

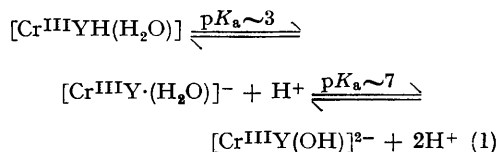
The Extent of Chelation in some Chromium(III)-EDTA Complexes

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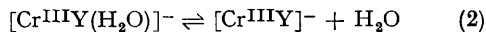
DETAILS of the preparations and experiments relating to the extent of chelation in some chromium(III)-EDTA complexes are reported here. Contrary to an earlier report¹ we have been unable to prepare the sexadentate complex $[\text{Cr}^{\text{III}}\text{Y}]^-$ from $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ (ethylenediaminetetraacetate or $\text{EDTA} \equiv \text{Y}^{4-}$). When the latter is treated with 0.1M-sodium hydroxide the product is in all probability the quinquedentate oxochromium(III) complex $[\text{Cr}^{\text{III}}\text{Y}(\text{O})]^{3-}$, and not² the quadridentate dihydroxo-complex $[\text{Cr}^{\text{III}}\text{Y}(\text{OH})_2]^{3-}$. The complex $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ in which the

EDTA is quinquedentate is well known.³⁻⁵ Acid-dissociation constants have been measured²⁻⁴ and are as shown in equation (1)



The most favourable conditions for the formation of a sexadentate complex $[\text{Cr}^{\text{III}}\text{Y}]^-$ 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)



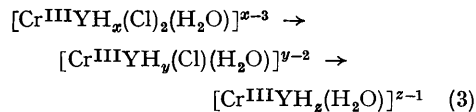
to be most favourable. From such solutions Hoard *et al.*¹ have prepared samples of the complexes $\text{Rb}, \text{CrY}, 2\text{H}_2\text{O}$ and $\text{NH}_4, \text{CrY}, 2\text{H}_2\text{O}$, which they claim are isomorphous with similar salts of $[\text{Co}^{\text{III}}\text{Y}]^-$ and $[\text{Al}^{\text{III}}\text{Y}]^-$ 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 $\text{Rb}, \text{CrY}, 2\text{H}_2\text{O}$ and $\text{NH}_4, \text{CrY}, 2\text{H}_2\text{O}$ 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 ($>300^\circ$), 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 $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ and the related conjugate-base form $[\text{CrY}(\text{H}_2\text{O})]^-$.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_3 have been identified. The reactions are all rapid and from visible spectra recorded within 3 min. of mixing, the only products are $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ and $[\text{Cr}^{\text{III}}\text{Y}(\text{H}_2\text{O})]^-$. Since the replacement of X^- by H_2O in complexes of the type $[\text{Cr}^{\text{III}}\text{YH}(\text{X})]^-$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{etc.}$) is unlikely to be rapid, we conclude that such reactions are of the outer-sphere type. Conversion of $[\text{Cr}^{\text{III}}\text{Y}]^-$ to $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ and $[\text{Cr}^{\text{III}}\text{Y}(\text{H}_2\text{O})]^-$ would also be expected to be slow.⁶

In aqueous solutions pH 8–9^{2–4} the complex $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ is present as $[\text{CrY}(\text{OH})]^{2-}$ ($\epsilon_{\text{max}} = 115$ at $594 \text{ m}\mu$, and 86 at $392 \text{ m}\mu$). At still higher pH's further spectral changes have been attributed to the conversion of $[\text{Cr}^{\text{III}}\text{Y}(\text{OH})]^{2-}$ into the quadridentate complex $[\text{CrY}(\text{OH})_2]^{3-}$, $pK_a = 12.2$,² ($\epsilon_{\text{max}} = 65$ at $575 \text{ m}\mu$ and 86 at $407 \text{ m}\mu$).

At 25° and in 0.1M -sodium hydroxide *ca.* 15 min. are required for this reaction to proceed to completion (rate constant *ca.* $5 \times 10^{-3} \text{ sec.}^{-1}$). The solutions obtained are stable for at least 24 hr. On acidifying to pH ~ 4.5 (buffered), the formation of $[\text{CrYH}(\text{H}_2\text{O})]$ and $[\text{CrY}(\text{H}_2\text{O})]^-$ is rapid and stopped-flow experiments have indicated a rate constant $> 10^3 \text{ sec.}^{-1}$. 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 $[\text{Cr}^{\text{III}}\text{Y}(\text{O})]^{3-}$.

Attempts to prepare the complex $[\text{Cr}^{\text{III}}\text{YH}(\text{Cl})]^-$ by treating $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ with concentrated hydrochloric acid resulted in a partial dissociation, *i.e.* uncoiling of the EDTA ligand. On cooling to 0° crystals of $[\text{Cr}^{\text{III}}\text{YH}_3(\text{Cl})_2(\text{H}_2\text{O})], 3\text{H}_2\text{O}$ (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 $[\text{Cr}^{\text{III}}\text{YH}_3(\text{Cl})_2(\text{H}_2\text{O})]$ 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 $\text{Rb}^+ [\text{CrYH}_2(\text{Cl})_2(\text{H}_2\text{O})]^- \cdot \text{H}_2\text{O}$ has also been prepared. In aqueous solutions pH 0–4, the complex $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ and its conjugate-base $[\text{Cr}^{\text{III}}\text{Y}(\text{H}_2\text{O})]^-$ are reformed, thus



where $x = 1$ or 2 , $y = 1$ or 2 (and possibly 0), and $z = 0$ or 1 . At pH 2 ($\mu = 1.0\text{M}$) and 10° the overall rate constant is $9 \times 10^{-3} \text{ sec.}^{-1}$. When scan spectra are recorded over the range $350\text{--}700 \text{ m}\mu$ 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 $[\text{H}^+]$ -dependence of the reaction will be reported in full elsewhere. Samples of $[\text{Cr}^{\text{III}}\text{YH}_3(\text{Br})_2(\text{H}_2\text{O})], 3\text{H}_2\text{O}$ can be prepared in a similar manner by treating $[\text{Cr}^{\text{III}}\text{YH}(\text{H}_2\text{O})]$ with hydrobromic acid.

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⁶ Cf. J. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 1958, 260.