Equilibrium and Kinetic Studies on the *N*-(2-Hydroxyethyl)ethylenediamine-*NN'N'*-triacetatochromium(III) Complex in Aqueous Perchlorate Media

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Acid dissociation constants for the chromium(III) complex of *N*-(2-hydroxyethyl)ethylenediamine-*NN'N'*-triacetic acid (H_3TOH) have been determined by potentiometric titration. The three species involved are $[Cr^{III}(TOH)(H_2O)]$, $[Cr^{III}(TOH)(OH)]^-$, and $[Cr^{III}(TO)(OH)]^{2-}$ and at 25 °C, $I = 0{\cdot}1$M (KNO_3): $pK_1 = 6{\cdot}02 \pm 0{\cdot}05$ and $pK_2 = 9{\cdot}85 \pm 0{\cdot}10$. When the pH is greater than *ca.* 13·1 de-chelation of the ligand from the metal ion occurs, and the kinetics of two consecutive slow steps, giving $[Cr^{III}(TO)(OH)_2]^{3-}$ and $[Cr^{III}(TO)(OH)_3]^{4-}$ respectively, have been studied by conventional spectrophotometry. There is no significant hydrogen-ion dependence and values of the rate constants at 25 °C, $I = 1{\cdot}0$M ($NaClO_4$) are $k_3 = 1{\cdot}7 \times 10^{-3}$ and $k_4 = 2{\cdot}0 \times 10^{-4}$ s^{-1}. A slower concurrent process, $k_{34} = 2{\cdot}0 \times 10^{-5}$ s^{-1} at 25 °C, has also been studied.

PREVIOUS investigations in these laboratories have been concerned with the characterization of ethylenediaminetetra-acetic acid (EDTA = H_4Y) complexes of chromium(III) in which the EDTA is only partly coordinated.[1] The kinetics of re-chelation of species assigned terdentate[2] and quadridentate[3] structures have been reported, where the final product is the quinquedentate complex $[Cr^{III}(YH)H_2O]$.[4] A sexidentate complex $[Cr^{III}(Y)]^-$ has not as yet been identified.[3] These studies are now extended to a consideration of the effect of pH on the chromium(III) complex of *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (H_3TOH).

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[1] R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 742.

[2] A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc.* (*A*), 1969, 655.

[3] R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc.* (*A*), 1971, 1494.

[4] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 1948, **31**, 459.

Bustin and Earley[5] have carried out potentiometric, spectrophotometric, and polarographic studies of chromium(III) complexes with *N*-substituted ethylenediaminetriacetic acid including H_3TOH. These authors reported no evidence for the existence of species formed by de-chelation of the ligand from the central metal ion at high pH.

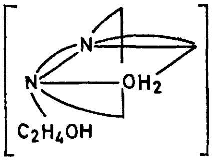
RESULTS

Spectroscopic Changes at pH 0—11.—Bustin and Earley[5] have assigned the formulae (I)—(III) corresponding to the complexes: $[Cr^{III}(TOH)(H_2O)]$, pH < 5; $[Cr^{III}(TOH)(OH)]^-$, pH *ca.* 8·0; and $[Cr^{III}(TO)(OH)]^{2-}$, pH > 11 respectively. The species present at low pH has the ligand bound in a quinquedentate manner, with the hydroxyethyl group unco-ordinated. The absence of an acid dissociation constant at pK_a *ca.* 3 precludes the presence of any uncomplexed carboxylate groups. U.v.-visible spectra of complexes (I)—(III) are shown in Figure 1 and peak positions and absorption coefficients are listed in Table 1. Solutions of all three are stable for 24 h. Absorption coefficients (ε) show serious differences from those reported in ref. 5, but are consistent with the value in ref. 6. Equation (1) represents the removal of a proton on addition of an equivalent of base, and well defined isosbestic

