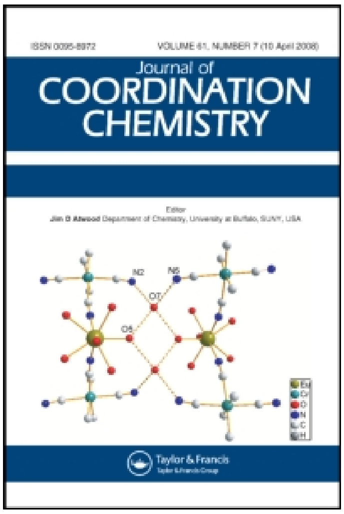

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CHROMIUM(III) COMPLEXES WITH DIETHYLENTRIAMINEPENTAACETIC ACID

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Complex formation by chromium(III) with diethylentriaminepentaacetic acid (DTPA) has been studied by potentiometry and spectrophotometry. In equimolar solutions or with a ligand excess, complexation is practically complete at pH > 1 and protonation equilibria have been calculated. Molar absorbtivities of the different species have been evaluated. Equilibrium constants for complex formation have been calculated in 1 mol dm^{-3} (Na,H)ClO$_4$ at 20°C.

Keywords: Stability constants, chromium(III), DTPA, complexes

INTRODUCTION

Complexes of chromium(III) with EDTA have been extensively investigated and stability constants of the 1:1 metal to ligand species are reported in the literature.[1-3] Kinetics of complex formation have also been studied and mechanisms of complexation postulated.[4,5] Chromium reacts with DTPA (H_5L) in acid medium forming violet complexes while a blue species is evidenced in alkaline medium, as is the case with EDTA. The metal to ligand molar ratio is 1:1 even in the presence of excess ligand.

Like EDTA, complexing of DTPA with hexaaquochromium(III) is generally slow and very much dependent on pH. Krumina *et al.*[6] calculated the equilibrium constants of the different protonated species from absorbance–pH curves in the pH range 2.5 to 4.5 and claimed that, in the presence of a ten-fold ligand excess (with $C_M = 0.002$ mol dm^{-3}), complex formation begins at pH > 2.5 and that the reaction is complete in about five hours at room temperature.

Our preliminary experiments showed that this is true only at pH values about 5, but that with decreasing pH the reaction rate markedly decreases and several days or high temperature are needed to complete the reaction. Furthermore, chromium complexation is practically complete at pH > 1, even in equimolar solutions. Therefore, a more detailed study was undertaken in order to characterize the prevailing species in aqueous solution and to calculate the corresponding equilibrium constants. Measurements were performed in a constant ionic medium, (Na,H)ClO$_4$ 1.0 mol dm^{-3}, and at 20°C.

EXPERIMENTAL

Distilled-deionised water and analytical grade reagents were used throughout.

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0.1 mol dm^{-3} chromium(III) stock solution was prepared from chromium(III) perchlorate (Alfa) dissolved in 0.01 mol dm^{-3} perchloric acid. Standardization of the solution was effected by iodometric titration after oxidation of chromium(III) to chromium(VI). 0.1 mol dm^{-3} DTPA stock solution was prepared by dissolving the appropriate quantity of diethylenetriaminepentaacetic acid (Fluka) with NaOH to pH = 4 to 5. The purity, checked by potentiometric titration with sodium hydroxide, was considered satisfactory.

Chromium(III)–DTPA complex solutions were prepared by dissolving the approximate quantity of diethylenetriaminepentaacetic acid chromium(III) (disodium salt) (Aldrich) in $NaClO_4$ (1.0 mol dm^{-3}). The water content and the purity of the solid salt was checked by thermal analysis. The weight loss between 50 and 300°C corresponds to 2.7 water molecules (8.5%), and a constant weight is reached at 620°C, corresponding to chromium oxide and sodium carbonate (calcd. on the anhydrous compound for $1/2.Cr_2O_3 + Na_2CO_3$:37.42%. Found: 37.2%). Titrations with perchloric acid were performed to standardize the salt solutions.

Potentiometric measurements were carried out with an AMEL 337 potentiometer, interfaced with an Apple computer, for automatic calculation of the formation function. An Ingold glass electrode was used, calibrated in concentration units, so in this work the symbol pH corresponds to $-\log[H^+]$. The reference was a double junction calomel electrode filled with $NaClO_4$ (1.0 mol dm^{-3}). A Hitachi Perkin Elmer 320 spectrophotometer, connected to a Perkin Elmer 3600 data station was used for spectrophotometric measurements.

