# *SEPARATION AND CHARACTERISATION*

# *OF*

# *CHROMIUM(III) CARBOXYLATE SOLUTIONS*

A thesis submitted to Rhodes University
for the degree of

MASTER OF SCIENCE

by

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# C O N T E N T S

# INTRODUCTION

The conversion of putrescible skin into the stable product leather, is described by the word 'tan', i.e. leather is collagen (skin protein) in the tanned state. The first criterion of the tanning potency of a substance is its capacity to form an irreversible combination with collagen, resistant to the action of water. The second criterion is the ability of the tanning agent to stabilize the collagen by improving its resistance to heat, proteinases, and swelling agents. The tanning agent supplies crosslinks between the protein chain and so compensate for the loss of internal cohesion of the weave structure in the skin brought about by the conditioning and pre-treatment before tanning.[1]

Tanning agents can be divided into two main classes: (1) the mineral tannages and (2) the tanning agents of an organic nature. Condensed tannins (catechol tannins), extracted from, for example, quebracho and wattle trees, and hydrolzable tannins (pyrogallol tannins), extracted from, for example, chestnut trees, are the most significant of the natural organic tanning agents. The reaction in vegetable tanning, is believed to involve the multipoint hydrogen bonding of the phenolic tannin to the peptide linkage of the collagen.[2]

The most significant mineral tannages are those with salts of chromium(III) and to a lesser extent, zirconium(IV) and aluminium(III).[3] Although aluminium salts were in use in Egyptian times, they were superceded in importance by chromium(III) salts; the first chrome leather was produced in 1884.[4] Chrome tanning agents are basic chromium(III) sulphate salts, which impart unique properties to leather. The high shrinkage temperature (the temperature at which a measureable shrinkage occurs when leather is gradually heated in water) of chromium tanned leather is indicative of the high degree of stabilization of the weave structure that chromium tanning can impart.[5]

The process of chrome tanning involves the co-ordination of chromium to the carboxyl groups of the collagen.

In addition, chromium(III) has the ability to form polynuclear complexes

which are large enough to bond to two carboxyl groups on separate protein chains, and thus stabilize the collagen lattice by cross-linking.[6]

Bjerrum's classical experiment in which he showed that the pH vs volume graph for the titration of the $Cr(H_2O)_6^{3+}$ ion by alkali was not retraced in the back titration by acid, implied that the initial basic species, $Cr(H_2O)_5OH^{2+}$, must undergo further reactions to give products that react only slowly with acids.[7] He proposed the formation of the polymerized products, $(CrOH)_2^{4+}$, $(Cr(OH)_2)_6^{6+}$ and $(Cr(OH)_{2,5})_{12}^{6+}$.

The initial steps in this olation process can be represented by the following equations.

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H^+ \quad \ldots\ldots (1)$$

$$[Cr(H_2O)_5OH]^{2+} + [Cr(H_2O)_6]^{3+} \longrightarrow [(H_2O)_4Cr(OH)_2Cr(H_2O)_5]^{5+} \longrightarrow$$

$$[(H_2O)_4Cr(OH)_2Cr(H_2O)_5]^{4+} \longrightarrow [(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+} \quad .. (2)$$

The acid dissociation constant of $Cr(H_2O)_6^{3+}$ has received much attention. pK Values ranging from 3,8 to 4,4 at different ionic strengths have been reported.[8]

Leather chemists were soon to realise that these polynuclear complexes existed in the basic chromium(III) solutions used in the tanning process.[9] The dinuclear complex, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, was proposed to exist in tanning liquors, to explain the fall in pH of the chromium tanning liquors when either heated or aged.[9] A molecular weight determination, by the freezing point depression method, on a basic and aged chromium(III) nitrate solution confirmed that dinuclear compounds were present.[10]

The titration of a refluxed solution of a basic chromium(III) salt by ammonium paramolybdate was interpreted to indicate the presence of a

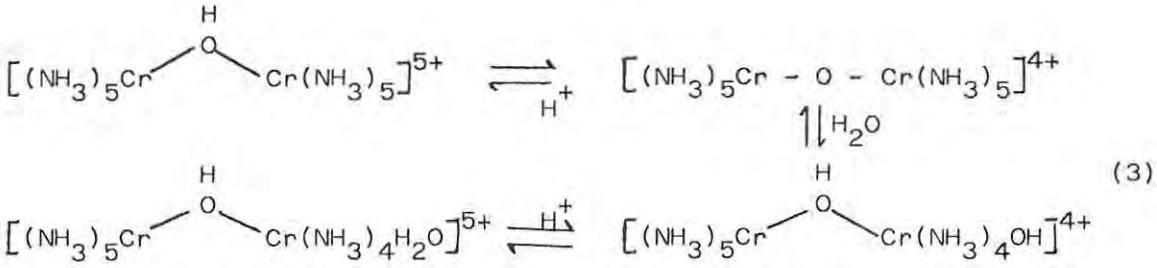
dinuclear oxygen bridged complex.[11] However, it was subsequently shown that depolymerization of the chromium(III) species and fragmentation of the polymolybdate tended to occur during the titration which invalidated this method.[12]

More recent work has been based on separation by ion exchange chromatography of the species present in refluxed chromium(III) nitrate and perchlorate solutions.[12-14] Three fractions were obtained, the first representing unreacted monomer, $Cr(H_2O)_6^{3+}$, followed by two new species of higher charge, viz. $(CrOH)_2^{4+}$ and $Cr_3(OH)_4^{5+}$. The nuclearity of the above species was determined from the ion exchange data.[14] In addition, the dinuclear nature of the second species, which had also been isolated from oxidized chromium(II) solutions,[15-17] was confirmed by cryscopic measurements.[14] An $^{18}O$ isotopic exchange study showed that the dinuclear species contained an hydroxo and not an oxo bridge.[17] Magnetic susceptibility data indicated that the trimer, $Cr_3(OH)_4^{5+}$, was linear.[14]

The presence of higher polymers was noted in solutions prepared in the presence of sodium hydroxide.[12-14,18] These high order polymeric species, in conjunction with the other three species previously mentioned, were recently detected in solutions of neutron irradiated crystals of potassium dichromate.[19]

Attempts to crystallize the dimers, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ and $Cr(H_2O)_5CrOHCr(H_2O)_5^{5+}$, from aqueous solutions have failed.[14] However, the existence of hydroxo and dihydroxo bridges is now well documented in the literature.[20]

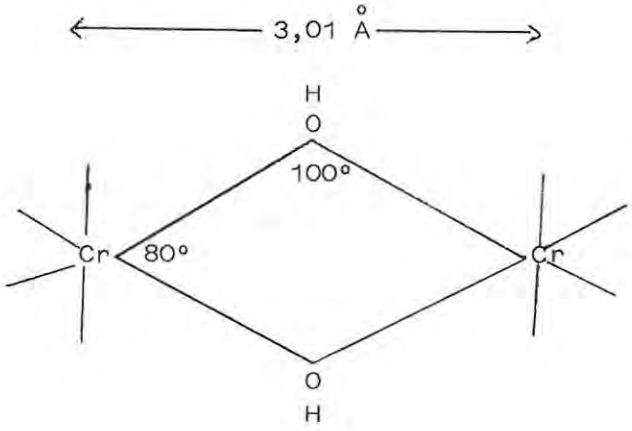
The dinuclear erthyro and rhodo chromium(III) complexes have been the subject of considerable interest since their discovery by Jorgensen in 1882.[21] It is now well established that these complexes are related by a common oxygen bridge and undergo the following transformations.[22]




(3)

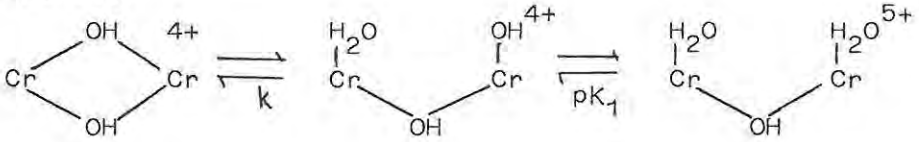
The hydroxo bridged complex was shown, by X-ray means, to be exceptionally strained with a Cr to Cr distance of 3,86 Å and a Cr OH Cr angle of 166°.[23-25] The oxo bridged species adopts a linear configuration, with the Cr to Cr distance decreasing to 3,67 Å through the formation of a system of $\pi$ molecular orbitals involving the Cr d$\pi$ and bridging Op$\pi$ orbitals.[25] The $\pi\pi$ bonding capacity gives oxo bridged complexes very distinctive UV-visible absorption spectra.[26]

Some dihydroxo bridged chromium(III) complexes (or diols) have been prepared as crystals suitable for X-ray structure elucidation, viz. $(en)_2Cr(OH)_2Cr(en)_2^{4+}$,[27-28] $(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$,[29-30] $(gly)_2Cr(OH)_2Cr(gly)_2^{4+}$,[31] $(mal)_2Cr(OH)_2Cr(mal)_2^{4+}$,[32] and $(pyrX)H_2OCr(OH)_2CrH_2O(pyrX)^{4+}$;[33] where en = ethylenediamine, phen = 1,10-phenanthroline, gly = glycinato, mal = malonato and pyrX = 4-hydroxo 2,6-dicarboxylatopyridine. The average distances and angles for the above complexes is shown below.




The incorporation of two bridges has reduced the CrOHCr angle and the Cr to Cr distance and distorted the chromium octahedra.

The reaction mechanism of the cleavage of mono and dihydroxo bridged dinuclear chromium(III) complexes has been extensively studied.[34] Diol bridged species have been shown to undergo reversible ring opening,



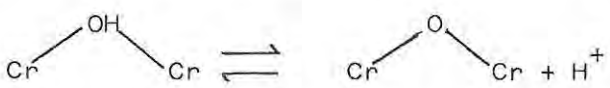
..... (4)

(Waters not involved in the above and in all subsequent reactions have been omitted for clarity).

Rate constants ( k ) for $(Ox)_2Cr(OH)_2Cr(Ox)_2^{4+}$,[35] $(en)_2Cr(OH)_2Cr(en)_2^{4+}$,[36] and $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$,[14] of $1{,}9 \times 10^{-3}\,sec^{-1}$, $4{,}9 \times 10^{-5}\,sec^{-1}$ and $1{,}5 \times 10^{-6}\,sec^{-1}$ respectively, were determined. It has been observed that the rate of cleavage of the diol bridge in $[(phen)_2Cr(OH)_2Cr(phen)_2]^{4+}$, is dependent on the hydrogen ion concentration.[34] This rate constant of $1 \times 10^{-4}\,mol^{-1}\,sec^{-1}$ relative to the rate constant for the protanation of a free hydroxo group of $10^{11} - 10^{12}\,mol^{-1}\,sec^{-1}$,[37] indicates that hydroxo bridge cleavage is a much slower reaction.

The acid dissociation constants ($pK_1$) for $(en)_2Cr(OH)(H_2O)Cr(en)_2^{5+}$,[38] $(H_2O)_4CrOHCr(H_2O)_4^{5+}$,[14] and $(NH_3)_5CrOHCr(NH_3)_4H_2O^{5+}$,[22] of 1, 1,6 and 2,8 respectively, relative to those for $Cr(H_2O)_6^{3+}$, $Cr(NH_3)_5H_2O^{3+}$ of 4,3 and 4,4,[8] respectively, indicates that the presence of a hydroxo bridge greatly increases the acidity of the complex.

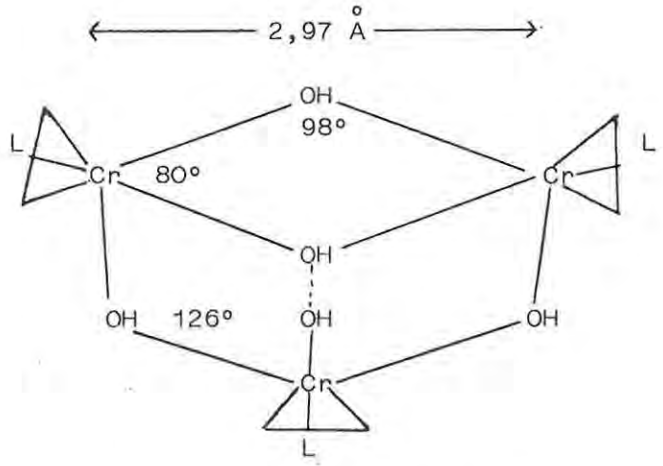
The deprotanation of the bridges to form oxo bridges, as shown in equation 5, occurs at high pH values, with $pK_1$ values of 7,60 and 12 having been reported for $(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$[39] and $(en)_2Cr(OH)_2Cr(en)_2^{4+}$,[38] respectively.(when phen = 1,10 phenanthroline).



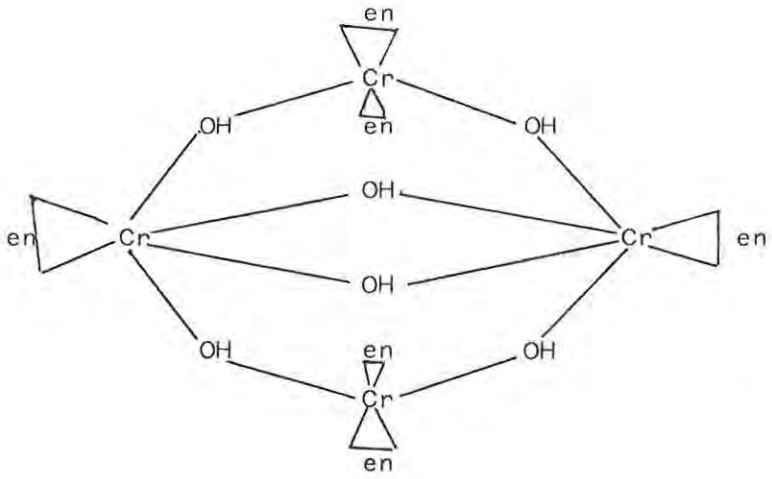
..... (5)

Other more complicated cyclic trinuclear and tetranuclear hydroxo bridged chromium(III) complexes have been prepared. Their structures

have been determined by X-ray diffraction,




L = 1,4,7 triazacyclononane




en= ethylenediamine

Two types of hydroxo bridges exist with the monohydroxo bridge having a larger Cr to Cr distance and Cr - OH - Cr bond angle than the dihydroxo bridge.

The relative affinity of a ligand for chromium(III) ions has been arranged in an order,[43] viz. perchlorate, nitrate, chloride, sulphate, formate, acetate, oxalate and hydroxyl. An attempt to connect this order to the dissociation constant of the acid[44] has been shown to only loosely hold when recent, reliable values were used.[45] However, it has been shown that perchlorate will only co-ordinate the chromium(III)

under very extreme conditions.[46]

Tanning with chromium(III) sulphate solutions, relies partly upon the diversity of the nature of the complexes present in solution.[3] Early work on the nature of chromium(III) sulphate solutions using conductimetric titrations, although not suitable for the structural assignment to complexes in solutions, was useful in showing the effect that the presence of sulphate ions had on the olation process.[47] More recent work, based upon sophisticated separation techniques, has allowed the isolation and characterisation of the various complexes present in chromium(III) sulphate and basic chromium(III) sulphate solutions, i.e in chromium tanning liquors. Ion exchange chromatography,[48-52] electrophoresis,[53] and gel filtration chromatography[54,55] have been used in the separation of these complexes.

Ion exchange chromatographic separations have proved more suitable for the separation of chromium(III) sulphate solutions. Very acidic chromium(III) sulphate solutions contain complexes with only monodentate sulphato ligands, $Cr(H_2O)_5SO_4^+$ and $Cr(H_2O)_4SO_4^-$.[48] The co-ordination mode of sulphato ligands may be ascertained from infra-red data.[56] The crystalline monosulphato complex has been prepared, $[Cr(SO_4)(H_2O)_5]Cl.0,5H_2O$, and infra-red bands at 1 002, 1 068 and 1 118 $cm^{-1}$ confirm that the sulphato ligand is monodentate.[49] The acid dissociation constant for this complex has been determined as pK = 4,65.[57]

The following new dinuclear sulphate complexes have been isolated, from less acidic solutions; $Cr(OH)_2SO_4Cr^{2+}$,[50,57] $CrOHSO_4Cr^{3+}$,[50,51], $CrOHSO_4CrSO_4^{2+}$,[57] and $Cr(OH)(SO_4)_2Cr^{2+}$.[57]
Only one of these complexes has been crystallized viz.

$$[(H_2O)_3CrOH(SO_4)_2Cr(H_2O)_3]Cl.0,5H_2O.$$[57]

The crystal structure of the related complex, $[(en)_2CrOHSO_4Cr(en)_2]_2(S_2O_6)_3.2H_2O$, also indicates that the sulphato ligand is bridged but the angle in the hydroxo bridge (137,4°) and the Cr - Cr distance (3,706 Å) show that the bridging ring is not strained.[58]

Results from this laboratory have also shown that a non ionic complex,

$(H_2O)_3Cr(OH)_2SO_4CrSO_4(H_2O)_2$, and an anionic complex, $(H_2O)_2SO_4Cr(OH)_2SO_4CrSO_4(H_2O)_2^{2-}$, exist in chromium(III) sulphate solutions.[59] Highly basic chromium(III) sulphate solutions contain complexes that have speculatively been assigned the formulae, $Cr_3(OH)_4SO_4^{3+}$ and $Cr_4(OH)_6SO_4^{4+}$.[60]

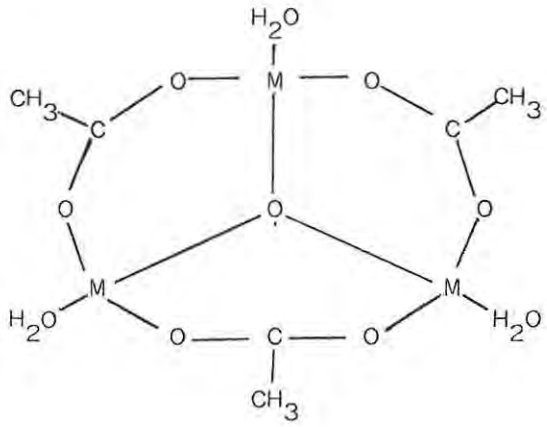
The method of preparation and the length of time before separation into the components have been shown to influence the relative concentration of the species formed.[53-55] For instance, the more basic the equilibrated solution, the higher the concentration of polynuclear, hydroxo bridged complexes.

Although basic chromium(III) sulphate salts are the main tanning agents, a more rapid and more uniform chromium tannage is achieved by the addition of salts of an organic acid, in particular formate or acetate. This effect called 'masking' results from competition for chromium co-ordination between the carboxyl groups of the collagen and the free organic acid.[1]

Some rather novel chromium(III) complexes were originally proposed to exist in 'masked' tanning liquors.[61] However, their presence has been refuted on stereochemical grounds.[45] A more recent approach using gel filtration and ion exchange chromatography has indicated that a wide variety of species are present in solutions prepared from a chromium(III) salt and sodium carboxylate.[46,47] The percentage of non ionic and lowly charged cationic species was found to increase with an increasing carboxylate concentration. A limited characterisation of the complexes present, was attempted.[62,63]

Simple mononuclear carboxylato chromium(III) complexes have been isolated from aqueous media. The acetate, $Cr(H_2O)_5OOCCH_3^{2+}$, was prepared by an indirect method via the reduction of $Co(NH_3)_5OOCCH_3^{3+}$ with $Cr(H_2O)_6^{2+}$.[64] The formate analogue was made, by the reduction of potassium dichromate with formic acid, in the presence of an excess of acid.[65] Ion exchange chromatography was used to recover the complexes and their nature was ascertained by analytical and spectral methods. A detailed kinetic study of the acetato complex was also carried out and the acid dissociation constant determined as $pK_1 = 4,35$.[64]

A green precipitate is formed from solutions made by the dissolution of chromium(III) hydroxide in hydrochloric acid and formic or acetic acids.[66] This chromium(III) carboxylate was first noted in 1919[67] and was assigned the formula, $[Cr_3(OH)_2(RCOO)_6]Cl.8H_2O$, where R = H or $CH_3$.[68] X-ray diffraction data has recently shown that the correct structure contains a triply bonded oxygen, contained within a cyclic framework.[69,70] The structure, as projected onto the $Cr_3O$ plane, is represented below,




The Cr to Cr distance of 3,28 Å was obtained.

The magnetic susceptibility data,[66,72] infra-red spectra[71,72] and visible spectra[72,73] of this and other similar iron and ruthenium complexes have been published.

The only reported dimeric chromium(III) complex containing a carboxylate bridge, $(en)_3CrOHOOCCH_3Cr(en)_2^{4+}$, has recently been prepared.[74] However, a number of cobalt(III) complexes containing carboxylato bridges have been isolated viz. $(NH_3)CoRCOO(OH)_2Co(NH_3)_3^{3+}$ [75] and $(NH_3)_4CoNH_2RCOOCo(NH_3)_4^{4+}$ [76] where R = $CH_3$ or H.

Economics[77] and the fear of environmental pollution[78] have made the practice of chromium recycling increasingly attractive to tanneries. The possibility that the recycling process may lead to the build up of complexes that are inert towards collagen, has been partially dispelled by recent work on the basic chromium(III) sulphate liquors.[77,79] The common use of salts of organic acids in the tanning process may mean

the formation of different complexes that are unreactive. It therefore seemed instructive to undertake a more detailed study of the complexes generated in aqueous media when chromium(III) ions react with sodium carboxylate, in particular sodium formate and acetate.

## EXPERIMENTAL

### 1. MATERIALS

(a) General. All chemicals that were used were of analytical grade. Distilled, de-ionised water was used in all experiments.

(b) Standard solutions. 0,1 N hydrochloric acid and 0,1 N sodium hydroxide standard solutions were made up to volume from standard ampoules.

(c) Sodium perchlorate. A stock 3 M solution was made by neutralising weighed amounts of sodium hydroxide with perchloric acid. Any carbon dioxide that was present in these solutions was removed by boiling. The solution was then cooled under an atmosphere of nitrogen.