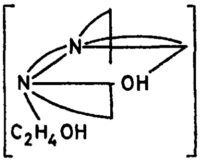
$$[Cr^{III}(TOH)(H_2O)] \overset{K_1}{\rightleftharpoons} [Cr^{III}(TOH)(OH)]^- + H^+ \quad (1)$$

points for the change are observed at 406 (ε = 88), 475 (ε = 46), and 570 nm (ε = 134 l mol⁻¹ cm⁻¹) over the pH range 4·8—5·8. On addition of a second equivalent of base spectroscopic changes associated with deprotonation of the free hydroxyethyl arm of the ligand are observed, equation (2). At pH 8·9—9·9 isosbestic points are observed at 390 (ε = 100), 507 (ε = 74), and 675 nm (ε = 51 l mol⁻¹ cm⁻¹). The interconversions (1) and (2) are too rapid to study by the stopped-flow technique; this is consistent with the assignments given above since protolytic equilibria are known to be rapid.

$$[Cr^{III}(TOH)(OH)]^- \overset{K_2}{\rightleftharpoons} [Cr^{III}(TO)OH]^{2-} + H^+ \quad (2)$$



(I)



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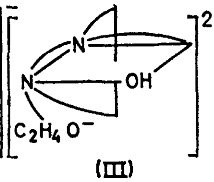

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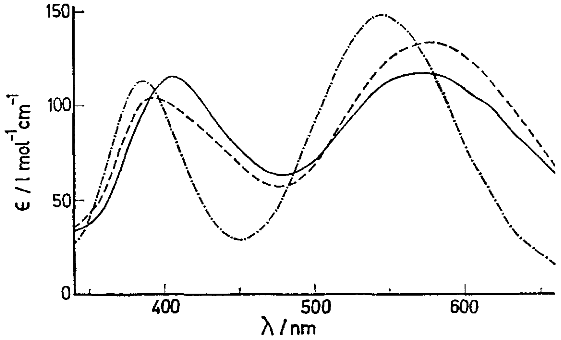

FIGURE 1 Spectra of the complexes $[Cr^{III}(TOH)(H_2O)]$ (—·—·—), $[Cr^{III}(TOH)(OH)]^-$ (– – – –), and $[Cr^{III}(TO)(OH)]^{2-}$ (——) at pH 4·1, 8·05, and 10·5 respectively. The colours are purple, blue A, and blue B respectively

TABLE 1

Details of peak positions in the u.v.-visible region for *N*-(2-hydroxyethyl)ethylenediaminetriacetate complexes of chromium(III)

Complex	Colour	λ/nm	ε/l mol⁻¹ cm⁻¹	λ/nm	ε/l mol⁻¹ cm⁻¹
$[Cr(TOH)(H_2O)]$	Purple	384·5	113	543	148
$[Cr(TOH)(OH)]^-$	Blue A	394	104	575	133
$[Cr(TO)(OH)]^{2-}$	Blue B	406	115	570	117
$[Cr(TO)(OH)_2]^{3-}$ [a]	Green A [b]	410	88	571	83
$[Cr(TO)(OH)_3]^{4-}$ [c]	Green B [d]	411	84	573	76

[a] Suggested formula, for possible structure see (IV). [b] Spectrum as recorded after 40 min of reaction at 25 °C, see Figure 2. [c] Suggested formula, for possible structure see (V). [d] Spectrum as recorded after 165 min of reaction at 25 °C, see Figure 2.

Acid Dissociation Constants.—These have been redetermined for equilibria (1) and (2) at ionic strength $I = 0{\cdot}1$M (KNO_3) by potentiometric titration. At 25 °C, from three independent determinations, $pK_1 = 6{\cdot}02 \pm 0{\cdot}05$ and $pK_2 = 9{\cdot}85 \pm 0{\cdot}10$, using $a_H = 0{\cdot}84$ for the activity of the hydrogen ion;[7] without any allowance for a_H, $pK_1 = 5{\cdot}55 \pm 0{\cdot}05$ and $pK_2 = 9{\cdot}66 \pm 0{\cdot}03$. Values obtained by Bustin and Earley[5] at 22 °C, $I = 0{\cdot}2$M ($NaClO_4$) are $pK_1 = 6{\cdot}44$ and $pK_2 = 9{\cdot}80$.

