

# Reaction of aquachromium(II) ions with 2,2'-bipyrimidine. A pulse radiolysis study

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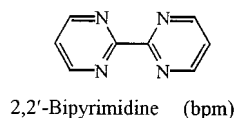
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Chromium(II) ion was generated from  $\text{Cr}(\text{NH}_3)_6^{3+}$  and hydrated electrons in the presence of 2,2'-bipyrimidine (bpm). The reaction of  $\text{Cr}(\text{NH}_3)_6^{3+}$  with  $e^-(\text{aq})$  has  $k = 4.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C. The  $\text{Cr}(\text{NH}_3)_6^{2+}$  so produced loses all the ammonia ligands with  $k > 10^5 \text{ s}^{-1}$ . A product complex with an absorption maximum at around 350 nm was formed in the reaction of chromium(II) ion and bpm. In the presence of a moderate excess of bpm an equilibrium is established on the 0.1 ms timescale with  $K_{\text{app}} = k_f [\text{bpm}] / k_b$ . Both the forward ( $k_f$ ) and back ( $k_b$ ) reactions are pH dependent in the range 3.5 to 8.6. At pH 3.5 and 8.6,  $k_f$  has the values of  $1.6 \times 10^8$  and  $4.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_b$  of  $4.3 \times 10^4$  and  $3.2 \times 10^3 \text{ s}^{-1}$ , respectively. The UV spectra of the reaction product(s) indicate that the absorbing product contains chromium(III) and bipyrimidine radical ligand. The first acid dissociation constant of chromium(II) ion was determined as  $1.4 \times 10^{-5} \text{ mol dm}^{-3}$ . At  $\text{pH} \leq 3.5$ , where all chromium species are predominantly in the aqua form, the proposed reaction scheme is  $(\text{H}_2\text{O})_6\text{Cr}^{2+} + \text{bpm} \xrightleftharpoons[k_{-1}]{k_1} (\text{H}_2\text{O})_5\text{Cr}^{\text{II}}(\text{bpm})^{2+} \xrightleftharpoons[k_{-2}]{k_2} (\text{H}_2\text{O})_4\text{Cr}^{\text{II}}(\text{bpm})^{2+} \xrightleftharpoons[k_{-3}]{k_3} (\text{H}_2\text{O})_4\text{Cr}^{\text{III}}(\text{bpm}^{\cdot-})^{2+}$  where  $[(\text{H}_2\text{O})_5\text{Cr}^{\text{II}}(\text{bpm})]^{2+}$  and  $[(\text{H}_2\text{O})_4\text{Cr}^{\text{II}}(\text{bpm})]^{2+}$  represent steady-state intermediates present in stoichiometrically negligible concentrations. On the 0.1 ms timescale,  $[(\text{H}_2\text{O})_4\text{Cr}^{\text{III}}(\text{bpm}^{\cdot-})]^{2+}$  is stable but undergoes changes at longer times. The protonated bpm molecule,  $\text{H}^+\text{bpm}$ , is reduced by 1-hydroxy-1-methylethyl radicals,  $k = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , yielding a diprotonated bpm radical,  $\text{H}_2\text{bpm}^{\cdot+}$ . No reaction was observed between  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and  $\text{H}_2\text{bpm}^{\cdot+}$  in pulse radiolysis experiments, which places the rate constant for this reaction at  $< 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

The availability of two chelating sites makes 2,2'-bipyrimidine (bpm) an interesting ligand for various aspects of metal coordination chemistry.<sup>1</sup> In addition to mononuclear complexes, bpm has been extensively used as a bridging ligand in binuclear and polynuclear complexes of different metals. Electrochemical investigations have shown that one-electron reduction of various bpm–metal complexes gives reduced species with the electron residing on the bpm ligand. The reduction potentials of the co-ordinated bpm in a number of metal complexes have been determined.<sup>2</sup> The visible and UV absorption spectra of the free bpm radical<sup>3</sup> and of the bpm radical ligand in some ruthenium(II) complexes<sup>4</sup> are known.

Rates and activation volumes for the reaction of a series of aliphatic radicals with chromium(II) ion have indicated that substitution on  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  occurs by an  $\text{I}_d$  mechanism.<sup>5</sup> Metal complexes having nitrogen heterocyclic ligand(s) are often reduced by this ion *via* a chemical mechanism, *i.e.* with formation of an intermediate ligand radical. However, relatively stable chromium(III)–ligand radical species are scarce. One such species is formed by the reaction of  $\text{Cr}^{2+}$  with pyrazine.<sup>6</sup>

In this work we have used pulse radiolysis to study the reaction between chromium(II) ion and bpm. Some other related reactions will also be described.



## Results and discussion

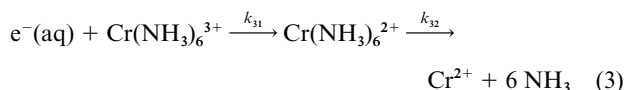
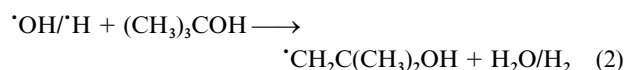
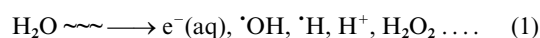
### General observations

The mixing of oxygen-free aqueous solutions of aquachromium(II) and bpm solutions produces an intensely absorbing species with an absorption maximum at around 350 nm. The

formation of this greenish yellow species is complete in the mixing time of our stopped-flow apparatus. The absorbance then decreases on the stopped-flow and conventional spectrophotometry timescale. The absorption spectrum resembles that of the bpm radical, as shown later in detail, suggesting a possibility that electron transfer process(es) may be involved. Preliminary experiments using *cis*- or *trans*- $[\text{Cr}(\text{[14]-aneN}_4)(\text{H}_2\text{O})_2]^{2+}$  have shown that the reaction of bpm with the *cis* complex produces a similar coloration, but that with the *trans* does not. This suggests that bpm binds to the metal in a bidentate fashion. We have therefore investigated the primary steps of the reaction between  $\text{Cr}^{\text{II}}(\text{aq})$  and bpm using pulse radiolysis;  $\text{Cr}^{\text{II}}(\text{aq})$  was produced in  $\approx 1 \mu\text{s}$ , in the presence of bpm, to study their reactions on the  $\mu\text{s}$ –ms timescale.

