# The Extent of Chelation in some Chromium(III)–EDTA Complexes

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DETAILS of the preparations and experiments relating to the extent of chelation in some chromium(III)–EDTA complexes are reported here. Contrary to an earlier report[1] we have been unable to prepare the sexadentate complex $[\mathrm{Cr^{III}Y}]^-$ from $[\mathrm{Cr^{III}YH(H_2O)}]$ (ethylenediaminetetraacetate or EDTA $\equiv \mathrm{Y^{4-}}$). When the latter is treated with $0{\cdot}1$M-sodium hydroxide the product is in all probability the quinquedentate oxochromium(III) complex $[\mathrm{Cr^{III}Y(O)}]^{3-}$, and not[2] the quadridentate dihydroxo-complex $[\mathrm{Cr^{III}Y(OH)_2}]^{3-}$

The complex $[\mathrm{Cr^{III}YH(H_2O)}]$ in which the EDTA is quinquedentate is well known.[3–5] Acid-dissociation constants have been measured[2–4] and are as shown in equation (1)

$$[\mathrm{Cr^{III}YH(H_2O)}] \overset{\mathrm{p}K_a\sim3}{\rightleftharpoons} [\mathrm{Cr^{III}Y\cdot(H_2O)}]^- + \mathrm{H^+} \overset{\mathrm{p}K_a\sim7}{\rightleftharpoons} [\mathrm{Cr^{III}Y(OH)}]^{2-} + 2\mathrm{H^+} \quad (1)$$

The most favourable conditions for the formation of a sexadentate complex $[\mathrm{Cr^{III}Y}]^-$ are (probably) at around pH 5,[6] when the unco-ordinated carboxyl group of the EDTA is unprotonated. Under these conditions one would expect the equilibrium in (2)

$$[\mathrm{Cr^{III}Y(H_2O)}]^- \rightleftharpoons [\mathrm{Cr^{III}Y}]^- + \mathrm{H_2O} \qquad (2)$$

to be most favourable. From such solutions Hoard *et al.*[1] have prepared samples of the complexes $Rb,CrY,2H_2O$ and $NH_4,CrY,2H_2O$, which they claim are isomorphous with similar salts of $[Co^{III}Y]^-$ and $[Al^{III}Y]^-$ and are therefore sexadentate. Since this is the only case in which a sexadentate chromium(III)–EDTA complex has been reported, we attempted to repeat this work. Samples of complexes which analysed satisfactorily for $Rb,CrY,2H_2O$ and $NH_4,CrY,2H_2O$ were obtained in good yields, but further experiments have shown that in both cases a water molecule remains co-ordinated to the chromium. Thus on leaving the samples to stand over $P_2O_5$ for seven days, and on heating to 120°, only one of the two water molecules is removed. On heating to higher temperatures using a thermogravimetric balance, decomposition occurs (>300°), before loss of the second water molecule. Diffuse reflectance spectra and spectra of aqueous solutions, pH 4—5, recorded within 1—2 min. of their preparation, are as expected for $[Cr^{III}YH(H_2O)]$ and the related conjugate-base form $[CrY(H_2O)]^-$.[4]

The products obtained in the reactions of chromium(II)–EDTA (pH 3—4) with a variety of oxidants including $Cl_2$, $Br_2$, $CrCl^{2+}$, $CrF^{2+}$, and $O_2$ have been identified. The reactions are all rapid and from visible spectra recorded within 3 min. of mixing, the only products are $[Cr^{III}YH(H_2O)]$ and $[Cr^{III}Y(H_2O)]^-$. Since the replacement of $X^-$ by $H_2O$ in complexes of the type $[Cr^{III}YH(X)]^-$ ($X^- = Cl^-$, $Br^-$, *etc.*) is unlikely to be rapid, we conclude that such reactions are of the outer-sphere type. Conversion of $[Cr^{III}Y]^-$ to $[Cr^{III}YH(H_2O)]$ and $[Cr^{III}Y(H_2O)]^-$ would also be expected to be slow.[6]

In aqueous solutions pH 8—9 [2—4] the complex $[Cr^{III}YH(H_2O)]$ is present as $[CrY(OH)]^{2-}$ ($\epsilon_{max} = 115$ at 594 mμ, and 86 at 392 mμ). At still higher pH's further spectral changes have been attributed to the conversion of $[Cr^{III}Y(OH)]^{2-}$ into the quadridentate complex $[CrY(OH)_2]^{3-}$, $pK_a = 12{\cdot}2$,[2] ($\epsilon_{max} = 65$ at 575 mμ and 86 at 407 mμ). At 25° and in 0·1M-sodium hydroxide *ca.* 15 min. are required for this reaction to proceed to completion (rate constant *ca.* $5 \times 10^{-3}$ sec.$^{-1}$). The solutions obtained are stable for at least 24 hr. On acidifying to pH ~ 4·5 (buffered), the formation of $[CrYH(H_2O)]$ and $[CrY(H_2O)]^-$ is rapid and stopped-flow experiments have indicated a rate constant $> 10^3$ sec.$^{-1}$. We suggest that this reaction is far too rapid for the conversion of a quadridentate chromium(III)–EDTA complex to a quinquidentate form, and that the complex formed at pH > 12 is in all probability $[Cr^{III}Y(O)]^{3-}$.

Attempts to prepare the complex $[Cr^{III}YH(Cl)]^-$ by treating $[Cr^{III}YH(H_2O)]$ with concentrated hydrochloric acid resulted in a partial dissociation, *i.e.* uncoiling of the EDTA ligand. On cooling to 0° crystals of $[Cr^{III}YH_3(Cl)_2(H_2O)],3H_2O$ (analysis, dehydration experiments, equivalent weight determinations) can be obtained within 1—2 hr. If solutions are allowed to stand for longer periods, *i.e.* overnight, there is further dissociation of the EDTA from the chromium. The complex $[Cr^{III}YH_3(Cl)_2(H_2O)]$ is most likely six-co-ordinate with the EDTA tridentate, but we cannot as yet entirely exclude a seven-co-ordinate structure in which the EDTA is quadridentate. The rubidium salt $Rb^+$ $[CrYH_2(Cl_2)(H_2O)]^-,H_2O$ has also been prepared. In aqueous solutions pH 0—4, the complex $[Cr^{III}YH(H_2O)]$ and its conjugate-base $[Cr^{III}Y(H_2O)]^-$ are reformed, thus

$$[\mathrm{Cr^{III}YH}_x(\mathrm{Cl})_2(\mathrm{H_2O})]^{x-3} \rightarrow [\mathrm{Cr^{III}YH}_y(\mathrm{Cl})(\mathrm{H_2O})]^{y-2} \rightarrow [\mathrm{Cr^{III}YH}_z(\mathrm{H_2O})]^{z-1} \qquad (3)$$

where $x = 1$ or 2, $y = 1$ or 2 (and possibly 0), and $z = 0$ or 1. At pH 2 ($\mu = 1{\cdot}0$M) and 10° the overall rate constant is $9 \times 10^{-3}$ sec.$^{-1}$. When scan spectra are recorded over the range 350—700 mμ three isosbestic points are observed. Such experiments are consistent with a slow–fast reaction sequence, *i.e.* the first stage in (3) is rate determining. Further details including the $[H^+]$-dependence of the reaction will be reported in full elsewhere. Samples of $[Cr^{III}YH_3(Br)_2(H_2O)],3H_2O$ can be prepared in a similar manner by treating $[Cr^{III}YH(H_2O)]$ with hydrobromic acid.

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