] K$[Cr(phen)(ox)_2]$,[12] and K$[Cr(bipy)(ox)_2]$[12] were performed essentially as previously described.

Electrochemical measurements were performed with either a Bioanalytical Systems Inc. CV-27 controller coupled with a Houston Instruments Omnigraphic 100 X–Y recorder, or with an AMEL model 473 controller linked to an EG and G PAR model 303A static mercury-drop electrode (s.m.d.e.) and a YEW model 3022 X–Y recorder. In all experiments the conventional three-electrode system was used with a platinum-wire auxiliary electrode and a Ag–AgCl reference electrode, with nitrogen or argon as the purge gas. Working electrodes were glassy carbon or dropping mercury (s.m.d.e.). Measurements were made on 10^{-3} mol dm^{-3} solutions of the complex in 0.1 mol dm^{-3} NaClO$_4$ as supporting electrolyte.

Pulse radiolysis experiments were performed with a van de Graaff electron accelerator which delivered electron pulses (3 μs) at *ca.* 1 MeV (1 eV = 1.60 × 10^{-19} J) through the thin wall of a cell with a 1-cm optical path, as previously described.[13] Dosimetry was performed with an aerated aqueous solution of potassium thiocyanate, employing values of ε = 7 600 dm^3 mol^{-1} cm^{-1} at 480 nm and $G(OH) = G[(CNS)_2^{-}] = 2.8$; a dose of approximately 40 Gy was observed. Solutions of complexes (10^{-3} mol dm^{-3}) in triply distilled water contained

t-butyl alcohol (0.1 mol dm^{-3}) to act as a scavenger of OH radicals.

Rate constants for reaction of chromium(III) complexes with e_{aq} (G_e 2.7) were detemined by monitoring the decay kinetics of e_{aq} at 580 nm in the presence of a known concentration of complex. Observed rate constants were measured for a series of four solutions of differing complex concentrations, and the second-order rate constant for formation of each chromium(II) transient was determined from the slope of a graph of observed rate constant *versus* complex concentration. Absorbance spectra of transients were constructed from averages of sets of optical density changes measured immediately after the electron pulse, at 5—20 nm intervals between 230 and 670 nm. Dosimetry permitted conversion of optical density into molar absorption coefficients. An internal check on the accuracy of the spectra was available, since absorption maxima and molar absorption coefficients for [Cr(bipy)$_3$]$^{2+}$ have been reported previously;[8] values of ε_{max} measured here agree to within *ca.* 10% with the literature values, and it is unlikely that the technique and facility we use can permit determinations with an error any smaller than that value. Rate constants for decay of transients were determined from sets of at least six signal-averaged independent traces recorded at two or three wavelengths in the visible region. A linear least-squares program calculated rate constants for the decay of the transients, which obeyed first-order kinetics.

Redox reactions between chromium(III) complexes and zinc(I) or cadmium(I) were initiated by pulse radiolysis of 0.01 mol dm^{-3} solutions of zinc(II) or cadmium(II) sulphate and containing variable amounts of chromium(III), but always $< 10^{-4}$ mol dm^{-3}. Variation of the pseudo-first-order decay at 310 nm was monitored, and this rate was first order in [Cr^{III}], allowing the electron-transfer rate constant to be determined from the slope of $k_{obs.}$ *versus* [Cr^{III}] plots in each case.

Results

Voltammetric studies of the series of chromium(III) complexes indicated that only for the tris(di-imine) complexes is quasi-reversible behaviour observed in neutral solution for the first redox step (Table 1). At a glassy carbon billet electrode, cathodic currents for the first reduction in all complexes of identical concentration are similar (although, as expected, smaller for the irreversible reactions). Since one-electron steps to chromium(II) have been established previously for [Cr(bipy)$_3$]$^{3+}$ and [Cr(phen)$_3$]$^{3+}$ complexes,[3-6] it appears that all complexes undergo an initial metal-centred one-electron reduction. While the first step is quasi-reversible for

