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Studies on kinetics and mechanism of imidazole substitution from *cis-equatorial*-[Cr(*S*-pdtra)(Him)]^0 complex in acidic and alkaline aqueous solutions [*S*-pdtra = (*S*)-propylenediaminetriacetate]†

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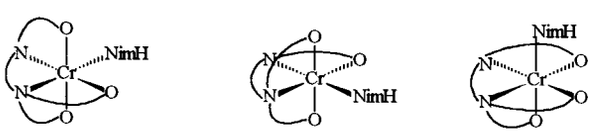
Aquation of the *cis-equatorial*-[Cr(*S*-pdtra)(Him)]^0 complex [*S*-pdtra = (*S*)-propylenediaminetriacetate] has been studied within the pH range 0–14. Liberation of imidazole in acidic medium leads to the *cis-eq*-[Cr(*S*-pdtra)(H_2O)]^0 complex. Deprotonation of coordinated imidazole in alkaline solutions stimulates a reversible one-end dechelation of *S*-pdtra, which precedes substitution of imidazole; a characteristic bell-shaped k_{obs} *vs.* [H^+] dependence is observed. The values of $\Delta S^{\ddagger} = -52.8$ J mol^{-1} K^{-1}, $\Delta H^{\ddagger} = 84.2$ kJ mol^{-1} and $\Delta V^{\ddagger} = -10.1$ cm^3 mol^{-1} for aquation in acidic medium are consistent with an I_a mechanism, whereas substitution of the imidazolate from the hydroxo complex with a tetradentate *S*-pdtra proceeds *via* an I_d mechanism on the basis of $\Delta S^{\ddagger} = 49.6$ J mol^{-1} K^{-1} and $\Delta H^{\ddagger} = 117.5$ kJ mol^{-1}. One-end dechelation of the *S*-pdtra ligand from the complex with imidazolate (pH > 13) is characterised by $k_{298} = 6.43 \times 10^{-3}$ s^{-1}, $\Delta S^{\ddagger} = -57.2$ J mol^{-1} K^{-1} and $\Delta H^{\ddagger} = 68.5$ kJ mol^{-1}.

In our previous studies [1–3] we observed distinct differences in the rate and mechanism of a monodentate ligand (X) substitution process between reactive *cis-equatorial*- and very inert *trans-equatorial*-[Cr(N,N′,O,O,O)(X)] type complexes. We found that partial dechelation of EDTA-like ligands can interfere with the substitution process.[3] Earlier a dechelation of chromium(III)–EDTA complex was examined in detail by Sykes and co-workers.[4] In the present study imidazole was used as a leaving group. Three possible geometrical isomers of the pentadentate EDTA-like ligand complexes are shown in Scheme 1.



cis-equatorial *trans-equatorial* *cis-axial*

Scheme 1 Geometrical isomers of [Cr(*S*-pdtra)(Him)]^0.

Imidazole is a typical representative of a large group of heterocyclic nitrogen donor atom ligands.[5,6] Imidazole and its derivatives are components of a variety of biologically important molecules, where they play a role as ligands,[5–7] and mainly for that reason coordination chemistry of these species is comprehensive and still under development. However, there are a limited number of papers on chromium(III) complexes with imidazole and its derivatives, *e.g.* refs. 8–17.

Imidazole normally coordinates to metal ions through the pyridine nitrogen, although it is potentially an ambidentate ligand, which can also bind *via* the pyrrole nitrogen.[5,18] In the case of the normal mode of bonding, coordination activates the acidity of the pyrrole hydrogen and the pK_a value is shifted from 14.4 to the typical range of 10–12.[19,20]

Thus, coordinated imidazole exists in strongly alkaline medium as an anionic ligand (im^-). Imidazole in its anionic form can act as a bridging ligand; several complexes with this type of im^- coordination have been found.[5,20] Imidazole is a "poor leaving group". The rate of its substitution in inert hexa-coordinate complexes is expected to be lower than that for NCS^- ion. For that reason it is an attractive leaving group in the case of such reactive complexes as *cis-eq*-[Cr(N,N′,O,O,O)(X)] type isomers. Deprotonation of coordinated imidazole activates neighbouring ligands, making them more labile,[20,21] but probably retards the rate of imidazole liberation. In this study we have examined kinetic effects which accompany deprotonation of coordinated imidazole in the *cis-eq*-[Cr(*S*-pdtra)(Him)]^0 complex.