Spectroscopic Changes at pH > 11.—In the case of the chromium(III)–EDTA system a green species is formed at pH > 12, which Furlani *et al.*[8] associated with the formation of a quadridentate EDTA complex. Other evidence has been obtained supporting this assignment.[3] With the chromium(III)–H_3TOH complex no spectroscopic changes are observed over the pH range 11—13, but evidence consistent with the formation of at least two other forms at pH > *ca.* 13·1 has now been obtained. Thus when the pH of solutions of $[Cr^{III}(TOH)(H_2O)]$ is adjusted to >13·1 at 25 °C, a colour change from blue to green-blue is observed within *ca.* 1 h. Visible spectra recorded after 40 and 165 min are shown in Figure 2. The similarity of these spectra to those reported by Furlani *et al.* for $[Cr^{III}(Y)(OH)_2]$ suggests that complex (IV) is present, or possibly the related quadridentate species in which the $C_2H_4O^-$ group is co-ordinated in place of a carboxylate group. The constant pK_3 corresponding to the formation of (IV) is clearly less favourable, and therefore of greater magnitude, than that for the analogous chromium(III)–EDTA complex.[8]

Kinetics of De-chelation.—Absorbance changes monitored at 575 nm for solutions of complex (III) at pH 13—14 were not as easy to interpret as those for the corresponding de-chelation reaction of the chromium(III)-EDTA complex.[3] At 25 °C the absorbance decreases relatively rapidly for *ca.* 200 min, during which time two stages of reaction

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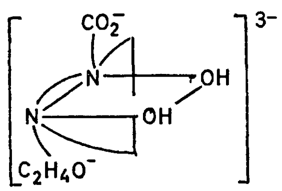
[5] D. I. Bustin and J. E. Earley, *J. Amer. Chem. Soc.*, 1967, **89**, 1818.

[6] T. R. Bhat and G. M. Phatak, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3058.

[7] Based on values in J. Kielland, *J. Amer. Chem. Soc.*, 1937, **59**, 1675.

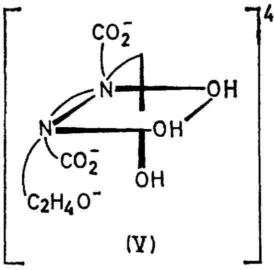
[8] C. Furlani, G. Morpurgo, and G. Sartori, *Z. anorg. Chem.*, 1960, **303**, 1.

are apparent, and slowly thereafter. A possible reaction sequence is (III) ⟶ (IV) ⟶ (V), where complex (V)



(IV)

has the structure indicated, or is some related tridentate species (see below). From graphs of absorbance against



(V)

time an estimate of the half-life was made, and the absorbance (OD_∞) on completion of the second stage was assumed to be as observed after seven half-lives. Plots of

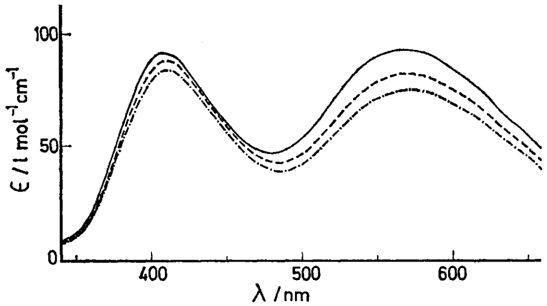


FIGURE 2 The de-chelation reaction of $[Cr^{III}(TO)(OH)]$ (——) at pH 13·4, 25 °C, and I = 1·0M (NaClO$_4$). Spectra obtained after 40 (– – – –) and 165 min (— · — · —) are predominantly the first and second decomposition products respectively, structures (IV) and (V)

log ($OD_t - OD_\infty$) against time t showed three stages as illustrated in Figure 3. The kinetics of the slow third stage were not investigated. Using a consecutive reaction treatment,[9] the theory of which has been outlined,[10] it was possible to evaluate constants k_3 and k_4 (Table 2) for the first and second stages, where the latter may be identified as the forward reactions in equilibria K_3 and K_4, which involve de-chelation and loss of a proton. The rate constant k_4 was obtained from the gradient of the linear portion in Figure 3. Extrapolation of this portion to the ordinate axis gives the intercept x which is defined as in (3), where A_0 is the initial concentration of complex,

$$x = A_0k_3(\epsilon_{IV} - \epsilon_{V})/(k_3 - k_4) \qquad (3)$$

and ϵ_{IV} and ϵ_V are for complexes (IV) and (V) respectively. This then enabled k_3 to be evaluated (see inset Figure 3) by plotting the left-hand side of equation (4) against time, t.