(d) Chromium(III) perchlorate. A solution containing chromium(VI) trioxide (60 g) and perchloric acid (330 mℓ of 60% $^{v}/_{v}$ solution) was converted to chromium(III) perchlorate by the addition of an excess of hydrogen peroxide (30% $^{v}/_{v}$). The volume of solution was reduced by heating, until on cooling, a blue crystalline precipitate formed. The precipitate was filtered, washed with propan-2-ol and dried under vacuum. The absence of any polymerisation was confirmed by the comparison between the ultra-violet and visible absorption spectrum of the precipitate and the literature values for $Cr(H_2O)_6^{3+}$.[48] The purity was checked by analysing the chromium content based on the formula, $Cr(H_2O)_6(ClO_4)_3.3H_2O$ (molecular weight 512,5).[80]

(e) Chromium(III) carboxylate. 50 mℓ of a solution of sodium carboxylate (0,2 M - 2 M) was added to 50 mℓ of a solution of chromium(III) perchlorate (0,2 M). In this way solutions with chromium to carboxylate ratios of 1:1, 1:2, 1:3 and 1:9 were prepared. The solutions (0,1 M in chromium) were refluxed for 1 hour. Basified solutions were made via dropwise addition of 20 mℓ of a solution of sodium hydroxide (0,25 M - 0,5 M) to 40 mℓ of a solution of sodium carboxylate (0,25 M - 2,5 M) and 40 mℓ of a solution of chromium(III) perchlorate (0,25 M). Stock solutions with chromium to carboxylate to

sodium hydroxide ratios of 1:1:1, 1:2:½, 1:2:1 and 1:3:1 were thus made. The pH of these solutions ranged from 2,7 to 4,6. Chromium(III) perchlorate and acetic acid, in a molar ratio of 1:3, were refluxed together for 1 hour.

(f) Pentaaquaformatochromium(III). 21 mℓ of 97% formic acid was added to a solution containing 0,6 g of sodium dichromate (or chromium(VI) trioxide), 3 mℓ of 11,8 M perchloric acid, and 21 mℓ of water. The resulting solution was allowed to stand at room temperature for 3 hours. The colour changed from orange to grey purple indicating that reduction of chromium(VI) to chromium(III) had taken place. The pentaaquaformatochromium(III) ion was isolated by ion exchange chromatography.[65]

(g) Pentaaquaacetatochromium(III) and the chlorinated acetic acid analogues. 20 mℓ of glacial acetic acid was added to a solution containing 0,6 g of sodium dichromate or chromium(VI) trioxide, 3 mℓ of 11,8 M perchloric acid and 21 mℓ of water. An excess of 30% $^{v}/_{v}$ hydrogen peroxide was added to reduce the chromium(VI) to chromium(III). The solution was allowed to stand until all effervesence ceased. The pentaaquaacetatochromium(III) ion was then isolated by ion exchange chromatography. This method was more satisfactory than the laborious procedure for the preparation of pentaaquaacetatochromium(III) that has been used previously.[64]

2. SEPARATION

(a) Ion exchange chromatography. A Beckman model 130 Spectrochrom analyser was used for the ion exchange separations. Water at 10 °C was circulated through the outer jacket of a Sephadex K25/45 column, with an inner diameter of 2,5 cm. The column was packed under gravity to a height of 20 cm with Dowex 50W-X2 (100 - 200 mesh, sodium form). The chromium solution under investigation was diluted with water to give a chromium concentration of 0,05 - 0,10 M and then loaded onto the top of the column. Water was pumped through to remove any anionic and neutral species. Elution was commenced with a dilute solution of sodium perchlorate (adjusted to pH = 4), the concentration of which was increased stepwise from 0,2 M to 3 M in order to remove all the +1, +2

and +3 species in turn. The conductivity, pH and absorbance (at 420 and 570 nm) of the eluant was automatically recorded. 10 mℓ fractions were collected in a refrigerated fraction collector. A typical ion exchange separation took up to nine hours.

The resin was regenerated by washing, first with a concentrated sodium citrate solution and then with a concentrated sodium chloride solution. Chromium was irreversibly bound to the resin in some cases. A dilute, hot basic perioxide solution was therefore used to convert this chromium(III) to chromium(VI) and since the latter forms anionic complexes it could be removed from the resin.[81]

(b) Electrophoresis. A high voltage Shandon electrophoresis apparatus was used for the electrophoretic separation of the chromium solutions. A strip of Whatman No. 1 paper (10 cm x 69 cm) was soaked in the electrolyte (0,1 N $NaClO_4$, pH = 3) and 5 $\mu$l of the chromium solution spotted on the centre of the paper. The damp strip of paper was placed between two insulating plastic sheets and positioned between the cooling platens. A constant voltage of 2000 V was applied for 45 minutes. The strip of paper was removed from the electrophoresis apparatus, dried in a horizontal position and the spots developed by spraying with a dilute solution of basic hydrogen peroxide. Densitometric traces were run across the paper using a Vitration Flying Spot Densitometer TLD 100, fitted with a blue filter.

(c) Gel filtration. A spectrochrom column with a diameter of 2 cm was packed to a height of 80 cm with Sephadex G 25 gel. 5 mℓ of a chromium solution (0,1 M in chromium) was loaded onto the column and then eluted with 0,1 M sodium perchlorate. The conductivity, pH and absorbance at 420 and 570 nm were automatically recorded.

## 3. ANALYTICAL METHODS

(a) Chromium concentration. Chromium was oxidized with hot, alkaline peroxide and the resulting chromate concentration spectrophotometrically determined at 373 nm ( $\varepsilon$ = 4815mol$^{-1}$cm$^{-1}$).[82] If magnesium ions were present, sodium citrate was added to prevent the precipitation of magnesium hydroxide.

(b) Formate analysis. A two step process was required for the analysis of the formate concentration of the complexes.[65] The formate ion was released from co-ordination to chromium, by boiling a known volume of the solution ($V_1$ = volume of chromium solution, [Cr] = chromium concentration of solution) with an excess of 1 M sodium carbonate. Formic acid was then separated from the chromium hydroxide that had formed, by redissolving the precipitate with acid and then loading the solution onto a cation exchange column (10 x 2 cm, Dowex 50 -X8, $H^+$ form). Chromium(III) was retained on the resin, and the effluent containing formic acid was then analysed in the following way.[83] The hot formate solutions were basified by the addition of sodium carbonate. Standard $KMnO_4$ solution ($N_1$ = normality of $KMnO_4$) was added to this solution until it had acquired a distinct pink colour ($V_2$ = volume of $KMnO_4$). It was then strongly acidified with dilute sulphuric acid and a known volume of standard 0,1 N sodium oxalate added. ($V_3$ = volume of sodium oxalate). Excess sodium oxalate was then back titrated against standard $KMnO_4$ at a temperature of 60 °C ($V_4$ = volume of $KMnO_4$). The overall reaction can be represented by the following equations.

$$MnO_4^{=} + 8H^+ + 5e = Mn^{++} + 4H_2O \quad \ldots\ldots (6)$$

$$HCOOH + O = H_2O + CO_2 \quad \ldots\ldots (7)$$

The molarity of the formate solution could be calculated from the normality of the formate solution ($N_3$) since the equivalent weight is half the molecular weight. The formate : Cr ratio could be calculated with the aid of the following expression.

$$\text{Formate : Cr} = \frac{N_1 N_3 (V_2 - V_3 + V_4)}{2V_1[Cr]} \quad \ldots\ldots (8)$$

where each term is as defined in the text.

(c) Acetate analysis. A method based on use of an anion exchange resin has previously been used for the analysis of the acetate content of chromium(III) complexes.[84] A simpler method more suitable for

routine application, in which a steam distillation apparatus is used, has been devised.[85] A known volume of the chromium acetate complex and 20 mℓ of 2 M sulphuric acid were heated in the steam distillation apparatus. The distillation was performed very carefully, under standardised conditions, in order to prevent contamination of the distillate with sulphuric acid and to ensure quantitative evolution of the acetic acid. The acetate : Cr ratio is given by the following expression.

$$\text{Acetate : Cr} = \frac{NV_2}{[Cr]V_1} \quad \ldots\ldots \quad (9)$$

where N and $V_2$ are the volume and normality in moles/litre of the sodium hydroxide and $[Cr]$ and $V_1$ are the concentration and volume of the chromium solution, respectively.

(d) Basicity. The method first developed for aluminium salts[86] and later adapted for chromium compounds[87] was used to determine the number of hydroxo groups per chromium atom. The method is based on the displacement of all co-ordinated groups (e.g. hydroxo and acetato) from an acidic solution of the chromium(III) complex by oxalate ions, with the formation of stable trioxalatochromium(III) ions. The displaced hydroxyl ions are neutralised by a known excess of acid present which is then back titrated with standard alkali. The reaction might be written:

$$Cr(OH)_xCH_3COO + 3C_2O_4 + yH \longrightarrow Cr(C_2O_4)_3 + (y - x)H + CH_3CO_2 \quad \ldots \quad (10)$$

(ionic charges have been omitted for clarity).

In order to ensure that the reaction went to completion, the mixture of chromium solution plus a large excess of potassium oxalate (3 g) and a known excess of acid was refluxed for 20 minutes. The solution was cooled and titrated with standard alkali to a pH of 7,5. The number of hydroxo groups per chromium atom for the chromium(III) species is given by the expression:

$$\text{OH : Cr} = \frac{V_1N_1 - V_2N_2}{[Cr]V_3} \quad \ldots\ldots \quad (11)$$

where $N_1$ and $V_1$ are the volume and normality in moles/litre of the excess acid, $N_2$ and $V_2$ are the volume and normality of standard alkali, and $[Cr]$ and $V_3$ are the concentration and volume of the chromium solution.

(e) Charge per chromium atom. The chromium solutions were loaded onto a magnesium (or sodium) column and eluted with neutral magnesium (or sodium) perchlorate. The fixed ion exchange capacity of a resin determines that the total normality of the eluant and eluate remains constant.[88] The charge per chromium atom ($^+$/Cr) of the complexes present in these solutions was thus determined from the difference in the eluent ion concentration in the original eluent and the eluate. The concentrations were measured by atomic absorption using a Varian Techtron Model 1000 Spectrophotometer. The charge per chromium atom is given by the following expressions,

$$^+/Cr = \frac{2[(Mg^{++})\text{eluent} - (Mg^{++})\text{eluate}]}{[Cr]\text{eluate}} \quad \ldots\ldots \quad (12)$$

$$^+/Cr = \frac{[(Na^{+})\text{eluent} - (Na^{+})\text{eluate}]}{[Cr]\text{eluate}} \quad \ldots\ldots \quad (13)$$

(f) pH. A Beckman pH meter E532, calibrated with buffer ampoules at pH 4 and 7, was used to measure the pH.

## 4. DETERMINATION OF ACID DISSOCIATION CONSTANTS

The acid dissociation constant (pK) of the equilibrium represented below, was determined potentiometrically with a Metrohm Model E436 automatic titrimeter.

$$Cr(H_2O)_5\,Y^{n+} \rightleftharpoons Cr(H_2O)_4\,Y\,(OH)^{(n-1)+} + H^+ \quad \ldots \quad (14)$$

where $Y = H_2O, \overset{O}{\overset{\|}{O}}CH, \overset{O}{\overset{\|}{O}}CCH_3, \overset{O}{\overset{\|}{O}}CCH_2Cl, \overset{O}{\overset{\|}{O}}CCHCl_2, \overset{O}{\overset{\|}{O}}CCCl_3$.

The rapid titration of a known volume of the chromium complex solution

by standard sodium hydroxide was monitored with a combination electrode (Metrohm EA 120). The electrode system was calibrated as a $H^+$ probe against standard perchloric acid made 0,5 M in perchlorate by the suitable addition of sodium perchlorate.[89,90] The value of $\bar{n}$ (the degree of protonation) was calculated for each point from the following adapted expression.[91]

$$\bar{n} = \frac{T_H - (NaOH) - [H^+]}{[COMPLEX]} \quad \ldots\ldots \quad (15)$$

where $T_H$ is the total concentration of ionizable acid ([complex] + [initial acid]). The acid dissociation constant at $\mu$ = 0,5 was calculated with the aid of the following expression.

$$pK = p[H^+] - \log \frac{1 - \bar{n}}{\bar{n}} \quad \ldots\ldots \quad (16)$$

The temperature of each experiment was controlled at either 10 °C, 15 °C, 20 °C or 25 °C by the circulation of water through the outer jacket of the titration vessel. All determinations were done in duplicate.

## 5. SPECTRAL DATA

(a) Ultra-violet and visible spectra. All spectra were recorded at 20 °C with a Beckman Model 35 Spectrophotometer.

(b) Infra-red spectra. All spectra were recorded with a Beckman IR-10 spectrophotometer. The chromium solutions were first concentrated by removing some of the water in a freeze dryer. The infra-red spectrum was then recorded for a drop of the concentrated solution between silver chloride discs.

## RESULTS AND DISCUSSION

### 1. SEPARATION OF COMPLEXES

Three techniques, viz. ion exchange chromatography, electrophoresis and gel filtration, were used in the separation of chromium complexes.

(a) Ion exchange chromatography. The elution patterns obtained on cation exchange chromatographic separation of the chromium(III) solutions using Dowex 50W-X2 resin in the sodium form are illustrated in Figs. 1 - 5.

The best separations of chromium(III) complexes were achieved when samples of low concentration were loaded onto the column, so that initially the solutes occupied only a narrow band.[92] This necessitated diluting those solutions with high carboxylate to chromium ratios.

Ion exchange processes involve electrostatic forces, so that a complex with a higher charge has a greater affinity for the resin and thus requires a solution of a higher ionic strength for its elution. Sodium perchlorate was specifically chosen as the eluent since the perchlorate ion shows little tendency to co-ordinate to chromium(III) ions.[46]

Chromium chloride solutions contain $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr(H_2O)_4Cl_2^{+}$ [59] whilst basified solutions of $Cr(H_2O)_6^{3+}$ contain $[Cr(OH)Cr]^{4+}$ and $[Cr_2OH_4]^{5+}$.[14] These solutions were thus separated, so that the elution characteristics of a +1 ion, a +2 ion, a +3 ion, Fig. 1a, a +4 and a +5 ion, Fib. 1b, could be compared to that of the unknown fractions, Figs. 2 - 5.

The elution profiles in Figs. 2 - 5, from the separation of chromium carboxylate solutions, show that a wide range of species are present. In fact, some solutions contained not only a number of species of different net charge but also a number of the same net charge. This is well illustrated in Fig. 3a, where a non-ionic species, a +1 species, two +2 species and a +3 species were separated from a 1:2:1 solution

of $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide.

An increase in the ratio of carboxylate to chromium, in the original solutions, resulted in a decrease in cationic character. This is illustrated by comparing Fig. 2a with Fig. 3c, which shows that a solution of 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate containing mainly +3 ions, was converted to one containing mainly +1 ions, when the ratio of $Cr(H_2O)_6^{3+}$ and sodium acetate was increased to 1:3. A non-ionic constituent became the dominant component in solutions containing high concentrations of sodium acetate but did not form under equivalent conditions when sodium formate was used, since a precipitate formed. This confirmed previous findings that acetate has a greater tendency to prevent precipitation of chromium hydroxide.[1]

The profiles also show how the method of preparation can influence the type of species generated and in particular how species of lower net charge were formed in the basified solutions. This trend is illustrated in a comparison of Fig. 2a and Fig. 2b. These diagrams show that a solution of 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate originally containing mainly +3 ions, contained more +2 ions when it was basified with sodium hydroxide.

The chromatographic column and the fraction collector were kept at 10 °C to minimise any degradation of the species both during and after their separation. This was found to be necessary since it was shown that the visible spectrum of the species changed with time. All characterisations were thus performed as soon as possible after the separation of a species from its parent solution.

Attempts to separate the chromium(III) carboxylate solutions using hydrogen ion columns and acid elutants were unsuccessful. The gradual conversion into higher charged species with the resultant tailing of the peaks caused a loss in the peak resolution. The possible protonation of the acetato groups at these low pH's appears unlikely as this only occurs at very acid concentrations (above 2 M).[64] Hydroxo bridge cleavage or terminal hydroxo protonation of the complexes at high acid concentrations are more feasible explanations. (see p.24).

(b) Electrophoresis. Different mobilities of the chromium(III) species form the basis of electrophoretic separations of the chromium(III) carboxylate solutions. The mobility of a species is dependent both on its charge and its size such that a species with the highest charge and the smallest size has the greatest mobility.[93]

The scan patterns of the electrophoretic separations are represented in Figs. 6 and 7. The net charges of the chromium(III) species were determined by comparison with the mobilities of standard mononuclear chromium(III) species of known charge (Fig. 6a). Non-ionic complexes migrate slightly towards the cathode due to endosmosis.[93] $R_f$ values given, are the ratios of the mobilities of the complexes relative to that of $Cr(H_2O)_6^{3+}$.

The electrophoretic separation profiles showed the same general trends with changing carboxylate concentration and basicity as were observed from the ion exchange work. However, there were significant differences chiefly due to the fact that electrophoresis separates on the basis of size as well as net charge. A comparison between the migration distance of an unknown fraction of known charge and a monomer of the same charge allowed predictions concerning their relative sizes to be made.

The major species isolated from ion exchange columns were reseparated by electrophoresis. This allowed both the purity of a fraction to be checked and the ion exchange fractions to be compared with those from the electrophoretic separations.

The main disadvantage of electrophoresis was that only the major components could be resolved into concise peaks. The minor constituents which were seen in ion exchange separations could not be conclusively identified after electrophoresis since the background noise was excessive. In addition, the very small initial volume of solution that was used for electrophoresis (5 $\mu$l) made collection and characterisation of the species impracticable.

(c) Gel Filtration. Gel filtration fractionates species present in chromium(III) solutions according to their molecular size by a molecular

sieve effect. Small molecules diffuse into gel grains and are thus retarded in their progress down the column. Large molecules cannot enter the gel pores and they thus move through the column faster and become separated from smaller ones.

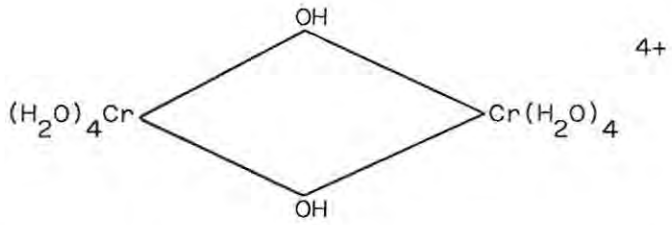
Dextran blue, a substance of very high molecular weight, was used to determine the elution volume of a solute that was completely excluded from the gel grains (Fig. 8a). The elution volume for a small mononuclear chromium(III) species, $Cr(H_2O)_6^{3+}$, was also determined (Fig. 8b). The elution profiles of the gel filtration of chromium(III) carboxylate solutions showed that there was a trend towards the formation of larger species as the carboxylate to chromium ratio was increased (Fig. 8 c and d). In fact, in solutions prepared from 1:9 $Cr(H_2O)_6^{3+}$ and sodium acetate, some species are sufficiently large to be completely excluded from the gel grains (Fig. 8). Unfortunately gel filtration, in general, did not separate the various species as well as ion exchange chromatography.

## 2. CHARACTERISATION OF NON-CARBOXYLATE COMPLEXES

The characteristation of the chromium complexes was based initially on their net charge. The nomenclature used to classify the individual complexes contains a term to represent this charge.

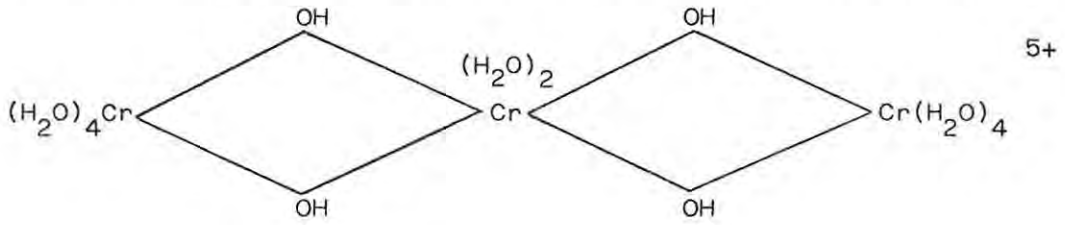
(a) Complex 3. This complex was separated as the only component from solutions of $Cr(ClO_4)_3.9H_2O$ (the starting material used in the preparation of all parent carboxylate solutions). Visible spectral data for complex 3 (Table 1) agreed closely with data for $Cr(H_2O)_6^{3+}$.[48] In addition, a solution of $CrCl_3.6H_2O$ is also known to contain $Cr(H_2O)_6^{3+}$,[59] and was thus used as the standard for determining the ion exchange characteristics (Fig. 1a) and electrophoretic mobility (Fig. 6a) of +3 fractions. A solution made from 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate or formate, was shown by electrophoretic separation (Fig. 6b) to also contain $Cr(H_2O)_6^{3+}$. Ion exchange separation of this solution gave a +3 fraction containing complex 3 and a carboxylato containing compound (see p.23). The presence of complex 3 was not detected in any solutions of higher carboxylate concentration.

(b) Complex 4. Refluxed solutions of $Cr(H_2O)_6^{3+}$ and basic solutions $Cr(H_2O)_6^{3+}$ are known to contain a +4 complex for which the following structure has been proposed.[14]




This complex was separated from these solutions by ion exchange chromatography (Fig. 1b) and identified by its visible spectrum (Table 1). Complex 4 was not detected in any chromium carboxylate solutions.

(c) Complex 5. Basified solutions of $Cr(H_2O)_6^{3+}$ are known to contain a +5 complex for which the following structure has been proposed,[14]




This complex was separated from these solutions by ion exchange chromatography (Fig. 1b) and identified by its visible spectrum (Table 1). Complex 5 was not detected in any chromium carboxylate solutions.

## 3. CHARACTERISTATION OF ACETATO COMPLEXES

(a) +3 Fraction.

(i) Complex $3a_1$. Ion exchange separation of a 1:1:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide solution (Fig. 2b) or 1:2 $Cr(H_2O)_6^{3+}$ and sodium acetate solution (Fig. 2c) gave a fraction of net charge +3. The fact that the ratio between the absorbance at 420 nm and the absorbance at 570 nm remained constant across the fraction indicated that only one complex ($3a_1$) was present (1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate solutions showed a variation of visible spectral data across the +3 fraction indicating that more than one complex was present, probably

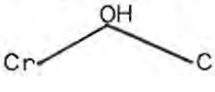
complex 3 and complex $3a_1$). The observation that only one peak was eluted when complex $3a_1$ was reloaded onto another ion exchange column confirmed this result. An electrophoretic separation of the fraction also revealed the presence of only complex $3a_1$.