Experimental

Materials

cis-eq-[Cr(*S*-pdtra)(Him)]^0 was prepared according to the following procedure. Equimolar amounts of *cis-eq*-[Cr(*S*-pdtra)(H_2O)]$^{0\,2}$ and imidazole were dissolved in methanol and the mixture was heated on a water bath. The solution was allowed to stand until it was almost condensed to dryness. Then methanol was added to the solution. This procedure was repeated until the solution became red from red violet. The red solution was evaporated to dryness. The solid was washed with diethyl ether and then filtered and dried {Found: C, 36.92; H, 5.06; N, 14.93. Calc. for [Cr(*S*-pdtra)(Him)]·H_2O = $CrC_{12}H_{19}N_4O_7$: C, 37.60; H, 5.00; N, 14.62%}. All other chemicals were of *pro analysi* grade and used without further purification. Solutions were prepared using doubly distilled water.

Kinetic and equilibrium studies

The products of aquation in acidic and basic (after acidification) medium were analysed by a chromatographic separ-

† *Supplementary data available*: Rate constants, activation parameters and UV–VIS spectral data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/91/, otherwise available from BLDSC (No. SUP 57452, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

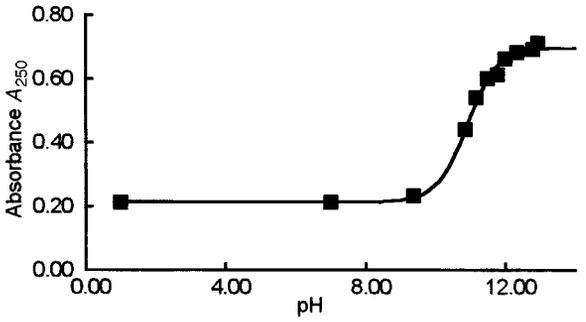


Fig. 1 Dependence of absorbance at 250 nm on the pH of the *cis-eq*-[Cr(*S*-pdtra)(Him)]^0 complex.

ation on Sephadex SP C-25 (H^+) and Sephadex DEAE A-25 (ClO_4^-). The two species were found: *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ and H_2im^+. The kinetic measurements were carried out at an ionic strength of 1.0 M ($NaClO_4$) at 25.0 ± 0.1 °C unless otherwise stated. Stock solutions of the complex were prepared by dissolving an appropriate amount of the solid complex directly before each experiment. The pH values were adjusted with phosphate buffer solutions, perchloric acid or sodium hydroxide, and measured with a CX-721 pH-meter equipped with a standard combined electrode. Kinetic runs as a function of temperature (55–75 °C) for the acid and base hydrolysis reactions were performed with a Specord M-40 spectrophotometer at 244 nm. Readings were taken until 90% (acid) or 75–80% (base) completion of the reaction. Olation and decomposition of the hydroxocomplex transform not more than 10% of the product after three half-lives of base hydrolysis. It was proved by acidification of the reaction mixture and chromatographic separation of *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ complex. The first-order rate constants were calculated using a non-linear least-squares method. Relative standard errors of single runs were 0.5–1.5%. Each kinetic run was repeated at least three times. Kinetic runs for the ring-opening reaction and hydrolysis in the pH range 4–12 were recorded with a Hewlett Packard 8453 diode-array spectrophotometer in the wavelength range 220–300 nm. The spectra were collected until 95% completion of the reaction. The first-order rate constants were calculated using the SPECFIT program.[22] Relative standard errors of single runs were below 1%. The effect of pressure on the rate of acid hydrolysis (5–150 MPa, $T = 45$ °C, $[H^+] = 0.1$ M, $\lambda = 560$ nm) was measured using the conventional pill-box technique; activation volume was calculated (linear least squares fit) from the slope of the ln k_{obs} *versus* pressure plot.