$$\log (OD_t - OD_\infty - xe^{-k_4t}) = k_3t + \text{constant} \qquad (4)$$

A variation of OD_∞, introduced by allowing 7 ± 1 half-lives to elapse, gave rate constants within ±10% of those listed. Finally we should add that, on consideration of a still wider range of OD_∞ values, three stages of reaction are still apparent and an essential part of our interpretation. The kinetics of both stages are first order in complex; no significant hydrogen-ion dependence of k_3 and k_4 is observed and we conclude that H_2O and not OH^- is displacing the chelate ligand. As in the case of the chromium(III)–EDTA complex[3] the aquo-ligand subsequently loses a proton. Because there is an additional slow reaction (see next section), which has not yet been allowed for, a study of the temperature dependence of k_3 and k_4 was not considered appropriate.

TABLE 2

Kinetic data (25 °C) for the two stage de-chelation of $[Cr(TO)OH]^{2-}$, [complex] = 3×10^{-3}M. Ionic strength, I, adjusted with NaClO$_4$

I/M	pH Initial	pH Final	[OH$^-$]/M	10^3k_3 [a]/s^{-1}	10^4k_4 [a]/s^{-1}
1·0	13·16	12·59		1·66	2·13
1·0	13·37	13·00		1·65	2·01
1·0	13·34	12·53		1·75	1·89
1·0 [b]	13·21	13·12		2·09	1·96
3·5			3·06	ca. 1·04	2·03
3·5			3·13	1·28	2·09
5·0			4·66	ca. 1·54	2·72

[a] Assuming OD_∞ is the absorbance after 7 half-lives, see text. Errors introduced by taking OD_∞ after 7 ± 1 half-lives are ±10%. [b] Ionic strength adjusted using LiClO$_4$.

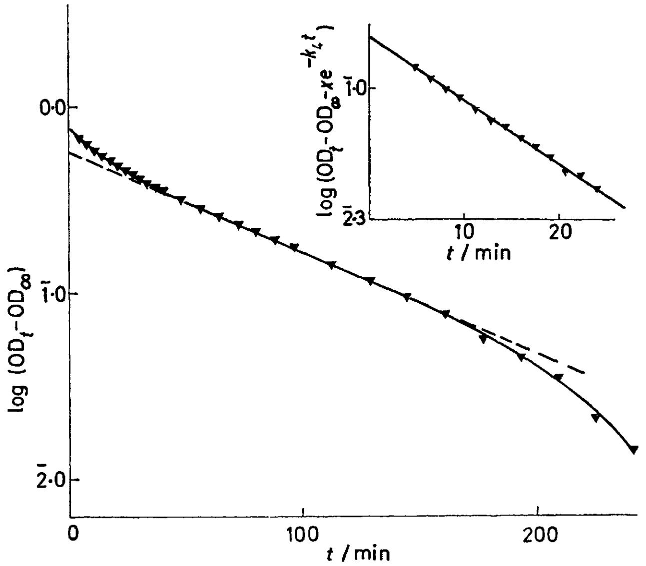


FIGURE 3 Illustration of the consecutive reaction treatment for the evaluation of the rate constants k_4 and k_3 (insert) for the de-chelation of $[Cr(TO)(OH)]^{2-}$. [NaOH] = 3·1M, [complex] = 3×10^{-3}M, 25 °C, and I = 3·5M (NaClO$_4$). A third stage in the reaction is apparent at $t > 200$ min

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[9] For a recent example see K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' Wiley, New York, 2nd edn., 1961, p. 167.

Solutions of complex (V) are unstable and the process of de-chelation continues. After a period of *ca.* 50 h at 25 °C all solutions at pH 13—14 become cloudy and precipitation occurs. The flocculent light green solid which is obtained was filtered off, washed with water and acetone, and then dried by suction. Analyses for chromium, as chromate, gave 34·3% and for carbon <0·2%. These figures suggest total stepwise de-chelation of the ligand from the metal to give a hydrated chromium oxide product, Cr_2O_3,nH_2O.[11] A light green solid is also precipitated from solutions of the chromium(III)–EDTA complex, after *ca.* 90 h (25 °C) at pH > 13; on analysis this gives for chromium 33·94% and for carbon <0·2%, in good agreement with the above.

Solutions of the green-blue chromium(III)–H_3TOH complex (2 h at pH 13·5) rapidly reverted to the blue and purple complexes on adding perchloric acid. Mixing effects arising from the drastic adjustment of pH made a stopped-flow study difficult.