[Cr(bipy)$_3$]$^{3+}$ [Figure 1(*a*)], even for [Cr(bipy)$_2$(ox)]$^+$ the parallel reduction is irreversible on the voltammetric time-scale [Figure 1(*b*)]. Subsequent, apparently one-electron redox processes occur for [Cr(bipy)$_3$]$^{3+}$ and the phen analogue, but are clearly complicated by phenomena possibly tied to ligand dissociation and complex rearrangement reactions (Figure 1). For the [Cr(bipy)$_2$(ox)]$^+$ and [Cr(bipy)(ox)$_2$]$^-$ ions, complicated reduction patterns with enhanced currents are observed at more negative potentials following the first reduction (Figure 2); some of these processes appear to be quasi-reversible in character. The behaviour is electrode dependent, since a d.c. polarogram of [Cr(bipy)$_2$(ox)]$^+$ showed two reduction waves with similar diffusion currents at -0.98 and -1.17 V, and no prior wave. Notably, cyclic voltammetry of [Cr(ox)$_3$]$^{3-}$ exhibited two simple irreversible waves with similar diffusion currents near -0.8 and -1.4 V, suggesting that the current-enhanced signals observed with [Cr(bipy)$_2$(ox)]$^+$ and [Cr(bipy)(ox)$_2$]$^-$ complexes involve particularly the bipy ligands. Results for the phen series closely parallel results for the bipy series.

While the nature of the voltammetric behaviour of the mixed oxalate–di-imine complexes at very negative potentials is complex, it does not impinge on the general observation that mixed oxalate–di-imine complexes undergo an initial irreversible one-electron reduction on the voltammetric time-scale, whereas the tris(di-imine) complexes show well behaved quasi-reversible behaviour. Reasonably, the variation may be related to rapid ligand dissociation in the former complexes compared with the relatively slow rate constants determined previously for [Cr(phen)$_3$]$^{2+}$ and [Cr(bipy)$_3$]$^{2+}$.[8,9] In order to define more clearly the process indicated by voltammetry, pulse radiolytic reduction of the complexes was investigated.

Reaction of all chromium(III) complexes with the definitive one-electron reductant the aquated electron (e_{aq}) led to the rapid formation of highly coloured intermediates, consistent with electron addition to the metal ion, at least by the completion of the electron pulse. This was confirmed by determination of the electronic spectra of the [Cr(phen)$_3$]$^{2+}$

Table 1. Reduction potentials from cyclic voltammograms of chromium-(III) complexes measured in aqueous 0.1 mol dm^{-3} NaClO$_4$ at a glassy carbon electrode
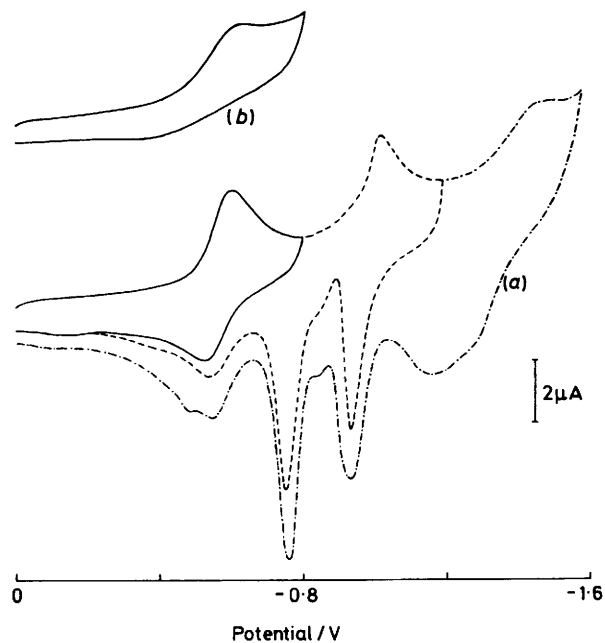
Complex	$E_{\frac{1}{2}}$/V (ΔE/mV)[a]
[Cr(bipy)$_3$]$^{3+}$ [b,c]	-0.56 (77), -0.98 (97), -1.4 (*ca.* 250)
[Cr(phen)$_3$]$^{3+}$ [b]	-0.58 (90), -0.89 (108), -1.3 (*ca.* 250)
[Cr(bipy)$_2$(ox)]$^+$ [d]	-0.62 (irrev.),[e] -0.97 (75),[f] -1.17 (130)[f]
[Cr(phen)$_2$(ox)]$^+$	-0.74 (irrev.),[e] -0.93 (90),[f] -1.25 (*ca.* 180)[f]
[Cr(bipy)(ox)$_2$]$^-$	-0.70 (irrev.),[e] *ca.* -1.2 (*ca.* 110)[f,g]
[Cr(phen)(ox)$_2$]$^-$	-0.77 (irrev.),[e] *ca.* -1.15 (*ca.* 140)[f,g]
[Cr(ox)$_3$]$^{3-}$	-0.79 (irrev.),[e] -1.40 (irrev.)[e]

