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Circular Dichroism and the Configuration of Deprotonated Tris-Tartrato Chromium-(III) Complex

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A complex with the composition $Cr(TH_{-1})_3$ (T = RR-tartrate^{2-}) has been characterised in solutions with excess of tartrate by circular dichroism (CD) and potentiometric data. The CD shows peaks $\epsilon_l - \epsilon_r/M^{-1}$ cm^{-1} *of +4.60 at 570 nm and –0.80 at 655 nm. Together with stereochemical considerations this strongly indicates that the complex $Cr(RR\text{-}TH_{-1})_3$ takes the Λ configuration. The partially protonated forms show less pronounced stereoselectivity.*

Introduction

The complexes of trivalent chromium provide perhaps the largest number of fascinating optical properties among the transition metals. For instance, the sharp spin-forbidden transitions from the $^4A_2$ ground state to the states deriving from ^2G in a trigonally distorted octahedral coordination site formed by oxygen atoms play a key role in the operation of the ruby laser. A number of D_3-symmetric Cr(III) complexes exhibit strong photoinversion in solution and this property has been used to produce partial optical enrichment by irradiation with circularly polarised light [1, 2]. Most recently it was shown that alkaline chromium(III) solutions containing racemic tartrate become optically active when exposed to circularly polarised light [2]. Mathieu [3] and Kuhn [4] in their classical papers on optical activity observed that chromium tartrate solutions exhibit strong circular dichroism in the absorption band at lowest energy. In fact the molar circular dichroism ($\Delta\epsilon = \epsilon_l - \epsilon_r/M^{-1}$ cm^{-1}) peak value at 580 nm (+3.6 Kuhn [4], +3.77 Mason [5], +4.6 this study) and the corresponding dissymmetry factor, $\Delta\epsilon/\epsilon$ = +0.081 at 555 nm (this study) are very large for an inorganic complex, though not so large as for some organic compounds (0.2 for certain dissymmetric ketones [6]). In his classical studies on dihedral metal complexes, Mason tentatively assigned the circular dichroism to a tris-tartrato complex [5] but no investigation clarifying the composition of the complex or the possible abundance of different configurational isomers and conformers has been carried out. With the aim of throwing some light on this matter we have studied solutions with high tartrate concentrations where the chromium can be expected to have saturated coordination and the formation of polynuclear complexes would be suppressed. Due to systematic errors caused by ionic strength variations it was not found relevant to extend the study to a traditional quantitative examination of the complex formation.

Methods

Solutions, 10 m*M* in Cr^{3+}, were prepared from $Cr(NO_3)_3\cdot9H_2O$ and $Na_2\text{-d-}C_4H_4O_6\cdot2H_2O$, both of *p.a.* quality. The Cr^{3+} concentration was determined by indirect complexometric titration according to Szekeres *et al.* [7]. The stoichiometric concentration of hydrogen ion, C_H, was varied by the addition of standardised NaOH or tartaric acid, $\text{d-}C_4H_6O_6$ *p.a.* The total concentration of tartrate was kept at 1.00 *M*. The fairly low solubility of sodium hydrogen tartrate sets an upper limit to the hydrogen ion concentration.

Since equilibrium was reached rather slowly the measurements were done a week after the preparation of the solutions. pH was measured with a Jena glass electrode U 9201 and circular dichroism with a JASCO J-41 dichrograph. Measurements repeated after another week confirmed that equilibrium was established.

The glass electrode was calibrated by pH-measurement of solutions that were similar to those above, *e.g.* with standardised NaOH and 1.00 *M* Na_2tartrate (but without Cr^{3+}). Measurement on corresponding chromium-free solutions with tartaric acid instead of NaOH made it possible to estimate the dissociation constants of tartaric acid (K_1 = 1.4 × 10^{-3} *M*, K_2 = 8.7 × 10^{-5} *M*). When the stoichiometric hydrogen ion concentration, the pH* of the chromium tartrate solutions, and the dissociation constants

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*For footnote, please see overleaf.

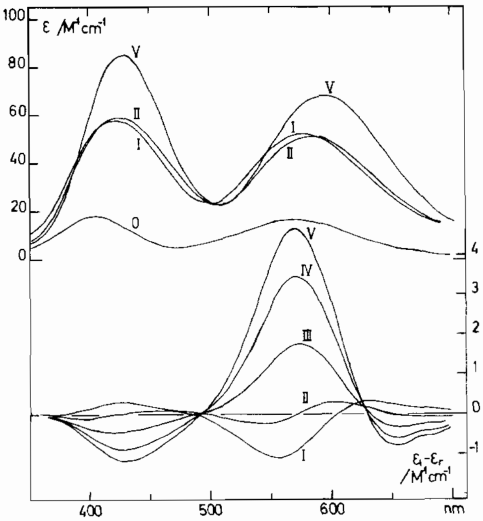

Figure 1. Absorbance (top) and circular dichroism (bottom) spectra of 0.010 *M* Cr^{3+} in aqueous 1.00 *M* tartrate solutions:

0. 0.010 *M* $Cr(NO_3)_3$
I. pH = 4.6, C_H = 0.200 *M*
II. pH = 6.3, C_H = −0.0100 *M*
III. pH = 7.0, C_H = −0.0250 *M*
IV pH = 7.6, C_H = −0.0286 *M*
V. pH = 11.7, C_H = −0.0357 *M*

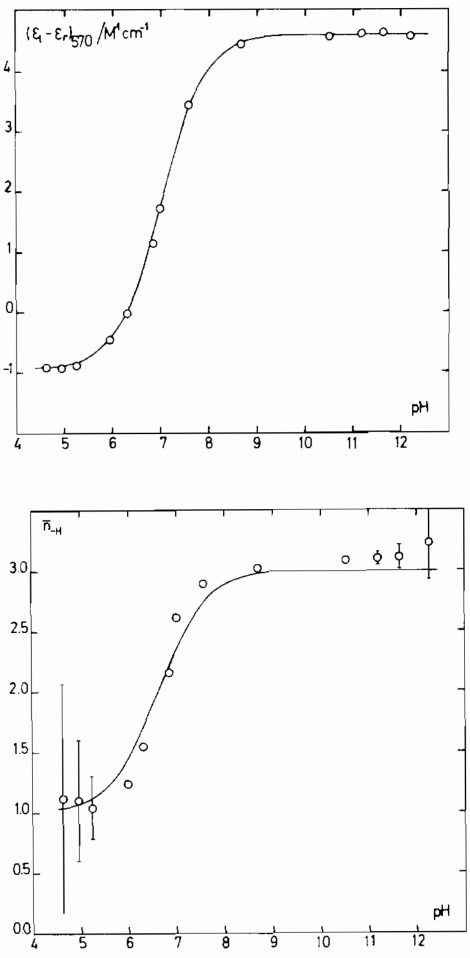

Figure 2. a) Observed circular dichroism (570 nm) *versus* pH (○). b) $\bar{n}_{-H}$ *versus* pH. Full lines represent an attempt to fit these data with a model including three complexes CrT_3H_{-1}, CrT_3H_{-2}, CrT_3H_{-3} with the β_n/β_{n-1} ratios 7 × 10^{-7} and 9 × 10^{-8} and specific circular dichroisms $\Delta\epsilon(M^{-1}$ $cm^{-1})$ = −0.92, −0.30, +4.60.

of tartaric acid are known, the average number of protons liberated from the chromium tartrate complexes can be calculated.

If we denote the tartrate ion $C_4H_4O_6^{2-}$ with T, we say that a complex with the formula $[CrT_yH_{-x}]^{3-2y-x}$ has lost x protons, irrespective of whether the protons have been derived from coordinated tartrate ions or water molecules. Then we define the stoichiometric hydrogen ion concentration, C_H, as $-C_{NaOH}$ or $2C_{C_4H_6O_6}$ and the average number of released protons is given by

$$\bar{n}_{-H} = \frac{-C_H + h - oh + [HT] + 2[H_2T]}{C_{Cr}} \qquad (1)$$

As can be seen from Fig. 2b the estimated errors in $\bar{n}_{-H}$ at low pH are very large since the numerator is now determined by the difference between two large quantities, C_H and the sum [HT] + 2[H_2T]; the calculated hydrogen tartrate concentrations are thus very sensitive to error in the pH measurements and subject to the uncertainty of the dissociation constants of tartaric acid.

Results

Fig. 1 shows how the circular dichroism of chromium(III) in the presence of excess of tartrate is very sensitive to pH. The very large specific CD at high pH suggests an almost complete stereospecificity. At lower pH the CD spectrum is of low intensity and resembles the mirror image of the high-pH spectrum though shifted by 10–15 nm to shorter wavelength. Fig. 2a shows CD at 570 nm *versus* pH.

From potentiometric measurements the amount of protons released was determined when the pH was changed from 4–12. As is clear from Fig. 2b, at

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[*] Strictly speaking it is the hydroxide ion concentration that is determined. At the formal representation as pH the ion product of water is taken as 1 × 10^{-14} M^2. This approximation also affects the numerical values of the dissociation constants given above but not the calculation of [HT] and [H_2T] in eq. (1). h is the only term of eq. (1) that is affected but this is of minor importance.

pH = 7 there is a sudden consumption of hydroxide ions leading to a result corresponding to a total release of three protons per chromium ion. As indicated by the bars in Fig. 2b the low pH range is uncertain and the apparent stabilisation at $\bar{n}_{-H} = 1$ may not be significant.

