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# Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. V. Identification of Reaction Products of the Perchloric Acid Hydrolysis of the *cis*- and of the *trans*-Diaquabis(1,2-ethanediamine)- and of the Tris(1,2-ethanediamine)chromium(III) Ions

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The title ions have been hydrolyzed in 1 M perchloric acid in the dark and the resulting mixtures of chromium(III) complexes have been separated by ion exchange chromatography. Large amounts of complexes coordinated with monoprotonated 1,2-ethanediamine ligand were found in the hydrolysis mixtures. Two new isomeric triamines and one pentaamine coordinated with one 2-aminoethylammonium ion ligand, and a diamine coordinated with two of these ligands were isolated in solution. Also a mixture of tetraamines, each coordinated with two 2-aminoethylammonium ion ligands was obtained in solution. By analogy with results for the chromium(III) ammonia system, *trans*-tetraamines and -diamines are not found as reaction products. Also from *trans*-tetraamine only *mer*-triamine is formed. Racemization of the *cis*-diaquabis(1,2-ethanediamine)chromium(III) ion has been observed, in contrast to the behaviour of the tris(1,2-ethanediamine)chromium(III) ion where no racemization could be detected.

As a continuation of our earlier studies of reactions of the ammineaquachromium(III) complexes,[1] it was of interest to us to investigate which effects would be observed for the chromium(III) amine bond breaking and isomerization reactions on introduction of a higher degree of stereochemical rigidity in the amine ligands studied. Therefore reactions of chromium(III) complexes coordinated with aliphatic amines were of particular interest, and as an introduction to this work we report here some initial results for the reactions of chromium(III) complexes coordinated with 1,2-ethanediamine.

Quantitative experiments on the acid hydrolysis of chromium(III) complexes of 1,2-ethanediamine were first carried out by Schläfer and coworkers, who studied the hydrolysis of the tris(1,2-ethanediamine)chromium(III)[2] and the *cis*-diaquabis(1,2-ethanediamine)chromium(III)[3] ions by spectrophotometric measurements, and of the optically active tris(1,2-ethanediamine)chromium(III)[4] ion by optical rotation experiments. The conclusions they reached about the initial stages of the tris(1,2-ethanediamine)chromium(III) hydrolysis reaction were later questioned by Jørgensen and Bjerrum,[5] who gave evidence for the production of the (2-aminoethylammonium)aquabis(1,2-ethanediamine)chromium(III) ion. Later the tetraaqua(1,2-ethanediamine)chromium(III) ion, postulated as an intermediate by Schläfer *et al.* was isolated in solution free of other chromium species by Garner *et al.*[6] who also investigated the aquation of this ion in an acid perchlorate medium, and were able to characterize the intermediate (2-aminoethylammonium)pentaaquachromium(III) ion. Our experience with the ammonia complexes of chromium(III) combined with the apparent robustness of the monoprotonated 1,2-ethanediamine ligand, questions the reported simplicity of the aquation

reactions of 1,2-ethanediamine complexes of chromium(III). Therefore we have undertaken a reinvestigation of this system and report here the characterization of reaction products from the acid hydrolysis of tris(1,2-ethanediamine)- and of the *cis*- and *trans*-diaquabis(1,2-ethanediamine)chromium(III) cations.

## EXPERIMENTAL

*Chemicals.** $[Cr(en)_3]Cl_3$,[7] $(+)_D$-$[Cr(en)_3]Cl_3$,[8] *cis*-$[Cr(en)_2Cl_2]Cl$,[7] $(-)_D$*cis*-$[Cr(en)_2(aq)_2]Br_3$,[9] *trans*-$[Cr(en)_2(aq)OH](ClO_4)_2$,[9] *fac*-$[Cr(en)(enH)Cl_3]Cl$,[10] $[Cr(en)(aq)_2Cl_2]Cl$,[11,12] $[Cr(O_2)_2(aq)(en)]$,[12] and $[Cr(en)(a)(aq)Cl_2]Cl$ [13] were all prepared by literature methods. Other chemicals, the Dowex 50 W X8 and the SP Sephadex C-25 ion exchange resins have been described earlier.[14] The chloride salts of racemic and optically active tris(1,2-ethanediamine)chromium(III) were converted into perchlorate salts by reprecipitation twice from water with 70 % perchloric acid. Solutions of the tris(1,2-ethanediamine)- and the *trans*-diaquabis(1,2-ethanediamine)-chromium(III) ions were made by directly dissolving the perchlorate salts in dilute perchloric acid. Mercury(II) accelerated chloride ligand hydrolysis in acid solution was used to generate aqua complexes from chlorido complexes. Such solutions were purified as follows: an amount of solution containing about 0.5 mequiv. of chromium(III) complex was charged onto a column (2 cm × 10 cm) packed with Sephadex ion exchange resin. Excess mercury(II) was removed by elution with 0.1 M sodium chloride solution and the chromium(III) complex left at the column top was next displaced with 1 M sodium perchlorate solution.