Central portions of this +3 fraction were used for analysis of hydroxo to chromium and acetate to chromium ratios. The average results from four determinations on fractions separated from different ion exchange runs are shown in Table 2. An empirical formula for complex $3a_1$ was thus derived, viz. $Cr_2(OH)_2CH_3COO$.

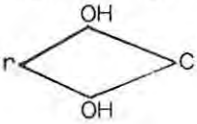
The nuclearity of the complex (i.e. dinuclear, trinuclear etc.) could not be determined on the basis of charge per chromium atom data. Charge per chromium atom determinations required an analysis of the concentration of original eluent and the concentration of the eluent in the +3 fraction. Unfortunately the difference between eluent and eluate concentration was small and together with the error associated with the atomic absorption method used in the analyses gave inconclusive results.

The molecular size of the complex was however deduced from electrophoresis (Fig. 6) and gel filtration (Fig. 8) data. A comparison of migration distances calculated from the electrophoretic scan patterns of the monomeric +3 ion, $Cr(H_2O)_6^{3+}$, and complex $3a_1$ indicated that the latter has a larger size. Gel filtration profiles confirmed this and showed that complex $3a_1$ is most probably dinuclear, since a known trinuclear complex, $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$, has a lower elution volume indicating that complex $3a_1$ has a smaller size. This agrees with the analytically determined empirical formula, $Cr_2(OH)_2CH_3COO$, which also has the correct net charge of +3 for a dinuclear complex. A tetranuclear complex $Cr_4(OH)_4(CH_3COO)_2$ is ruled out since its net charge would be +6.

The hydroxo to chromium ratio of 1 for a dinuclear complex could be explained by the presence of either an oxo bridge, Cr - O - Cr, or a single hydroxo bridge together with a terminal hydroxo group,




, or two hydroxo bridges,

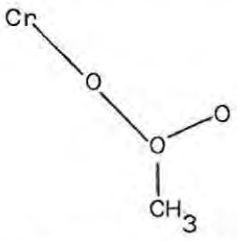



. Complex

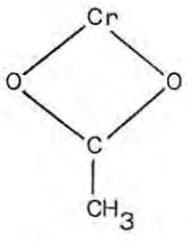
$3a_1$ has the visible spectral features of weak, broad d - d bands, typically encountered in the spectra of chromium(III) complexes.[94] (Fig. 9 and Table 2). In contrast, complexes in which the presence of an oxo bridge has been positively identified, show a number of sharp, intense peaks due to extensive $\pi$ bonding in the Cr - O - Cr group.[21-23] Investigations have also shown that these oxo bridges only exist at pH values higher than those encountered in these separations ( > 12).[38] Oxo bridging can thus be ruled out.

The visible absorption spectrum of complex $3a_1$ did not change immediately on acidification to an acid concentration of 1 M. However, a gradual change did occur with time. A terminal hydroxo group is hence unlikely to be present in complex $3a_1$, since a terminal hydroxo group would have been protonated under these conditions of measurement and an immediate change in the spectrum would be expected. The visible absorption spectrum of an acidified solution (1 M in hydrogen ion concentration) of complex $3a_1$ did however change gradually with time. Hydroxo bridge cleavage reactions in acid media are known to be slow[34] and this type of reaction would explain the observed spectral changes in acid media, if the remaining possibility, $Cr(OH)_2Cr$, is present in species $3a_1$. In general, chromium(III) complexes with dihydroxo bridges have been well documented.[20]

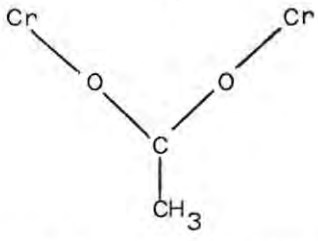
Acetato ligands can co-ordinate to chromium ions in one of three ways, represented below.




(a) Monodentate




(b) Bidentate, chelated



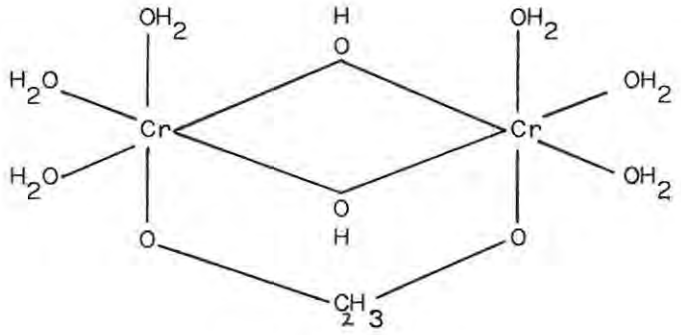

(c) Bidentate, bridged

Results of crystal structure determination on a compound with an acetato ligand chelated to ruthenium, $Ru(CH_3COO)(CO)(PMe(Ph)_2)_3$,[95] indicate that the narrow bite (90°) between the ligand and the metal introduces much strain to the structure. Such a strained structure would not be

expected to exist in solution.

The distinction between monodentately bound acetato groups (a) and bidentately bound acetato groups (c) has concerned many investigators.[96] Infra-red studies have demonstrated that the separation, $\Delta$ V, between the asymmetric and symmetric C - O stretching frequencies in acetato complexes, reflects the type of bond. $\Delta$ V decreases in the order : monodentately bound acetato, free acetate and bidentate or bridged acetato. These general features are illustrated in Table 3 which compares literature data for various cobalt compounds whose structures are now well established. The data for complex $3a_1$ and other related compounds are also included in Table 3. It is clear that $\Delta$ V values for complex $3a_1$ are lower than those for the corresponding free acetate ion indicating a bridging acetato group. A similar argument was used to predict bridging in the case of the analogous complex, $[(en)_2Cr(OH)(CH_3COO)Cr(en)_2]^{4+}$.[74]

The best structure for complex $3a_1$ that fits all the available facts is shown below,




The cobalt analogue of the above compound is known, viz. $[(NH_3)_3Co(OH)_2CH_3COOCo(NH_3)_3]^{3+}$.[75] The infra-red evidence that indicated a bridging acetato group, (Table 3) has been confirmed by X-ray analysis.[97] Further X-ray evidence has shown that when acetato bridges across two metal atoms, the organic framework remains rigid while the M - O -C angle varies from 121° for $\mu$-tetraacetato-diaquadi=chromium(II) with a Cr - Cr distance of 2,4 Å[98] to 150° (calculated from published data[70]) for a Cr - Cr distance of 3,3 Å[70] for

μ-oxo-μ-hexaacetato-triaquatrichromium(III).

(b) +2 Fraction.

The ion exchange elution properties and electrophoretic mobility of $[Cr(H_2O)_5Cl]^{2+}$ (present in chromium(III) chloride solutions[59]) was used as the standard for the +2 fraction.

(i) Complex $2a_1$. The ion exchange separation of an acidic solution prepared by the reduction of Cr(VI) to Cr(III) in the presence of excess acetic acid (Fig. 1c) and a refluxed solution of 1:3 $Cr(H_2O)_6^{3+}$ and acetic acid, gave a fraction whose elution characteristics (Fig. 1c) and visible absorption spectrum (Table 1) agreed with the literature data[64] for $[Cr(H_2O)_5CH_3COO]^{2+}$.

It was shown in the previous section that a distinction between an acetato group co-ordinated monodentately to a metal ion and one co-ordinated bidentately or bridged could be made on the basis of infra-red data. The separation between the asymmetric and symmetric C - O stretching frequencies (ΔV) was shown to be larger for a monodentately bonded acetato groups, compared to that for sodium acetate (Table 3).

Attempts to measure the stretching frequencies of $[Cr(H_2O)_5CH_3COO]^{2+}$ were only partially successful. Fig. 10 shows the infra-red spectra of dilute and concentrated (by freeze drying) aqueous solutions of complex $2a_1$. The dilute spectrum shows a single symmetric C - O stretching vibration at 1400 $cm^{-1}$ for the monodentate acetate ligand. Unfortunately, the strong O - H bending vibration at 1615 $cm^{-1}$ prevented the detection of the asymmetric C - O stretching vibration. However, on concentrating the solution in order to remove some of the excess water, a new band appeared at 1450 $cm^{-1}$. This was probably due to decomposition of complex $2a_1$ to a bidentate acetato complex since on dilution of the concentrated solution, the visible spectrum was observed to be different from that of the original $2a_1$ complex. The asymmetric C - O stretching band at 1570 $cm^{-1}$ in the concenrated spectrum (Fig. 10) therefore cannot really be used to calculate Δ V for complex $2a_1$. Nevertheless, using this value (it could well be at a higher frequency but is unlikely to be at a lower frequency) gives with the band at 1400 $cm^{-1}$ a Δ V value of 170 $cm^{-1}$. This is greater than that for free acetate, but is consistent with a monodentate acetato ligand.[100]

(ii) Complex $2a_2$. Ion exchange separation of a 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate solution produced a small fraction whose elution characteristics resembled that of an ion with a net charge of +2 (Fig. 2a). The fact that the ratio between absorbances at 420 and 570 nm changed across the fraction indicated more than one complex was present. An OH/Cr ratio of 0,30 from a sample taken from the centre of this fraction indicated that the fraction could be a mixture of $[Cr(H_2O)_5CH_3COO]^{2+}$ ($2a_1$) and an unknown basic acetato chromium(III) complex ($2a_2$). No attempt was made to separate and characterise this complex since it represented only a minor component of the parent solution.

(iii) Complex $2a_3$. Ion exchange separations of solutions of 1:1:1 $Cr(H_2O)_6^{3+}$ sodium acetate, sodium hydroxide (Fig. 2b) gave a major blue fraction, $2a_3$, of net charge +2. Visible spectral data across this +2 fraction, from separations of 1:1:1 solutions (Fig. 2b), indicated that complex $2a_3$ was slightly contaminated by a minor impurity (probably $2a_{1,2}$) in the tailing portion. However, reloading and eluting a central portion of fraction $2a_3$ onto another ion exchange column indicated that the complex was pure. An electrophoretic separation of a central portion of this fraction also indicated that only one complex was present. The blue +2 fraction ($2a_3$) from an ion exchange separation of a 1:2 solution, showed a greenish leading edge indicating the presence of another complex ($2a_4$ see p.30 ) with a slightly lower ion exchange selectivity than complex $2a_3$. However, central portions were again shown to be pure complex $2a_3$.

The analytical data for complex $2a_3$ is shown in Table 2 and indicates an empirical formula of, $CrOHCH_3COO$. The simplest structure corresponding to this empirical formula is the mononuclear complex, $[Cr(OH)CH_3COO(H_2O)_4]^+$. This complex could be formed by the following type of equilibrium.

$$[Cr(H_2O)_5CH_3COO]^{2+} \rightleftharpoons [Cr(H_2O)_4(OH)CH_3COO]^{+} + H^{+} \quad \ldots\ldots \quad (17)$$

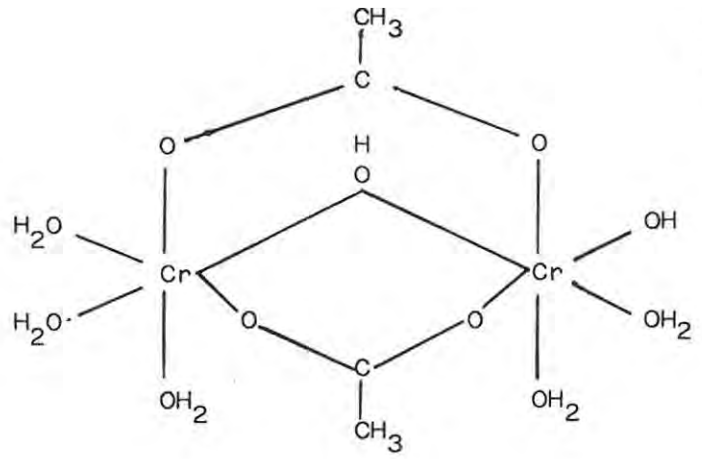
The visible spectrum of $[Cr(H_2O)_4(OH)CH_3COO]^+$ could however not be determined, by adding alkali to complex $2a_1$, due to the lability of

the hydroxo complex. However, the net charge of this complex is +1 whereas the net charge of complex $2a_3$ is known to be +2 which rules out the mononuclear complex as a possibility for complex $2a_3$.

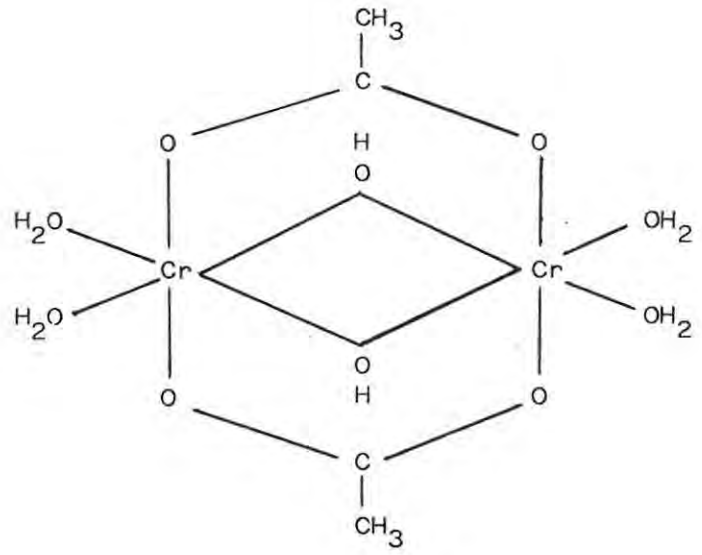
Charge per chromium atom determinations gave an average value of 1,08 from four separations in which a magnesium elutant was used. A net charge of +2 and a charge per chromium atom of 1 indicates that complex $2a_3$ is therefore dinuclear, $[Cr_2(OH)_2(CH_3COO)_2]^{2+}$. In addition, gel filtration of complex $2a_3$ and the dinuclear complex $3a_1$ showed similar elution properties, indicating that complex $2a_3$ is dinuclear.

Concentrated solutions of complex $2a_3$ were used to measure the infra-red spectrum. A rediluted solution of complex $2a_3$ was found to have the same visible absorption spectrum and thus no decomposition was assumed to have occurred during concentrating by freeze drying. The difference ($\Delta\nu$) between the symmetric C - O stretching frequency and the symmetic stretching frequency (Table 3) of 105 $cm^{-1}$ indicates that the acetato groups are bridged. Monodentately bridged acetato group could not be completely eliminated as a possibility since it was previously shown that their presence was difficult to detect due to changes in the infra-red spectra of complex $2a_1$ as water was removed. However, the absence of a peak at 1400 $cm^{-1}$ (found for the monodentate complex $2a_1$, $[Cr(H_2O)_5CH_3COO]^{2+}$ see p.26) was taken as evidence that in complex $2a_3$ both acetato groups are bridging.

The OH/Cr ratio of 1 could be explained by an oxo bridge, a bridged hydroxo group together with a free hydroxo group or two bridged hydroxo groups. Visible spectral data (Table 1) indicated that an oxo bridge is not present (see p.24). The following structures for complex $2a_3$ would thus be possible,



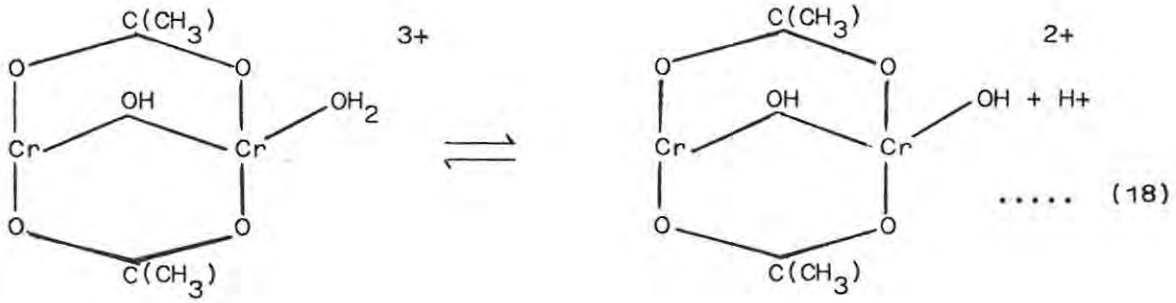

I




II

Structure I contains cis-acetato bridges whilst structure II has trans-acetato bridges. Only one hydroxo bridge is stereochemically possible for structure I whilst two are possible for structure II. The distinction between the two structures was made by the addition of acid to complex $2a_3$. Ten seconds was the minimum amount of time between acid addition and spectrophotometric measurement that could be achieved. At high acid concentrations (1 M), an immediate (i.e. within the above timescale) change in visible absorption spectrum was observed as shown

in Fig. 11. This very fast protonation indicates that a terminal hydroxo group, i.e. structure I, is probably present in complex $2a_3$. The pK for the equilibrium,




..... (18)

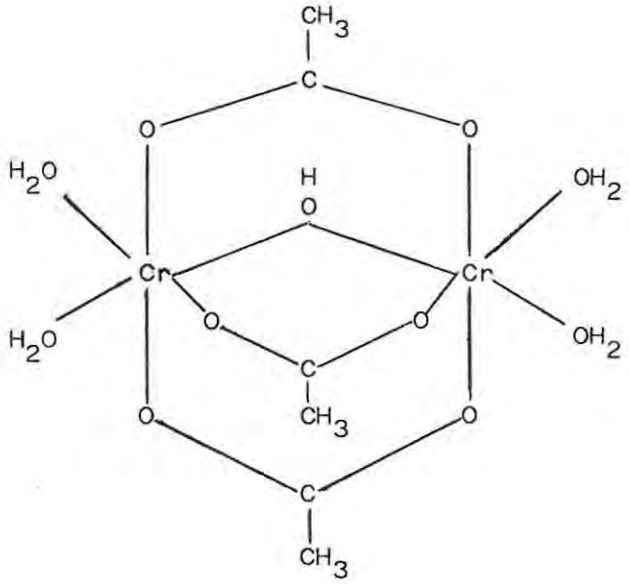
Complex $3a_2$ Complex $2a_3$

was determined by standard spectrophotometric techniques[91] as 0,6 at 25 °C and $\mu$ = 0,5. Complex $3a_3$ is thus much more acidic relative to related mononuclear complexes, $Cr(H_2O)_6^{3+}$ pK = 4,3,[8] and $[Cr(H_2O)_5CH_3COO]^{2+}$ pK = 4,8 (see later). However other hydroxo bridged chromium(III) complexes have also been found to be more acidic, viz. $[(3en)_2H_2OCrOHCrH_2O(en)_2]^{5+}$ (pK = 1),[38] $[(H_2O)_5CrOHCr(H_2O)_5]^{5+}$ (pK = 1,6)[14] and $[(NH_3)_5CrOHCr(NH_3)_4H_2O]^{5+}$ (pK = 2,8).[22]

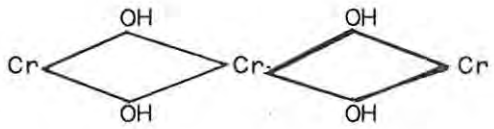
The reversibility of equilibrium (18) was proved by reloading to acid solution of complex $3a_2$ onto a sodium column. Complex $2a_3$ was recovered on elution of the column with a neutral elutant.

(iv) Complex $2a_4$. Ion exchange separation of solutions prepared from 1:2 $Cr(H_2O)_6^{3+}$ and sodium acetate contained a +2 fraction, mainly consisting of complex $2a_3$ but the leading edge of this fraction was found to be contaminated by a greenish complex $2a_4$ (Fig. 2c). Complex $2a_3$ was shown previously to form a protonated analogue (complex $3a_2$) of higher charge when it was acidified (see equilibrium (18)). The separation of complex $2a_4$ from complex $2a_3$ utilised this reaction. An acidified elutant (0,2 M $Na^+$ and 0,2 M H+) shifted equilibrium (18) to the left, thus changing the ion exchange properties of the $2a_3/3a_2$ equilibrium mixture. A neutral eluent was then used to remove complex $2a_4$ from the column for characterisation purposes. In this way complex $2a_4$ could be well separated from complex $2a_3$ (Fig. 2d).

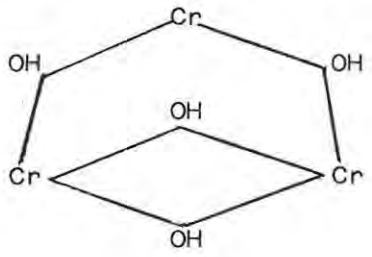
An empirical formula, $Cr_2OH(CH_3COO)_3$, was derived from the analytical data in Table 2. This formula corresponds with the net charge of +2 for the complex. The dilute nature of this minor component precluded any further characterisation of it. However, the following structure is possible,




(v) Complex $2a_5$. Ion exchange separation of a 1:2:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide solution gave a separate bluish-violet fraction ($2a_5$) of net charge +2 (Fig. 3a). Visible spectral data (Table 1) across this fraction indicated that only one complex was present. The analytical data (Table 2) gives an empirical formula of, $Cr_3(OH)_4(CH_3COO)_3$, for complex $2a_5$. This formula agrees with the net charge of +2 for this complex. Complex $2a_5$ represented only a minor component in the chromium carboxylate solutions and thus no detailed characterisation was carried out. Two types of trinuclear chromium(III) hydroxo bridged complexes are known, viz. linear,[14]



and cyclic,[40]




(non bridging ligands omitted for clarity).

Structures based on these two frameworks with three co-ordinated acetate groups are possible for complex $2a_5$.

(c) +1 Fraction

(i) Complex 1a. Ion exchange separations of solutions of 1:3 $Cr(H_2O)_6^{3+}$ and sodium acetate gave a major green fraction, 1a, (Fig. 3b) whose elution characteristics and visible spectrum agreed with the literature data[73] for $Cr_3O(CH_3COO)_6^{+1}$, a trinuclear complex with bridging acetato groups and a central oxo bridge. The visible absorption spectra for complex 1a is given in Fig. 9 which shows the extra sharp bands characteristic of the presence of an oxo bridge.[21-23] The formula was confirmed by the determination of the OH:Cr and acetate:Cr ratios (Table 2). Complex 1a was also found to be present in solutions of higher basicity and carboxylate concentration.