### Reduction of $\text{Cr}(\text{NH}_3)_6^{3+}$ by hydrated electrons

The reaction was studied at neutral or near neutral pH. The rate constant was measured in deaerated, neutral solutions containing  $0.1 \text{ mol dm}^{-3}$  2-methylpropan-2-ol and various concentrations ( $0$ – $30 \mu\text{mol dm}^{-3}$ ) of  $\text{Cr}(\text{NH}_3)_6^{3+}$ . The alcohol was added in order to convert hydroxyl radicals and hydrogen atoms, formed in reaction (1), into unreactive  $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  radicals, reaction (2). The decay kinetics of  $e^-(\text{aq})$  was followed



spectrophotometrically at 700 nm. It was of pseudo-first order with respect to  $[\text{Cr}(\text{NH}_3)_6^{3+}]$ . From these data the second-order rate constant  $k_{31} = (4.9 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was calculated. The value is very similar to known rate constants for the reduction of some chromium(III) amino complexes and  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  with hydrated electrons.<sup>7,8</sup>

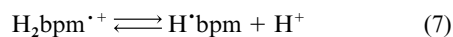
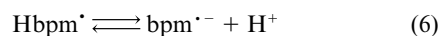
Conductivity measurements at pH 4.0 and  $1 \text{ mmol dm}^{-3}$   $\text{Cr}(\text{NH}_3)_6^{3+}$  were performed to determine the rate of loss of the ammonia ligands after the reduction of the metal center. After pulse irradiation with the dose producing  $\approx 1 \mu\text{mol dm}^{-3}$  of  $\text{Cr}^{2+}$ , the solution conductivity showed a strong decrease that was fully developed within *ca.* 5  $\mu\text{s}$  after the pulse, the time when the first quantitative measurements were possible with the set-up used. The conductivity signal did not change further, up to 10 ms. The observed decrease was  $G\Delta\lambda = -2840$  ( $G = 1$  corresponds to *ca.* 0.1  $\mu\text{mol}$  of charged species per joule of absorbed energy and generally denotes the number of chemically changed species per 100 eV of absorbed energy,  $\text{eV} \approx 1.60 \times 10^{-19} \text{ J}$ ;  $\lambda$  denotes specific conductivity). Considering the overall change in ion concentration according to the processes expressed by eqns. (1)–(4) and taking into account that at pH 4.0 ammonia is fully protonated ( $\text{p}K = 9.25$ ), the change in the specific conductivity should be as in eqn. (5) taking  $\lambda(\text{H}^+) = 315$ ,

$$\Delta\lambda = \lambda(\text{H}^+) - \lambda[\text{Cr}(\text{NH}_3)_6^{3+}] + \lambda(\text{Cr}^{2+}) + 6[\lambda(\text{NH}_4^+) - \lambda(\text{H}^+)] = -1245 \text{ S cm}^2 \text{ equiv.}^{-1} \quad (5)$$

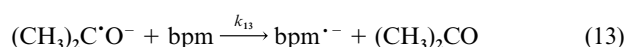
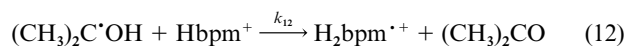
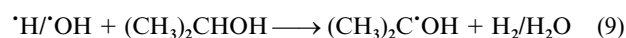
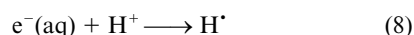
$\lambda(\text{NH}_4^+) = 65$  and  $\approx 60 \text{ S cm}^2 \text{ equiv.}^{-1}$  for the difference in specific conductivity between  $\text{Cr}(\text{NH}_3)_6^{3+}$  and  $\text{Cr}^{2+}$ . This gives  $G = 2.3$  from the measured  $G\Delta\lambda$  value mentioned above, which is very close to the full yield of hydrated electrons in the radiolysis of water ( $G = 2.7$ ). This result demonstrates that reduction of  $\text{Cr}(\text{NH}_3)_6^{3+}$  to  $\text{Cr}^{2+}$  is accompanied by the release of all six ammonia ligands, with the rate constant  $k_{32} > 10^5 \text{ s}^{-1}$ .

#### Reduction of 2,2'-bipyrimidine by 1-hydroxy-1-methylethyl radicals

It is known that one-electron reduction of bpm can be conveniently achieved by pulse radiolysis.<sup>3</sup> The reaction with hydrated electrons has a rate constant of  $2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at pH 7. The resulting radical is known to exist in three forms with respect to protonation, eqns. (6) and (7) with  $\text{p}K_6 = 12.5$  and  $\text{p}K_7 = 4.5$ , as determined from the difference in their optical absorption spectra.<sup>3</sup>



We investigated the reduction of bpm by  $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$  radical. No reduction of bpm was observed at neutral pH. However, at low pH the protonated form,  $\text{Hbpm}^+$ , was reduced very efficiently, and the rate constant of  $k_{12} = 5.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was determined. This was measured in deaerated aqueous solution containing  $1 \text{ mol dm}^{-3}$  propan-2-ol at pH 1, where all primary water radicals were converted into  $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$  during the pulse (reactions 1, 8 and 9).