*Separation of hydrolysis mixtures.* The technique employed for isolation of the chromium(III) complexes from the hydrolysis mixtures was based upon a combination of ion exchange methods in acid and basic solution.

By elution upon Sephadex columns (2 cm × 10 cm) at about 20 °C with sodium perchlorate solution made 1 mM acid with perchloric acid complete separation between amineaqua species of different charges was obtained. A definite but incomplete separation between species of equal charges was seen. For such species the elution took place more readily the greater the number of coordinated water molecules, as was likewise observed for the ammonia complexes. Also, as with the ammonia complexes, *trans* isomers were eluted prior to corresponding *cis* isomers and *mer* isomers prior to corresponding *fac* isomers.

By elution upon Sephadex columns (2 cm × 10 cm) at about 20 °C with ammonium ion-ammonia buffer solutions the tri-, di-, and monopositively charged cations could be separated from each other, and from uncharged or anionic species not retained by the cation exchanger. Contrary to the acid elution where all species are stable in the time necessary for the elution to take place, some rather fast reactions proceed in basic solution. The most notable of these are the chelation reactions of the triamines and the pentaamine, where the tetraamine is formed within a few minutes at room temperature from the triamines, and the hexaamine, also significantly but substantially slower, is formed from the pentaamine.

The individual chromium(III) complexes were isolated from mixtures prepared by hydrolysis in the dark in 1 M perchloric acid as follows.

*Tris(1,2-ethanediamine)chromium(III).* This ion was eluted free of other chromium(III) species by elution with acid 0.5 M sodium perchlorate solution after removal of other chromium(III) species by elution with an 0.1 M ammonium chloride – 0.05 M ammonia buffer solution. In order to avoid contamination with rechelated pentaamine, however, only the column band of tripositive species from an acid 0.5 M sodium perchlorate elution was subjected to the basic elution. In a typical experiment optically active hexaamine was boiled for 5 min and the unhydrolyzed hexaamine recovered with unchanged optical activity.

*(2-Aminoethylammonium)aquabis(1,2-ethanediamine)chromium(III).* Basic elution with an 0.1 M ammonium chloride – 0.01 M ammonia buffer solution was used to remove all anionic, neutral, or monopositively charged species. The pentaamine and hexaamine remaining at the column top were next separated by acid 0.5 M sodium perchlorate solution. In a typical experiment pentaamine ion was isolated from hexaamine solution boiled for 1 min.

cis-*Diaquabis(1,2-ethanediamine)chromium-(III).* After an acid 0.5 M sodium perchlorate elution, to isolate the tripositive ions, recovery of monopositively charged species in a basic 0.1 M ammonium chloride – 0.05 M ammonia buffer solution elution allowed the isolation of tetraamminediaqua ions. In one experiment pure *cis* isomer was isolated in this way from the hexaamine which had been boiled for 5 min. In another experiment active *cis* isomer maintained at 60 °C for 1.35 and 3.17 h was recovered with 48 % and 15 %, respectively, of the initial optical activity.

For the remaining cations described below acid sodium perchlorate elution only was employed for their isolation. In all cases fractionation of the column eluate was used to confirm

* All chemicals are written without water of crystallization since this may vary with the history of the compound. The following ligand abbreviations are used in chemical formula throughout the paper: a = ammonia, aq = water, en = 1,2-ethanediamine, enH = 2-aminoethylammonium ion.