Non-retention of Complex.—A slow reaction concurrent with k_3 and k_4 is effective at pH 13—14. This has been identified by sampling the reactant solution and adding perchloric acid to pH < 3 when the purple complex (I) reforms. No subsequent change in colour intensity was observed at pH < *ca.* 3 over 3 h. The absorbance due to (I) decreases with each sample and plots of log $(OD_t - OD_\infty)$ against time, where values of OD_∞ were as observed just prior to precipitation of the hydrated chromium oxide, gave satisfactory linearity for >30 h (25 °C). Some non-linearity was detected over the first 3 h but, in view of the small absorbance changes, it was not clear whether this was indicative of an initial stage. On varying OD_∞ by ±10%, which from graphs of absorbance against time was considered a reasonable allowance, rate constants (Table 3) varied by ±25%. At 25 °C k_{34} evaluated in this way is $(2\cdot0 \pm 0\cdot5) \times 10^{-5}\ s^{-1}$. Similar experiments with the chromium(III)–EDTA complex at pH *ca.* 13·5 showed that this also exhibits a slow k_{34} step, an approximate rate constant of $8\cdot4 \times 10^{-6}\ s^{-1}$ being obtained at 25 °C. Processes which may be involved are de-chelation of the ligands by alternative routes to that involving complexes (IV) and (V). An initial step might be the displacement of a nitrogen atom before that of adjacent oxygen atoms.[12] At pH < 3 the free ligand co-ordinates only very slowly to hexa-aquochromium(III).[13]

TABLE 3

Rate constants k_{34} for the non-retention of complex, concurrent with k_3 and k_4, [complex] = 3×10^{-3}M, pH 13—14, I = 1·0M ($NaClO_4$)

Temp. °C	10^5k_{34} [a] s^{-1}
25	2·06
	1·91
	2·02
35	5·22
	5·22
45	18·73
	17·75

[a] On varying OD_∞ by ±10% rate constants vary by ±25%. We consider this a satisfactory estimate of the accuracy of these values.

DISCUSSION

The value of pK_1 for the chromium(III)–H_3TOH complex at 25 °C and I = 0·1M (KNO_3) is 6·02 ± 0·05 using $a_H = 0\cdot84$ [7] and 5·55 ± 0·05 using the hydrogen-ion concentration, whereas previously [5] a value of 6·5 was obtained at I = 0·2M ($NaClO_4$). There is little doubt that pK_1 corresponds to deprotonation of the water ligand as in equation (1). A pK value of 7·5 has been reported for the corresponding chromium(III)–EDTA complex.[8,13] The value obtained for pK_2 = 9·8 is lower than might have been expected for the deprotonation of an ethanolic hydroxy-group as in equation (2), without any accompanying changes. We note that removal of the proton does not greatly effect the colour of the complex (Blue A ⟶ Blue B, Table 1), which is consistent with deprotonation occurring at a position remote from the metal chromophore.

Additional changes in which the deprotonated hydroxyethyl arm becomes co-ordinated to the metal ion are possible. Thus Tanner and Higginson [14] have identified the sexidentate cobalt(III)–H_3TOH complex, in which deprotonation and co-ordination of the hydroxyethyl group is observed. Also Bhat *et al.*[15] have presented evidence for co-ordination of the ethanolic oxygen atom in H_3TOH complexes of antimony(III) and bismuth(III), and similar behaviour is apparent for the iron(III) complex.[16] Other studies with hydroxyethyl-amino acids based on the ammonia structure have indicated that the ethanolic group is involved in chelate formation.[17] Although Chaberek and Martell [18] were unable to prove conclusively that the hydroxyethyl group participates in chelate formation in complexes of H_3TOH and divalent metal ions, they consider the ligand to have potentially sexidentate chelating properties.

It is not clear how co-ordination of the deprotonated hydroxyethyl arm of the ligand can occur in the present case, unless a carboxylate group becomes unco-ordinated or the metal ion assumes a seven-co-ordinate structure. The latter does not seem a strong possibility for chromium(III), although we do not rule out a weak interaction with the $C_2H_4O^-$ arm of the ligand whereby the central metal ion can supplement its octahedral co-ordination. The most likely of all these possibilities is co-ordination of the hydroxyethyl oxygen atom in place of a carboxylate group, in which case equation (2), while still applicable, no longer represents a simple protolytic reaction. Although a slow rate process might be expected for this

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[11] See for example F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' Interscience, 3rd edn., 1972, p. 833.