The concentration of bpm in the reactive, protonated form was calculated using  $K = 4 \text{ dm}^3 \text{ mol}^{-1}$  for  $[\text{Hbpm}^+]/[\text{bpm}][\text{H}^+]$ .<sup>9</sup> In basic solution, where the radical derived from propan-2-ol deprotonates into the more strongly reducing  $(\text{CH}_3)_2\text{C}^{\bullet}\text{O}^-$  ( $\text{p}K = 12.2$ ),<sup>10</sup> reaction (13) was observed to occur with  $k_{13} = 1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . An  $\text{N}_2\text{O}$ -saturated solution containing  $1 \text{ mol dm}^{-3}$  NaOH and  $0.1 \text{ mol dm}^{-3}$  propan-2-ol produced  $(\text{CH}_3)_2\text{C}^{\bullet}\text{O}^-$  as the only radical (reactions 1, 9–11). The above observations and the rate constants are in accord with the previously obtained results for other nitrogen-containing heterocyclic molecules in their reactions with  $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}/(\text{CH}_3)_2\text{C}^{\bullet}\text{O}^-$  radicals.<sup>11</sup>

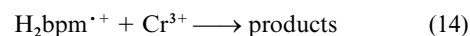
Optical absorption spectra of the one-electron reduced bpm in its different protonation forms measured in this work were very similar to those published previously<sup>3</sup> and will be discussed later. As expected, the spectra were not dependent on the reducing species used, indicating the occurrence of electron transfer in reactions (12) and (13).

#### Decay kinetics of 2,2'-bipyrimidine radicals

The radicals  $\text{bpm}^{\bullet-}$ ,  $\text{Hbpm}^+$  and  $\text{H}_2\text{bpm}^{\bullet+}$  decay on the ms timescale. The kinetics was not simple first or second order. Whereas individual intensity (absorbance) vs. time signals could be rather well fitted according to a second-order rate law, change of the initial radical concentration (by changing the dose of high energy radiation per pulse) caused insufficient change of the decay rates. For example, in the presence of  $1 \text{ mol dm}^{-3}$  NaOH,  $0.1 \text{ mol dm}^{-3}$  propan-2-ol and  $0.1 \text{ mmol dm}^{-3}$  bpm in water,  $\text{bpm}^{\bullet-}$  decayed with a first half-life of 583 and 415  $\mu\text{s}$  when formed with the initial concentrations of 0.6 and 3.0  $\mu\text{mol dm}^{-3}$ , respectively. The other two forms, the neutral radical and the radical cation, are somewhat shorter lived species. The first half-life of *ca.* 200  $\mu\text{s}$  was observed for both radicals at a dose per pulse resulting in the initial concentration of the respective radicals of 2.0  $\mu\text{mol dm}^{-3}$ .

#### Reaction of $\text{H}_2\text{bpm}^{\bullet+}$ radical with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$

To avoid hydrolysis of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  the reaction was studied in  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$ . At this acidity  $\text{e}^-(\text{aq})$  could not be used as the primary agent to reduce bpm, and  $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$  radical was employed instead. As described above, this radical reduces  $\text{Hbpm}^+$  cation effectively but it is relatively unreactive toward  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ .<sup>12</sup>



Experiments were performed in deaerated aqueous solution containing  $0.1 \text{ mol dm}^{-3}$  propan-2-ol,  $1 \text{ mmol dm}^{-3}$  bpm, and  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$ . The spectra immediately after the pulse, and the decay kinetics of  $\text{H}_2\text{bpm}^{\bullet+}$  radical cation formed, were measured in the absence and in the presence of  $1.4 \text{ mmol dm}^{-3}$   $\text{Cr}^{3+}$  [for these measurements the perchlorate salt of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  was used]. Neither of the characteristics of  $\text{H}_2\text{bpm}^{\bullet+}$  was influenced by the presence of  $\text{Cr}^{3+}$ . Considering that an acceleration of  $\text{H}_2\text{bpm}^{\bullet+}$  decay kinetics by a factor of 2 would be easily detectable, it was concluded that  $t_{1/2}$  of reaction (14) must be  $> 200 \mu\text{s}$ , and consequently  $k_{14} < 2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , if the reaction occurs at all.

#### Reaction of $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ with 2,2'-bipyrimidine

This was investigated in deaerated solutions containing  $0.1 \text{ mol dm}^{-3}$  2-methylpropan-2-ol,  $5 \text{ mmol dm}^{-3}$   $\text{Cr}(\text{NH}_3)_6^{3+}$ , and bpm at various concentrations in the range which ensured that at least 95% of hydrated electrons were scavenged by  $\text{Cr}^{\text{III}}$ . The concentration of protons in the investigated solutions was varied between pH 3 and 9. Owing to the low dose per pulse applied ( $\approx 1 \mu\text{mol dm}^{-3}$  of reduced  $\text{Cr}^{\text{III}}$ ), practically no significant change of the bulk pH occurred due to the protonation of

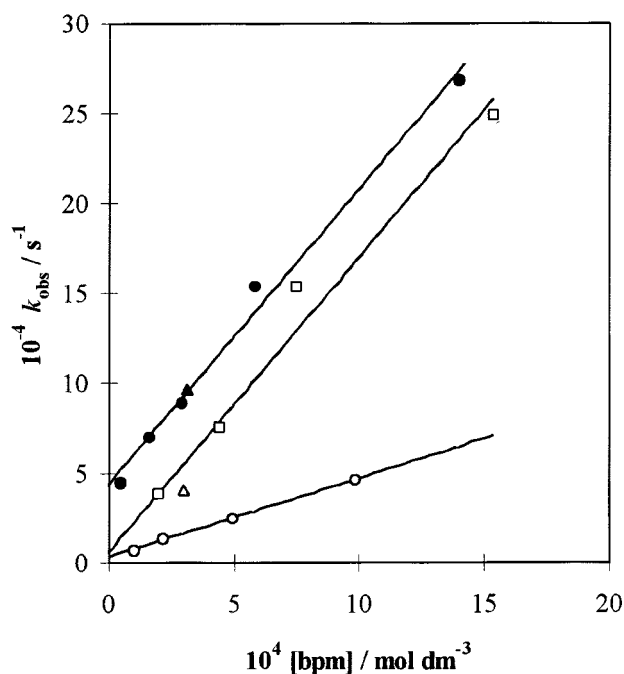


Fig. 1 First-order-rate constant,  $k_{\text{obs}}$ , for the reaction between chromium(II) ion and bpm as a function of bpm concentration at different pH: O, 8.6;  $\Delta$ , 4.1;  $\square$ , 3.9;  $\bullet$ , 3.5;  $\blacktriangle$ , 3.0.