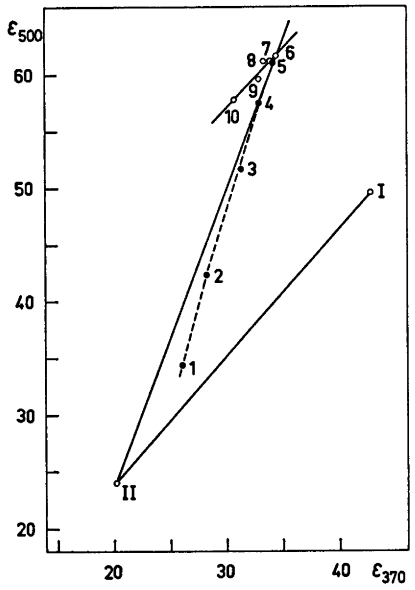


*Fig. 1.* Fractionation of hydrolysis mixture obtained by boiling tris(1,2-ethanediamine)-chromium(III) ions in 1 M perchloric acid for 3 min. The molar extinction coefficient at 500 nm for ten succesive fractions eluted after the main portion of tetrapositive pentaamine is plotted as a function of the molar extinction coefficient at 370 nm for these same fractions. Points I and II are the pure pentaamine and pure pentapositive diamine, inserted for comparative purposes. Incomplete separation mainly between pentapositive tetraamine and diamine is seen, but since the points, depicted by filled circles, are not situated on a straight line that passes through the pure pentapositive diamine, also some pentaamine must be present, mainly in the first fractions. The marked difference in fractionation behaviour before and after fraction 6 makes it likely that this fraction is free of pentapositive diamine. Constant spectra of successive fractions were, however, not obtained as depicted by the open circles. Complete visible absorption spectra of the first and the last pure tetraamine fraction, points 6 and 10 respectively, are given in Fig. 4.

the isomeric purity of the species.

*Bis(2-aminoethylammonium)diaqua(1,2-ethanediamine)chromium(III)*. Results of a fractionation experiment of the band of pentapositively charged species formed by boiling a hexaamine solution for 3 min are exhibited in Fig. 1. In order to get measurable amounts of the tetraamines, hexaamine hydrolyzate was charged onto a Sephadex column (2 cm × 15 cm) until the yellow hexaamine colour was mainly

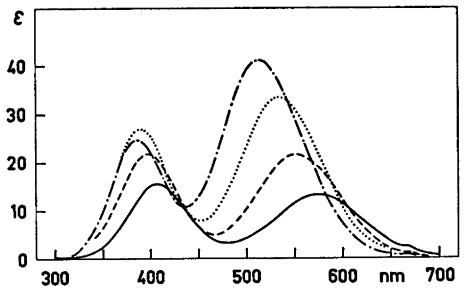


*Fig. 2.* Visible absorption spectra of compounds prepared as described in the text. ———, $[Cr(aq)_6]^{3+}$; - - -, $[Cr(enH)(aq)_5]^{4+}$; ···, *cis*-$[Cr(enH)_2(aq)_4]^{5+}$; — · —, $[Cr(en)(aq)_4]^{3+}$.

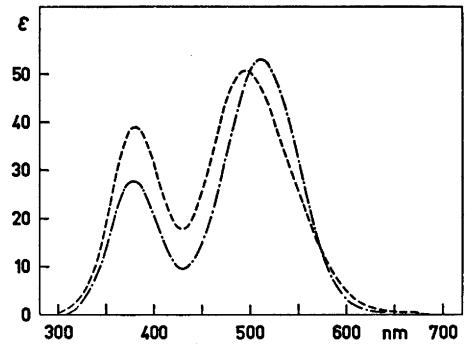


*Fig. 3.* Visible absorption spectra of compounds prepared as descibed in the text. - - -, *mer*-$[Cr(en)(enH)(aq)_3]^{4+}$; — · —, *fac*-$[Cr(en)(enH)(aq)_3]^{4+}$.

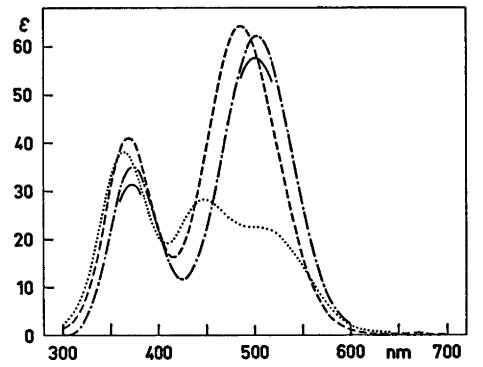


*Fig. 4.* Visible absorption spectra of compounds prepared as described in the text. · · ·, *trans*-$[Cr(en)_2(aq)_2]^{3+}$; - - -, *cis*-$[Cr(en)_2(aq)_2]^{3+}$; — · —, first; and ———, last fraction of the $[Cr(en)(enH)_2(aq)_2]^{5+}$ mixture. (Points 6 and 10 of Fig. 1, respectively).