[a] Ambient temperature, neutral pH; measured *versus* Ag-Ag$^+$; 100 mV s^{-1} scan rate. [b] One-electron steps. [c] Corresponding $E_{\frac{1}{2}}$ values at the s.m.d.e. (pulsed d.c.) are -0.56, -0.88, and -1.43 V. [d] Reductions at the s.m.d.e. observed at only -0.98 and -1.17 V. [e] E_p (cathodic) cited for apparently one-electron irreversible steps. [f] Multi-electron or adsorption-enhanced signal. [g] Complex response pattern.
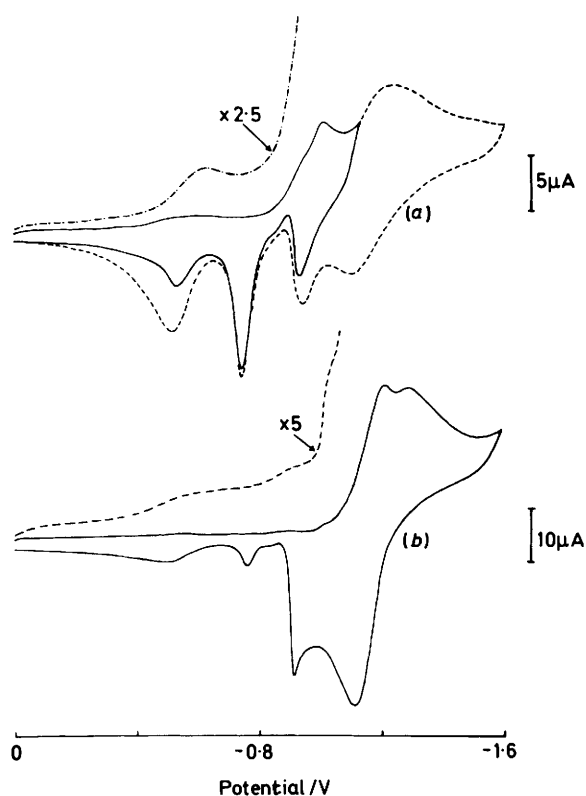

Figure 1. Cyclic voltammograms of (*a*) [Cr(bipy)$_3$]$^{3+}$ with various switching potentials, and (*b*) [Cr(bipy)$_2$(ox)]$^+$ measured in aqueous 0.1 mol dm^{-3} NaClO$_4$ at a glassy carbon working electrode

Figure 2. Cyclic voltammograms of (a) $[Cr(bipy)_2(ox)]^+$ and (b) $[Cr(bipy)(ox)_2]^-$ measured in 0.1 mol dm^{-3} NaClO$_4$ at a glassy carbon working electrode. Complex concentrations (10^{-3} mol dm^{-3}) and working electrode are identical throughout the study

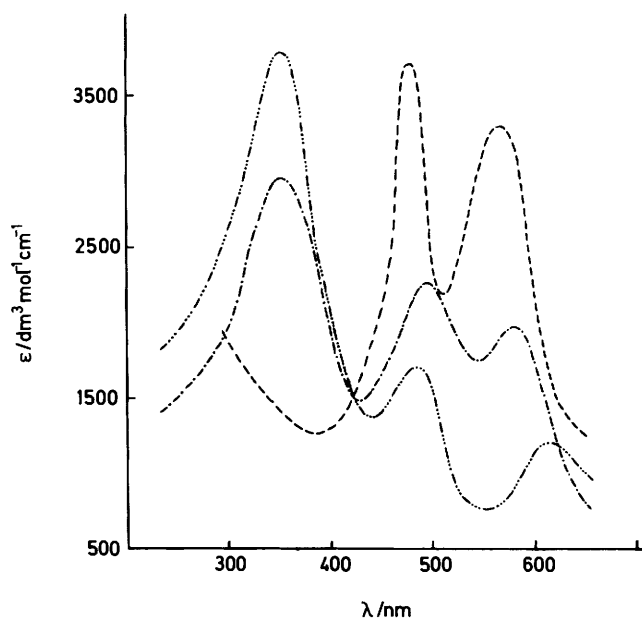**Table 2.** Rate constants for formation and decay of transients in the reaction of chromium(III) complexes with e_{aq} at 23 °C, and electronic spectral data for transients recorded immediately after the pulse