[12] For a recent example in which a chelated nitrogen ligand of a chromium(III) complex is displaced see S. C. Pyke and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2445.

[13] R. E. Hamm, *J. Amer. Chem. Soc.*, 1953, **75**, 5670.

[14] S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1966, 537.

[15] T. R. Bhat, R. K. Iyer, and J. Shankar, *Z. anorg. Chem.*, 1966, **343**, 329.

[16] R. Skochdopole and S. Chaberek, *J. Inorg. Nuclear Chem.*, 1959, **11**, 222.

[17] S. Chaberek, R. C. Courtney, and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5057; 1953, **75**, 2185.

[18] S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 1477.

change, we have been unable to detect any such step in this study. Moreover, since a rapid step (rate constant 330 s^{-1} at 25 °C) has been detected for the re-chelation of a carboxylate group of EDTA to chromium(III) at pH *ca.* 4,[3] any argument based on rates may not be valid. Whatever the precise nature of (2), it seems reasonably certain that complexes (III)—(V) can be represented by $[Cr^{III}(TO)(OH)]^{2-}$, $[Cr^{III}(TO)(OH)_2]^{3-}$, and $[Cr^{III}(TO)(OH)_3]^{4-}$ respectively.

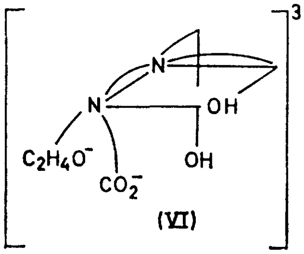
We were unable to obtain an accurate value for pK_3 for the formation of the dihydroxy complex (IV) because of the occurrence of subsequent de-chelation; a value greater than 13·0 and probably *ca.* 13·3 is apparent from these studies. The corresponding pK_3 for the chromium(III)–EDTA complex is 12·2.[8] The rate constant for the formation of (IV), $k_3 = 1{\cdot}7 \times 10^{-3}$ s^{-1} at 25 °C and $I = 1{\cdot}0$M ($NaClO_4$), is of the same order of magnitude as the value $4{\cdot}8 \times 10^{-3}$ s^{-1} (25 °C) observed for the corresponding step in the chromium(III)–EDTA de-chelation reaction.[3]

Partial de-chelation of EDTA from chromium(III) has been observed when solutions of $[Cr^{III}(YH)(H_2O)]$ are reacted with concentrated hydrochloric or hydrobromic acids.[1] Terdentate complexes of general formula $[Cr^{III}(YH_3)(X)_2(H_2O)]$ (X = Cl or Br) have been identified. If the reaction time exceeds *ca.* 20 min there is further uncoiling of the ligand from the metal. When re-chelation occurs a slow-fast reaction sequence is observed,[2] which is consistent with de-chelation of adjacent carboxylate and amine groups.

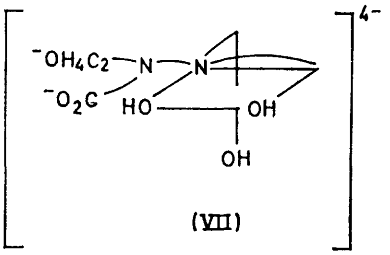
Hamm[13] and, more recently, Murry[19] have studied the chelation of EDTA to hexa-aquochromium(III). In the latter work at pH 2·50—3·30 the first slow step in the reaction is attributed to co-ordination of a carboxylate group. The product is assigned the formula $[Cr(H_2O)_5(YH_3)]^{2+}$. The second slow step has an inverse hydrogen-ion dependence and therefore most likely corresponds to co-ordination of an adjacent amine nitrogen atom. This follows since in the pH range investigated the amine but not the carboxylate groups are extensively protonated. Formation of the remaining chelate rings to give $[Cr^{III}(Y)(H_2O)]^-$ is rapid.