Protolytic equilibrium. The spectra of the studied complex in the pH range 1–13 were recorded using a HP 8453 diode array spectrophotometer equipped with a stopped-flow unit. The absorbances at a few wavelengths (245, 250 and 255 nm) were extrapolated to zero-time (acidic solutions of complex at pH = 3 were mixed with buffer solutions of appropriate pH) and calculation of the acidity constant K_a was based on eqn. (1), where A = absorbance at particular pH, A_1 = absorbance of

$$A = \frac{A_1 + A_2 \cdot 10^{(\mathrm{pH} - \mathrm{p}K_a)}}{1 + 10^{(\mathrm{pH} - \mathrm{p}K_a)}} \quad (1)$$

a protonated form and A_2 = absorbance of a deprotonated form. A typical pH dependence of absorbance is presented in Fig. 1.

Results and discussion

Qualitative observations

The entering process of imidazole into the coordination sphere of the *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ complex, followed by its liberation as the result of aquation, obeys a simple stereoretentive pattern [eqn. (2)]. The assumption of *cis-eq*-configuration of

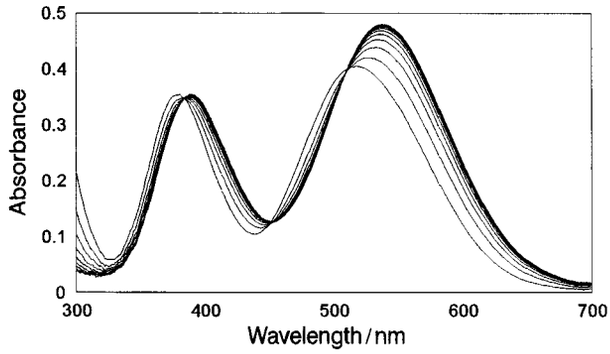


Fig. 2 Spectral changes observed during acid hydrolysis of *cis-eq*-[Cr(*S*-pdtra)(Him)]^0. Reaction conditions: $[Cr(III)]_T = 5 \times 10^{-3}$ M, $[H^+] = 0.1$ M, $I = 1.0$ M, $T = 40$ °C, time interval = 4800 s.

$$\textit{cis-eq}\text{-}[Cr(S\text{-pdtra})(H_2O)]^0 \xrightarrow{+Him} \textit{cis-eq}\text{-}[Cr(S\text{-pdtra})(Him)]^0 \xrightarrow{+H_2O} \textit{cis-eq}\text{-}[Cr(S\text{-pdtra})(H_2O)]^0 \quad (2)$$

the imidazole complex therefore seems to be justified. Also in alkaline medium, [Cr(*S*-pdtra)$(OH)]^-$ complexes formed from *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ or from [Cr(*S*-pdtra)$(Him)]^0$ are transformed to the *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ isomer after acidification. No isomerization reactions were observed in our studies.

Liberation of coordinated imidazole is a very slow process over the whole pH range, $t_{1/2}$ (298 K) ≈ 10 h. The simplicity of the studied system in acidic medium (only one reaction is observed and the rate is independent of $[H^+]$) strongly contrasts with a complex behaviour in alkaline solution where several reactions are observed spectroscopically and the rates depend on $[OH^-]$ in a complicated way.

Acidic solutions

Visible spectral changes recorded during aquation of the *cis-eq*-[Cr(*S*-pdtra)(Him)]^0 complex in acidic medium are presented in Fig. 2.