An infra-red spectrum of a concentrated solution of $[Cr_3O(CH_3COO)_6.3H_2O].Cl$ prepared according to the literature,[66] is shown in Fig. 12. The assignments in Table 4 are based on those for sodium acetate.[99] Infra-red data for $[Cr_3O(CH_3COO)_6.3H_2O].Cl$ have been published, giving an asymmetric C- O stretching frequency at 1595 $cm^{-1}$ and a symmetric C - O stretching frequency at 1515 $cm^{-1}$.[71] The latter value differs from the value now found (see Table 4). However, discrepancies between frequencies given for the iron analogue of the above compound in the same publication and more recently published values[72] put the earlier infra-red data in doubt. The separation between the asymmetric and symmetric C - O stretching frequencies, $\Delta V$,

determined in the present study, viz. 155 $cm^{-1}$, is less than that for sodium acetate ($\Delta V$ = 164 $cm^{-1}$)[99] indicating a bridging nature for the acetato group. This has been confirmed by an X-ray crystallographic determination of the structure of this complex.[70]

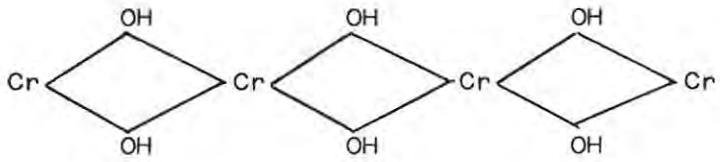
(d) Non-ionic fraction

(i) Complex $Oa_1$. A minor non-ionic component was found in solutions prepared from a 1:3 $Cr(H_2O)_6^{3+}$ and sodium acetate. A basified 1:3 solution and solutions with higher carboxylate to chromium ratios (Fig. 3c, d) were found to contain mainly non-ionic fractions. The fact that the ratio between the absorbance at 420 and 570 nm changed across the non-ionic fraction after gel filtration (Fig. 8) indicated that more than one complex was present.

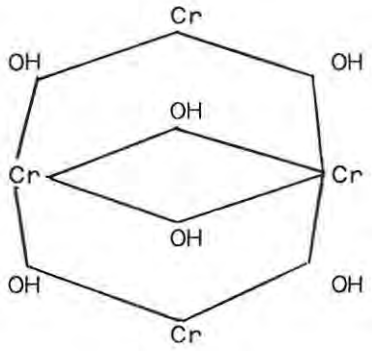
Non-ionic complexes are, of course, not retained on cation or anion exchange columns. However, it was found that if the pH of the non-ionic fraction was raised to above 9 and then reloaded onto an anion exchange column, some chromium bound to the resin. The remainder of the solution, which was now free of any sodium acetate was collected as a dilute pink solution (complex $Oa_1$).

Analysis of the pink solution (Table 2) gave an empirical formula of $Cr_2(OH)_3(CH_3COO)_3$. The visible spectrum (Table 1) did not indicate the presence of an oxo bridge. In addition, the visible spectrum did not change immediately on the addition of strong acid, thus excluding the possibility of terminal hydroxo groups. This suggests that all the hydroxo groups are bridging. On the other hand, a dinuclear structure for complex $Oa_1$, with three bridging hydroxo groups would be unique, as attempts to prepare chromium(III) complexes with this grouping have all failed.[40] However, a tetranuclear structure for complex $Oa_1$ is more likely since gel filtration of a mixture of complex $Oa_1$ and the trinuclear complex, 1a, (Fig. 8), suggests that the former comples has a larger molecular size. This would give the formula, $Cr_4(OH)_6(CH_3COO)_6$, for complex $Oa_1$.

Two types of tetranuclear chromium(III) hydroxo bridged complexes are known, viz. linear,[14]




and cyclic,[41-42]




(non bridged ligands omitted for clarity). Structures based on these two frameworks with co-ordinated acetato groups are possible for Complex $Oa_1$. Flexible models indicate that all the acetato groups of complex $Oa_1$ cannot be bridging in the above structure. Infra-red data, with a symmetric C - O stretching band at 1460 $cm^{-1}$ and a distinct shoulder at 1415 $cm^{-1}$ suggests that in fact both bridging and mondentate acetato groups are present. Attempts to prepare crystalline material for further characterisation of complex $Oa_1$, were unsuccessful.

## 4. CHARACTERISATION OF FORMATO COMPLEXES

### (a) +3 Fraction

(i) Complex $3f_1$. Ion exchange separations of either 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide or 1:2 $Cr(H_2O)_6^{3+}$ and sodium formate solutions gave a fraction of net charge +3 (Fig. 4c, 5a). The fact that the ratio between the absorbance at 420 nm and 570 nm did not change across the fraction, indicates that only one complex, $3f_1$, is present (a + 3 fraction, separated from 1:1 $Cr(H_2O)_6^{3+}$, and sodium formate solutions showed a variation of visible spectral data indicating that two complexes are present, probably complex 3 and $3f_1$).

Analytical determination of the OH:Cr and formate:Cr ratios (Table 5) gave the empirical formula, $Cr_2(OH)_2HCOO$, for complex $3f_1$. It was not feasible to determine the nuclearity of this complex by the determination of the charge per chromium atom (for the same reasons as discussed for complex $3a_1$). The nuclearity was instead deduced as dimeric from electrophoretic and gel filtration evidence using the same arguments that were used for other dimeric compounds (e.g. complex $3a_1$).

The OH:Cr ratio could be explained by 1) an oxo bridge, 2) a terminal hydroxo and a bridged hydroxo and 3) two bridged hydroxo groups. The visible absorption spectrum of complex $3f_1$ (Fig. 13) indicates that an oxo bridge is not present. Acidification of a solution of complex $3f_1$ (up to a concentration of 1 M) did not change its visible absorption spectra immediately as would be expected if a terminal hydroxo group was present. A dihydroxo bridge, $Cr(OH)_2Cr$, is the only grouping which satisfies the above findings for complex $3f_1$.

Investigators have distinguished between monodentately bound formato and bridged formato groups, on the basis of infra-red spectral data.[96] Table 7 shows data for sodium formate and for various formato cobalt(III) complexes whose structures are well established. The separation between the asymmetric and symmetric stretching frequencies

($\Delta$ V) has been shown to decrease in the order: monodentate bound formato, free formate and bridged formato. A concentrated solution of complex $3f_1$ showed infra-red bands attributable to the asymmetric and symmetric C - O stretching vibrations that were separated by a $\Delta V = 170\ cm^{-1}$ (Table 7). This value indicates that the formato group is bridging. It is therefore suggested that complex $3f_1$ has the formula, $[(H_2O)_3Cr(OH)_2HCOOCr(H_2O)_3]^{3+}$, which is the formate analogue of the acetate containing complex, $3a_1$.

(b) +2 Fraction

(i) Complex $2f_1$. The reduction of Cr(VI) to Cr(III) by formic acid has been shown to produce a significant concentration of $[Cr(H_2O)_5HCOO]^{2+}$.[65] The separation of this complex by ion exchange chromatography is shown in Fig. 4a. The visible spectral data (Table 6) agreed with published data for this complex.[65] Analytical data (Table 5) confirmed the above formula for this complex.

Problems were encountered in the measurement of the infra-red spectrum of complex $2f_1$. By analogy with the cobalt compound, $[Co(NH_3)_5HCOO]^{2+}$, (Table 7) a chromium complex containing a monodentately co-ordinated formato group would be expected to absorb at above $1600\ cm^{-1}$ (asymmetric C - O stretching mode). Unfortunately, water absorbs strongly at $1620\ cm^{-1}$ (OH bending mode) and this broad band prevented the detection of the asymmetric C - O stretching vibration. Two symmetric C - O stretching bands were observed at $1360\ cm^{-1}$ and $1300\ cm^{-1}$. The latter is probably related to the monodentately bound formato ligand of complex $2f_1$. The former increased in intensity in a concentrated sample of this fraction relative to the band at $1300\ cm^{-1}$ but decomposition also took place (as determined by a change in the visible spectrum on dilution of the concentrated sample) suggesting that the band at $1360\ cm^{-1}$ is probably related to a bidentate formato decomposition product. A distinct asymmetric C - O stretching band could not even be detected in the concentrated infra-red spectrum due to the overlying OH bending band. This precluded the determination of a $\Delta$ V value for complex $2f_1$.

(ii) Complex $2f_2$. Two major +2 fractions were separated by ion

exchange from solutions of 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide, or 1:2 $Cr(H_2O)_6^{3+}$ and sodium formate, and 1:2:½ $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide (Figs. 4, 5). The first fraction contains only complex $2f_3$ (see below). The fraction ($2f_{1,2}$) with the higher ion exchange selectivity coefficient showed a change in the visible spectral data across the peak, suggesting the presence of at least two complexes. Attempts to separate this mixture proved unsuccessful (Fig. 4d).

Charge per chromium atom ($^+$/Cr) determinations on the composite fraction ($2f_{1,2}$) gave an average value of 1,30 from four determinations with both sodium and magnesium eluents. The net charge was known to be +2. These values could be rationalised by the proposal that the fraction contains a mixture of a chromium(III) monomer and a chromium(III) dimer. A monomer with a +2 charge would have a $^+$/Cr = 2 whilst a dimer would have a $^+$/Cr = 1. The $^+$/Cr atom value could thus be explained by the presence of a mixture of 50% monomer and 50% dimer.

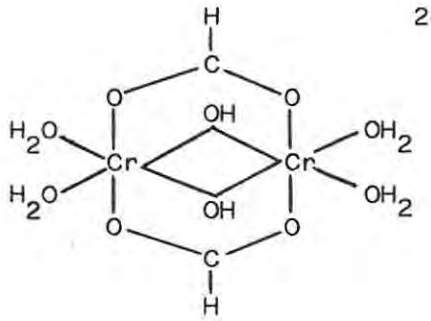
Analytical determinations on this fraction gave an OH:Cr ratio of 0,70 formate Cr ratio of 1,03. If the fraction was assumed to be pure then the empirical formula, $Cr_3(OH)_2(HCOO)_3$, would be indicated. This structure would have a net charge of +4 which would contradict the known net charge value of +2. A mixture containing 50% of $[Cr(H_2O)_5HCOO]^{2+}$ (i.e. complex $2f_1$) and 50% of a dimer, of formula, $[Cr_2(OH)_2(HCOO)_2]^{2+}$ (i.e. complex $2f_2$) would however also agree with the above data.

Ion exchange separations of a solution of 1:1 $Cr(H_2O)_6^{3+}$ and sodium formate gave a minor +2 fraction with an OH:Cr ratio of 0,30. This low value therefore indicates the presence of more $[Cr(H_2O)_5HCOO]^{2+}$ in the above mixture, viz. 70%.

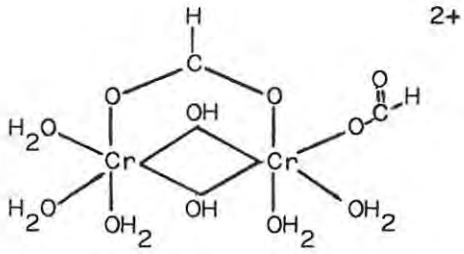
Complex $2f_1$, contains no co-ordinated hydroxo group and would thus not be expected to be susceptible to acid addition. However, attempts to separate this complex from complex $2f_2$ by using an acidified eluent were unsuccessful since tailing of the peaks occurred (Fig. 4d) due to decomposition (probably as a result of hydroxo bridge cleavage of the dimer in the acid media).

The visible absorption spectrum of this fraction was found to change slowly when the pH was decreased to 1. The spectrum was monitored with time and was found to become constant after 8 minutes. This would exclude the possibility of terminal hydroxo groups and thus indicates the presence of a dihydroxo bridge in complex $2f_2$.

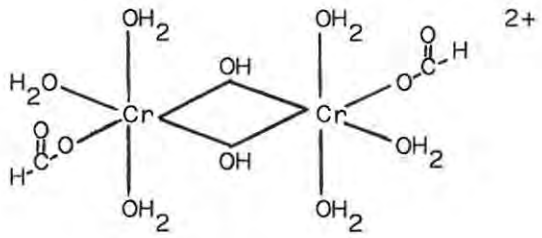
The mode of co-ordination of the formato groups in complex $2f_2$ could not be determined since separation from complex $2f_1$ was not achieved. The following structures would thus be possible for complex $2f_2$,




III




IV




IV

(iii) Complex $2f_3$. Ion exchange separations of solutions of 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide, 1:2 $Cr(H_2O)_6^{3+}$ and sodium formate, and 1:2:½ $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide gave two +2 fractions of net charge +2 (Figs. 4, 5). The fraction of higher ion exchange selectivity has been discussed above. The fraction with the lower ion exchange selectivity coefficient was present in higher concentrations in basified solutions. The fact that the ratio between the absorbance at 420 nm and 570 nm did not change across the fraction indicates that only complex $2f_3$ was present.

The analytical data from complex $2f_3$ is given in Table 5. The empirical formula, Cr(OH)HCOO, was derived. The simples structure of this formula is the mononuclear complex, $[Cr(H_2O)_4(OH)HCOO]^+$. This complex would be formed by the following type of equilibrium,

$$[Cr(H_2O)_5HCOO]^{2+} \rightleftharpoons [Cr(H_2O)_4(OH)HCOO]^+ + H^+ \quad \ldots\ldots \quad (19)$$

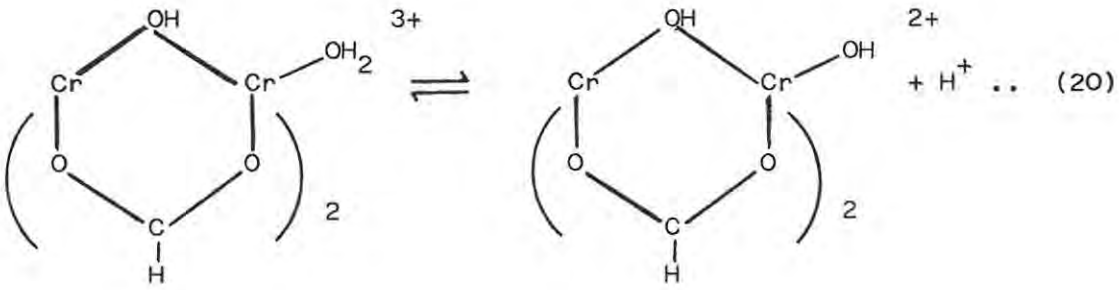
The visible spectrum of this complex was determined by recording the spectra of solutions of $[Cr(H_2O)_5HCOO]^{2+}$ to which increasing amounts of sodium hydroxide had been added (Fig. 14). Linear plots of extinction coefficient versus OH:Cr ratios (extrapolated to 1) at various fixed wavelengths (Fig. 15) gave absorption maxima at 431 and 585 nm and extinction coefficients of 31 and 19 $mol^{-1}cm^{-1}$, respectively for $[Cr(H_2O)_4(OH)HCOO]^+$. Comparing these values with those for complex $2f_3$ (Table 6) excluded this mononuclear complex as the structure for complex $2f_3$. In any case, the net charge of the mononuclear complex is +1 whereas the net charge of complex $2f_3$ has been found to be +2.

Charge per chromium atom determinations on complex $2f_3$ gave a value of 1,05. The net charge is +2 and therefore a dimeric nature for the complex is indicated. This was confirmed from electrophoretic and gel filtration separations using the same arguments as that for other dimeric species, (see complex $3a_1$).

It has been shown previously, with reference to Table 7, that infra-red spectra could be used to distinguish between a formato group co-ordinated to a metal in a monodentate or bidentate bridged fashion (see complex $3f_1$). A concentrated solution of complex $2f_3$ showed bands attributable to the asymmetric and symmetric stretching vibrations (Table 7) that were separated by a $\Delta V$ value of 185 $cm^{-1}$. This separation indicated that both the formato groups are bridging. (Redilution of the complex gave the same visible absorption spectrum showing that no decomposition had taken place on freeze drying). However, the presence of monodentately bound formato groups could not be excluded since it was shown previously (see complex $2f_1$) that their presence was difficult to detect because of the changes in the infra-red spectrum that had been demonstrated to occur during freeze drying. The absence of a peak at 1300 $cm^{-1}$ in the spectrum of complex $2f_3$ is,

however, taken as evidence that both formato groups are bridging.

The visible absorption spectrum of complex $2f_3$ (Table 6) indicated that an oxo bridge is not present. Acidification of this complex gave an immediate change in the visible spectrum thus indicating that a terminal hydroxo group is present. The pK for this equilibrium,




$3f_2$ $2f_3$

was determined as 0,4 (at 20 °C, $\mu$ = 0,5) by standard spectroscopic titration techniques.[91] The pK value is in accordance with the value of 0,6 for the acetate analogue, complex $3a_2$ (equilibrium 18).

Complex $2f_3$ is likely to contain cis arrangement of the bridging formato groups (see structure I for the acetate analogue, complex $2a_3$) since on stereochemical grounds this structure can only have one bridging hydroxo group. Complexes $2f_3$ and $2f_2$ have the same empirical formula but complex $2f_2$ was however found to contain a dihydroxo bridge.

(c) +1 Fraction

(i) Complex $1f_1$. Ion exchange separations of 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide solution gave a minor blue fraction of net charge +1 (Fig. 4c). Separations of solutions with higher carboxylate to chromium ratios gave a major green fraction with the same net charge (Fig. 5). The fact that the ratio between the absorbance at 420 nm and 570 nm changed across both fractions indicated that neither fraction was pure. Attempts to separate the fractions into their components by the use of a lithium column and a lithium eluent failed.

The trinuclear compound, $[Cr_3O(HCOO)_6(H_2O)_3].Cl$ was prepared by a known method.[66] The structure of the acetate analogue of this complex has been determined and shown to contain a central oxo group bridged to three chromium atoms and to contain bridging carboxylate groups.[70] The visible spectrum of a solution of $[Cr_3O(HCOO)_6(H_2O)_3].Cl$ was determined (Table 6) and shows the absorption bands typical of the presence of an oxo group.

The visible absorption spectrum of the major green +1 fraction separated from solutions of high carboxylate to chromium ratios (Fig. 5) approached that of the trinuclear complex. It was thus deduced that this green +1 fraction contained mainly complex $1f_1$, $[Cr_3O(HCOO)_6(H_2O)_3]^+$.

The infra-red spectrum of complex $1f_1$, has been measured previously but only one band at 1550 $cm^{-1}$ was reported in the region of the C - O stretching vibrations.[71] The infra-red spectrum of complex $1f_1$ (Table 7) however shows two C - O stretching bands. The $\Delta V$ value of 260 $cm^{-1}$ for this complex agrees well with a value of 255 $cm^{-1}$ for the iron analogue.[72] Both values are higher than the value for sodium formate of 201 $cm^{-1}$, indicating that complex $1f_1$ and its iron analogue are exceptions to the rule,[96] that bidentate formato groups have $\Delta V$ values less than that for sodium formate. This could possibly be due to the unusual structure of these trinuclear complexes.

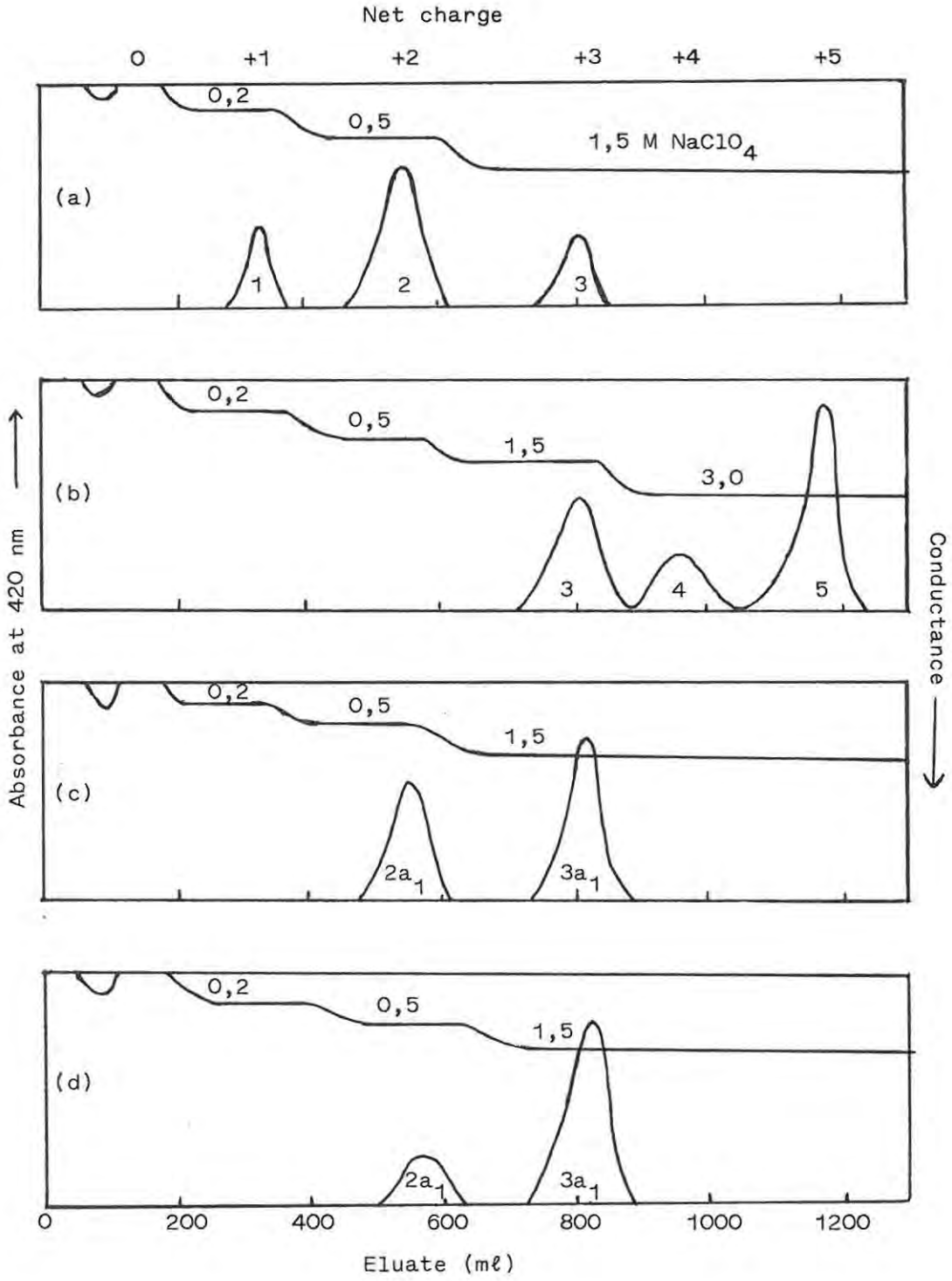



Figure 1. Elution patterns of cation exchange chromatographic separations using Dowex 50W-X2 resin (Na form).