The attempt to describe the CD and $\bar{n}_{-H}$ data with a model based only on the complexes CrT_3H_{-n}, n = 1,2,3, is represented by the full lines in Fig. 2. It should be noted however that this attempt is tentative and that other models may describe our data equally well.

At pH > 11 the CD spectrum is practically insensitive (change less than 2%) to a change in tartrate concentration down to 0.6 *M*. This is strong evidence for a saturated coordination. At pH = 4.6 the decrease in tartrate concentration immediately results in an increase of the negative CD deflection (finally reaching a maximum change of about 40% at *ca.* 0.5 *M* tartrate). From this we can conclude that at low pH in the 1.00 *M* tartrate solution there must be an equilibrium between complexes with different tartrate coordination numbers. Thus the model corresponding to the lines in Fig. 2 is not strictly adequate at low pH.

Discussion

From the fact that the CD in the alkaline range is independent of the tartrate concentration it can be concluded that a complex with saturated coordination is formed. The simultaneous release of up to three protons supports the concept of a complex, $Cr(TH_{-1})_3$, with three tartrates in chelate coordination. Polynuclear species can be dismissed since the specific CD is independent of the total Cr(III) concentration in the range 0.001–0.01 *M*, at a large excess of tartrate. As mentioned, the measurements do not give any firm basis for characterisation of the complex composition at low pH.

The absolute configuration of the $Cr(RR\text{-}TH_{-1})_3$ complex can be safely concluded as Λ. This follows from the empirical rule for the rotational strength of the lowest spin-allowed d–d transition in trigonal d^3, d^6 complexes with planar chelate rings [5]. The CD pattern (*cf.* Fig. 4) at the lowest spin and magnetic dipole allowed transition $^4T_{2g} \leftarrow {}^4A_{2g}$, which has a strong positive peak at 570 nm and a weaker negative component at 655 nm, closely resembles the corresponding CD features of the tris-acetylacetonato and tris-oxalato chromium(III) complexes [2]. This

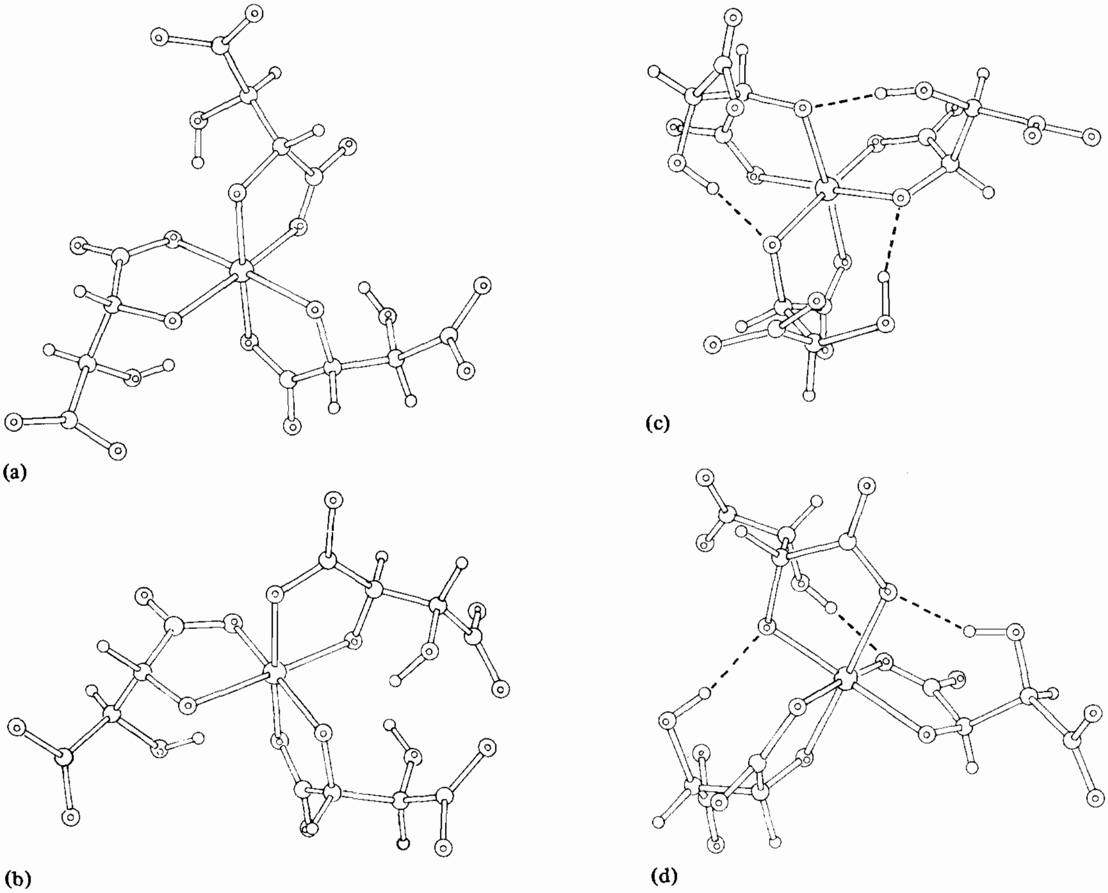

Figure 3. Configurations of tris-F-tartrato Cr(III): a) Δ-*fac*, b) Δ-*mer*, c) Λ-*fac*, d) Λ-*mer*.

configuration is also supported by the negative CD of the corresponding band in mixed tartrate-bridged binuclear chromium complexes [8] where the Δ configuration has to be adopted for steric reasons [9].