released ammonia, reactions (3) and (4), at the pH employed. Under these conditions the formation of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  was completed within the pulse. After the pulse the formation of an optical absorption with  $\lambda_{\text{max}}$  at around 350 nm was monitored. The absorption change obeys first-order kinetics with the pseudo-first-order rate constant being proportional to the bpm concentration. This is shown in Fig. 1 for pH 8.6, 3.9 and 3.5, which also incorporates single points at pH 4.1 and 3.0. The straight lines obtained for the three pH values have intercepts which are real, outside of the experimental error, so that the kinetics is of the general form (15). Both the slope  $a$  and inter-

$$k_{\text{obs}} = a[\text{bpm}] + b \quad (15)$$

cept  $b$  are pH dependent and their values are given in Table 1. The values at pH 3 are assumed, based on the observation that the  $k_{\text{obs}}$ , measured at a single bpm concentration, falls on the line obtained for pH 3.5. The value of  $k_{\text{obs}}$  at pH 4.1, also measured at a single bpm concentration, falls between those at pH 8.6 and 3.9, and thus does not allow an estimate of  $a$  and  $b$ .

The rate expression (15) points to the operation of reverse reaction(s) on the  $10^2 \mu\text{s}$  timescale. The spectral measurements presented in the next section endorse this observation.

The decay of the 350 nm absorption is of mixed order with a first half-life of ca. 1 ms and is not significantly influenced by the change of dose.

Another observation should be mentioned for measurements at pH < 5. Namely, in more acidic solutions the exponential fitting of the formation curves was less satisfactory if the dose was increased above  $\approx 5$  Gy, and the obtained half-lives were rather sensitive to the doses applied. This resulted in higher values for  $k_{\text{obs}}$  at lower intensity ( $G\epsilon$ ) values as the dose and, consequently, initial  $\text{Cr}^{2+}$  concentration was increased. This indicates an interference by an additional second-order process most probably involving reactions of  $\text{Cr}^{2+}$  with  $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2$  and/or  $\text{H}_2\text{O}_2$  formed in the solution in approximately the same yield. Therefore all measurements of  $k_{\text{obs}}$  shown in Fig. 1 were done by using a constant dose producing only  $1 \mu\text{mol dm}^{-3}$  of  $\text{Cr}^{2+}$  per pulse of irradiation.

The forward rate constant  $a$  is significantly changed between pH 8.6 and 3.9. The bpm is a weak base with  $\text{p}K_{\text{a}} = 0.6^9$  and is

Table 1 Dependence of the experimental rate constants  $a$  and  $b$  on pH\*

pH	$a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$b/\text{s}^{-1}$
8.6	$(4.4 \pm 0.08) \times 10^7$	$(3.2 \pm 0.4) \times 10^3$
3.9	$(1.6 \pm 0.2) \times 10^8$	$(0.6 \pm 1.3) \times 10^4$
3.5	$(1.6 \pm 0.1) \times 10^8$	$(4.3 \pm 0.5) \times 10^4$
3.0	$\approx 1.6 \times 10^8$	$\approx 4.3 \times 10^4$

\* Uncertainties quoted are standard errors.

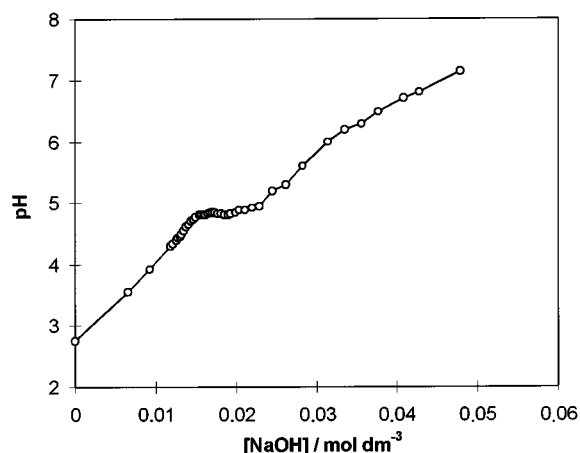
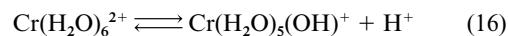


Fig. 2 The pH as a function of NaOH concentration added to a solution of  $0.0386 \text{ mol dm}^{-3}$  chromium(II) ions.