(a) 100 mℓ (0,1 M in Cr) chromium chloride, aged 1 day.

(b) 100 mℓ (0,1 M in Cr) of 1:1 refluxed solution of $Cr(H_2O)_6^{3+}$ and sodium hydroxide.

(c) 150 mℓ (0,05 M in Cr) of solution prepared by the reduction of Cr(VI) to Cr(III) in the presence of excess acetic acid.

(d) 100 mℓ (0,1 M in Cr) of 1:3 refluxed solution of $Cr(H_2O)_6^{3+}$ and acetic acid.

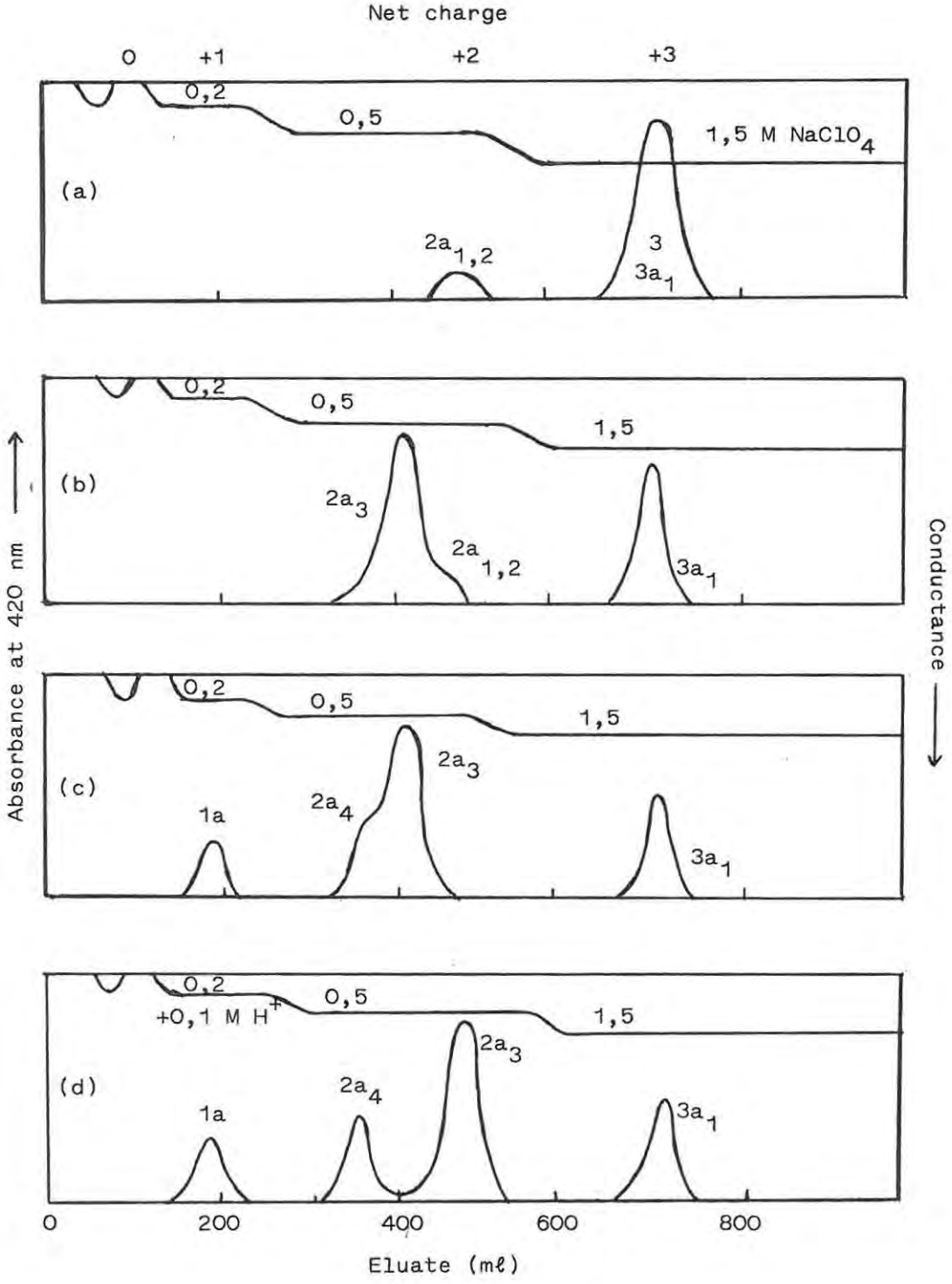



Figure 2. Elution patterns of cation exchange chromatographic separations using Dowex 50W-X2 resin (Na form). 100 mℓ (0,1 M in Cr) of a refluxed solution of

(a) 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate,

(b) 1:1:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide,

(c) and (d) 1:2 $Cr(H_2O)_6^{3+}$ and sodium acetate.

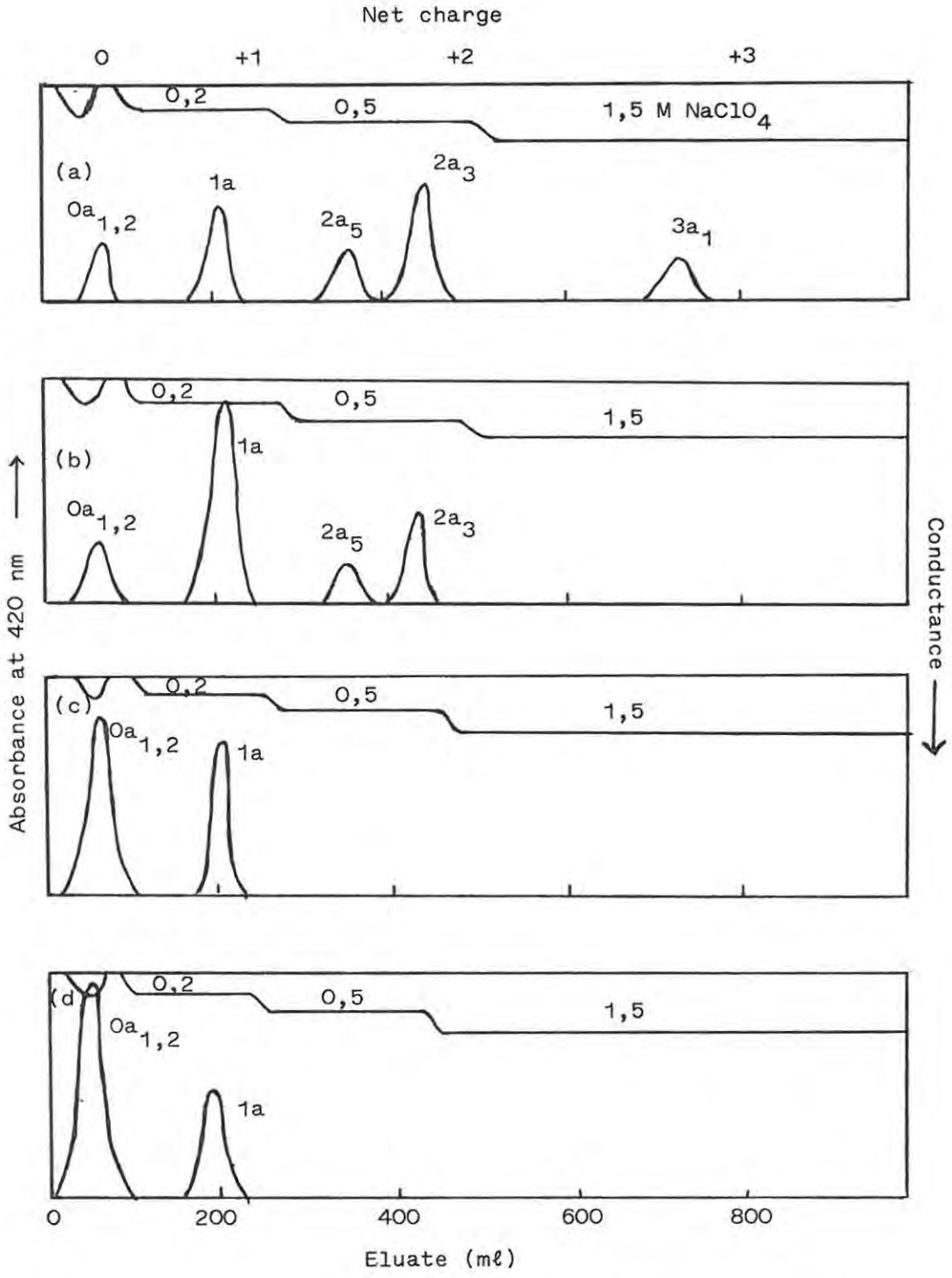



Figure 3. Elution patterns of cation exchange chromatographic separations using Dowex 50W-X2 resin (Na form). 150 mℓ (0,05 M in Cr) of a refluxed solution of

(a) 1:2:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide

(b) 1:2 $Cr(H_2O)_6^{3+}$ and sodium acetate,

(c) 1:3:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide,

(d) 1:9 $Cr(H_2O)_6^{3+}$ and sodium acetate.

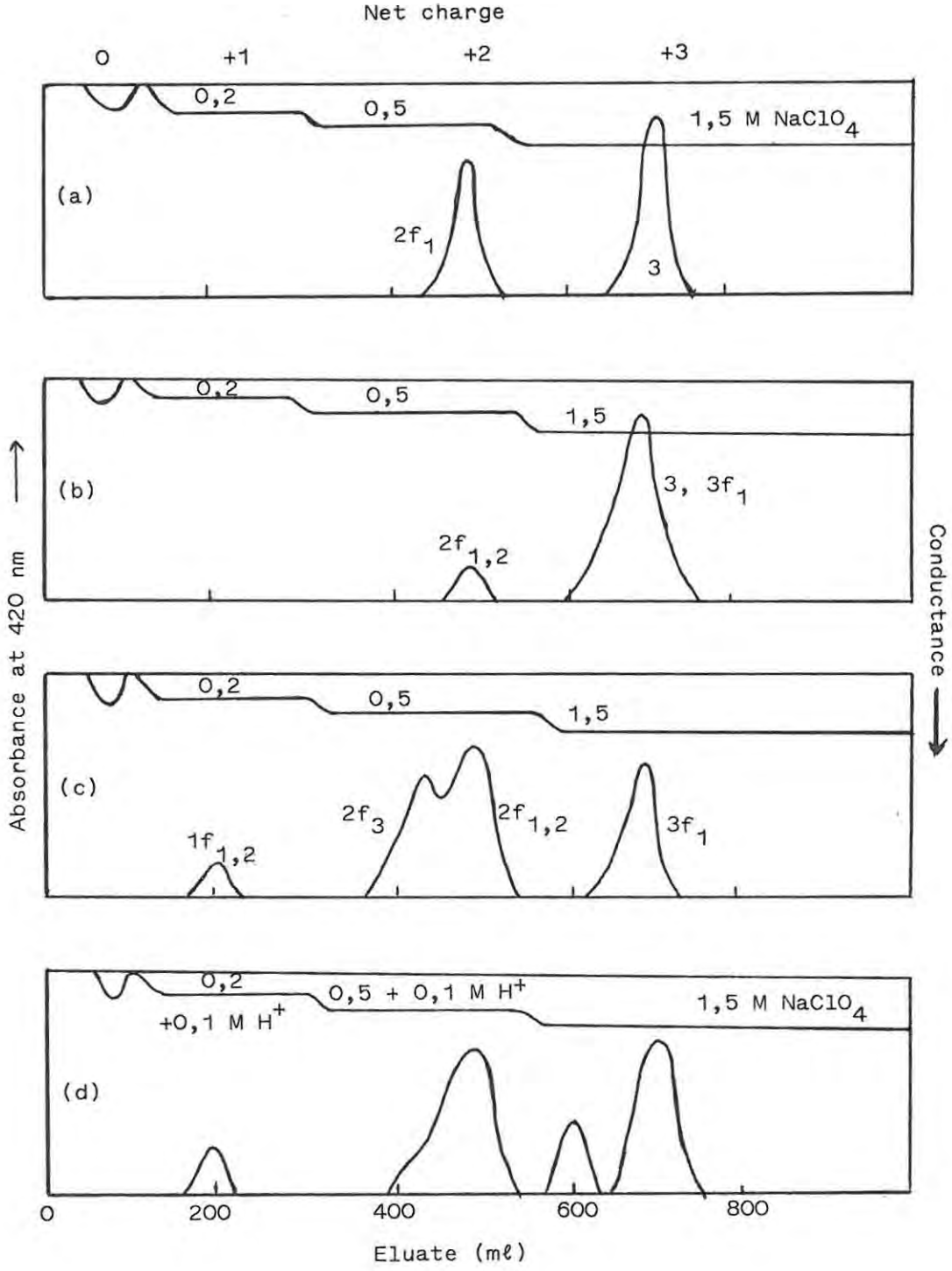



Figure 4. Elution pattern of cation exchange chromatographic separations using Dowex 50W-X2 resin (Na form).

(a) 150 mℓ (0,05 M in Cr) of solution prepared by the formic acid reduction of Cr(VI to Cr(III). 100 mℓ (0,1 M in Cr) refluxed solution of

(b) 1:1 $Cr(H_2O)_6^{3+}$ and sodium formate,

(c) and (d) 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide.

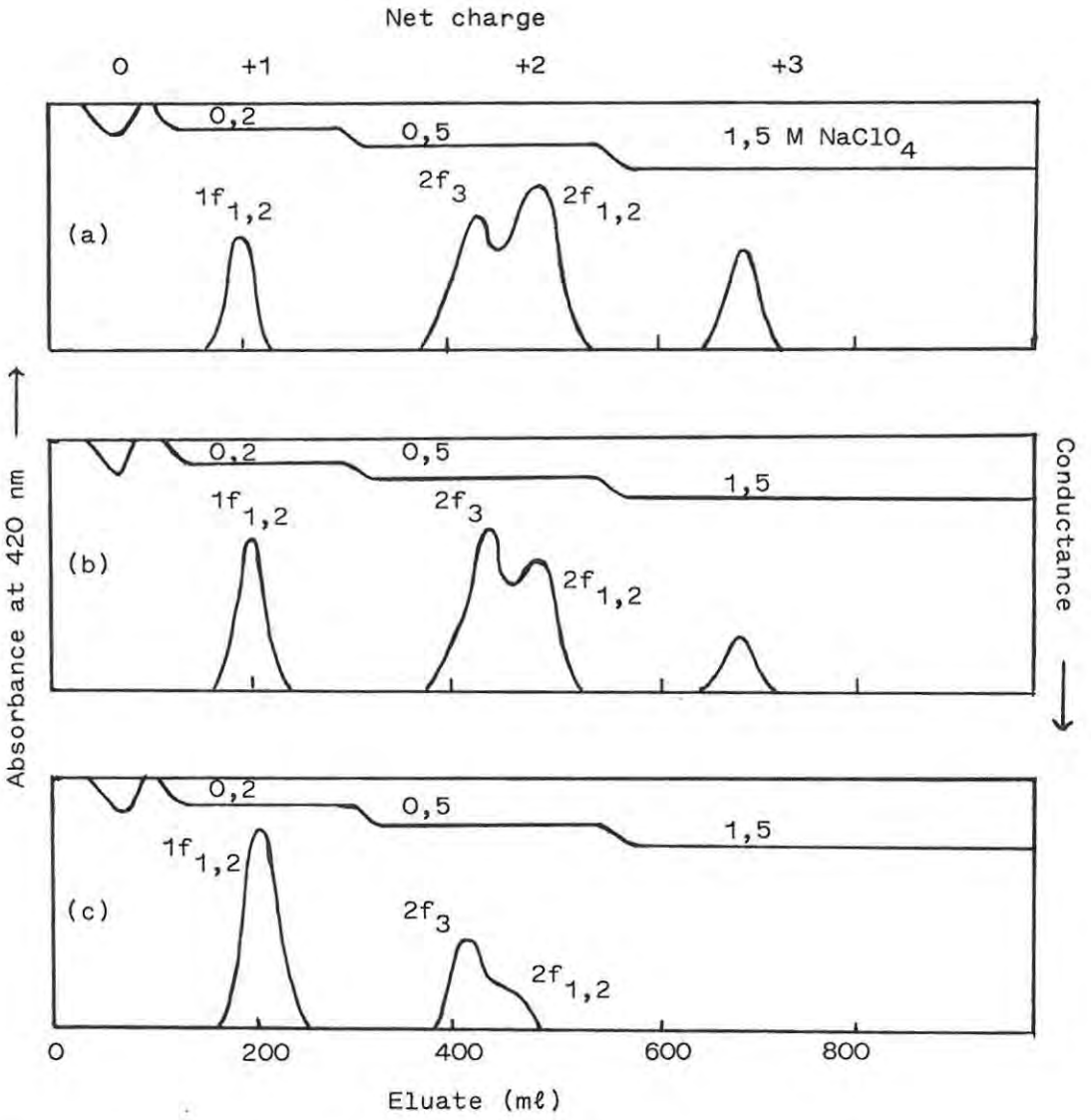



Figure 5. Elution pattern of cation exchange chromatographic separations using Dowex 50W-X2 resin (Na form ). 150 mℓ (0,05 M) in Cr of

(a) 1:2 $Cr(H_2O)_6^{3+}$ and sodium formate,

(b) 1:2:½ $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide,

(c) 1:3 $Cr(H_2O)_6^{3+}$ and sodium formate.

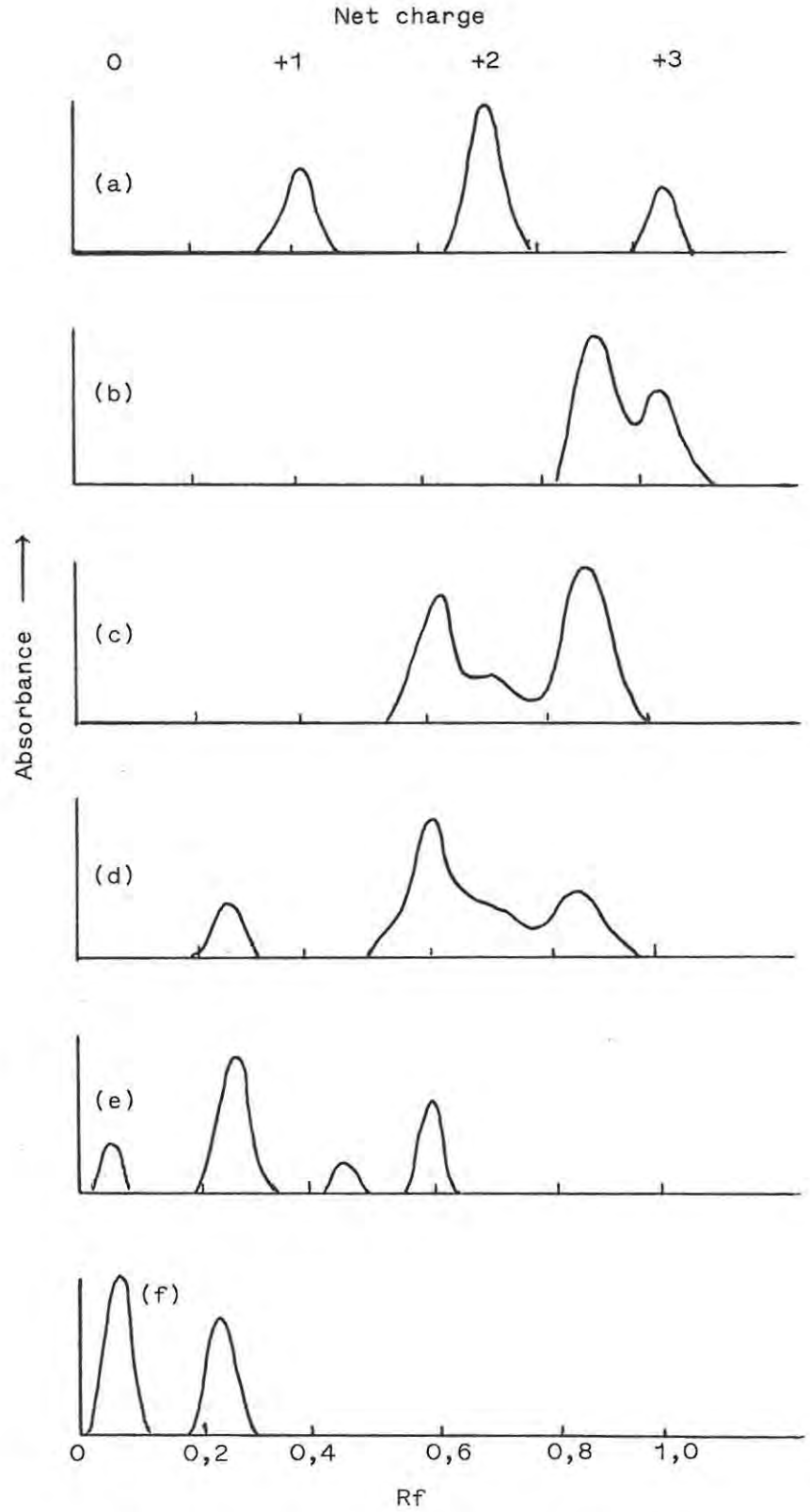



Figure 6. Scan patterns of paper electrophoretic separations of solutions of

(a) Chromium chloride, (b) 1:1 $Cr(H_2O)_6^{3+}$ and sodium acetate, (c) 1:1:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide, (d) 1:2 $Cr(H_2O)_6^{3+}$ and sodium acetate, (e) 1:2:1 $Cr(H_2O)_6^{3+}$, sodium acetate and sodium hydroxide, (f) 1:3 $Cr(H_2O)_6^{3+}$ and sodium acetate.