The fact that the three protons are released at a much lower pH than would be expected if the hydroxyl oxygen was not coordinated, demonstrates the presence of the five-membered carboxylate–hydroxyl chelate ring. This form of coordination in fact frequently occurs in tartrate complexes in the solid state [10, 11].

Figure 3 shows some possible arrangements of the tartrate ions in a tris-tartrato complex. From the models it is evident that the five-membered ring must be practically planar. In the figure we have placed the tartrate carboxyl groups in a *trans* conformation, which seems to be the exclusively occurring conformation in solid RR-tartrates [10]. In the completely deprotonated tartrate ion this conformation should be stabilised by 13 kJ mol^{-1} according to a calorimetric study of vanadyl tartrates [12, 13].

The structures in Fig. 3 show the *facial* and the *meridional* isomers of each of the two possible absolute configurations. Among the different alternative combinations based on transoid conformations the Δ-*mer* form seems improbable since it would imply repulsive steric interaction. Of the remaining three structures the Λ forms, particularly the Λ-*fac*, can be stabilised by hydrogen bonds. In the Λ-*fac* isomer the remaining hydroxyl proton of each tartrate can form a hydrogen bond with the deprotonated coordinated hydroxyl oxygen of the adjacent tartrate ligand.

From the $\bar{n}_H$ and CD data in Fig. 2 it can be shown that introducing one proton in Λ-$Cr(TH_{-1})_3$ immediately leads to a tremendously decreased total CD, *i.e.* that the absence of all three protons is necessary for the Λ stereospecificity. It is possible that a decreased chelating tendency of the protonated tartrate ligand leads to coordination of one water molecule or a fourth tartrate ion. The greater mobility of a unidentate tartrate may drastically change the possibilities for hydrogen bonding.

The variation of the CD with the tartrate concentration at low pH demonstrates the appearance of a complex with a changed number of tartrates in the coordination sphere. The fairly strong CD indicates the presence of complexes with at least two chelate rings also in this pH range. However the reversed CD sign shows that the Δ configuration now predominates. The spectrum resembles the mirror image of that assigned to the Λ-$Cr(TH_{-1})_3$ complex (shown in Fig. 4) but has about four times lower magnitude and is shifted about 15 nm towards lower energy. The shift would be expected according to the spectrochemical series if the release of the tartrate hydroxyl protons is seen as an analogue to change of ligand from H_2O to OH^-. The shift is also observed for the $^4T_{2g} \leftarrow {}^4A_{2g}$ absorption band whose position in the protonated complexes in fact agrees with that of the aqueous chromium complex (*cf.* 0, I and V in Fig. 1). The sharp $^2E_g \leftarrow {}^4A_{2g}$ transition at 667 nm in the aqueous complex is shifted to 709 nm in $Cr(TH_{-1})_3$, which is surprising in that the energy separation of these states should be practically independent on the ligand field [14]

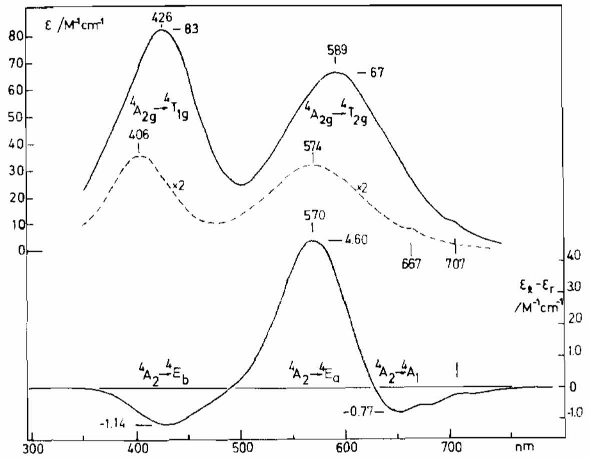

Figure 4. Spectral characteristics of Λ-$Cr(RR\text{-}TH_{-1})_3$; $\Delta\epsilon/\epsilon$ = +0.081 at 555 nm. For comparison the ϵ of $Cr(H_2O)_6^{3+}$ is displayed; broken line.

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