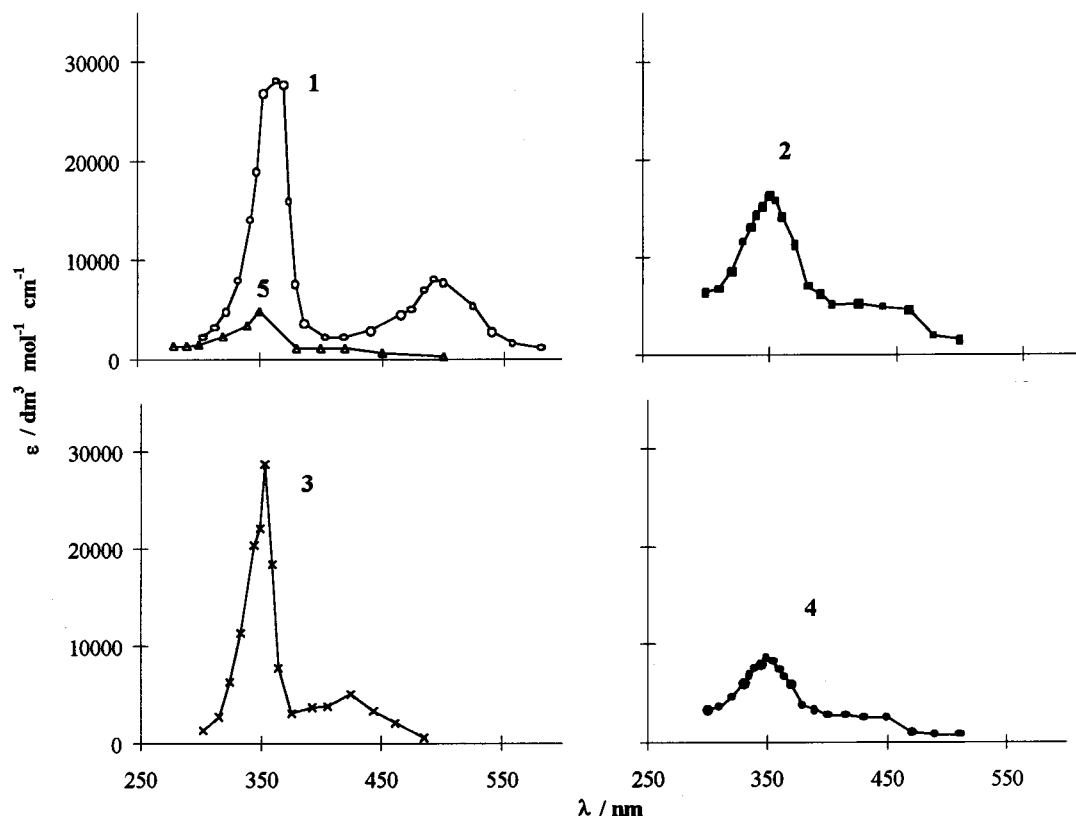
unprotonated in the pH range studied. However, the hydrolysis of  $\text{Cr}^{2+}$ , eqn. (16), may be the cause of the pH dependence of  $a$ .



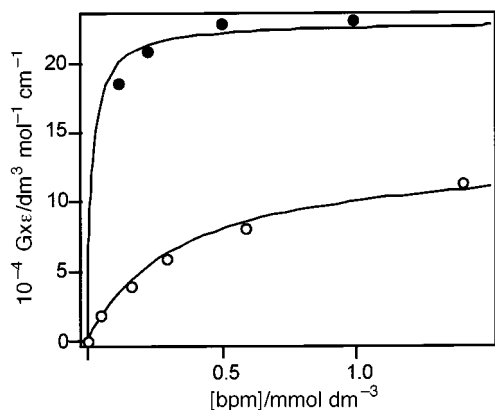
A thorough study of the hydrolysis of aquachromium(II) species has not been done thus far, and we have tested equilibrium (16) by titrating  $\text{Cr}^{2+}$  with a solution of NaOH.

**Hydrolysis of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ .** Solutions of  $0.0386 \text{ mol dm}^{-3}$   $\text{Cr}^{2+}$  were titrated with  $1 \text{ mol dm}^{-3}$  and  $0.1 \text{ mol dm}^{-3}$  NaOH under argon at  $25^\circ\text{C}$  and  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ ) using Cole-Parmer Chemcodet pH-meter. A typical titration curve is depicted in Fig. 2. A first plateau is achieved between pH 4.8 and 4.9. We assume that it corresponds to the first deprotonation step of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ , eqn. (16), giving a  $\text{p}K_{\text{a}1}$  value of 4.85 or  $K_{\text{a}1} = 1.4 \times 10^{-5} \text{ mol dm}^{-3}$ . Accordingly, at pH < 3.9 more than 90% of aquachromium(II) species is in the  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  form. The titration curve above pH 5 is more complex, and at pH 8.6 a mixture of different hydrolytic species is probably present at equilibrium. We did not further investigate this problem.

**Optical absorption spectra.** Optical absorption spectra of the products formed in the reaction of bpm with chromium(II) ions at pH 8.6 and 3.5 are shown in Fig. 3, spectra (4) and (5), respectively. They were obtained by pulse radiolysis spectrophotometric measurements and taken at the time of maximum intensity for each trace. A correction for the decay was negligible on this timescale. Corrections were made, however, for the absorption formed within the pulse which was clearly distinguishable from the next slower stage due to the investigated reaction (15). The former was observable at all wavelengths with the maximum intensity of up to  $(G\epsilon) \approx 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at around 350 nm. This absorption belongs to the free bpm radicals formed by reduction of bpm by hydrated electrons. Although these radicals were formed in a very low yield [under the experimental conditions, over 95% of hydrated electrons reacted with chromium(III) ions], they were visible due to their high molar absorptivities.<sup>3</sup>



**Fig. 3** Optical absorption spectra: (1) bpm radical anion,  $\text{bpm}^{\bullet-}$ , observed in  $\text{N}_2\text{O}$ -saturated aqueous solution containing  $0.1 \text{ mol dm}^{-3}$  propan-2-ol,  $1 \text{ mol dm}^{-3}$  NaOH and  $0.1 \text{ mmol dm}^{-3}$  bpm; (2) neutral radical  $\text{Hbpm}^\bullet$ , observed in deaerated aqueous solution containing  $0.1 \text{ mol dm}^{-3}$  2-methylpropan-2-ol and  $0.2 \text{ mmol dm}^{-3}$  bpm at pH 8.0; (3) radical cation  $\text{H}_2\text{bpm}^{\bullet+}$ , observed in deaerated aqueous solution containing  $0.1 \text{ mol dm}^{-3}$  propan-2-ol,  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  and  $0.2 \text{ mol dm}^{-3}$  bpm; (4) and (5) species formed upon reaction of  $\text{Cr}^{\text{II}}$  with bpm at pH 8.6 and 3.5 observed in deaerated aqueous solution containing  $5 \text{ mmol dm}^{-3}$   $\text{Cr}(\text{NH}_3)_6^{3+}$ ,  $0.1 \text{ mol dm}^{-3}$  2-methylpropan-2-ol and  $0.5 \text{ mmol dm}^{-3}$  bpm.



**Fig. 4** Absorbance at 350 nm of species formed upon reaction of  $\text{Cr}^{\text{II}}(\text{aq})$  and bpm expressed as  $(G\epsilon)$ , as a function of bpm concentration at pH 8.6 (●) and 3.5 (○). The curves are fitted according to eqn. (18).