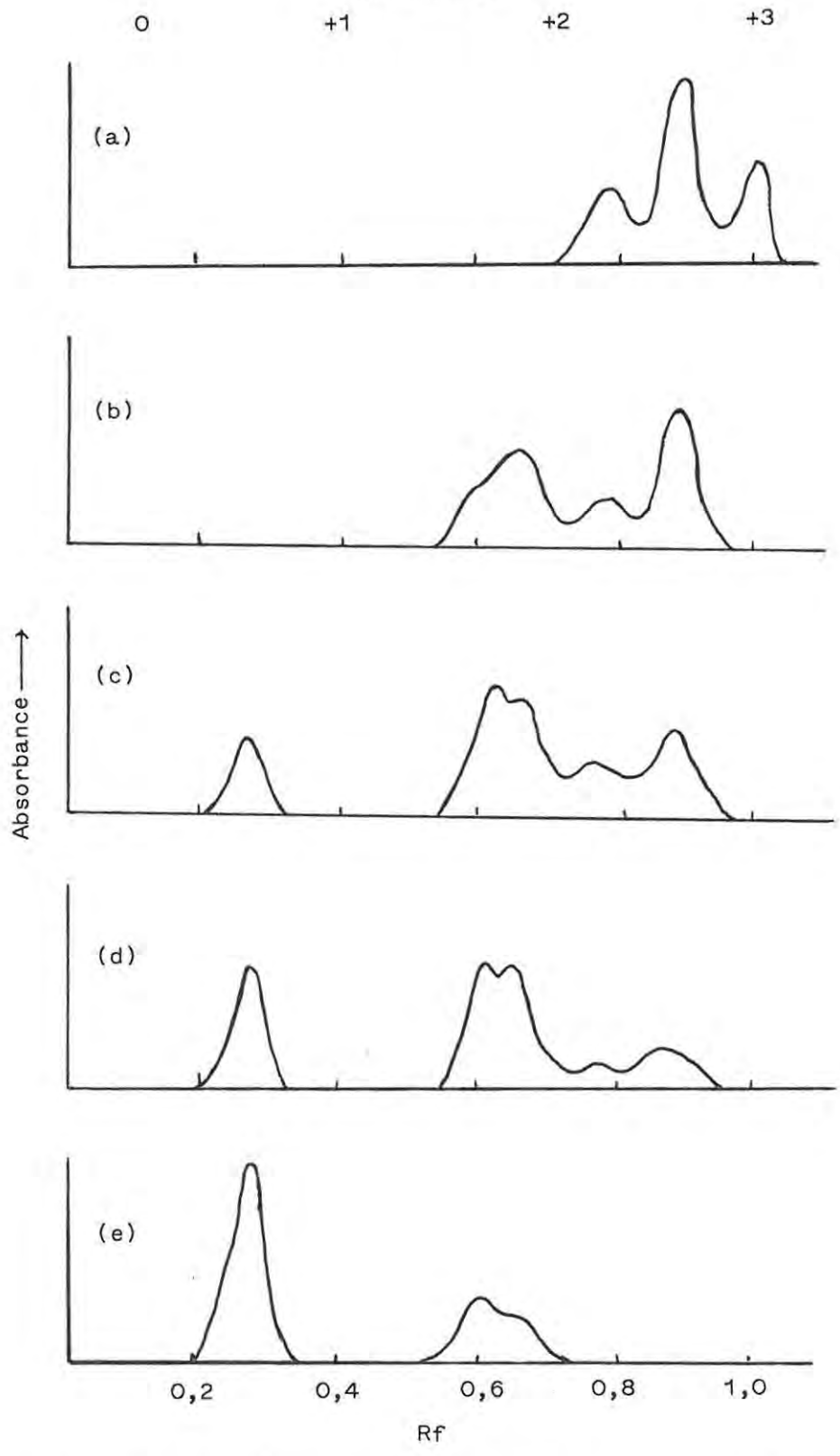



Figure 7. Scan patterns of paper electrophoretic separations. Refluxed solution of (a) 1:1 $Cr(H_3O)_6^{3+}$ and sodium formate, (b) 1:1:1 $Cr(H_2O)_6^{3+}$, sodium formate and sodium hydroxide, (c) 1:2 $Cr(H_2O)_6^{3+}$ and sodium formate, (d) 1:2 $Cr(H_2O)_6^{3+}$, sodium formate and hydoroxide and (e) 1:3 $Cr(H_2O)_6^{3+}$ and sodium formate.

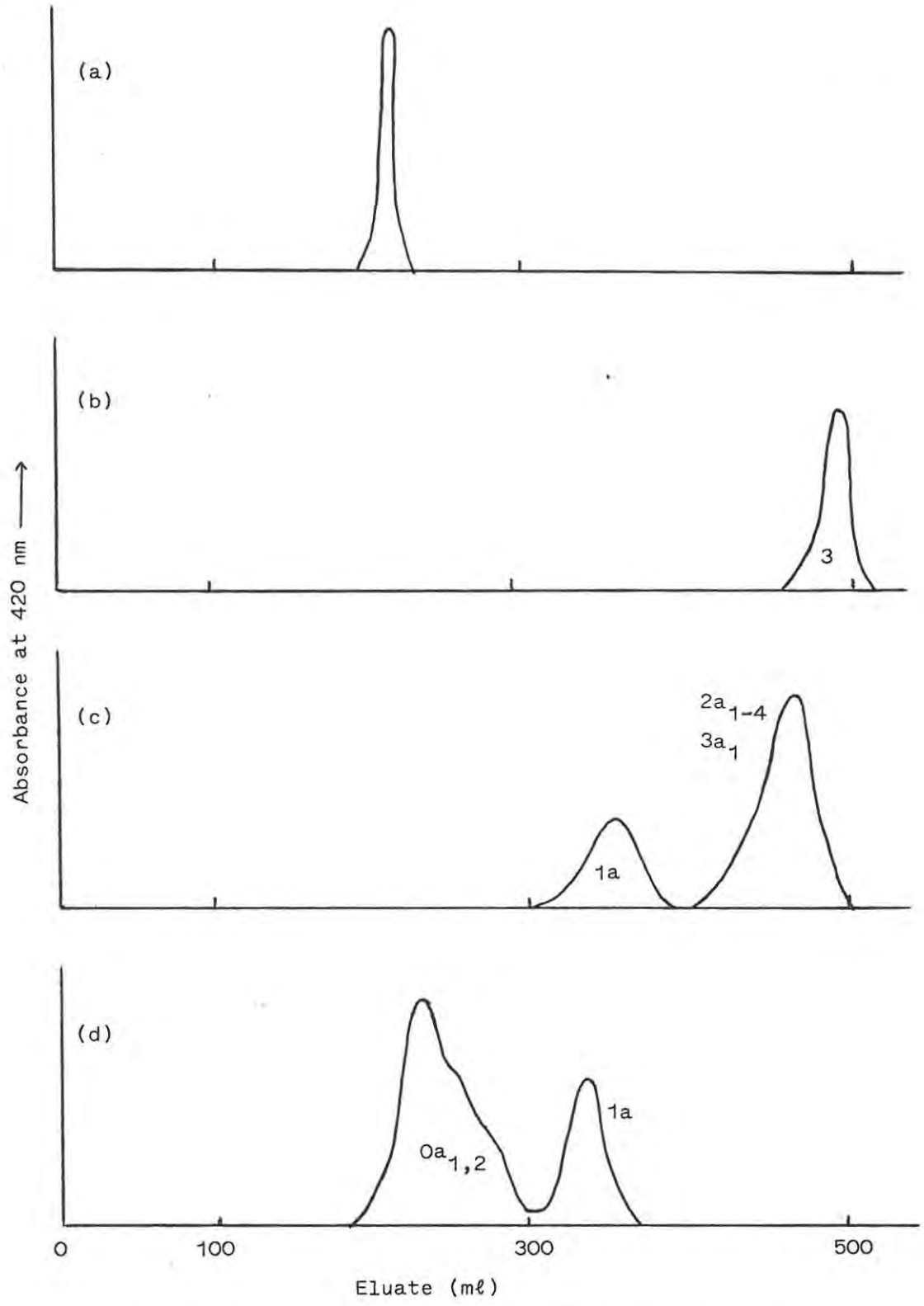



Figure 8. Elution profiles of gel filtration chromatographic separation (Elutant 0,1 M $NaClO_4$) Sephadex G25. 5 mℓ of

(a) Dextran Blue, (b) $Cr(H_2O)_6^{3+}$, (c) 1:2 refluxed solution of $Cr(H_2O)_6^{3+}$ and sodium acetate, (d) 1:9 reluxed solution $Cr(H_2O)_6^{3+}$ and sodium acetate, eluted with 0,1 M $NaClO_4$ (pH 4).

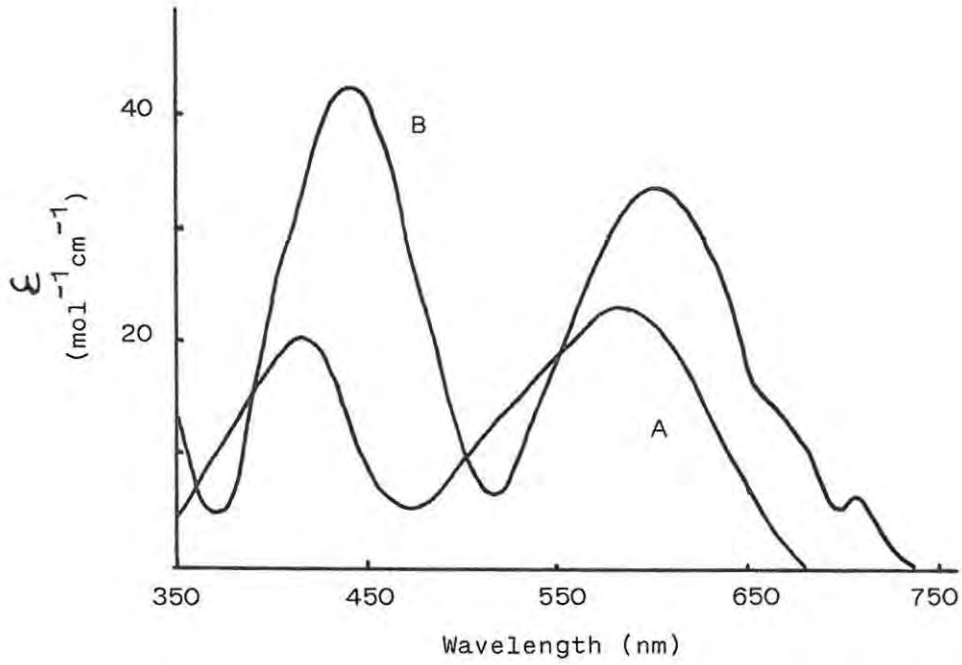



Figure 9. Visible absorption spectra of complex $3a_1$ (A) and complex 1a (B).

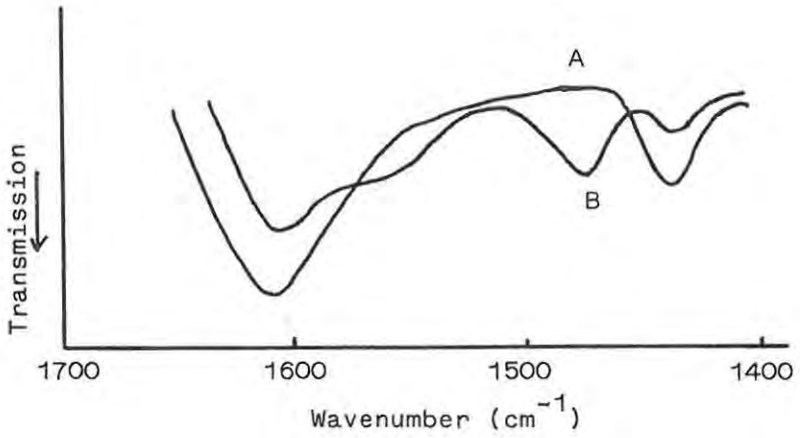



Figure 10. Infra-red spectrum of dilute (A) and concentrated (B) solutions of complex $2a_1$.

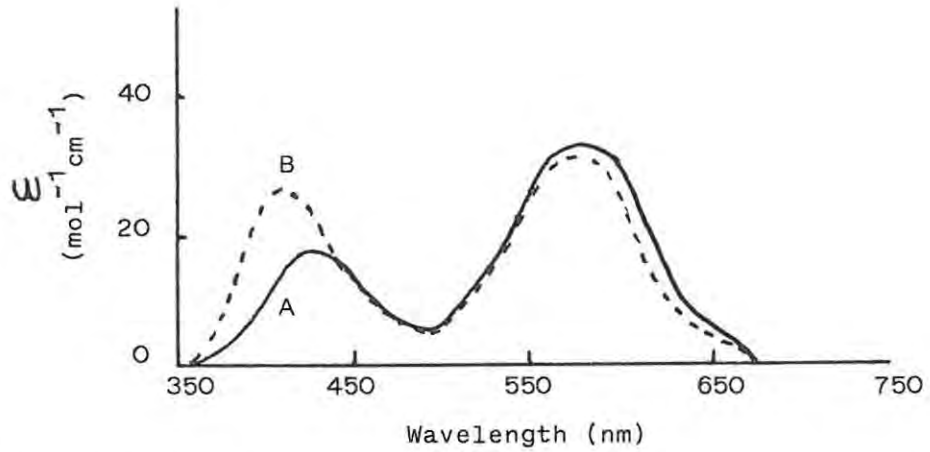



Figure 11. Change in visible spectrum on the conversion of complex $2a_3$ (A) to complex $3a_2$ (B).

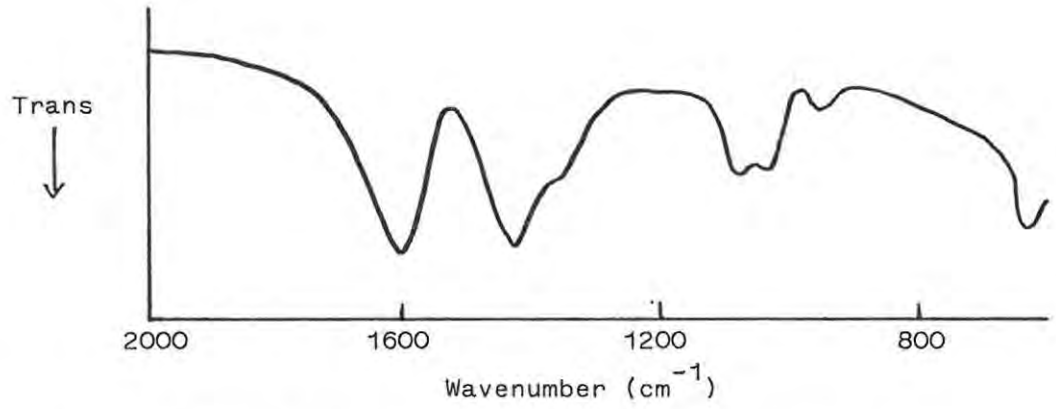



Figure 12. Infra-red spectrum of a concentrated solution of $[Cr_3O(H_3COO)_6 3H_2O]Cl$. Measured as thin film between AgCl discs.

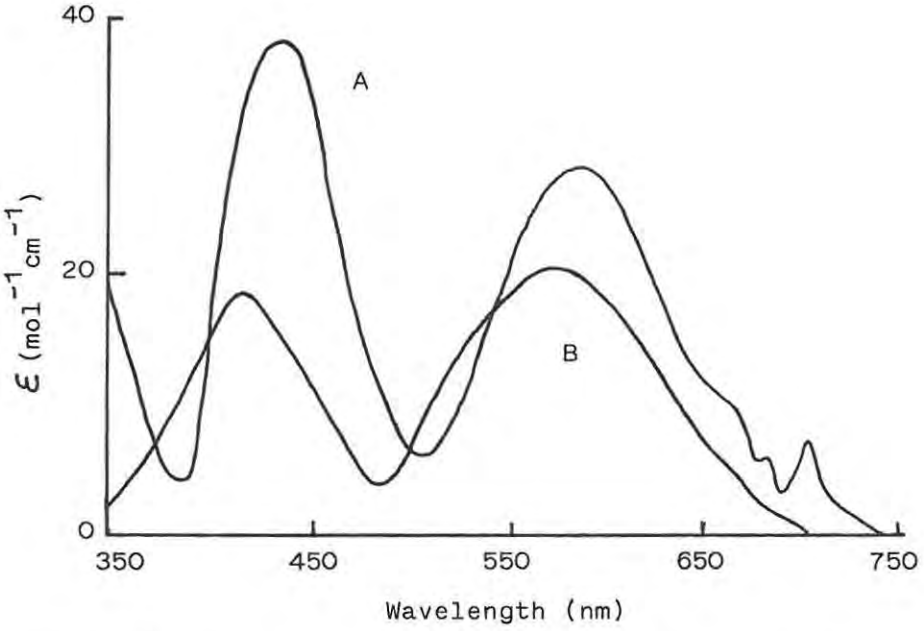



Figure 13. Visible absorption spectra of (A) complex $1f_1$, $[Cr_3O(HCOO)_6 3H_2O]^+$ and (B) complex $3f_1$.

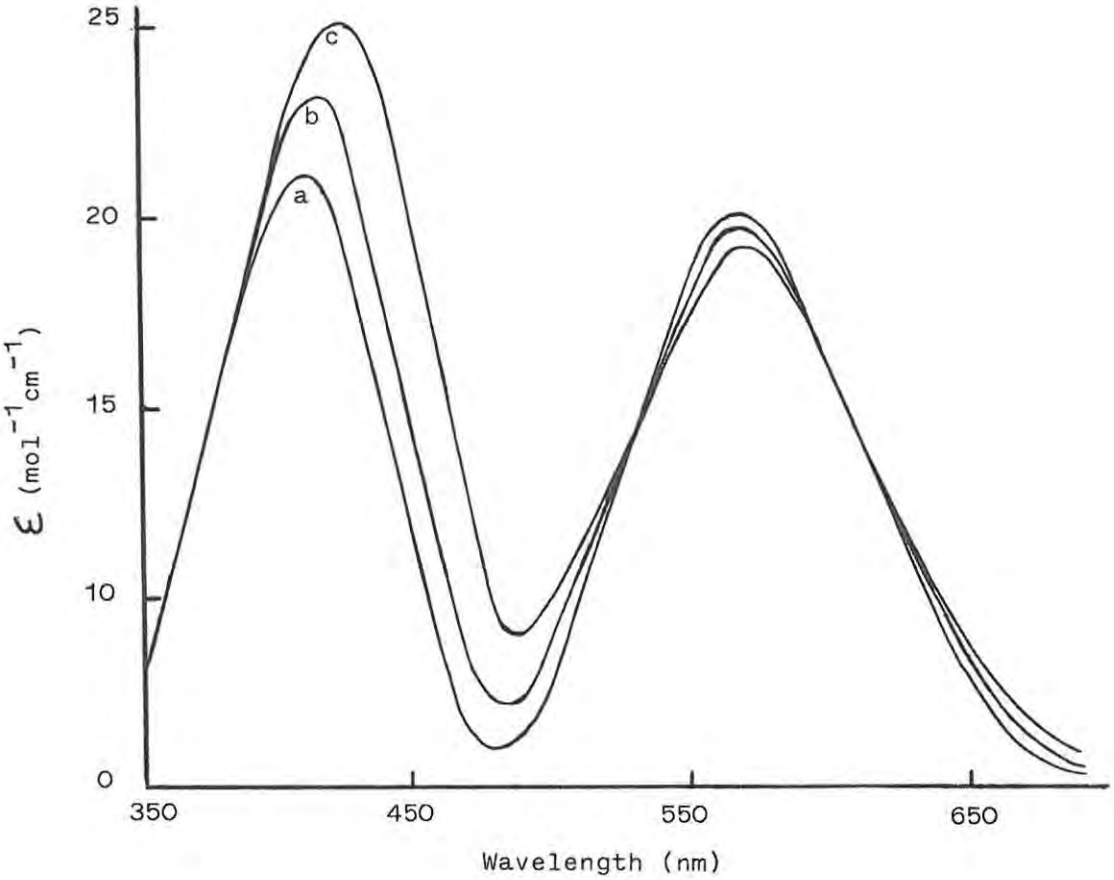



Figure 14. Visible spectra of complex $2f_1$ on titration against sodium hydroxide at OH:Cr ratios of (a) 0, (b) 0,25 and (c) 0,55.

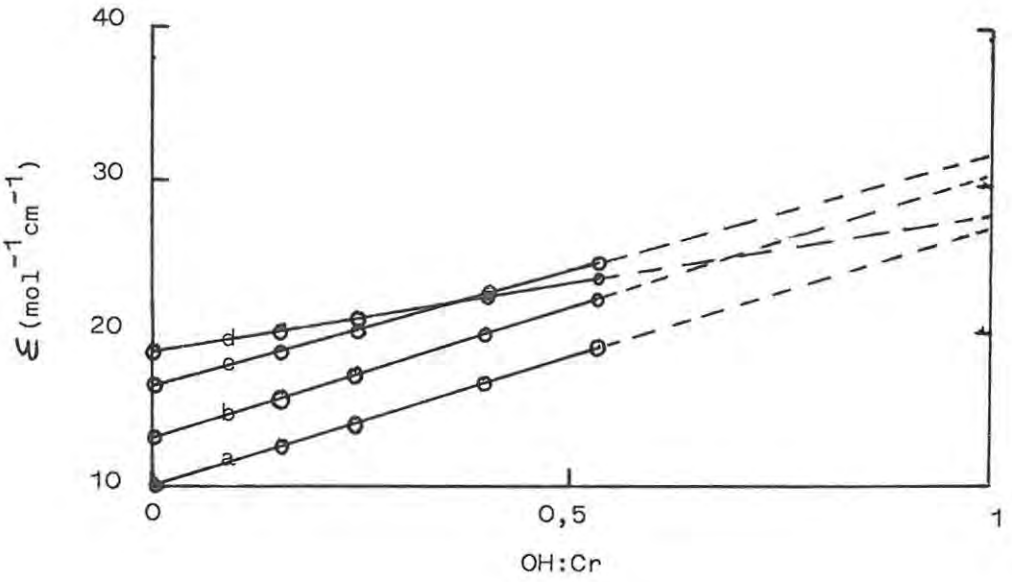



Figure 15. Change in extinction coefficient of complex $2f_1$ on titration against sodium hydroxide. Values extrapolated to OH:Cr = 1 (a) 450 nm, (b) 440 nm, (c) 430 nm, (d) 420 nm.