RESULTS AND DISCUSSION

Potentiometric and spectrophotometric methods have been applied to evaluate acid-base equilibria for the different protonated species. Starting with the 1:1 complex (concentration between 0.01 and 0.005 mol dm^{-3} dissolved in 1.0 mol dm^{-3} $NaClO_4$), titrations both with perchloric acid and with sodium hydroxide were performed. Formation functions, $\bar{n} = \bar{n}(pH)$, were calculated and stability constants were obtained by the curve-fitting method proposed by Sillèn.[7] In acid medium, three protonated forms were evident, $[Cr(HL)(H_2O)]^-$, $[Cr(H_2L)(H_2O)]$, and $[Cr(H_3L)(H_2O)]^+$, the equilibrium constants for which are reported in Table I. These forms show two absorption maxima at 545 and 386 nm, shifted in the normal complex to 570 and 391 nm, respectively (Fig. 1). Also three isosbestic points are evidenced.

From the curve A = f(pH), the first protonation constant can be calculated. The plot is conveniently reported as $\log(A^\circ_1 - A)/(A - A^\circ_2)$ vs pH at constant λ (545 nm). A straight line is obtained, the intercept of which on the x axis represents the value of pK (Fig. 2). A°_1 and A°_2 are the limiting values of absorbance of the two species ($= \varepsilon b C$). The successive protonation constants cannot be obtained by spectrophotometric measurements, as molar absorptivities of the protonated species are practically the same.

TABLE I
Spectroscopic and equilibrium constant results.

quilibrium	−log K	Isosbestic points (nm)
r$(H_3L)(H_2O)]^+ \rightleftharpoons [Cr(H_2L)(H_2O)] + H^+$	1.45 ± 0.1[a]	
r$(H_2L)(H_2O)] \rightleftharpoons [Cr(HL)(H_2O)]^- + H^+$	2.85 ± 0.05[a]	
r$(HL)(H_2O)]^- \rightleftharpoons [CrL(H_2O)]^{2-} + H^+$	6.13 ± 0.02[a]	578
	6.17 ± 0.05[b]	475
		409
rL$(H_2O)]^{2-} \rightleftharpoons [CrL(OH)]^{3-} + H^+$	7.65 ± 0.02[a]	569
	7.64 ± 0.05[b]	477
		419

Potentiometric method. [b] Spectrophotometric method

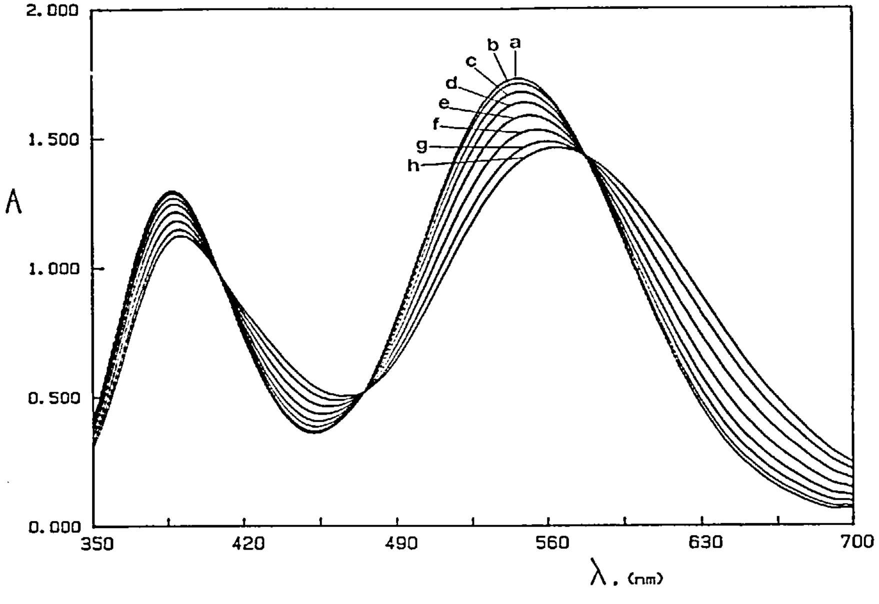


FIGURE 1 Absorption spectra as a function of pH for the system Cr(III)-DTPA in acid medium; a) pH = 4.15, b) pH = 4.82, c) pH = 5.30, d) pH = 5.61, e) pH = 5.90, f) pH = 6.20, g) pH = 6.49, h) pH = 6.76.

In alkaline medium, dissociation of coordinated water occurs and a blue species is formed. This form shows two maxima, at 392 and at 585 nm, with two shoulders at 713 and 430 nm (Fig. 3). Also in this case, a dissociation constant was calculated from the absorbance–pH curve. In Table II, spectral characteristics of the species are summarized.