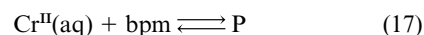
Molar absorptivities of the species (4) and (5) were calculated from the dosimetry data, taking  $G = 2.7$  for the yield of hydrated electrons and assuming their quantitative conversion into  $\text{Cr}^{2+}$  and further into the absorbing products. At pH 8.6 the obtained  $\epsilon = 8700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}} = 350 \text{ nm}$  (Fig. 3 and Table 2) could be taken as the absolute value. As can be seen in Fig. 4, at pH 8.6 the yield of the species, expressed as the  $G\epsilon$  value, does not change at  $[\text{bpm}] \geq 0.5 \text{ mmol dm}^{-3}$ . This is, however, not so for the product formed at pH 3.5 where the full yield was not reached even at the highest bpm concentration employed,  $1.4 \text{ mmol dm}^{-3}$ . The molar absorptivities for spectrum (5) can be taken therefore only as relative values.

Fig. 3 shows also the spectra of bpm radicals in different states of protonation. The radical anion  $\text{bpm}^{\bullet-}$ , spectrum (1),

was obtained in the presence of  $1 \text{ mol dm}^{-3}$  NaOH where  $(\text{CH}_3)_2\text{C}^-\text{O}$  was used as the reduction agent in a  $\text{N}_2\text{O}$ -saturated system. Thus, the molar absorptivities were calculated by using  $G[(\text{CH}_3)_2\text{C}^-\text{O}] = G(\text{bpm}^{\bullet-}) = 6.1$ . Spectrum (2) represents the neutral radical  $\text{Hbpm}^\bullet$  obtained at pH 8 where bpm was reduced by hydrated electrons,  $G[\text{e}^-(\text{aq})] = G(\text{Hbpm}^\bullet) = 2.7$ . Finally, spectrum (3) shows the radical cation  $\text{H}_2\text{bpm}^{\bullet+}$  measured in the presence of  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  and propan-2-ol, where all primary water radicals were converted into  $(\text{CH}_3)_2\text{C}^-\text{OH}$  ( $G = 6.1$ ) which then reduced bpm quantitatively. The relevant spectral data are compiled in Table 2. For all three bpm radicals the wavelengths of the maximum absorption are the same as previously obtained,<sup>3</sup> whereas the corresponding molar absorptivities are systematically lower by a factor of *ca.* 0.8. We have not explored this discrepancy further.

Fig. 4, showing an increase in the yield with the increase of bpm concentration, indicates that the absorbing product is in equilibrium with the reactants, consistent with the kinetic observation, eqn. (15).

**Apparent equilibrium constants.** Assuming the simplest equilibrium scheme, eqn. (17), and assuming that the product P is



the only absorbing species at 350 nm, one can fit the data in Fig. 4 by eqn. (18), where  $(G\epsilon)_e$  is the equilibrium absorbance at a

$$(G\epsilon)_e = (G\epsilon)_p K_s [\text{bpm}] / (1 + K_s [\text{bpm}]) \quad (18)$$

bpm concentration from Fig. 4,  $(G\epsilon)_p$  is the full yield of the absorbing product P and  $K_s$  is an apparent equilibrium constant. Fitting gives  $K_s = (2.9 \pm 0.4) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  for pH 3.5 and  $(6.0 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  for pH 8.6.

**Table 2** Molar absorptivities at wavelengths of maximum absorption of free and co-ordinated 2,2'-bipyrimidine radical

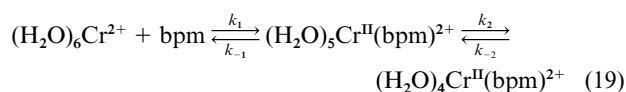
Species	pH	$\lambda_1/\text{nm}$	$\epsilon_1/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_2/\text{nm}$	$\epsilon_2/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\text{p}K_a$	Ref.
$\text{bpm}^{\cdot -}$	$\approx 14$	360	28 000	495	8 000	—	*
	13.0	360	>20 000				3
$\text{Hbpm}^{\cdot}$	8.0	350	16 500	450	3 800	12.5	*
	7.0	350	$\approx 20 000$				3
$\text{H}_2\text{bpm}^{\cdot +}$	$\approx 0$	355	28 700	430	5 000	4.5	*
	4.0	360	40 000				3
$\text{Cr-bpm}$	8.6	350	8 700	$\approx 430$	1 500		*
	3.5	355	>4 800				*
$[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpm}^{\cdot -})]^+$		340	21 500	460	13 400	7.2	4
$[\text{Ru}^{\text{II}}(\text{bpy})(\text{bpm})(\text{bpm}^{\cdot -})]^+$		340	21 200	440	13 300	6.9	4
$[\text{Ru}^{\text{II}}(\text{bpm})_2(\text{bpm}^{\cdot -})]^+$		330	19 000	450	11 500	6.8	4
		(340)					

\* This work.

Based on reaction (17) and rate expression (15) one can calculate an apparent equilibrium constant  $K_k = a/b$  from the kinetic data in Table 1;  $K_k = 3.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  for pH 3.5 and  $1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$  for pH 8.6.

The  $K$  values for pH 3.5 obtained in two different ways are in reasonable agreement, while those for pH 8.6 show a higher degree of discrepancy. A reason for the latter probably comes from the higher uncertainty of the intercept  $b$  at higher pH. Though it was determined with an acceptable standard deviation,  $b = (3.2 \pm 0.4) \times 10^3 \text{ s}^{-1}$ , a contribution to such a relatively low value of the intercept by side (parallel) radical reactions could be significant.