Table 1

Visible spectral data for acetato complexes

| Complex | Wavelength (nm) ($\varepsilon$)$mol^{-1}cm^{-1}$ | Wavelength (nm) ($\varepsilon$)$mol^{-1}cm^{-1}$ |
|---|---|---|
| 3 | 408 (15,6) | 574 (13,4) |
| 4 | 418 (22,5) | 582 (18,9) |
| 5 | 426 (31,4) | 580 (19.7) |
| $3a_1$ | 411 (18,4) | 574 (21,9) |
| $3a_2$ | 419 (27,5) | 576 (35,2) |
| $2a_1$ | 410 (22,2) | 570 (24,4) |
| $2a_3$ | 419 (19,5) | 576 (35,2) |
| $2a_4$ | 432 (25,4) | 580 (35,2) |
| $2a_5$ | 410 (24,1) | 566 (29,2) |
| 1a | 437 (38,0) | 579 (32,0) |
| $0a_1$ | 412 (29,7) | 563 (39,4) |

Table 2

Analytical data for acetato complexes

| Complex | OH:Cr | Acetate:Cr | Empirical formula |
|---|---|---|---|
| $3a_1$ | 0,98 | 0,56 | $Cr_2(OH)_2CH_3COO$ |
| $2a_1$ | 0,00 | 1,04 | $CrCH_3COO$ |
| $2a_3$ | 1,03 | 1,00 | $CrOHCH_3COO$ |
| $2a_4$ | 0,60 | 1,50 | $Cr_2OH(CH_3COO)_3$ |
| $2a_5$ | 1,37 | 1,08 | $Cr_3(OH)_4(CH_3COO)_3$ |
| 1a | 0,71 | 1,99 | $Cr_3(OH)_2(CH_3COO)_6$ |
| $0a_1$ | 1,54 | 1,52 | $Cr_2(OH)_3(CH_3COO)_3$ |

See Appendix for worked examples.

Table 3

Infra-red spectral data ($cm^{-1}$)

| Compound | Vas(CO) | Vs(CO) | ΔV | Ref. |
|---|---|---|---|---|
| $Na(CH_3COO)$ | 1 578 | 1 414 | 164 | 99 |
| $[Co(NH_3)_5(CH_3COO)](ClO_4)_2$ | 1 603 | 1 380 | 223 | 76 |
| $[(NH_3)_4Co(CH_3COO)(NH_2)Co(NH_3)_4]Cl_4$ | 1 530 | 1 410 | 120 | 76 |
| $[(NH_3)_3Co(OH)_2(CH_3COO)Co(NH_3)_3]Cl_3$ | 1 535 | 1 440 | 95 | 75 |
| $[(en)_2Cr(CH_3COO)OHCr(en)_2](ClO_4)_4$ | 1 552 | 1 418 | 134 | 74 |
| $[triaz\ Rh(OH)_2CH_3COORh\ triaz]3ClO_4$ | 1 560 | 1 455 | 105 | 100 |
| $3a_1$ | 1 540 | 1 450 | 90 | THIS WORK |
| $2a_1$ | 1 570 | 1 400 | 170 | THIS WORK |
| $2a_3$ | 1 560 | 1 455 | 105 | THIS WORK |
| 1a | 1 600 | 1 445 | 155 | THIS WORK |

Table 4

Infra-red spectral data ($cm^{-1}$)

| $NaCH_3COO$[a] | $Cr_3O(CH_3COO)_6 3H_2O^+$ | $Fe_3O(CH_3COO)_6 3H_2O^+$[b] | Band Assignment |
|---|---|---|---|
| 1 578 | 1 600 | 1 595 | Vas(COO) |
| 1 443 | | | $\delta CH_3$ |
| 1 430 | | | $\delta CH_3$ |
| 1 414 | 1 445 | 1 450 | Vs(COO) |
| | 1 345 | 1 352 | |
| | | 1 240 | |
| 1 042 | 1 090 | 1 052 | $p_r CH_3$ |
| 1 009 | 1 040 | 1 035 | $p_r CH_3$ |

[a] Ref. 99. [b] Ref. 72.

Table 5

Analytical data for formato complexes

| Complex | OH:Cr | Formate:Cr | Empirical formula |
|---|---|---|---|
| $3f_1$ | 0,99 | 0,52 | $Cr_2(OH)_2(HCOO)$ |
| $2f_1$ | 0,00 | 1,02 | CrHCOO |
| $2f_3$ | 1,01 | 1,02 | Cr(OH)HCOO |
| $1f_1$ | 0,67 | 2,02 | $Cr_3(OH)_2(HCOO)_6$ |

See Appendix for worked examples

Table 6

Visible spectral data for formato complexes

| Complex | Wavelength (nm) $(\varepsilon)mol^{-1}cm^{-1}$ | Wavelength (nm) $(\varepsilon)mol^{-1}cm^{-1}$ |
|---|---|---|
| $3f_1$ | 410 (18,8) | 574 (20,9) |
| $3f_2$ | 408 (24,8) | 576 (30,7) |
| $2f_1$ | 412 (20,3) | 575 (20,9) |
| $2f_3$ | 417 (20,3) | 577 (29,7) |
| $1f_1$ | 440 (38,1) | 585 (28,7) |

Table 7

Infra-red spectral data ($cm^{-1}$)

| Compound | Vas(CO) | Vs(CO) | ΔV | Ref. |
|---|---|---|---|---|
| NaHCOO | 1 567 | 1 366 | 201 | 99 |
| $[Co(NH_3)_5HCOO]Br_2$ | 1 640 | 1 345 | 295 | 76 |
| $[(NH_3)_4Co(NH_2)HCOOCo(NH_3)_4]^{4+}$ | 1 570 | 1 365 | 205 | 76 |
| $[(NH_3)_4Co(OH)\ HCOOCo(NH_3)_4]^{4+}$ | 1 550 | 1 355 | 195 | 75 |
| $[(en)_2Cr(OH)HCOOCr(en)_2]^{4+}$ | 1 569 | 1 379 | 190 | 74 |
| $^3f_1$ | 1 530 | 1 360 | 170 | THIS WORK |
| $^2f_3$ | 1 550 | 1 365 | 185 | THIS WORK |
| $^1f_1$ | 1630 | 1 370 | 260 | THIS WORK |

## 5. DETERMINATION OF EQUILIBRIUM CONSTANTS

Acid dissociation constants (pK) of the pentaaquachromium(III) complexes in the following equilibrium were determined by potentiometric means,

$$[Cr(H_2O)_5Y]^{2+} \rightleftharpoons [Cr(H_2O)_4(OH)Y]^{+} + H^{+} \quad \ldots\ldots \quad (21)$$

where Y = $H_2O$, $CH_2CO_2$, $CH_2ClCO_2$, $CHCl_2CO_2$, $CCl_3CO_2$, HCOO. Typical titration curves for the change in pH of these complexes during potentiometric titration with standard sodium hydroxide (at temperatures ranging from 10 °C - 25 °C) are shown in Fig. 16. Data from these titrations was substituted into expressions 15 and 16 and values for $\bar{n}$ (the degree of protonation) and pK calculated (Table 8).

Polymerization has been shown previously to cause problems in the determination of pK values for this type of equilibrium.[101] The generation of hydrogen ions by the formation of hydroxo bridges (see equilibrium 2 ) results in incorrect pK values being determined at high $\bar{n}$ values. This is illustrated in Fig. 17 which shows that the problem is particularly serious for $[Cr(H_2O)_5CH_3COO]^{2+}$ as has been noted previously.[64] However $Cr(H_2O)_6^{3+}$ and $[Cr(H_2O)_5HCOO]^{2+}$ maintain a constant pK over a wide range of $\bar{n}$ values.

The pK data for this equilibrium from the present study are compared with data from previous work in Table 8. The pK value determined for $Cr(H_2O)_6^{3+}$ is in agreement with the published value[8] at the same ionic strength and temperature. However, a significant difference is noted between the determined pK values for $[Cr(H_2O)_5CH_3COO]^{2+}$ and published values.[64] Some of this difference can be attributed to the different ionic strengths used in the determinations, a general effect which has been noted previously.[101]

The pK value for $[Cr(H_2O)_5HCOO]^{2+}$ is seen from Table 8 to be in the same range as the value determined for the acetato analogue. The pK values for the acetato and formato complexes are both higher than that for $Cr(H_2O)_6^{3+}$, indicating that carboxylate co-ordination reduces the acidity of the complexes relative to $Cr(H_2O)_6^{3+}$. A similar trend has been observed for $[Cr(H_2O)_4Cl_2]^{+}$.[8]

pK Values and temperature are related by the following expression,[102]

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \qquad \ldots\ldots \quad (22)$$

The slope and intercept of a plot of lnK vs $\frac{1}{T}$ were used to calculate the change in enthalpy ($\Delta$ H) and the change in entropy ($\Delta$ S). The temperature dependence of the lnK value for equilibrium (21) of the various complexes is illustrated in Fig. 18. $\Delta$ H and $\Delta$ S values were derived from these plots by least squares analysis and are listed in Table 9. The complexes all have similar $\Delta$ H and similar $\Delta$S values.

In the same way that the $pK^H$ value of chloro substituted acetic acid depends on the degree of substitution (Table 10) and is associated with the inductive effect,[103,104] it was found that the pK values for equilibrium (21) varied depending on the substituent (Table 10). A direct linear correlation was found between the pK for equilibrium (21) and the $pK^H$ value for the free ligand as illustrated in Fig. 19. This indicates that the effect on the acidity of a co-ordinated water molecule can to some extent be related to the electron withdrawing properties, i.e. basicity, of the co-ordinated substituted acetato ligand. The effect can either be transmitted through or across the metal cation. The same effect has been noted for a series of cobalt compounds, trans-$Co(dmgH)_2$ (substituted pyridine) $(H_2O)^+$, where dmg = dimethylglyoximate.[101] In both cases, the variation in the pK value for the co-ordinated water is much less than the variation in the $pK^H$ value for the co-ordinated ligand (as shown by the slope of $>1$ in Fig. 19). This indicates that the effect of an electron withdrawing group on an acetate ligand that is co-ordinated to chromium(III) is greatly attenuated by the time the protons of the co-ordinated water have been reacted.

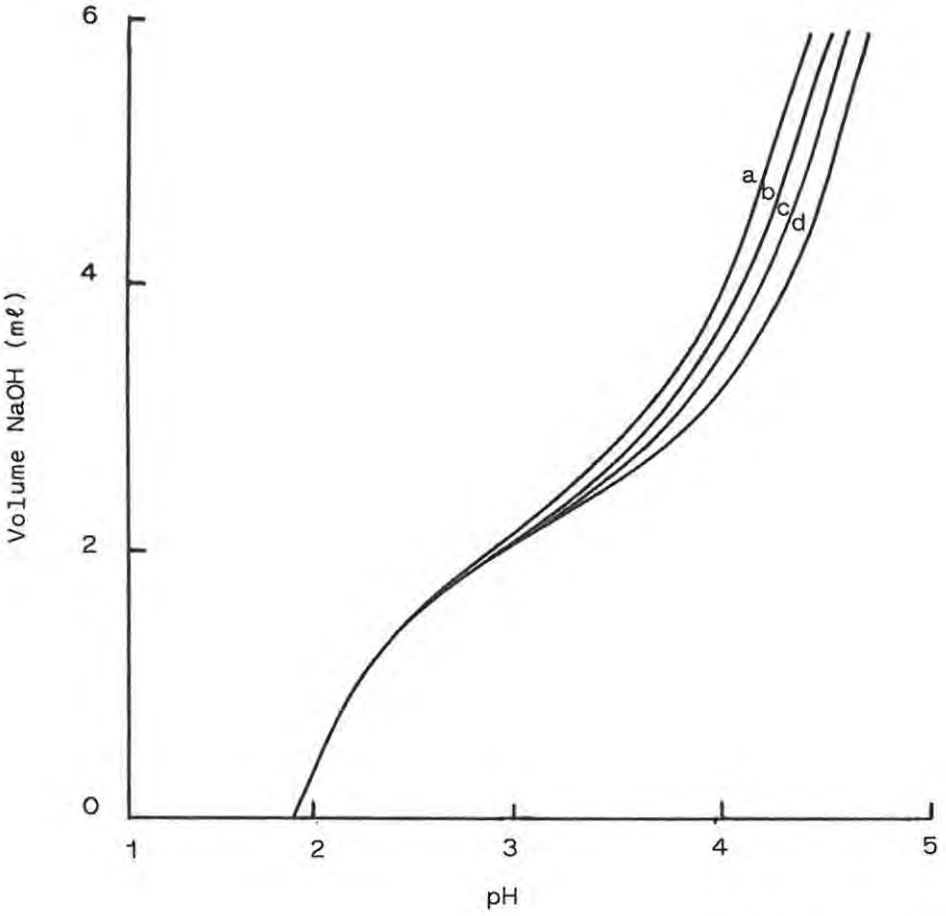



Figure 16. Potentiometric titration curves of $[Cr(H_2O)_5HCOO]^{2+}$ at temperatures, (a) 10 °C, (b) 15,5 °C, (c) 20 °C and (d) 25 °C. [NaOH] = 0,1 N, [Complex] = 0,7960 mequiv. $T_H$ = 1,004 mequiv.

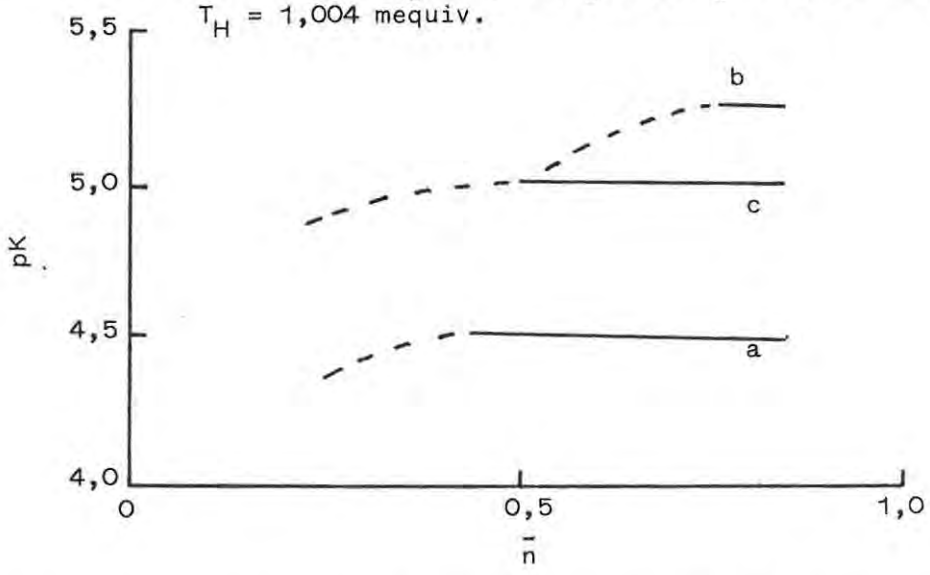



Figure 17. The relation between the pK value and $\bar{n}$ for equilibrium 21 at 10 °C for complexes, (a) $Cr(H_2O)_6^{3+}$, (b) $[Cr(H_2O)_5CH_3COO]^{2+}$ and (c) $[Cr(H_2O)_5HCOO]^{2+}$. (broken lines indicate non-equilibrium conditions).

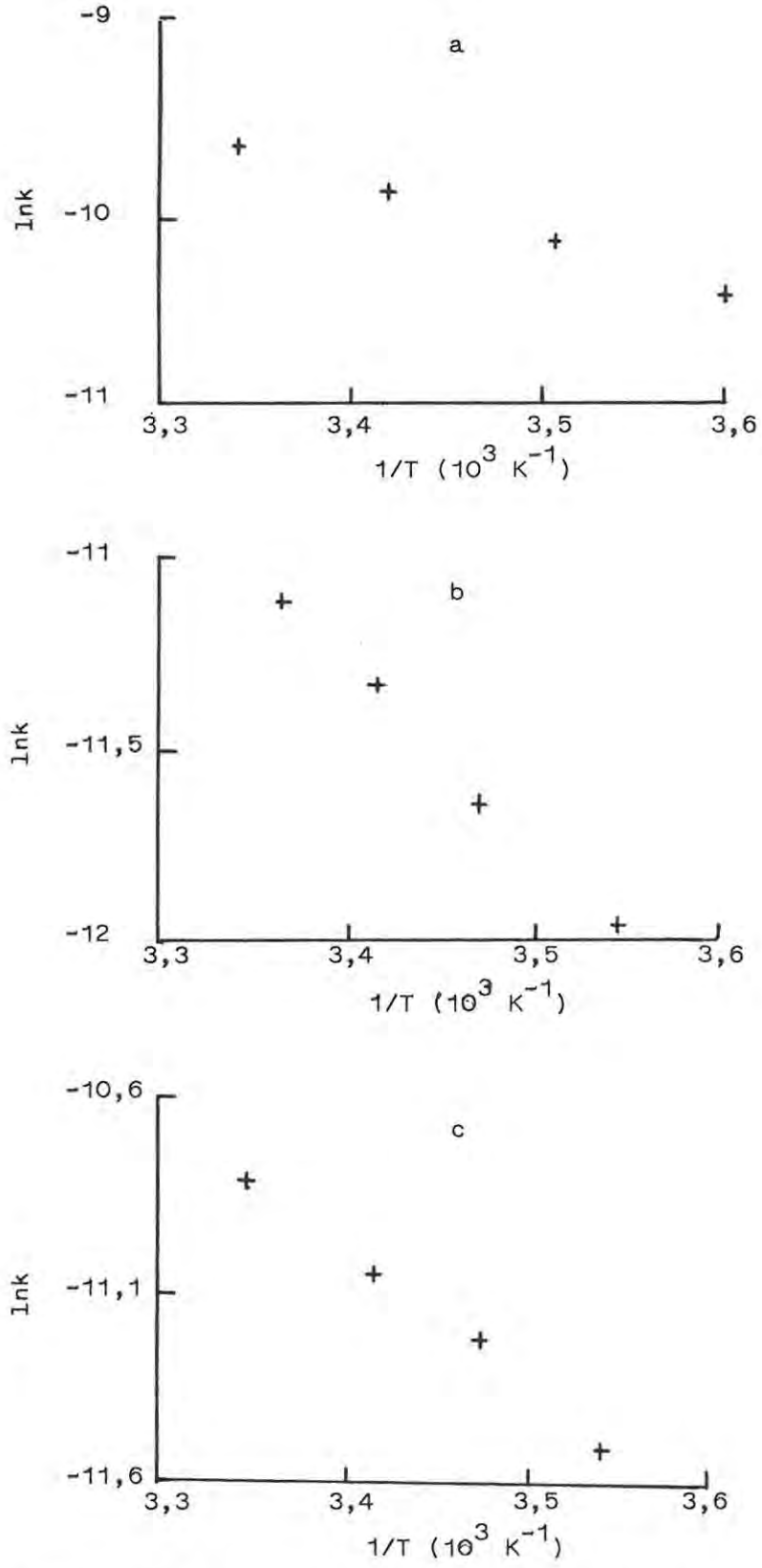



Figure 18. The relation between pK values and temperature for equilibrium 21 for complexes, (a) $Cr(H_2O)_6^{3+}$, (b) $[Cr(H_2O)_5CH_3COO]^{2+}$ and (c) $[Cr(H_2O)_5HCOO]^{2+}$

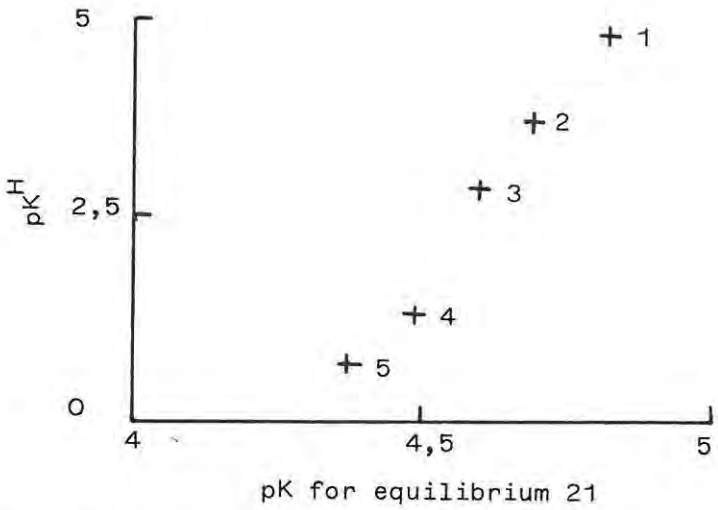



Figure 19. Relation between $pK^H$ values of the free ligands and pK values for equilibrium 21 at 25 °C for the following complexes, $[Cr(H_2O)_5RCOO]^{2+}$ where R represents, (1) $CH_3$, (2) H, (3) $CH_2Cl$, (4) $CHCl_2$ and (5) $CCl_3$.