Complex	$10^{-10}k_f$/dm^3 mol^{-1} s^{-1}	k_d/s^{-1}	Electronic spectrum, $\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1})
$[Cr(bipy)_3]^{3+}$	8.0	0.1,[a] 0.38[b]	565 (3 700), 475 (4 100)[c]
$[Cr(phen)_3]^{3+}$	7.7	9 × 10^{-3d}	560 (3 900), 475 (4 200)
$[Cr(bipy)_2(ox)]^+$	4.0	8.9 × 10^3	580 (2 000), 495 (2 400), 350 (3 200)
$[Cr(phen)_2(ox)]^+$	3.8	9.8 × 10^3	575 (1 600), 480 (2 500), 340 (2 900)
$[Cr(bipy)(ox)_2]^-$	1.9	7.4 × 10^4	610 (1 100), 485 (1 700), 350 (4 300)
$[Cr(phen)(ox)_2]^-$	1.6	8.0 × 10^4	600 (600), 470 (2 000), 340 (3 500)
$[Cr(ox)_3]^{3-}$	0.65[e]		

[a] Ref. 8. [b] Ref. 9. [c] Lit.[8] cites 562 (ε 4 300) and 467 nm (ε 4 000 dm^3 mol^{-1} cm^{-1}). [d] Ref. 6. [e] Ref. 17; ref. 18 cites a value of 1.8×10^{10} dm^3 mol^{-1} s^{-1}.

and $[Cr(bipy)_3]^{2+}$ complexes generated radiolytically; the calculated spectrum of the latter agrees well with the reported spectrum[8] (Table 2). Rate constants of formation of chromium(II) were all $>10^{10}$ dm^3 mol^{-1} s^{-1} (Table 2). Previously, measured rate constants for reactions of e_{aq} with phen alone (2.1×10^{10} dm^3 mol^{-1} s^{-1})[14] and $[Cr(OH)(OH_2)_5]^{2+}$ (6.0×10^{10} dm^3 mol^{-1} s^{-1})[15] have been reported, and are also fast. Moreover, values for formation of $[Co(bipy)_3]^{2+}$ (8.3×10^{10} dm^3 mol^{-1} s^{-1}) and $[Co(phen)_3]^{2+}$ (7.5×10^{10} dm^3 mol^{-1} s^{-1}) reported earlier[16] are very close to the values measured for the chromium(II) analogues in this study. Reactions of e_{aq} in both systems are with complexes of similar size and charge. Notably, k_f diminishes as the positive charge on the complex falls, with a roughly two-fold decrease for every change in charge by $+2$. One literature value[17] of k_f for $[Cr(ox)_3]^{3-}$ reacting with e_{aq} is about twelve times smaller than the values for $[Cr(phen)_3]^{3+}$ and $[Cr(bipy)_3]^{3+}$ reacting, although a value only four times smaller appeared earlier.[18]

The electronic spectra of the series of chromium(II) transients are somewhat similar in shape, except that a transition occurring in the visible region near 350 nm for the mixed complexes is absent or shifted to the ultraviolet for the tris-(di-imine) complexes (Figure 3). Maxima observed at 475 and 565 nm for the $[Cr(bipy)_3]^{2+}$ ion are shifted slightly to lower energy in the mixed oxalate–bipy complexes. There is a steady diminution in molar absorption coefficients as the number of di-imine ligands co-ordinated to the chromium(II) decreases. Spectra for the phen series are very similar to those observed for bipy (Table 2). Reported spectra were recorded immediately after the pulse (3 μs), and constructed from experimental optical density changes measured at 5-nm intervals near maxima and

Figure 3. Electronic spectra of chromium(II) transients determined immediately after the electron pulse (3 μs). Complexes are $[Cr(bipy)_3]^{2+}$ (– – – –), $[Cr(bipy)_2(ox)]$ (– · – · –), and $[Cr(bipy)(ox)_2]^{2-}$ (– ·· – ·· –)

minima. Cited maxima are estimated to be defined to within 5 nm, while molar absorption coefficients are defined to $ca. \pm 10\%$.

