Separation of the *cis/trans* Isomers of Bis(L-aspartato)- and Tris-(L-alaninato)-chromium(III) Complexes. Kinetic Studies on the Ring-opening of Isomers of Bis-L-(aspartato) Chelate

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Abstract

Bis-(L-aspartato)chromium(III) trihydrate and tris-(L-alaninato)-chromium(III) monohydrate complexes were prepared according to literature methods [1]. The isomers in each of these complexes were separated using a CM Sephadex cation exchanger and sodium iodate as the eluting solvent. Characterization of the isomers was by elemental analysis and spectroscopy. The kinetics of the ring-opening of the aspartato-chelating complex was monitored at constant $[H^+]$.

Introduction

Chromium(III) complexes of amino acids have been extensively investigated during the last decade [2–4]. However, not much work has been reported on the separation of the isomers of these complexes. The acid catalysed opening of chelate rings in transition metal complexes is well documented, and detailed kinetic studies have been reported for phosphato [5] oxalato [6] and carbanato [7] complexes.

Boreham and Buckingham [8] reported the oxygen exchange chelate ring-opening in $Co(en)_2(glyO)^{2+}$. Hay and Basak [9] investigated the stability of $Co(en)_2(-alaO)^{2+}$ in acidic media and also the kinetic and mechanistic work on the ring-opening reaction. Faustres and Daffe [10] studied the protonation equilibrium $(Co(en)_2(glyO)^{2+} + D^+ \rightleftharpoons (Co(en)_2(glyOD)^{3+}$ in strongly acidic solution by ^1H NMR spectroscopy. As far as reports indicate, there has not been any work on the separation of the *cis/trans* isomers of bis-(L-aspartato)chromium(III) trihydrate and tris-(L-alaninato)chromium(III) monohydrate complexes and no studies of the isomers of the former complexes have been reported.

Experimental

CM Sephadex cation exchange resin was stirred into warm water (50 °C) and set aside for 1 h. The swollen resin was then carefully packed into the chromatographic column. 50 cm^3 solution of sodium iodate (1.98 g, 0.01 M) was then run down the column. 5.4 g of bis-(L-aspartato)chromium(III) trihydrate complex dissolved in 10 cm^3 ethanol was run into the chromatographic column and the sodium iodate solution allowed to drip down the column for 2 h. (The level of the iodate solution was always kept above that of the aspartato complex in the column.) After 2 h, the deep red colour of the solution of the bis-(L-aspartato)complex gradually gave way to violet and red colours forming two adjacent layers in the column. The eluting process was continued for another 1 h, after which period the violet and red layers became quite distinct. The layers were then collected separately with dry receivers. Crystals were recovered by rotary evaporation, and the analytical data of each isomer is given in Table I. The isomers of the tris-(L-alaninato)-chromium(III) monohydrate complex were similarly separated, and their analytical data is also given in Table I.

TABLE I. Isomers of Bis-L-(aspartato)- and Tris-L-(alaninato)chromium(III) Complexes

Isomer colour	Melting point (°C)	Analysis (found (calc.)) C	H	N
$Cr(NH_2CH(COO)CH_2COO)_2 \cdot 3H_2O$				
red	255	23.50(23.69)	4.31(4.35)	7.65(7.61)
violet	257	23.62(23.69)	4.38(4.35)	7.58(7.61)
$Cr(NH_2CH_2CH_2COO)_3 \cdot H_2O$				
red	261	33.50(33.33)	5.60(5.55)	12.83(12.77)
violet	263	33.21(33.33)	5.48(5.55)	12.73(12.77)

Kinetics

Nitric acid solutions of the isomers of bis-(L-aspartato)chromium(III) trihydrate adjusted to $I = 0.1$ M KNO_3 were thermostated on a Perkin-Elmer 420 spectrophotometer by circulating water. Measurements were monitored at 310 nm where a decrease