Table 8

pK Data for equilibrium 21 for complexes $Cr(H_2O)_5Y$ at various temperatures

| Ligand Y | Temperature (°C) 10 | 15 | 20 | 25 | Medium | Ref. |
|---|---|---|---|---|---|---|
| $H_2O$ | | | 4,26 | | 0,5 M $NO_3^-$ | 8 |
| | 4,72 | 4,61 | 4,50 | 4,35 (±0,05) | 1 M $LiClO_4$ | 8 |
| | 4,56 | 4,45 | 4,35 | 4,25 (±0,02) | 0,5 M $NaClO_4$ | THIS WORK |
| $CH_3CO_2$ | 4,54 | 4,41 | 4,28 | 4,17 (±0,01) | 1 M $LiClO_4$ | 64 |
| | 5,22 | 5,09 | 4,99 | 4,86 (±0,03) | 0,5 M $NaClO_4$ | THIS WORK |
| $HCO_2$ | 5,01 | 4,90 | 4,81 | 4,71 (±0,02) | 0,5 M $NaClO_4$ | THIS WORK |

See Appendix for a worked example

Table 9

Change in enthalpy ($\Delta H$) and entropy ($\Delta S$) for equilibrium 21 for complexes $Cr(H_2O)_5Y$

| Ligand Y | H (kcal/mol) | S (cal/mol) | Medium | Ref. |
|---|---|---|---|---|
| $H_2O$ | 8 ± 1 | 6 ± 3 | 1 M $LiClO_4$ | 8 |
| $H_2O$ | 9 ± 1 | 10 ± 2 | 0,5 M $NaClO_4$ | THIS WORK |
| $CH_3COO$ | 6 ± 2 | -2 ± 5 | 1 M $LiClO_4$ | 64 |
| $CH_3COO$ | 9 ± 2 | 8 ± 4 | 0,5 M $NaClO_4$ | THIS WORK |
| HCOO | 8 ± 1 | 5 ± 2 | 0,5 M $NaClO_4$ | THIS WORK |

Table 10

pK Data for equilibrium 21 for complexes $Cr(H_2O)_5Y$ and acid dissociation constants $pK^H$ for the related free ligand (HY)[a]

| Ligand | pK | $pK^H$ |
|---|---|---|
| $CH_3CO_2$ | 4,86 | 4,76 |
| $CH_2ClCO_2$ | 4,61 | 2,87 |
| $CHCl_2CO_2$ | 4,50 | 1,26 |
| $CCl_3CO_2$ | 4,38 | 0,66 |

[a] Ref. 103

## 6. INVESTIGATION OF THE VISIBLE ABSORPTION SPECTRA

The theory of visible absorption spectra of octahedral compounds with $O_h$ symmetry is well known.[105] The three spin allowed d - d transitions arising from a $d^3$ configuration (i.e. chromium(III) complexes, $CrX_6$) in an octahedral field are $^4T_{2g} \longleftarrow {}^4A_{2g}(V_1)$, $^4T_{1g}(F) \longleftarrow {}^4A_{2g}(V_2)$, and $^4T_{1g}(P) \longleftarrow {}^4A_{2g}(V_3)$. The first two transitions for the simple octahedral complex, $Cr(H_2O)_6^{3+}$, occur at 17400 $cm^{-1}$ and 24600 $cm^{-1}$, respectively, whereas the third at 37800 $cm^{-1}$ tends to be partially obscured by a neighbouring, high intensity band.[105] In chromium(III) octahedral complexes, the lowest energy spin allowed band ($V_1$) gives 10 Dq directly which represents the crystal field perturbation, a measure of the orbital energy difference between the metal $e_g$ and $t_{2g}$ energy levels.

In quadrate fields (e.g. $Cr(X)_5Y$), a new parameter Dt is introduced to describe the visible spectra because of the added axial field.[106] The spectra are interpreted on the basis of the assumption that axial fields are perturbative additions to the cubic fields. The $^4T_{1g} \longleftarrow {}^4A_{2g}$ transition ($V_1$) is predicted to be split into two transitions,

$$^4B_2 \longleftarrow {}^4B_1 = 10Dq_x \qquad \ldots\ldots (23)$$

$$^4E \longleftarrow {}^4B_1 = 10Dq_x + \frac{35}{4}Dt \qquad \ldots\ldots (24)$$

$$= \frac{15}{2}Dq_x + \frac{5}{2}Dq_y \qquad \ldots\ldots (25)$$

where $Dq_x$ and $Dq_y$ for $CrX_5Y$ represent the splitting in a cubic field.

The position of the visible absorption maxima for a series of different monosubstituted pentaaquachromium(III) complexes is given in Table 11. Splitting has been observed in the iodo and chloro systems whilst an asymmetric appearance of the $^4T_{2g}$ band suggests the presence of a second component in the bromo and other complexes.[106] Whenever the expected splitting is of the order of 2000 $cm^{-1}$ or less only one band has been observed. If the assumption is made that this band ($V_1$) represents the transition, $^4E_1 \longleftarrow {}^4B_1$, in the complex $Cr(H_2O)_5Y$, then Dt and $Dq_y$ can be calculated using the expressions 24 and 25

(taking $Dq_x$ = 1739 $cm^{-1}$). The values are given in Table 11. The values for $Dq_y$, calculated from the spectra of $Cr(H_2O)_5Y$ complexes compare favourably with values given in the literature[105] for $CrY_6$. The calculated Dt values also agree closely with the values that have been determined from a simple crystal field model.[106] The arrangement of the ligands on the basis of the magnitude of the $Dq_y$ value follows the spectrochemical series, viz.
$I < Br < Cl < F < H_2O < \underline{NCS} < NH_3 < CN$.[105] The values in Table 11 establish that the carboxylates have nearly the same position as water in this series.

A small systematic change in $Dq_y$ is observed in Table 11 on changing the substituent on the acetato ligands, i.e. $CH_3CO_2$, $CH_2ClCO_2$, $CHCl_2CO_2$, $CCl_3CO_2$. The introduction of successive electron withdrawing chloro groups decreases the $Dq_y$ value. This could be explained by a reduction in the repulsion between metal $e_g$ electrons and the electrons of the co-ordinated oxygen atom (of the carboxylate). This would result in a decrease in the separation between the $e_g$ and $t_{2g}$ levels as the electron withdrawing effect increases, i.e. $Dq_y$ would decrease.

The other important ligand present in the chromium(III) carboxylate complexes is the hydroxo ligand. The $Dq_y$ for the complex $[Cr(NH_3)_5OH]^{2+}$ has been measured as 1455 $cm^{-1}$.[106] This value would put terminal hydroxo ligands closer to fluoride than to water in the spectrochemical series. However, the visible spectrum of the hydroxo bridged complex, $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ has a low energy band ($V_1$) at 17180 $cm^{-1}$.[14] This complex can be considered to be a <u>cis</u>-isomer of $MX_4Y_2$ (where X = $H_2O$ and Y = OH) and the $Dq_y$ can then be calculated from the following expression[106] assuming band $V_1$ is the $^4B_1 \longleftarrow {}^4E$ transition,

$$V_1 = \frac{15}{2}Dq_x + \frac{5}{2}Dq_y \qquad \ldots\ldots \quad (26)$$

A value of $Dq_y$ = 1655 $cm^{-1}$ for the above complex was thus calculated. The bridged hydroxo ligand therefore also occurs near to water and near to carboxylate in the spectrochemical series.

The ligand-field splitting, 10 Dq, can also be calculated from the lowest energy visible absorption band ($V_1$) for the other hydroxo bridged

chromium(III) carboxylate complexes (Table 1 and 6), if the average environment rule[105] is applied, i.e. the magnitude of 10 Dq is a result of an average effect of all the ligands. The 10 Dq values for the acetate and formato complexes are shown in Table 12. These values are all similar to that of water, as would be expected since it was shown above that carboxylato and bridged hydroxo ligands occur close to water in the spectrochemical series.

Table 11

Spectrochemical data for $Cr(H_2O)_5Y$ complexes

| Y | $V_1$(kK) [a] | | Dt($cm^{-1}$) | Dt($cm^{-1}$) [b] Theoretical | $Dq_y$($cm^{-1}$) | Literature [c] value $Dq_y$($cm^{-1}$) |
|---|---|---|---|---|---|---|
| I | 15,41 | 17,25 | -226 | -206 | 947 | |
| Br | 16,08 | | -150 | -156 | 1 215 | |
| Cl | 16,45 | 17,03 | -107 | -120 | 1 363 | 1 318 |
| F | 16,84 | | - 67 | - 37 | 1 503 | 1 490 |
| $CCl_3CO_2$ | 17,33 | | - 7 | | 1 715 | |
| $HCO_2$ | 17,39 | | 0 | | 1 739 | |
| $H_2O$ | 17,39 | | 0 | 0 | 1 739 | 1 739 |
| $CHCl_2CO_2$ | 17,41 | | + 2 | | 1 747 | |
| $CH_2ClCO_2$ | 17,33 | | + 9 | | 1 799 | |
| $CH_3CO_2$ | 17,54 | | + 17 | | 1 799 | |
| NCS | 17,54 | | + 17 | 7 | 1 799 | 1 770 |
| $NH_3$ | 18,12 | | + 83 | 119 | 2 031 | 2 155 |
| CN | 19,20 | 17,50 | +207 | 260 | 2 463 | 2 670 |

[a] Ref. 105 [b] Ref. 106 [c] Ref. 105

Table 12

Spectrochemical data for chromium(III) carboxylate complexes

| Complex | 10 Dq($cm^{-1}$) | Complex | 10 Dq($cm^{-1}$) |
|---|---|---|---|
| $0a_1$ | 17 760 | $2a_3$ | 17 360 |
| $2a_5$ | 17 670 | $3a_2$ | 17 360 |
| $2a_1$ | 17 540 | $3f_2$ | 17 360 |
| $3a_1$ | 17 420 | $2f_3$ | 17 330 |
| $3f_1$ | 17 420 | 1a | 17 270 |
| $2f_1$ | 17 390 | $2a_4$ | 17 240 |
| | | $1f_1$ | 17 090 |

## SUMMARY

The complexes present in chromium(III) carboxylate solutions (acetate or formate) were separated using ion exchange chromatography, electrophoresis and gel filtration. Eight cationic species and one non-ionic species with charges from 0 to +3 and nuclearities ranging from mononuclear to quadranuclear were isolated from chromium(III) acetate solutions. Six cationic species with charges from +1 to +3 and nuclearities ranging from mononuclear to trinuclear were isolated from chromium(III) formate solutions. The empirical formulae for these complexes were determined by analytical methods. Infra-red spectroscopy was used to distinguish between monodentate and bidentate bridged carboxylate ligands. An immediate change in the visible spectrum of a complex on its acidification was used as evidence that a terminal hydroxo group was present. The following major, novel complexes were isolated, $[(H_2O)_3Cr(OH)_2(RCOO)Cr(H_2O)_3]^{3+}$ and $[(H_2O)_3Cr(OH)(RCOO)_2Cr(H_2O)_2OH]^{2+}$, where R = H or $CH_3$. The pK values for the protonated version of the latter were determined as 0,6 for the acetato complex and 0,4 for the formato complex (at a temperature of 20 °C and ionic strength of 0,5).

Acid dissociation constants for complexes with the formula, $[Cr(H_2O)_5Y]^{2+}$, where Y = $HCO_2$, $CH_3CO_2$, $CH_2ClCO_2$, $CHCl_2CO_2$, $CCl_3CO_2$, were determined at 25 °C and $\mu$ = 0,5 as 4,71, 4,84, 4,49, 4,61 and 4,38, respectively. The temperature variation of the acid dissociation constant for the complex where, Y = $HCO_2$, was used to determine the change in enthalpy and entropy, viz. $\Delta H$ = 8,0 Kcal/mol and $\Delta S$ = 5 cal/mol.

Analysis of the visible spectral data for the chromium(III) carboxylate and the hydroxo bridged chromium(III) complexes showed that water, bridged hydroxo groups and carboxylato groups all occur close to each other in the spectrochemical series.

## APPENDIX

### Table 13

Determination of the OH:Cr ratio using expression (11)

| $V_2$(mℓ) | $V_3$(mℓ) | [Cr] (M) | OH:Cr |
|---|---|---|---|
| | Complex $3a_1$ | | |
| 3,97 | 10,00 | 0,0104 | 0,99 |
| 3,54 | 10,00 | 0,0154 | 0,95 |
| 3,34 | 10,00 | 0,0173 | 0,96 |
| 3,21 | 10,00 | 0,0183 | 0,98 |
| | Complex $2a_3$ | | |
| 3,71 | 10,00 | 0,0128 | 1,01 |
| 3,41 | 10,00 | 0,0154 | 1,02 |
| 3,00 | 10,00 | 0,0185 | 1,08 |
| 3,60 | 10,00 | 0,0141 | 0,99 |
| | Complex $2a_4$ | | |
| 4,40 | 40,00 | 0,0025 | 0,60 |
| 4,02 | 60,00 | 0,0026 | 0,63 |
| 4,42 | 40,00 | 0,0025 | 0,58 |
| | Complex $2a_5$ | | |
| 2,00 | 40,00 | 0,0056 | 1,34 |
| 3,40 | 8,00 | 0,0147 | 1,36 |
| 1,37 | 20,00 | 0,0129 | 1,41 |
| | Complex 1a | | |
| 2,63 | 10,00 | 0,0343 | 0,69 |
| 2,00 | 10,00 | 0,0416 | 0,72 |
| 2,54 | 10,00 | 0,0346 | 0,71 |
| | Complex $0a_1$ | | |
| 3,05 | 25,00 | 0,0051 | 1,56 |
| 2,80 | 20,00 | 0,0072 | 1,53 |
| 2,93 | 20,00 | 0,0067 | 1,54 |
| | Complex $3f_1$ | | |
| 2,02 | 20,00 | 0,0149 | 1,02 |
| 2,47 | 20,00 | 0,0132 | 0,96 |
| 2,31 | 20,00 | 0,0110 | 0,98 |
| | Complex $2f_3$ | | |
| 3,10 | 10,00 | 0,0190 | 1,00 |
| 0,88 | 20,00 | 0,0200 | 1,03 |
| 3,50 | 25,00 | 0,0060 | 1,00 |
| | Complex $1f_1$ | | |
| 2,95 | 10,00 | 0,0301 | 0,68 |
| 1,62 | 20,00 | 0,0264 | 0,64 |
| 2,06 | 20,00 | 0,0210 | 0,70 |

$V_1$ = 5 mℓ, $N_1$ = 0,1 N, $N_2$ = 0,1 N

Table 14

Determination of the acetate:Cr ratio using expression (9)

| $V_1$(mℓ) | $V_2$(mℓ) | [Cr] (M) | Acetate:Cr |
|---|---|---|---|
| | | Complex $3a_1$ | |
| 2,01 | 20,00 | 0,0183 | 0,55 |
| 1,54 | 20,00 | 0,0154 | 0,50 |
| 1,63 | 20,00 | 0,0136 | 0,60 |
| 1,54 | 25,00 | 0,0112 | 0,55 |
| | | Complex $2a_1$ | |
| 4,37 | 10,00 | 0,0420 | 1,05 |
| 4,18 | 10,00 | 0,0394 | 1,07 |
| 3,80 | 10,00 | 0,0376 | 1,01 |
| | | Complex $2a_3$ | |
| 2,58 | 20,00 | 0,0134 | 0,96 |
| 3,02 | 20,00 | 0,0151 | 1,00 |
| 3,69 | 20,00 | 0,0179 | 1,01 |
| 2,90 | 20,00 | 0,0135 | 1,04 |
| | | Complex $2a_4$ | |
| 3,25 | 40,00 | 0,0056 | 1,43 |
| 0,88 | 10,00 | 0,0059 | 1,53 |
| 4,44 | 40,00 | 0,0071 | 1,55 |
| | | Complex $2a_5$ | |
| 3,53 | 60,00 | 0,0056 | 1,07 |
| 4,05 | 30,00 | 0,0129 | 1,09 |
| 1,55 | 10,00 | 0,0147 | 1,09 |
| | | Complex 1a | |
| 6,70 | 10,00 | 0,0343 | 1,95 |
| 8,49 | 10,00 | 0,0416 | 2,04 |
| 6,85 | 10,00 | 0,0346 | 1,99 |
| | | Complex $0a_1$ | |
| 3,14 | 40,00 | 0,0051 | 1,54 |
| 4,32 | 40,00 | 0,0072 | 1,50 |
| 4,07 | 40,00 | 0,0067 | 1,52 |

$N_1$ = 0,1 N

Table 15

Determination of the formate:Cr ratio using expression 8

| $V_1$ (mℓ) | $V_4$ (mℓ) | [Cr] (M) | Formate:Cr |
|---|---|---|---|
| | Complex $3f_1$ | | |
| 23,10 | 20,00 | 0,0149 | 0,54 |
| 27,05 | 25,00 | 0,0282 | 0,50 |
| 23,60 | 20,00 | 0,0173 | 0,52 |
| | Complex $2f_1$ | | |
| 25,90 | 25,00 | 0,0118 | 1,02 |
| 26,50 | 25,00 | 0,0126 | 1,03 |
| 28,40 | 25,00 | 0,0208 | 1,01 |
| | Complex $2f_3$ | | |
| 26,80 | 20,00 | 0,0162 | 1,05 |
| 25,50 | 15,00 | 0,0178 | 1,03 |
| 28,10 | 20,00 | 0,0190 | 1,00 |
| | Complex $1f_1$ | | |
| 36,20 | 10,00 | 0,0410 | 2,00 |
| 41,20 | 20,00 | 0,0263 | 2,02 |
| 37,60 | 20,00 | 0,0215 | 2,05 |

$N_1$ = 0,10 N, $N_2$ = 0,10 N, $V_2$ = 40 mℓ, $V_3$ = 60 mℓ

Table 16

Charge per chromium atom determination using expression 12 and 13

| $[Mg^{++}]_{eluent}$ (M) | $[Mg^{++}]_{eluate}$ (M) | $[Cr]_{eluate}$ (M) | $^{+}/Cr$ |
|---|---|---|---|
| | Complex $2a_3$ | | |
| 0,105 | 0,055 | 0,0845 | 1,18 |
| 0,140 | 0,105 | 0,0741 | 0,95 |
| 0,140 | 0,125 | 0,0272 | 1,10 |
| | Complex $2f_3$ | | |
| 0,079 | 0,075 | 0,0075 | 1,07 |
| 0,010 | 0,095 | 0,0173 | 1,04 |
| $[Na^{+}]_{eluent}$ (M) | $[Na^{+}]_{eluate}$ (M) | $[Cr]_{eluate}$ (M) | $^{+}/Cr$ |
| | Complex $2f_3$ | | |
| 0,578 | 0,550 | 0,0256 | 1,09 |
| 0,560 | 0,535 | 0,0279 | 0,90 |

Table 17

Determination of equilibrium constants at various temperatures for equilibrium 21, where Y = $HCO_2$ using expression 15 and 16

| | | Temperature (°C) | | | |
|---|---|---|---|---|---|
| | | 10,0 | | 15,5 | |
| NaOH (mequiv) | $\bar{n}$ | $[H^+]10^4$ (M) | pK | $[H^+]10^4$ (M) | pK |
| 0,310 | 0,872 | 0,661 | 5,01 | 0,871 | 4,89 |
| 0,335 | 0,840 | 0,513 | 5,01 | 0,676 | 4,89 |
| 0,360 | 0,809 | 0,417 | 5,01 | 0,550 | 4,89 |
| 0,385 | 0,778 | 0,347 | 5,01 | 0,457 | 4,89 |
| 0,410 | 0,746 | 0,288 | 5,01 | 0,380 | 4,89 |
| 0,435 | 0,715 | 0,245 | 5,01 | 0,324 | 4,89 |
| 0,460 | 0,683 | 0,214 | 5,00 | 0,282 | 4,89 |
| 0,485 | 0,652 | 0,186 | 5,00 | 0,240 | 4,89 |
| 0,510 | 0,621 | 0,166 | 5,00 | 0,214 | 4,88 |
| 0,535 | 0,589 | 0,145 | 5,00 | 0,191 | 4,88 |
| 0,560 | 0,558 | 0,132 | 4,98 | 0,166 | 4,88 |
| 0,585 | 0,526 | 0,117 | 4,98 | 0,151 | 4,87 |
| 0,610 | 0,495 | 0,105 | 4,97 | 0,138 | 4,85 |
| 0,635 | 0,464 | 0,095 | 4,96 | 0,123 | 4,85 |
| 0,660 | 0,432 | 0,085 | 4,95 | 0,112 | 4,83 |
| 0,685 | 0,401 | 0,076 | 4,95 | 0,102 | 4,83 |
| 0,710 | 0,369 | 0,069 | 4,93 | 0,093 | 4,80 |

$T_H$ = 1,004 mequiv  [Complex] = 0,7960 mequiv

Table 18

Determination of equilibrium constants at various temperatures for equilibrium 21, where Y = HCOO, using expressions 15 and 16

| NaOH (mequiv) | $\bar{n}$ | Temperature (°C) 20,0 $[H^+]10^4$ (M) | 20,0 pK | 25,0 $[H^+]10^4$ (M) | 25,0 pK |
|---|---|---|---|---|---|
| 0,310 | 0,872 | 1,047 | 4,81 | 1,318 | 4,71 |
| 0,335 | 0,840 | 0,832 | 4,80 | 1,047 | 4,70 |
| 0,360 | 0,809 | 0,661 | 4,81 | 0,832 | 4,71 |
| 0,385 | 0,778 | 0,550 | 4,81 | 0,692 | 4,71 |
| 0,410 | 0,741 | 0,468 | 4,80 | 0,603 | 4,69 |
| 0,435 | 0,715 | 0,398 | 4,80 | 0,513 | 4,69 |
| 0,460 | 0,683 | 0,347 | 4,79 | 0,447 | 4,68 |
| 0,485 | 0,652 | 0,302 | 4,79 | 0,389 | 4,69 |
| 0,510 | 0,621 | 0,269 | 4,78 | 0,347 | 4,67 |
| 0,535 | 0,589 | 0,240 | 4,78 | 0,309 | 4,67 |
| 0,560 | 0,558 | 0,214 | 4,77 | 0,282 | 4,65 |
| 0,585 | 0,526 | 0,191 | 4,77 | 0,251 | 4,65 |
| 0,610 | 0,495 | 0,174 | 4,75 | 0,229 | 4,63 |
| 0,635 | 0,464 | 0,155 | 4,75 | 0,209 | 4,62 |
| 0,660 | 0,432 | 0,145 | 4,72 | 0,191 | 4,60 |
| 0,685 | 0,407 | 0,132 | 4,71 | 0,169 | 4,60 |
| 0,710 | 0,369 | 0,117 | 4,70 | 0,151 | 4,59 |

$T_H$ = 1,004 mequiv  [Complex] = 0,7960 mequiv

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