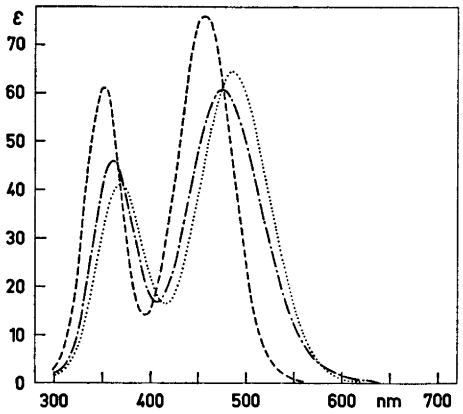


*Fig. 5.* Visible absorption spectra of compounds prepared as described in the text. · · ·, *cis*-$[Cr(en)_2(aq)_2]^{3+}$; — · —, $[Cr(en)_2(enH)(aq)]^{4+}$; - - -, $[Cr(en)_3]^{3+}$.

concentrated at the column bottom. The adsorbed species were then eluted with acid 1 M sodium perchlorate solution. The large amounts of chromium(III) species present account for the incomplete separation between tetrapositive and pentapositive species.

fac-*(2-Aminoethylammonium)triaqua(1,2-ethanediamine)chromium(III)*. Due to the limited column lengths necessitated by the instability of some of the chromium(III) species, this ion was never isolated pure in solution from the hydrolysis mixture of tetrapositive ions. Chloride ligand hydrolysis of crude impure *fac*-$[Cr(en)(enH)Cl_3]Cl$ generated, however, a mixture of the *fac* triamine ion and the tetraaqua(1,2-ethanediamine)chromium(III) ion which were easily separated from each other by acid 0.5 M sodium perchlorate elution.

mer-*(2-Aminoethylammonium)triaqua(1,2-ethanediamine)chromium(III)*. This ion was the only triamine hydrolysis product of the *trans*-diaquabis(1,2-ethanediamine)chromium(III)ion. In one experiment the *trans* tetraamine was boiled for a few seconds then rapidly cooled to room temperature. This treatment generated the *mer* triamine as the only tetrapositive cation, which consequently was readily obtained pure in solution by elution with acid 0.5 M sodium perchlorate solution.

*Tetraaqua(1,2-ethanediamine)chromium(III)*. This ion was only with difficulty separated from other tripositive cations in the hydrolysis mixtures, although Dowex columns operated with 2 M sulfuric acid or Sephadex columns operated with acid 0.1 M sodium sulfate were able to affect this separation. Hydrolysis of the *cis* tetraamine gave always mixtures of tripositive cations, whereas the *trans* tetraamine isomer when boiled for 10 min formed the pure diamine ion, indistinguishable from the one produced both from $[Cr(en)(aq)_2Cl_2]Cl$ and from $[Cr(O_2)_2(aq)(en)]$.

*Bis(2-aminoethylammonium)tetraaqua- and (2-aminoethylammonium)pentaaquachromium-(III) ions*. These two cations are the only pentapositive and tetrapositive species produced by hydrolysis of the *cis*-diaquabis(1,2-ethanediamine)- and the tetraaqua(1,2-ethanediamine)chromium(III) ions, respectively. Therefore they were readily prepared pure in solution by acid 0.5 M sodium perchlorate elution upon Sephadex. Typical reaction times at the boiling point of the solution were about 10 min for production of substantial amounts of the diamine and 3 h for production of the monoamine.

Visible absorption spectra of the compounds prepared and purified as described above are given in Figs. 2 – 5.

## RESULTS AND DISCUSSION

All aqua(1,2-ethanediamine)chromium(III) isomers with the diamine as a chelate ligand have previously been characterized in solution. As the displacement of the bidentate diamine ligand takes place in two distinct steps, with monoprotonated unchelated diamine complex as intermediate in acid solution, tetra-, penta-, and hexapositive cations are possible aquation products of the initial tripositive cations.