The simplest interpretation of the kinetic behavior, eqn. (15), and the yield, eqn. (18), would be to assume that the reaction between  $\text{Cr}^{\text{II}}(\text{aq})$  and bpm gives substitution product  $[\text{Cr}^{\text{II}}(\text{H}_2\text{O})_4(\text{bpm})]^{2+}$ , with bpm bound to chromium(II) in a bidentate mode. The substitution would proceed through a monodentate bound intermediate as shown in eqn. (19) for

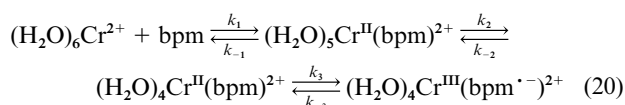


pH  $\leq 3.9$ , where  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  is the predominant  $\text{Cr}^{\text{II}}(\text{aq})$  species. Applying a steady state approximation for the intermediate,  $d[\text{Cr}(\text{H}_2\text{O})_5(\text{bpm})^{2+}]/dt = 0$ , gives  $a = k_1 k_2 / (k_{-1} + k_2)$  and  $b = k_{-1} k_{-2} / (k_{-1} + k_2)$ . The consequence of the likely situation of  $k_2 \gg k_{-1}$  is that the forward reaction is controlled by substitution of the first water in  $\text{Cr}(\text{H}_2\text{O})_6^{2+}$  with  $a = k_1 = 1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

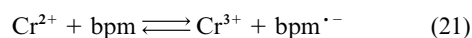
By use of pulse radiolysis or flash photolysis techniques, rates of  $\text{Cr}^{2+}$  reactions with a considerable number of neutral species have been determined. Most of them are reactions with aliphatic radicals.<sup>5,13</sup> Though the span is within a factor of 10, most of the rate constants fall between  $1 \times 10^8$  and  $3.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 25 °C. The rate constant for the reaction of benzyl radical is  $8.5 \times 10^7$ ,<sup>14</sup> of tetranitromethane  $1.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>15</sup> and of molecular oxygen  $1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .<sup>15,16</sup> In addition to the rate constants, activation volumes determined for a series of 10 aliphatic radicals have strongly indicated an  $\text{I}_d$  substitution mechanism.<sup>5</sup> The rate constant  $k_1 = 1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (which includes the outer sphere association constant) for bpm in eqn. (19) is in good accord with these observations.

While it is reasonable to assume the reaction course of eqn. (19), it is likely that  $[\text{Cr}^{\text{II}}(\text{H}_2\text{O})(\text{bpm})]^{2+}$  is not the product of the reaction on the timescale considered here. The product spectra (4) and (5) in Fig. 3 have some resemblance with that of  $\text{bpm}^{\cdot -}$  radical. The absorption maxima and the corresponding molar absorptivities for the Cr-bpm product, free bpm radical, and bpm radical co-ordinated to  $\text{Ru}^{\text{II}}$  are given in Table 2. In all cases the positions of the maxima are very similar, while differences in the molar absorptivities are more pronounced. Though

a possibility that the absorption of Cr-bpm comes from metal to ligand charge transfer cannot be completely ruled out, this is not likely, since none of the transition metal complexes having one bpm ligand exhibits absorption in this spectral region. It is more likely that subsequent to reaction (19), an intramolecular electron transfer occurs to give  $\text{bpm}^{\cdot -}$  radical bound to chromium(III), eqn. (20).



A change in the redox potentials of bpm and  $\text{Cr}^{\text{II}}$  upon formation of the  $\text{Cr}^{\text{II}}\text{-bpm}$  complex should be large enough to allow electron transfer. Literature data for the first reduction potentials of co-ordinated bpm, and those of free bpm in different solvents, are listed in Table 3. The half wave reduction potential of free bpm in acetonitrile is  $E_2 = -1.8 \text{ vs. SCE}$ . The data for aqueous solution are apparently not available. However, the first reduction potential of bpm co-ordinated to  $\text{Ru}^{\text{II}}$  in  $\text{Ru}(\text{bpm})_3^{2+}$  is only about 60 mV different in water from the one in  $\text{CH}_3\text{CN}$ . For the purpose of an estimate, one can assume for free bpm in water that  $E_2$  is also  $-1.8 \text{ V vs. SCE}$  or  $-1.56 \text{ V vs. NHE}$ . This gives a standard reaction potential  $E^\circ \approx -1.15 \text{ V vs. NHE}$  or equilibrium constant  $K \approx 3.7 \times 10^{-20}$  for reaction (21),



ruling out the outer sphere reduction of bpm by  $\text{Cr}^{2+}$ . However, upon co-ordination to a metal center, the  $E^\circ$  of bpm (electrochemically determined as  $E_2$ ) is notably changed. Inspection of  $E^\circ$  (or  $E_2$ ) in Table 3 reveals several common observations for different metals. Upon co-ordination with one of the two chelate sites available to bpm ligand,  $E^\circ$  undergoes a large positive change in the range of 0.73 to 1.0 V. Once one bpm ligand is bound additional bpm ligands do not further change  $E^\circ$  significantly. Co-ordination of a bpm ligand by both chelate sites brings a new significant positive change in  $E^\circ$ . In binuclear  $[\{\text{Ru}(\text{bpy})_2\}_2(\text{bpm})]^{4+}$ ,  $E_2$  is increased by 0.61 V, from  $-1.02 \text{ V}$  for the mononuclear  $[\text{Ru}(\text{bpy})_2(\text{bpm})]^{2+}$ , to  $-0.41 \text{ V}$ . An even more pronounced change of 0.73 V occurs upon transformation from mononuclear  $[\text{Re}(\text{CO})_3\text{Cl}(\text{bpm})]$  to binuclear  $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{bpm})]$ .