With the facility available, we were unable to measure decay rates for the $[Cr(phen)_3]^{2+}$ and $[Cr(bipy)_3]^{2+}$ ions because they are too long lived ($k_d > 0.1$ s^{-1}). However, decay rates for the mixed oxalate–di-imine complexes were at least 10^4 times faster and first order, consistent with much more rapid ligand dissociation. Decay of both $[Cr(bipy)(ox)_2]^{2-}$ and $[Cr(phen)-$

Table 3. Rate constants for electron transfer between chromium(III) complexes and zinc(I) or cadmium(I) in neutral aqueous solution [*]

Reductant	Oxidant	$10^{-9}k_{obs}$ $dm^3 mol^{-1} s^{-1}$
Zn^I	$[Cr(bipy)_3]^{3+}$	1.85
	$[Cr(phen)_3]^{3+}$	1.70
	$[Cr(bipy)_2(ox)]^+$	2.20
	$[Cr(phen)_2(ox)]^+$	2.10
	$[Cr(bipy)(ox)_2]^-$	2.20
	$[Cr(phen)(ox)_2]^-$	2.15
Cd^I	$[Cr(bipy)_3]^{3+}$	1.75
	$[Cr(phen)_3]^{3+}$	1.65
	$[Cr(bipy)_2(ox)]^+$	2.25
	$[Cr(phen)_2(ox)]^+$	2.45
	$[Cr(bipy)(ox)_2]^-$	2.15
	$[Cr(phen)(ox)_2]^-$	2.40

[*] Temperature, 23 °C; reaction initiated by pulse radiolysis.

$(ox)_2]^{2-}$ is about ten times faster than decay of $[Cr(bipy)_2(ox)]^+$ and $[Cr(phen)_2(ox)]^+$ complexes (Table 2). The sharply diminished kinetic stability of the mixed-ligand complexes agrees with the voltammetric evidence.

The chromium(III) complexes also undergo rapid reduction when treated with zinc(I) or cadmium(I) ions (Table 3). The metal(I) ions can be generated essentially exclusively from radiolysis of solutions containing at least a 100-fold excess of metal(II) ions over chromium(III) ions. Decay of both zinc(I) and cadmium(I) is a process readily monitored at 310 nm,[19] and this decay rate is mediated by electron transfer between zinc(I) or cadmium(I) and any oxidant present, such as the chromium(III) complexes. Observed second-order rate constants for the redox reactions between cadmium(I) or zinc(I) and the chromium(III) complexes are all close to 2×10^9 dm³ mol⁻¹ s⁻¹, with no significant variation with charge or ligand type apparent.

Discussion

Multidentate ligands with heterocyclic nitrogen donors apparently stabilize a number of metal ions, particularly in lower oxidation states. In the chromium and iron triads, for example, tris(phenanthroline) complexes of chromium, iron, and ruthenium are relatively stable in a range of oxidation states in various solvents; the tris(1,2-diaminoethane) equivalents, if known, do not show similar stability. The metal–ligand bonding interactions which can act to stabilize di-imine complexes, in particular, have been described at length.[20] However, variation in the number of di-imine ligands by substitution of other chelates or unidentate ligands can affect physical properties and reactivities, particularly where substitution-labile groups replace di-imine ligands. For the present series, for example, it is known that the mechanism of racemization of the chiral complexes changes from a trigonal-twist process for the tris-(di-imine) systems to a rearrangement involving one-ended dissociation of an oxalate ligand when only one di-imine is co-ordinated.[21] Here, we observe a marked change in redox stability when oxalate replaces phen or bipy in the co-ordination sphere.