A distinct decrease in energy for the $^4A_{2g} \longrightarrow {}^4T_{2g}$ transition (pseudo-O_h symmetry approximation) from 522 to 562 nm, and an increase in intensity of this band are consistent with substitution of imidazole by a water molecule, taking into account the known positions of Him and H_2O in the spectrochemical series. The presence of three isosbestic points at 385, 455 and 508 nm for at least four half-lives of the aquation process suggests the existence of only two Cr(III) species in the reaction mixture. The products of aquation were separated chromatographically and identified spectroscopically as *cis-eq*-[Cr(*S*-pdtra)$(H_2O)]^0$ and H_2im^+. Thus aquation of the studied imidazole complex in acidic medium proceeds according to a simple stoichiometry [eqn. (3)].

$$\textit{cis-eq}\text{-}[Cr(S\text{-pdtra})(Him)]^0 + H_2O \xrightarrow{+H^+} \textit{cis-eq}\text{-}[Cr(S\text{-pdtra})(H_2O)]^0 + H_2im^+ \quad (3)$$

Reaction (3) follows a first order rate law and the rate constant (k_1) is independent of pH, at least within the range 0–3; data from a few runs at pH = 6 gave only a slightly higher value for k_1. Summarising the results for acidic media one can conclude that formally possible partial dechelation of the *S*-pdtra ligand is not observed; it neither interferes with the rate of substitution of imidazole, nor is seen in the spectra. The activation parameters: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ were determined from the temperature and pressure dependences of k_1 (Table 1), respectively (SUP 57452).

Table 1 Rate and activation parameters for substitution of [Cr(*S*-pdtra)(Him)]^0 and [Cr(*S*-pdtra)(NCS)]$^-$ [a]

	[Cr(*S*-pdtra)(Him)]^0		[Cr(*S*-pdtra)(NCS)]$^-$
	pH = 1	pH = 13	pH = 1
$\Delta H^{\ddagger}$/kJ mol^{-1}	84.2 ± 0.3	117.5 ± 2.4	67.2
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	−52.8 ± 0.9	+49.6 ± 7.2	−65.6
$\Delta V^{\ddagger}$/cm^3 mol^{-1}	−10.1 ± 0.9		
k_{298}/s^{-1}	1.93×10^{-5}	6.4×10^{-6}	3.9×10^{-3}

[a] Ref. 2.

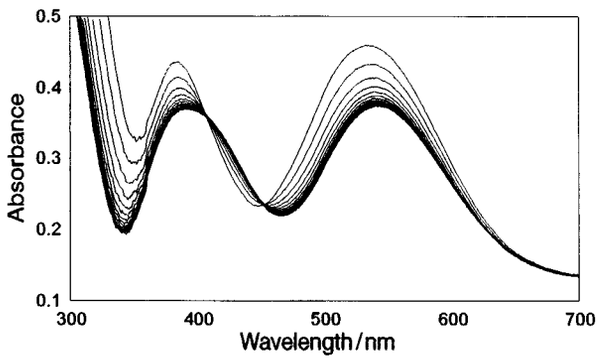


Fig. 3 Spectral changes observed during dechelation of *cis-eq*-[Cr(*S*-pdtra)(Him)]^0. Reaction conditions: $[Cr(III)]_T = 5 \times 10^{-3}$ M, $[OH^-]$ = 0.1 M, I = 1.0 M, T = 25 °C, time interval = 60 s.

As seen from Table 1, the rate of substitution of imidazole is exceptionally low as for a *cis-equatorial* isomer; the rate constant at 298 K is two orders of magnitude lower than that for liberation of the NCS^- ion.[2] However, the mechanism of both reactions is analogous and can be classified as an I_a-type because of high negative values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$. Substitution of Him, a neutral ligand, should not cause significant changes in solvation during the activation processes, which simplifies the interpretation of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$.

Alkaline solutions

Preliminary observations. Two kinds of processes, which precede substitution of coordinated imidazole, have been observed spectroscopically in alkaline media. Both are reversible upon acidification.

(i) Instant spectral changes within the pH range 9.5–12, especially distinct in the UV range (Fig. 1), which can be assigned to deprotonation of coordinated imidazole [eqn. (4)].

$$[Cr(N,N',O,O,O)(Him)]^0 + H_2O \overset{K_a}{\rightleftharpoons} [Cr(N,N',O,O,O)(im)]^- + H_3O^+ \quad (4)$$

The determined value of K_a of 1.4×10^{-11} mol dm^{-3} (pK_a = 10.85 ± 0.05) at 298 K (I = 1.0 M), is within the range found for coordinated imidazole.[19,20]