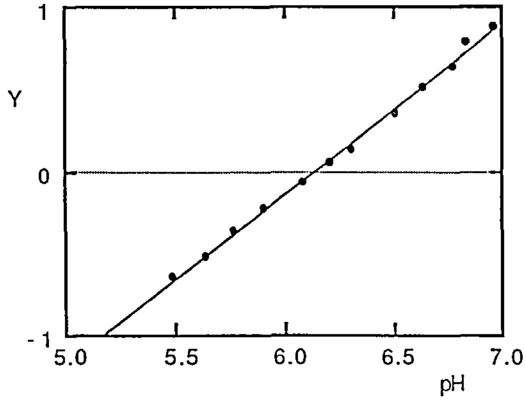


FIGURE 2 Logarithmic analysis of the absorbance–acidity plot with respect to the spectra of Fig. 1; $\lambda = 545\,\text{nm}$, $Y = \log(A^\circ_1 - A)/(A - A^\circ_2)$.

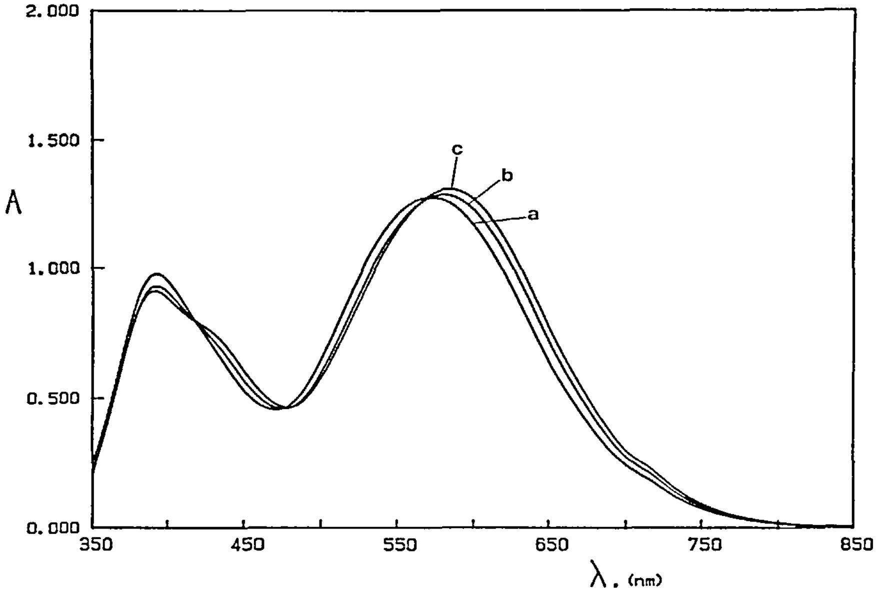


FIGURE 3 Absorption spectra as a function of pH for the system Cr(III)–DTPA in alkaline medium; a) pH = 6.88, b) pH = 7.53, c) pH = 8.21.

At pH < 0.5 dissociation of the complex is evident, but equilibrium is reached only by heating the solution for several hours. In order to obtain the value of the conditional formation constant for the equilibrium $Cr^{3+} + L' \rightleftharpoons CrL'$ the equations $[CrL'] = A/A^\circ \cdot C_L$, $[Cr^{3+}] = C_M - [CrL']$ and $[L'] = C_L - [CrL']$, where L′ is the total ligand not bound to the chromium ion, were used. The value of A/A° was measured at a fixed pH value (A is the actual value of the absorbance corrected for the absorbance of the metal ion, A° the limiting value when the complex is quantitatively formed).

TABLE II
Spectroscopic data for the complexes.

Species	λmax(nm)	ε($M^{-1}cm^{-1}$)
$[Cr(H_3L)(H_2O)]^+$	545	157
	386	117
$[Cr(H_2L)(H_2O)]$	545	157
	386	117
$[Cr(HL)(H_2O)]^-$	545	157
	386	117
$[CrL(H_2O)]^{2-}$	570	130
	391	98
$[CrL(OH)]^{3-}$	713 (sh)	
	585	120
	430 (sh)	
	392	78

In $HClO_4$ 1 mol/dm^{-3} we obtain log K′ = 2.83 ± 0.05. From the values of overall protonation constants of the ligand (β_{0il}), reported in the literature[8] for our experimental conditions of ionic strength and temperature, the stability constant for the equilibrium $Cr_{aq}^{3+} + H_3L^{2-} \rightleftharpoons CrH_3L^+$ is obtained by $K_c = K'/\alpha_{H_3L}$, where $\alpha_{H_3L} = \beta_{131}[H^+]^3/(1 + \Sigma\beta_{0il}[H^+]^i)$. By inserting numerical values, we obtain log $K_c = 10.55$.