The inertness of the series of complexes in the chromium(II) oxidation state is clearly impaired by the presence of even one oxalate ligand. Decay of the mixed-ligand complexes is up to 10^6 times faster than decay of the tris(di-imine) complexes. The implication is that dissociation of oxalate is much more rapid than loss of a di-imine ligand. The relative flexibility of oxalate permits a facile one-ended dissociation not available for phenanthroline at least,[21] and this dissociation may be the rate-determining step. However, general rearrangements of ligands in the chromium(II) co-ordination sphere may occur on a very rapid time-scale. Notably, anodic maxima observed at -0.55, -0.75, and -0.94 V in the cyclic voltammetry of $[Cr(bipy)_3]^{3+}$ can also be identified in the anodic sweeps following cathodic sweeps for $[Cr(bipy)_2(ox)]^+$ and $[Cr(bipy)(ox)_2]^-$. The implication is that rapid rearrangement of bipy (and likewise of phen) ligands in the series occurs following reduction, facilitated by loss of oxalate, so that even from $[Cr(bipy)(ox)_2]^-$ some $[Cr(bipy)_2(OH_2)_2]^{2+}$ and $[Cr(bipy)_3]^{2+}$ ions could form.

The enhanced currents observed in reductions of the mixed-ligand complexes support rapid ligand rearrangements if they arise from complexes with $E_{\frac{1}{2}}$ values more positive than the precursors being formed and immediately reduced, or initiating some electron-transfer reactions. Alternatively, the waves may be related to electron addition to the di-imine. The first reduction wave of heteroaromatic compounds in aprotic solvents is markedly enhanced by the presence of a proton donor such as water,[22] where the anion formed from electron transfer rapidly adds a proton to form a radical with a more anodic $E_{\frac{1}{2}}$ value. This may not be the case here, since ligand-centred electron additions occur in $[Cr(phen)_3]^{3+}$ only at very negative potentials, and in dry acetonitrile only the fourth wave near -1.8 V is markedly enhanced by water addition.[4] The complex nature of the voltammetric responses precludes detailed analysis, and the chemistry, beyond initial dissociation, is not a prime interest of this study. However, the marked drop in stability of the chromium(II) complex occurring on introduction of even one oxalate chelate indicates a significant role for oxalate in the dissociation process.

Rate constants for formation of the chromium(II) complexes (k_f) versus complex charge show a clear trend in the series, with complex anions slowest. Complex ion size and the number of each type of co-ordinated ligand vary throughout the series, modifying solvation effects and possible pathways for electron transfer. From the observation that k_f for $[CoL_3]^{2+}$ and $[CrL_3]^{2+}$ are essentially the same, despite the different redox potentials and d-electron configurations for the two metal ions, it appears that ion charge and size are important determinants for these reactions with e_{aq}. The reactions are very fast, and essentially diffusion controlled. In this case, the results fit the general observation that, for diffusion-controlled reactions of metal complexes, differences in rate may be accounted for by changes in charge and radii.[23]

The apparently significant part played by oxalate in limiting the stability of the chromium(II) complexes is supported by the observation that, while $[Cr(phen)_2(ox)]$ decays ca. 10^6 times faster than $[Cr(phen)_3]^{2+}$, the $[Cr(phen)(ox)_2]^{2-}$ ion decays less than 10 times faster again. Introduction of a second oxalate ligand would have a minor effect on lability, if one oxalate ligand is sufficient to initiate dissociation and subsequent rearrangement reactions.

Spectra of all six transient chromium(II) complexes have been determined prior to decay, and show minor shifts in positions of the maxima in the visible region, but almost stepwise decrease in molar absorption coefficients with the number of di-imine donors. This is not unreasonable since $[CrL_3]^{2+}$ ions are known to be highly coloured,[7–9] yet $[Cr(OH_2)_6]^{2+}$, which would be spectroscopically like $[Cr(ox)_3]^{4-}$, does not absorb strongly in the visible region. The colour of these ions is presumably largely tied to specific metal–di-imine bonding interactions.