The occurrence of one-sided (*O′N′*) co-ordination of EDTA to chromium(III),[19] and the apparent one-sided de-chelation (*O″N″*) of EDTA from chromium(III) on treatment with hydrochloric and hydrobromic acids,[1] suggests that in the experiments reported here de-chelation may well be occurring in a one-sided manner, and that complexes (IV) and (V) should perhaps be written as in (VI) and (VII) respectively. However the assignment of formulae to the products at high pH is very much dependent on the structure of the product in equation (2), and it remains uncertain whether (IV) is a precise representation or requires some modification as suggested above.

From this discussion it seems likely that the predominant sequence in the co-ordination of EDTA and related ligands to chromium(III) is *O′N′O′N″O″*, where carboxylate groups designated *O′* are bonded to *N′*, *etc.* and where *O″* remains unco-ordinated. This may be an over-simplification, however, since Margerum[20] has detected several forms of 1 : 1 complexes during the chelation of EDTA to metals ions. Evidence has also been obtained[21] suggesting that isomerization can occur in complexes of metal ions and multidentate ligands of this type; thus the chelating ligand is able to change the sites at which it is co-ordinated to the central atom.



(VI)



(VII)

EXPERIMENTAL

Solutions of hexa-aquochromium(III) perchlorate were prepared by reduction of a solution of chromium trioxide in perchloric acid with hydrogen peroxide; the excess of hydrogen peroxide was decomposed in the presence of platinum black. To prepare *N*-(2-hydroxyethyl)ethylenediaminetriacetatochromium(III), $[Cr(TOH)H_2O]$, a solution of hexa-aquochromium(III) perchlorate was heated (80—90 °C, *ca.* 3 h) with slightly less than an equivalent amount of *N*-(2-hydroxyethyl)ethylenediamine-*NN′N′*-triacetic acid (Koch–Light, AnalaR grade) in acid solution (*ca.* 0·1M-perchloric acid). The product, separated from unchanged chromium(III) and polymeric products using a Dowex 50W-X8 cation-exchange column with distilled water as eluant, could not be crystallized.

Visible and u.v. spectra were measured on Unicam SP 800 (recording) and SP 500 (manual) spectrophotometers. Molar absorption coefficients of $[Cr(TOH)H_2O]$ were calculated on the basis of the chromium concentration which was determined spectrophotometrically as chromate. Absorption coefficients of other species (Table 1) were determined by direct comparison with the values found for $[Cr(TOH)(H_2O)]$. The latter agree well with that obtained by Bhat and Phatak,[6] but all our values differ by *ca.* 50% from those quoted by Bustin and Earley.[5]

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[19] W. V. Murry, *Diss. Abs.*, 1968, **28***B*, 4901.

[20] D. W. Margerum, *J. Phys. Chem.*, 1959, **63**, 336.

[21] K. Bernauer and C. Bernhard, personal communication of unpublished results on the *N*-(2-hydroxyethyl)ethylenediamine-*NN′N′*-triacetatocobalt(III) complex.

The ionic strength of solutions was adjusted to $I = 1{\cdot}0\text{M}$ with sodium perchlorate (B.D.H., AnalaR). The pH of solutions were measured on a Radiometer pH-meter 4 which was calibrated with standard buffer solutions of pH 6·50 ± 0·02 (20 °C), and checked against 0·1M-sodium hydroxide, $I = 1{\cdot}0\text{M}$ ($NaClO_4$). Radiometer glass (type G202B) and calomel electrodes (type K401) were used.

Kinetic experiments in which the rate constants k_3 and k_4 were determined were monitored on a Unicam SP 500 spectrophotometer fitted with a thermostatted cell housing. The rate constant k_{34} for the concurrent reaction was determined by sampling the reactant solution over periods of up to 100 h. The samples (3 ml) were quenched by addition to 0·25M-perchloric acid (22 ml), and the absorbance of the purple complex $[Cr(TOH)(H_2O]$, was measured at 543 nm.

Acid dissociation constants were determined by potentiometric titration, actual values being computed using a programme for dibasic acids which incorporated a correction for the hydroxide-ion concentration. The end-points in such titrations were estimated before computation by carrying out a Gran treatment.[22] In order to ensure a constant ionic strength of $I = 0{\cdot}1\text{M}$ (initially 0·1M-KNO_3) in the titrations, we used 0·1M-NaOH made up with 0·05M-KNO_3. All titrations were carried out in a thermostatted cell at 25 °C.

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