Sodium perchlorate solution is an effective eluting agent for the separation of chromium(III) amine species of different charges upon SP Sephadex C-25 cation exchange resins. With hydrolyzed solutions of both tetraaqua(1,2-ethanediamine)chromium(III) and *trans*-diaquabis(1,2-ethanediamine)chromium(III) ions only column bands indicative of tri- and tetrapositive species, respectively, are observed, whereas with hydrolyzed solutions of both *cis*-diaquabis(1,2-ethanediamine)chromium(III) and tris(1,2-ethanediamine)chromium(III) ions, also a column band indicative of pentapositive species appears. Evidence for the production of hexapositive species was never obtained, but in view of the very limited amounts of tetraamine with two nonchelated diamine ligands present in solu-

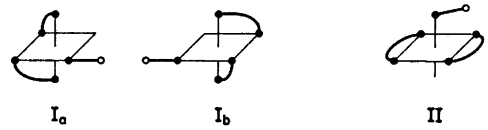


*Fig. 6.* Possible pentaamineaquachromium(III) isomers.

tions of hydrolyzed tris(1,2-ethanediamine)chromium(III), this is readily understood.

The two geometrical isomers of the (2-aminoethylammonium)aquabis(1,2-ethanediamine)-chromium(III) ion, one of which exists in optically active forms are shown in Fig. 6. Hydrolysis of optically active tris(1,2-ethanediamine)chromium(III) ions yields optically active pentaamine, of which different column eluates are indistinguishable as judged from the visible absorption spectra. Consequently, either pentaamine isomer II is not present in significant amounts, or elution behaviour or visible absorption spectra of the two isomers are almost identical. These latter possibilities seem unlikely from a comparison with the fractionation experiments with the bis(2-aminoethylammonium)diaqua(1,2-ethanediamine)chromium(III) mixtures, and therefore the pentaamine solution isolated is believed not to contain appreciable amounts of isomer II (see Fig. 6). Also the reaction mechanism, previously postulated by us [1] which rationalizes the chromium(III) ammine hydrolysis and isomerization reactions by assuming that these reactions takes place *via* an intermediate of increased coordination number with an approximately pentagonal bipyramidal structure, predicts that pentaamine isomer II cannot be formed directly from the tris(1,2-ethanediamine)chromium(III) ion but only by an isomerization reaction of the pentaamine isomer I.

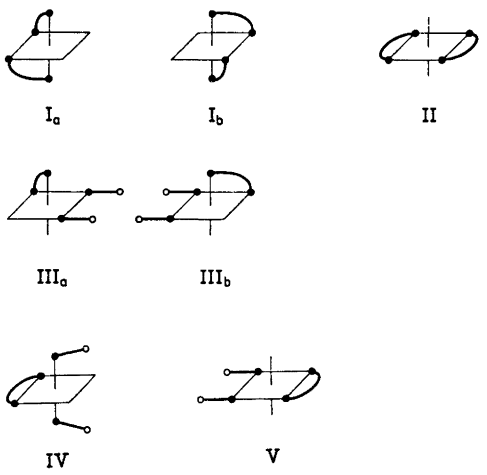


*Fig. 7.* Possible tetraaminediaquachromium(III) isomers.

Two geometrical isomers of diaquabis(1,2-ethanediamine)chromium(III) and three geometrical isomers of bis(2-aminoethylammonium)diaqua(1,2-ethanediamine)chromium(III) are possible. Two of these five tetraamine ions exist in optically active forms as shown in Fig. 7. In the hydrolysis experiments the *cis*-diaquabis(1,2-ethanediamine)chromium(III) ion is the only tripositive tetraamine species observed. From optically active tris(1,2-ethanediamine)-chromium(III) this tetraamine is produced optically active, but with reduced optical activity compared to that of the pure optical isomer, whereas the optical activity of the unhydrolyzed tris(1,2-ethanediamine)chromium(III) ion remains unchanged. Again the observations are consistent with the proposed substitution mechanism, which cannot account for racemization of the tris(1,2-ethanediamine)chromium(III) ion except by diamine rechelation, but leaves a number of posibilities for production of partly racemized *cis*-diaquabis(1,2-ethanediamine)-chromium(III) ions.