(ii) The deprotonation is followed by a slow (on a few minutes time-scale), but much faster than substitution of imidazole, process with first order behaviour (at constant pH) (Fig. 3). A red shift in the region of the d–d transitions and a decrease of the band intensity, as well as reversibility of this reaction, can be rationalised by the assumption of a one-end dechelation of the *S*-pdtra ligand through cleavage of the Cr–O bond, stimulated by imidazolate and followed by entrance of a H_2O molecule (which is deprotonated to OH^-) into the created vacant position [eqn. (5)].

$$[Cr(N,N',O,O,O)(im)]^- \overset{H_2O,\ OH^-}{\rightleftharpoons} [Cr(N,N',O,O)(OH)(im)]^{2-} \quad k_2, k_{-2} \quad (5)$$

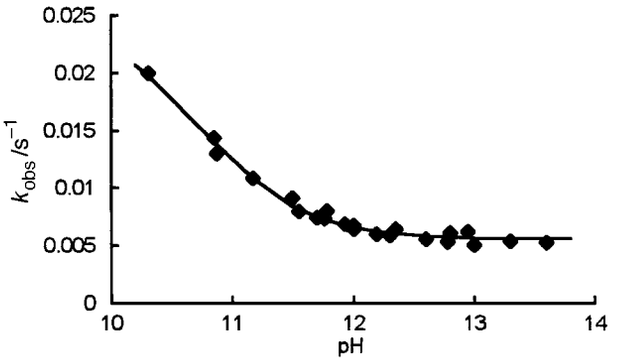


Fig. 4 pH profile for the ring opening reaction (dechelation) of the *cis-eq*-[Cr(*S*-pdtra)(Him)]^0 complex; T = 25 °C, $[Cr(III)]_T = 4 \times 10^{-4}$ M, I = 1.0 M.

The dependence of the observed rate constant for reaction (5) on $[H^+]$ is shown in Fig. 4.

The rate of reaction (5) decreases with an increase in pH and a minimum in k_{obs} is reached near pH = 13 (Fig. 4). [Cr(N,N′,O,O)(OH)(Him)]$^-$ is involved in the protonation/deprotonation equilibria but it is kinetically not important in reforming the pentadentate species [Cr(N,N′,O,O,O)(im)]$^-$. The dechelation equilibrium moves towards the pentadentate [Cr(N,N′,O,O,O)(im)]$^-$ as the pH falls because it is the stability of either the species [Cr(N,N′,O,O)(OH)(im)]$^{2-}$ or [Cr(N,N′,O,O)(OH)(Him)]$^-$ which provides the driving force for the reaction even though they are not kinetically involved. Thus the spectral changes (Fig. 3) become smaller when the pH drops from 13 to 10 and the error in k_{obs} increases beyond acceptable limits. The equilibrium position of reaction (5) depends on pH and is shifted practically to the left at pH near 10.

The limited set of data for k_{obs} *vs.* $[H^+]$ (Fig. 4) and the quite narrow pH range where the penta- ⟷ tetra-dentate coordination of the *S*-pdtra ligand can be observed, require using a very simplified reaction pattern for formulation of the rate law. For the forward process [reaction (5)] it is assumed that deprotonation of imidazole stimulates dechelation and the hydroxo complex with tetradentate *S*-pdtra is formed practically exclusively *via* the k_2 path [reaction (5)]. However, for the reverse process at least two alternative pathways should be considered since the product of partial dechelation can exist (at pH 10–14) in several protolytic forms: with protonated and deprotonated imidazole, with OH^- or H_2O where the water ligand is expected to be present only in small amounts (expected pK_a for the coordinated H_2O is 7–8). The proposed model [reaction (6)] assumes that the k_{-2} is a pseudo-rate constant not connected with any particular process. The tautomeric forms {[Cr(N,N′,O,O)(H_2O)(im)]$^-$ and [Cr(N,N′,O,O)(OH)(Him)]$^-$} are treated as one pseudo-species 'c', besides the intermolecular protolytic process converting [Cr(N,N′,O,O)(OH)(Him)]$^-$ to [Cr(N,N′,O,O)(OH)(im)]$^{2-}$ is omitted.