Electron-transfer reactions between radiolytically generated zinc(I) and cadmium(I) and various metal complexes have been reported previously.[24] Reactions with $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, for example,[25] are rapid and presumably outer sphere in mechanism, while recent studies with macrobicyclic hexa-amine complexes where the outer-sphere mechanism must

operate are also rapid.[26] At least between metal(I) and $[Cr(bipy)_3]^{3+}$ or $[Cr(phen)_3]^{3+}$, reactions should involve outer-sphere electron transfer. With mixed-ligand complexes, there exists the possibility of electron transfer *via* an oxalate bridge between the chromium(III) centre and the metal(I) centre. Since E° values for the chromium complexes are all very similar, the observation throughout of similar electron-transfer rate constants with either zinc(I) or cadmium(I) is not unreasonable even for an activation-controlled process. While E° values for the $Zn^{II}-Zn^{I}$ and $Cd^{II}-Cd^{I}$ couples have not been established finitely,[24,27] they are known to be similar, so again electron-transfer rate constants could be similar. However, the rate constants observed are all close to the estimated diffusion-controlled rate for such a reaction of 1×10^9 to 4×10^9 dm^3 mol^{-1} s^{-1}.[25] The reactions may be diffusion controlled, with the limiting rate constant near 2.5×10^9 dm^3 mol^{-1} s^{-1}. In this case there is no opportunity to apply the basic equations of the Marcus theory,[28] applicable only for an activation-controlled process, although with electron-transfer reactions which are slower, self-exchange rate constants for the metal(II)–metal(I) systems may be definable.[26]

Acknowledgements

References

1 A. Fischerova, *Collect. Czech. Chem. Commun.*, 1965, **30**, 1771.
2 I. G. Murgulescu, T. Oncescu, and Z. Simon, *Rev. Roum. Chim.*, 1967, **12**, 737.
3 S. Herzog and H. Aul, *Z. Naturforsch., Teil B*, 1960, **15**, 617; S. Herzog, *Chem. Tech. (Berlin)*, 1956, **8**, 544.
4 M. C. Hughes and D. J. Macero, *Inorg. Chem.*, 1976, **15**, 2040.
5 D. M. Soignet and L. G. Hargis, *Inorg. Chem.*, 1972, **11**, 2349.
6 D. M. Soignet and L. G. Hargis, *Inorg. Chem.*, 1972, **11**, 2921.
7 A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, 1960, **29**, 42.
8 J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, 1964, **86**, 1019.
9 B. R. Baker and B. D. Mehta, *Inorg. Chem.*, 1965, **4**, 848.
10 F. K. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1953, 3570.
11 J. A. Broomhead, M. Dwyer, and N. Kane-Maguire, *Inorg. Chem.*, 1968, **7**, 1388.
12 J. A. Broomhead, *Aust. J. Chem.*, 1962, **15**, 228.
13 H. A. Boucher, A. M. Sargeson, D. F. Sangster, and J. C. Sullivan, *Inorg. Chem.*, 1981, **20**, 3719.
14 W. L. Waltz, Doctoral dissertation, Northwestern University, 1976.
15 M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 973.
16 W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941.
17 R. R. Hentz, Farhataziz, and E. M. Hansen, *J. Chem. Phys.*, 1972, **56**, 4485.
18 A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 289.
19 G. V. Buxton and R. M. Sellers, *J. Chem. Soc., Faraday Trans. 1*, 1975, 558.
20 See, for example, C. K. Jorgensen, 'Inorganic Complexes,' Academic Press, London, 1963.
21 G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, 1977, **16**, 929.
22 B. J. Tabner and J. R. Yandle, *J. Chem. Soc. A*, 1968, 381; G. J. Haijtink, J. van Schoeten, E. deBoer, and V. Aalbensberg, *Recl. Trav. Chim. Pays-Bas*, 1954, **73**, 355; P. H. Given and P. E. Peover, *J. Chem. Soc.*, 1960, 385.
23 M. Anbar and E. J. Hart, *Adv. Chem. Ser.*, 1968, **81**, 79.
24 G. V. Buxton and R. M. Sellers, *Coord. Chem. Rev.*, 1977, **22**, 195.
25 D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1969, **73**, 1091.
26 G. A. Lawrance, E. Miles, D. F. Sangster, and A. M. Sargeson, unpublished work.
27 J. H. Baxendale and R. S. Dixon, *Z. Phys. Chem. (Frankfurt)*, 1964, **43**, 161; J. Navon and D. Meyerstein, *J. Phys. Chem.*, 1970, **74**, 4067.
28 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Chem. Phys.*, 1965, **43**, 3477.