One of these possibilities was investigated further: optically active *cis*-diaquabis(1,2-ethanediamine)chromium(III) ions were kept in 1.0 M perchloric acid at 60 °C, and the optical activity of the isolated unhydrolyzed *cis*-tetraamine measured as a function of time. Since the *trans*-tetraamine has never been found in hydrolyzed solutions of the *cis* isomer, and is also known to hydrolyze appreciably faster than the *cis* isomer, the *trans*-tetraamine ion cannot be of importance as an intermediate for the $(-)_D$-*cis* to $(+)_D$-*cis* racemization reaction. We have therefore interpreted our preliminary kinetic data as showing that the reaction:

$$(-)_D\text{-}cis[Cr(en)_2(aq)_2]^{3+} \underset{k}{\overset{k}{\rightleftharpoons}} (+)_D\text{-}cis[Cr(en)_2(aq)_2]^{3+}$$

occurs in acid solution at 60 °C and has a rate constant, $k$, of about $8 \times 10^{-5}$ s$^{-1}$.

Only small amounts of tetraamines with two unchelated diamines are present in hydrolyzed solutions of tris(1,2-ethanediamine)chromium-(III) ions. In Fig. 1 results of a fractionation experiment with the column band of pentapositive species are exhibited. Because of the very large amounts of hydrolyzed tris(1,2-ethanediamine)chromium(III) ion solution em-

*Table 1.* Comparison with literature values of spectral characteristics of compounds prepared and purified as described in the text.

| Complex | Medium | $\lambda_1$ max (nm) | $\varepsilon_1$ max [l/(mol cm)] | $\lambda_2$ max (nm) | $\varepsilon_2$ max [l/(mol cm)] | $\varepsilon_1$ max/ $\varepsilon_2$ max | Ref. |
|---|---|---|---|---|---|---|---|
| $[Cr(en)_3]^{3+}$ | 1.0 M HCl | 457 | 75.8 | 351 | 60.8 | 1.25 | *b* |
| | 1 M $NaNO_3$ | 457 | 76.5 | 351 | 60.7 | | 15 |
| $[Cr(en)_2(enH)(aq)]^{4+}$ | 0.5 M $HClO_4$ + 1.0 M $NaClO_4$ | 474 | 60.8 | 361 | 45.7 | 1.33 | *b* |
| *cis*-$[Cr(en)_2(aq)_2]^{3+}$ | 0.25 M $HClO_4$ + 1.0 M $NaClO_4$ | 486 | 64.2 | 368 | 41.2 | 1.56 | *b* |
| | 1 M $NaNO_3$ | 484 | 67.0 | 367 | 42.5 | | 15 |
| ?-$[Cr(en)(enH)_2(aq)_2]^{5+}$ [a] | 0.5 M $HClO_4$ + 1.0 M $NaClO_4$ | 502 | 62.1 | 372 | 34.9 | 1.78 | *b* |
| *trans*-$[Cr(en)_2(aq)_2]^{3+}$ | 1.0 M $HClO_4$ | 447 | 28.2 | 364 | 38.1 | 0.74 | *b* |
| | 1 M $NaNO_3$ | 442 | 29.3 | 361 | 39.2 | | 15 |
| *fac*-$[Cr(en)(enH)(aq)_3]^{4+}$ | 0.25 M $HClO_4$ + 1.0 M $NaClO_4$ | 511 | 52.9 | 378 | 27.8 | 1.90 | *b* |
| *mer*-$[Cr(en)(enH)(aq)_3]^{4+}$ | 0.25 M $HClO_4$ + 1.0 M $NaClO_4$ | 495 | 50.7 | 380 | 38.9 | 1.30 | *b* |
| $[Cr(en)(aq)_4]^{3+}$ | 0.25 M $HClO_4$ + 1.0 M $NaClO_4$ | 512 | 41.3 | 387 | 24.7 | 1.67 | *b* |
| | 0.1 – 3 M $HClO_4$ | 512 | 41.7 | 385 | 24.3 | | 6 |
| *cis*-$[Cr(enH)_2(aq)_4]^{5+}$ | 0.5 M $HClO_4$ + 1.0 M $NaClO_4$ | 534 | 33.3 | 391 | 26.8 | 1.23 | *b* |
| $[Cr(enH)(aq)_5]^{4+}$ | 0.25 M $HClO_4$ + 1.0 M $NaClO_4$ | 551 | 21.5 | 397 | 21.4 | 1.01 | *b* |
| | 3 M $HClO_4$ | 549 | 22.2 | 396 | 21.5 | | 6 |

[a] See legend to Fig. 1. [b] This work.