$$\begin{array}{l} [Cr(N,N',O,O,O)(Him)]^0 \\ \quad +H_3O^+ \uparrow\downarrow K_a \\ [Cr(N,N',O,O,O)(im)]^- \underset{k_{-2},\ -H_2O}{\overset{k_2,\ +H_2O}{\rightleftharpoons}} \left[\begin{array}{l} [Cr(N,N',O,O)(H_2O)(im)]^- \\ \quad \uparrow\downarrow \text{rapid eq.} \\ [Cr(N,N',O,O)(OH)(Him)]^- \end{array}\right] \quad (6) \\ \qquad\qquad +H_2O \uparrow\downarrow K'_a \\ [Cr(N,N',O,O)(OH)(Him)]^{2-} + H_3O^+ \end{array}$$

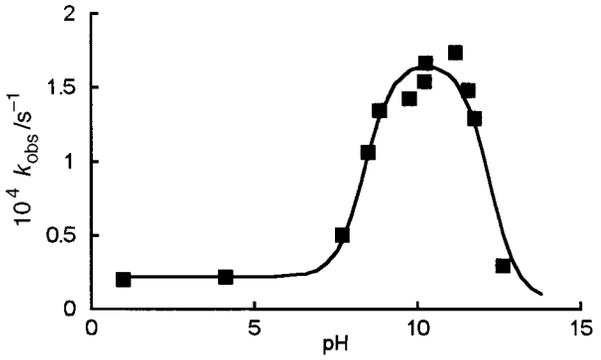


Fig. 5 pH dependence of the substitution rate constant for the release of imidazole from the *cis-eq*-[Cr(*S*-pdtra)(Him)]^0 complex; $T = 25$ °C, $[Cr(III)]_T = 1 \times 10^{-4}$ M, $I = 1.0$ M.

The proposed model is presented by the reaction sequence (6) and leads to the rate law (7):

$$k_{obs} = \frac{k_2K_aK_a' + (k_2K_a + k_{-2}K_a)[H^+] + k_{-2}[H^+]^2}{K_aK_a' + (K_a + K_a')[H^+] + [H^+]^2} \quad (7)$$

At pH ≥ 13, eqn. (7) reaches its limiting form [eqn. (8)], since

$$k_{obs} = k_2 \quad (8)$$

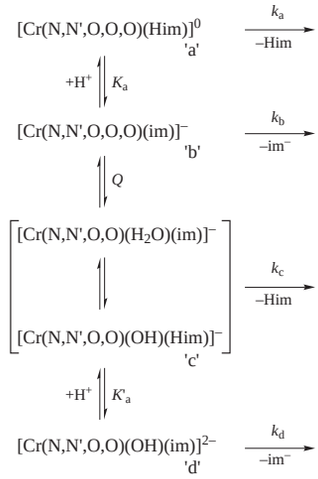
$K_a = 1.4 \times 10^{-11}$ mol dm^{-3} (independent spectrophotometric determination) and the value of K_a' is expected to be of the same order. The constant value of the k_{obs} at pH > 13 means, in terms of this model, that the value of k_{-2} cannot be higher than one order of magnitude as compared to k_2. According to this model, the limiting value of k_{obs} is the first order rate constant for the one-end dechelation of *S*-pdtra from the complex with imidazolate. The limiting k_{obs} was determined at three different temperatures (20, 25 and 35 °C) and the calculated activation parameters are: $\Delta H^‡ = 68.5 \pm 0.3$ kJ mol^{-1} and $\Delta S^‡ = -57.2 \pm 1.0$ J mol^{-1} K^{-1}. The negative value of $\Delta S^‡$ for dechelation is controlled mainly by an increase in hydration caused by the free carboxylate group.

The composite form of eqn. (7) allows the calculation of the parameters with satisfactory accuracy only with a fixed value for K_a (=1.4×10^{-11} mol dm^{-3}). The calculated parameter values are as follows: $k_2 = (5.58 \pm 0.14) \times 10^{-3}$ s^{-1}; $k_{-2} = (2.49 \pm 0.11) \times 10^{-2}$ s^{-1}; $K_a' = (1.71 \pm 0.17) \times 10^{-11}$ mol dm^{-3}.