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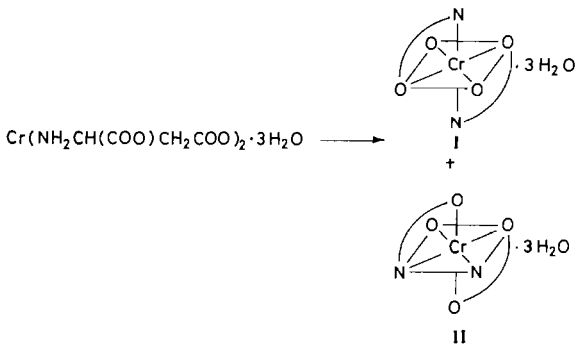
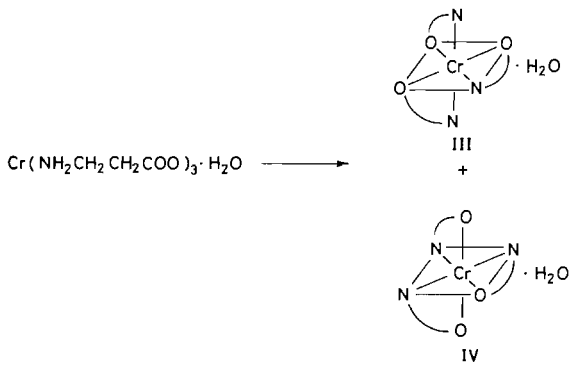
in absorbance was noticed. Values of the observed first-order rate constant (k observed) at constant pH were evaluated from a log ($A_\infty - A_t$) *versus* time curve and each rate constant is a mean of duplicate runs.

Results and Discussion

The bis-(L-aspartato)chromium(III) trihydrate complex gave *trans*-amine-*cis*-carboxylate structure **(I)** as the red isomer and *trans*-carboxylate-*cis*-amine **(II)** as the violet isomer.



Similarly the tris-L-(alaninato)chromium(III) monohydrate gave *trans*-amine-*cis*-carboxylate (structure **(III)**) as the red isomer while the *trans*-carboxylate-*cis*-amine **(IV)** is the violet isomer.



The isomers are listed in Table I together with the analytical data. All the complexes are stable in air at room temperature, but easily decompose in moist air. The important infrared spectral bands are shown in Table II. The –OH stretching frequency for the aspartatoisomeric complexes indicate strong broad bands in the 3400–3450 cm^{-1} range attributed to H-bonding. This phenomenon is absent in the alaninato isomeric complexes which show strong sharp bands in the electronic spectra of these complexes indicating the ground state as $^4A_{2g}$, the first and second excited states as $^4T_{2g}$ and $^4T_{1g}$ respectively. The $^4T_{2g}$ transitions are observed in the UV spectra as two bands for each isomer (Table II).

TABLE II. IR Spectra and UV Spectra for Isomers of Bis-L-(aspartato)- and Tris-L(-alaninato)chromium(III) Complexes

Isomer colour	IR (cm^{-1}) (OH)	(C=O)	UV (cm^{-1}) $^4A_{2g} \rightarrow {}^4T_{2g}$	
			ν_1	ν_2
$Cr(NH_2CH(COO)CH_2COO)_2 \cdot 3H_2O$				
red	3400–3450	1730	18500	25300
violet	3410–3450	1735	25450	37000
$Cr(NH_2CH_2CH_2COO)_3 \cdot H_2O$				
red	3500	1750	18100	24750
violet	3510	1760	25280	37250

On dissolution of the *cis*/*trans* isomers of the bis-(L-aspartato)chromium(III) trihydrate complex in dilute HNO_3, studies indicate frequency shifts to lower wavelengths in the UV absorption spectra of these isomers. It is therefore assumed that the protons catalyse the opening of the chelate rings, and the mechanism in Scheme 1 is postulated. Characterization of the products of the ring-opening reaction was not possible as they could not be isolated in pure forms. Plots of k (observed) *vs.* $[H^+]$ are linear and pass through the origin as shown in Fig. 1. (k observed = observed first-order rate constant at constant pH). The plots show a first-order dependence on $[H^+]$ corresponding to the above reaction scheme for both isomers.