*Table 2.* Comparison between chromium(III) complexes equivalently coordinated with ammonia and 2-aminoethylammonium ions.

| Complex | $\lambda_1$ max (nm) | $\varepsilon_1$ max [l/(mol cm)] | $\lambda_2$ max (nm) | $\varepsilon_2$ max [l/(mol cm)] |
|---|---|---|---|---|
| $[Cr(a)(aq)_5]^{3+}$ | 547 | 19.9 | 396 | 18.6 |
| $[Cr(enH)(aq)_5]^{4+}$ | 551 | 21.5 | 397 | 21.4 |
| *cis*-$[Cr(a)_2(aq)_4]^{3+}$ | 526 | 27.0 | 386 | 21.3 |
| *cis*-$[Cr(enH)_2(aq)_4]^{4+}$ | 534 | 33.3 | 391 | 26.8 |
| *mer*-$[Cr(en)(a)(aq)_3]^{3+}$ | 491 | 41.3 | 378 | 33.1 |
| *mer*-$[Cr(en)(enH)(aq)_3]^{4+}$ | 495 | 50.7 | 380 | 38.9 |

ployed in order to get measurable amounts of these tetraamines, incomplete separation between the eluted chromium(III) species is seen to have occurred. The fractions of pentapositive species are seen to consist of at least two components in addition to the *cis*-bis(2-aminoethylammonium)tetraaquachromium(III) ion. The latter fractions of pentapositive species had spectra typical of *cis*-tetraaminediaquachromium(III) species. As the elution progresses the maximum of the first spin-allowed band is shifted towards the blue from the 502 nm of the first fraction believed to be free of the *cis*-diamine. This makes it less plausible that hexapositive triamines are eluted after the pentapositive species, as from Table 2 it seems to be a general feature that the position of the first spin-allowed band of 2-aminoethylammonium complexes of chromium(III) is shifted towards the red compared to complexes equivalently coordinated with ammonia, and first spin-allowed band positions of 502 and 513 nm for the *mer*- and *fac*-triamminetriaquachromium(III) ions, respectively, are observed.

The structure of the *cis*-tetraaminediaquachromium(III) isomers III and IV (Fig. 7) accounts well for both visible absorption spectra and elution behaviour of the pentapositive tetraamine species isolated from tris(1,2-ethanediamine)chromium(III) hydrolyzates. Since the maximum of the first spin-allowed band of the tetraamine fractions is shifted towards the red compared to that of the *mer*-(2-aminoethylammonium)triaqua(1,2-ethanediamine)chromium(III) ions, and substitution of water with an amine nitrogen donor atom is expected to be accompagnied by a blue shift, the first tetraamine fractions are tentatively assumed to contain most of the *cis*-tetraamine not derivable from the *mer*-triamine, by exchange of a coordinated water molecule with a 1,2-aminoethylammonium ion ligand, *i.e.* isomer IV. Tetraamine isomer III should in principle be expected to be produced optically active from the active tris(1,2-ethanediamine)chromium(III) ion. However, such dilute column eluates of this tetra-

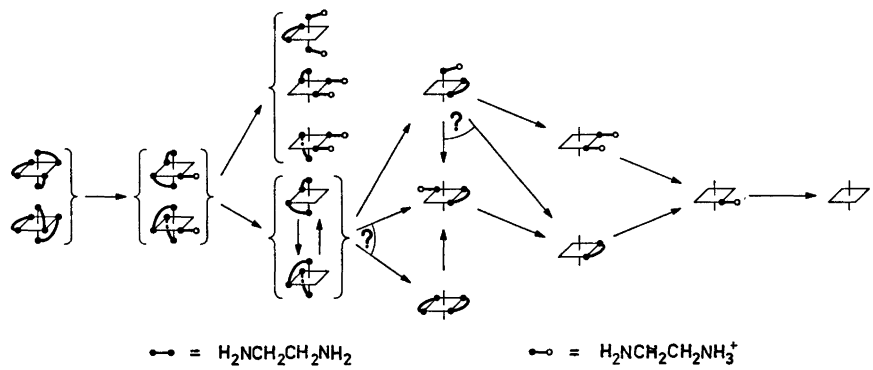


*Fig. 8.* Reaction scheme for the acid hydrolysis of 1,2-ethanediamine complexes of chromium(III).

amine were always obtained, that measurements of well defined rotations could not be performed, which is as would be expected even with a molar rotation of the active tetraamine comparable to that of the tris(1,2-ethanediamine)chromium(III) ion.