Substitution of imidazole. Reactions (4) and (5) or (6) precede a very slow ($t_{1/2} \approx 10$ h at 298 K) process of liberation of coordinated imidazole, which results in formation of [Cr(*S*-pdtra)(OH)]$^-$ as the main product. However, partial decomposition of this species is observed for conversions >50%. Reproducible kinetic data can be obtained only for low concentrations of Cr(III) (≈10^{-4} M) and measurements were carried out in the UV range where absorbance changes are determined mainly by breakage of the Cr(III)–imidazole bond. The dependence of the observed pseudo-first-order rate constant on pH is of a characteristic bell-shaped form (Fig. 5).

The proposed rationalisation for the observed pH dependence of k_{obs}' (Fig. 5), takes into account protolytic and dechelation preequilibria (4) and (6), and is based on the assumption that the rate of liberation of Him is higher than that for imidazolate (im$^-$). Imidazole is substituted from two complexes with pentadentate *S*-pdtra ('a', 'b') and at least from two complexes with tetradentate *S*-pdtra ('c', 'd').

The hydroxo complexes 'c' and 'd' are expected to be far more labile than species 'a' and 'b'. According to the postulated reaction pattern (9), the pseudo-first-order rate constant (k_{obs}') describing the rate of imidazole substitution *via* four parallel reaction paths is given by eqn. (10), where the protolytic equi-



(9)

$$k_{obs}' = \frac{k_a[H^+]^2 + (k_bK_a + k_cK_aQ)[H^+] + k_dK_aK_a'Q}{[H^+]^2 + (K_a + K_aQ)[H^+] + K_aK_a'Q} \quad (10)$$

librium constants are as before [eqns. (4) and (6)] and Q describes the equilibrium process between species 'b' and tautomeric forms of species 'c'.

The two limiting forms of eqn. (10) have a simple interpretation: (i) at a pH about two units higher than the pK_a for the coordinated imidazole, pH > 13, $k_{obs}' \approx k_d$ and represents practically exclusively the reaction of species 'd', *i.e.* substitution of the imidazolate from the hydroxo complex with tetradentate *S*-pdtra. This conclusion is consistent with the practically constant value of k_{obs}' observed within the [OH$^-$] concentration range 0.2–0.7 M. The rate constants and activation parameters for this case are presented in Table 1. (ii) In acidic medium, $k_{obs}' = k_a$ represents the rate constant for substitution of Him from the complex with pentadentate *S*-pdtra; data in Table 1. The higher value of $\Delta H^‡$ and the high positive value for $\Delta S^‡$ for the k_d path, in comparison to the k_a path, are consistent with an interchange dissociative or dissociative mode of activation, characteristic for chromium(III) complexes labilised by an OH$^-$ ligand.[23] However, it is worthwhile to note that substitution of two different ligands is compared, *viz.* Him and im$^-$.

The maximum of the k_{obs}' ([H$^+$]) curve (Fig. 5) occurs at pH ≈ 10.5, where the k_c path, liberation of the imidazole from the hydroxo complex with tetradentate *S*-pdtra, seems to be predominant because the complex 'b' with imidazolate and pentadentate *S*-pdtra is expected to be less labile. From the plot (Fig. 5) we can estimate the k_c value as 1.7×10^{-4} s^{-1}. The values calculated from the fit of the data to eqn. (10) with a fixed k_d value (6.4×10^{-6} s^{-1}) are: $k_a = (2.2 \pm 0.9) \times 10^{-5}$ s^{-1}, $(k_bK_a + k_cK_aQ) = (7.0 \pm 2.2) \times 10^{-13}$ mol dm^{-3} s^{-1}, $(K_a + K_aQ) = (4.2 \pm 1.4) \times 10^{-9}$ mol dm^{-3}, and $(K_aK_a'Q) = (2.6 \pm 1.1) \times 10^{-21}$ mol^2 dm^{-6}.

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