There are no systematic literature data on changes in the oxidation potential of metal centers upon co-ordination of bpm, but it could be expected that they change to more negative values. Both trends in  $E^\circ$ , those for bpm ligand and the metal center, could bring about a change in standard potential of the reaction of  $\text{Cr}^{2+}$  with bpm, eqn. (20), to enable the electron transfer within  $[\text{Cr}^{\text{II}}(\text{H}_2\text{O})_4(\text{bpm})]^{2+}$ . If the apparent equilibrium constant at pH 3.5, between  $2.9 \times 10^3$  and  $3.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ , is assigned to the equilibrium between  $\text{Cr}^{2+} + \text{bpm}$  and

**Table 3** Reduction potentials of free and co-ordinated 2,2'-bipyrimidine

Compound	$E^\circ/V$ vs. NHE	$E_2/V$ vs. SCE or SSCE	Solvent	Ref.
bpm		-1.8	CH <sub>3</sub> CN	17
bpm		-1.75	thf	2(h), 2(o)
bpm		-1.73	dmf	2(a), 2(r)
[Ru(bpy) <sub>2</sub> (bpm)] <sup>2+</sup>	-0.83	-1.02	H <sub>2</sub> O, CH <sub>3</sub> CN	2(n)
[{Ru(bpy) <sub>2</sub> }_2(bpm)] <sup>4+</sup>		-0.41	CH <sub>3</sub> CN	2(a), 2(r)
[Ru(bpy)(bpm)] <sup>2+</sup>	-0.77	-0.95	H <sub>2</sub> O, CH <sub>3</sub> CN	2(s)
Ru(bpm) <sub>3</sub> <sup>2+</sup>	-0.73	-0.97	H <sub>2</sub> O	2(d)
[Ir(bpm) <sub>2</sub> Cl] <sup>+</sup>		-0.80	CH <sub>3</sub> CN	2(d)
[RhH <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (bpm)] <sup>+</sup>		-1.34	CH <sub>3</sub> CN	2(j)
[{RhH <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (bpm)] <sup>2+</sup>		-0.67	CH <sub>3</sub> CN	2(j)
[Re(CO) <sub>3</sub> Cl(bpm)]		-1.03	CH <sub>3</sub> CN	2(k)
[{Re(CO) <sub>3</sub> Cl}_2(bpm)]		-0.30	CH <sub>3</sub> CN	2(k)
[(bpy) <sub>2</sub> Ru(bpm)Re(CO) <sub>3</sub> Cl] <sup>2+</sup>		-0.41	CH <sub>3</sub> CN	2(k)
[Ru{(bpm)Re(CO) <sub>3</sub> Cl}_3] <sup>2+</sup>		-0.21	CH <sub>3</sub> CN	2(k)
[{Ru <sup>II</sup> (bpy) <sub>2</sub> (bpm)} <sub>2</sub> Ir <sup>III</sup> Cl] <sup>5+</sup>		-0.03	CH <sub>3</sub> CN	2(g)

[Cr<sup>III</sup>(H<sub>2</sub>O)<sub>4</sub>(bpm<sup>•-</sup>)]<sup>2+</sup> {assuming steady states, the concentrations of [Cr<sup>III</sup>(H<sub>2</sub>O)<sub>5</sub>(bpm)]<sup>2+</sup> and [Cr<sup>III</sup>(H<sub>2</sub>O)<sub>4</sub>(bpm)]<sup>2+</sup> intermediates are negligible}, the corresponding standard reaction potential is  $E^\circ \approx 0.21$  V vs. NHE. This would mean that the standard potential of reaction (20) has become more positive by 1.36 V as compared to the potential for reaction (21). Admittedly, this is a large change, somewhere between the changes achieved by mononuclear and binuclear co-ordination of bpm to some ruthenium(II) or rhenium(III) metal centers.

For reaction (20) to operate in accordance with experimental rate expression (15) one has to assume steady state approximation for intermediates [Cr<sup>III</sup>(H<sub>2</sub>O)<sub>5</sub>(bpm)]<sup>2+</sup> and [Cr<sup>III</sup>(H<sub>2</sub>O)<sub>4</sub>(bpm)]<sup>2+</sup>, with  $a$  being an overall forward and  $b$  an overall reverse rate constant.

A possibility of formation of Cr<sup>III</sup> and bpm<sup>•-</sup> as reaction products in an outer sphere reaction is excluded on thermodynamic grounds, and their formation by the dissociation of Cr<sup>III</sup>(bpm<sup>•-</sup>)<sup>2+</sup> species is highly unlikely on the timescale involved due to the substitution inertness of the chromium(III) center.

The chromium(III)-bipyrimidine ligand radical species, [Cr<sup>III</sup>-(H<sub>2</sub>O)<sub>4</sub>(bpm<sup>•-</sup>)]<sup>2+</sup>, as proposed in this mechanism, is a relatively stable entity on the timescale relevant to this study. Its destiny on the timescale longer than 1–2 ms is currently being investigated. Relatively stable chromium(III)-ligand radical species with nitrogen heterocycles are not unknown. Kinetic and thermodynamic properties of chromium(III) complexes containing pyrazine radical ligand have been described previously.<sup>6</sup>

## Experimental

2,2'-Bipyrimidine (Lancaster Synthesis) was purified by recrystallization from ethanol and by sublimation. The salt [Cr(NH<sub>3</sub>)<sub>6</sub>][ClO<sub>4</sub>]<sub>3</sub> was prepared and purified according to the literature procedure.<sup>18</sup> All other chemicals employed were commercially available analytical grade used as obtained. The solutions were prepared with deionized Millipore-filtered water the quality of which corresponded to triply distilled water. The desired pH values were adjusted by HClO<sub>4</sub> or NaOH. All the experiments were done at ambient temperature.

The pulse radiolysis experiments were carried out using 1.55 and 3.8 MeV Van de Graaff accelerators delivering 0.1–2 μs pulses of high energy electrons. The total energy absorbed by the investigated system was typically in the range 1–10 Gy per pulse. Further details of the set-up, detection techniques and pulse radiolysis method have been described elsewhere.<sup>19</sup> Dosimetry was based on the HO<sup>•</sup> radical induced oxidation of thiocyanate in a N<sub>2</sub>O-saturated solution using  $\epsilon[(\text{SCN})_2^{\bullet-}] = 7200$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at 500 nm,  $\Delta\lambda = -360$  S cm<sup>2</sup> equiv.<sup>-1</sup> for the conductivity change, and  $G = 5.5$ . All the experiments were performed with continuously flowing solutions.

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