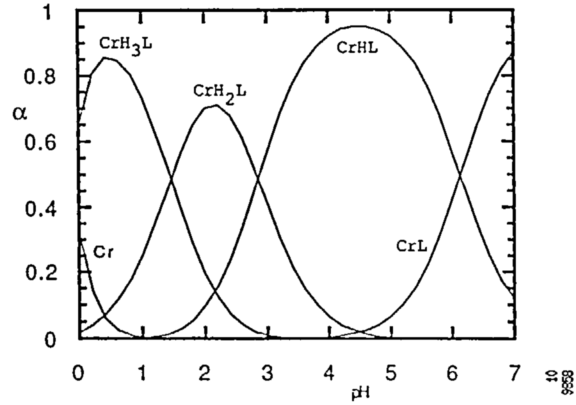


FIGURE 4 Distribution diagram for the chromium(III)–DTPA system under equimolar conditions.

From the stepwise protonation equilibria for the complex species previously calculated, the overall stability constants can be derived. The values are summarized in Table III, together with protonation constants for DTPA. By using these values, the distribution diagram of Figure 4 is reported for equimolar solutions of metal and ligand.

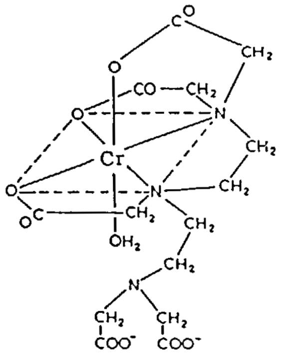
TABLE III
Overall formation constants for proton[8] and chromium(III) ion; T = 20°C, ionic strength 1.0 mol dm^{-3} (Na,H)ClO$_4$.

$\log \beta_{011} = 9.48$
$\log \beta_{021} = 17.74$
$\log \beta_{031} = 21.93$
$\log \beta_{041} = 25.53$
$\log \beta_{051} = 27.61$
$\log \beta_{061} = 28.83$
$\log \beta_{071} = 29.58$

$\log \beta_{101} = 22.05$
$\log \beta_{111} = 28.18$
$\log \beta_{121} = 31.03$
$\log \beta_{131} = 32.48$

β_{pqr} represents the formation constant for the equilibrium $pCr + qH + rL \leftrightarrow Cr_pH_qL_r$, with charges omitted for clarity, and L being the (5−) anion.

Chromium(III) forms with DTPA in aqueous solution five different species. In the pH range 4 to 7 the monoprotonated form exists in equilibrium with the normal chelate. At pH = 3 two further protons are bound to the complex. At pH > 7 a monohydroxochelate is formed. One water molecule is bound to the metal ion. The suggested structure is shown below.



DTPA behaves as a pentadentate ligand, one iminodiacetic group being free from coordination. This is confirmed by experimental evidence concerning mixed complexes with other metal ions.[9]

A similar structure was detected during an NMR investigation in aqueous solution of the cobalt(III)-DTPA complex.[10] In the case of EDTA, only one protonated species was evidenced (pK = 2.27).[2] In this case the ligand seems to act as a pentadentate, one carboxylic group being free from coordination.[11]

REFERENCES

1. R.L. Pecsok, L.D. Shield and W.P. Schefer, *Inorg. Chem.*, **3**, 114 (1963).
2. C. Furlani, G. Morpurgo and G. Sartori, *Z. Anorg. Chem.*, **303**, 1 (1960).
3. J. Korsse, G.A.J. Leurs and P.W.F. Louwrier, *Talanta*, **32**, 451 (1985).
4. R.E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).
5. A.G. Sykes and R.N.F. Thorneley, *J. Chem. Soc. A*, 655 (1969).
6. V.T. Krumina, K.V. Astakov and S.A. Barkov, *Russian J. Phys. Chem.*, **43**, 1567 (1969).

7. L.G. Sillèn, *Acta Chem. Scand.*, **10**, 186 (1956).
8. J. Kragten and L.G. Deknop Weever, *Talanta*, **30**, 623 (1983).
9. A. Napoli, to be published.
10. B.B. Smith and R.H. Betts, *J. Am. Chem. Soc.*, **91**, 7749 (1969).
11. F.P. Dwyer and F.L. Garvan, *J. Am. Chem. Soc.*, **82**, 4823 (1960).