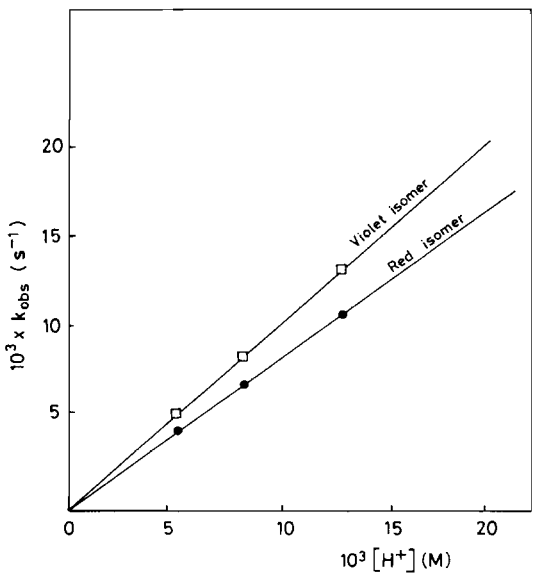
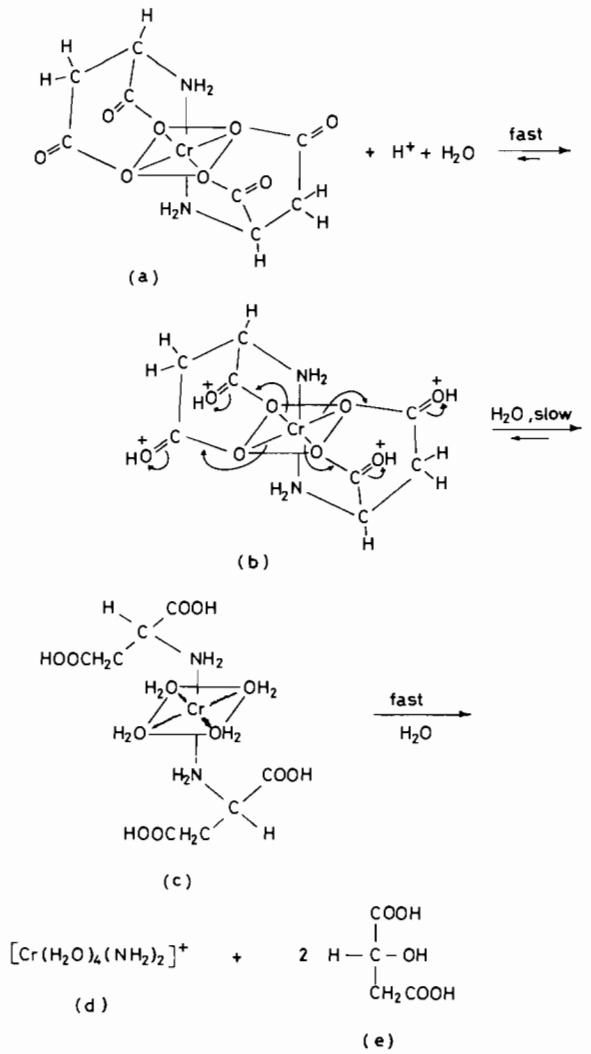


Fig. 1. Acid catalysed ring-opening of the isomers of $Cr(NH_2CH(COO)CH_2COO)_2 \cdot 3H_2O$ at 25 °C in HNO_3 solutions.



Scheme 1.

For these schemes:

$$\text{Rate} = kk' \frac{[\text{isomeric complex}]\,[H^+]}{1 + k[H^+]}$$

But $k[H^+] \ll 1$

$$\text{Rate} = kk'[\text{isomeric complex}]\,[H^+]$$
$$= k_H\,[\text{isomeric complex}]\,[H^+]$$

The dependence of the isomers of bis-L-(aspartato)chromium(III) trihydrate complexes on temperature was further studied at 35 °C and 45 °C (Table III). It has been shown that an acid catalysed exchange process between H_2O and COO groups bound to a transition metal gives rise to discrimination between the two oxygen atoms, as the electron-rich centre is favoured [8, 9]. Acid catalysed ring-opening usually involves protonation of the carbonyl oxygen in a rapid equilibrium step and this is then followed by a slow rate determining step involving the opening of the chelate ring with a cleavage of the Cr–O bond as the above scheme indicates.

TABLE III. Acid Catalysed Ring-opening of Bis-L-(aspartato)chromium(III) Trihydrate Chelate (Kinetic Measurements)

Temperature (°C)	$[H^+] \times 10^{-3}$ (M)	$k_{obs} \times 10^3$ (s^{-1})		k_H ($M^{-1}\,s^{-1}$)	
		red isomer	violet isomer	red isomer	violet isomer
25	6.0	4.3	4.40	0.70	0.72
	9.0	6.60	6.80	0.73	0.74
	12.0	8.20	8.50	0.72	0.73
	15.0	11.0	11.50	0.71	0.72
	18.0	16.0	17.0	0.74	0.71
35	1.0	1.80	2.0	1.90	2.0
	2.0	3.30	4.0	1.70	1.85
	3.0	7.50	8.50	1.80	1.90
	4.0	11.50	12.60	1.74	1.95
	5.0	15.0	16.50	1.85	1.90
45	1.0	2.50	2.60	2.70	2.80
	2.0	4.20	4.55	2.10	2.30
	3.0	6.85	7.0	2.35	2.42
	4.0	10.0	11.10	2.60	2.65
	5.0	14.50	16.0	2.50	2.70

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