Significant amounts of tetrapositive triamines are present in hydrolyzed tris(1,2-ethanediamine)chromium(III) ion solutions even after comparatively short reaction times. The inconsistency between this fairly rapid production and the somewhat slower appearance of these same triamine ions from the main isolated tetraamine reaction product [the *cis*-diaquabis-(1,2-ethanediamine)chromium(III) ion] indicate that a significant amount of the triamines are formed *via* other tetraamines than this latter tetraamine species. In the chromium(III) ammine system the *trans*-diaqua species is not formed in detectable amounts.[1] If this holds true also for the chromium(III) 1,2-ethanediamine system tetraamine isomers II and V should not be expected to play any important role in the aquation reactions. Therefore, although always present in small amounts tetraamine isomers III and IV are formed in quantities comparable to the *cis*-diaquabis(1,2-ethanediamine)chromium(III) ion but removed substantially faster by the subsequent aquation.

The minor amounts of pentapositive tetraamine ions present in solution of hydrolyzed tris(1,2-ethanediamine)chromium(III) ions and the tedious procedure for the preparation of only very dilute solutions of mixtures of these tetraamine ions prevented the investigation of the further reactions of these species. Reaction products with fewer than three diamines coordinated were more conveniently studied by hydrolyzing the *cis*- and *trans*-diaquabis(1,2-ethanediamine)chromium(III) ions, since far less complicated reaction mixtures were obtained by hydrolysis of these two cations than by hydrolysis of the tris(1,2-ethanediamine)chromium-(III) ion.

Two tetrapositive triamine ions are possible, and these may be labelled *mer* and *fac*, respectively, if the coordinated water is considered. From the *trans* tetraamine ion one of these triamine ions is produced fairly rapidly compared to the speed at which a mixture of the two triamines are produced from the *cis* tetraamine ion. For this latter tetraamine ion the complexity of the tetrapositive column band is further enhanced by the fact that the initial tetraamine ion is so robust that further aquation produces the tetrapositive monoamine ion, (2-aminoethylammonium)pentaaquachromium-(III), within reaction times suitable for production of significant amounts of triamine ions. Although the triamine ion produced from the *trans* tetraamine ion was easily isolated free of other chromium species in solution, the mixture of tetrapositive species produced by hydrolysis of the *cis* tetraamine isomer was not easily converted into solutions of pure substances. Therefore solutions of the triaminetriaqua ion obtained by mercury(II) accelerated chloride hydrolysis of the (2-aminoethylammonium)trichlorido(1,2-ethanediamine)chromium(III) ion was examined. Such solutions contained one pure triamine ion, different from the one isolated from the *trans* tetraamine ion hydrolyzates, and less readily eluted on ion exchange columns than this latter triamine ion. From the positions and shapes of the first spin-allowed absorption bands given in Table 1 and Fig. 3, the elution behaviour, and their mode of formation if comparisons with the chromium(III) ammine system are valid, a *mer* triaqua structure is assigned to the triamine isomer obtained from the *trans* tetraamine ion, and to the other triamine isomer a *fac* triaqua structure is assigned.

By the further aquation the *cis*-tetraaqua-(1,2-ethanediamine)chromium(III) ion appears from both these triamine ions. From the *fac* triamine, however, also a pentapositive diamine can be isolated. The visible absorption spectrum and the mode of formation of this ion indicated a *cis* diamine structure, wherefore it must be the *cis*-bis(2-aminoethylammonium)tetraaquachromium(III) ion. Only the monoamine ion, (2-aminoethylammonium)pentaaquachromium-(III), is a possible aquation product of both diamine ions, and from the monoamine ion only the hexaaquachromium(III) ion is a possible reaction product in acid solution.

A summary of all these qualitative results is given in Fig. 8. Two question marks are seen in this kinetic scheme. These are caused by the considerably faster reactions of the *trans* than of the *cis*-diaquabis(1,2-ethanediamine)chromium(III) and the likewise faster reaction of the *mer*- than of the *fac*-(2-aminoethylammonium)-

triaqua(1,2-ethanediamine)chromium(III) ions, which do not allow distinction to be made between direct slow aquation or slow isomerization followed by rapid aquation. The eventual kinetic importance of undetected species and other reaction pathways in this system must await a complete quantitative investigation. The semiquantitative results reported here seem, however, to make doubtful the quantitative conclusions reached in some earlier works within this field.

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