Chromium(III) Complexes of Macrocyclic Amine Ligands. Preparation and Properties of Some Chromium(III) Complexes of 1,5,9,13-Tetraazacycloclohexadecane

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Chromium(III) reacts in anhydrous solvents with the title cyclic tetraamine, cycnt, to give species containing the Cr(cyctn) moiety, which exists in the cis and in at least two trans configurations: these have been characterized as solids and in solution. Transformations between these three configurations have been investigated in aqueous solution containing hydroxide, fluoride, chloride or perchlorate ions, and can be summarized as:

cis $\leftrightarrow$ (u)-trans $\rightarrow$ (s)-trans

with the trans configurations labelled (u) and (s) for unstable and stable, respectively. Characterization of two (s)-trans-[Cr(cyctn)Cl(OH$_2$)]$^{2+}$ isomers suggests that the stable trans-Cr(cyctn) moiety is unsymmetrical with respect to axial coordination.

The replacement of simple ligands by macrocyclic ligands greatly modifies the reactivity of metal ions, and this seems an important feature of many processes. Structural parameters are obviously of importance, and both electronic and steric effects play dominating roles. The effect of coordinating macrocyclic ligands to a chromium(III) center is, however, a relatively little explored field, despite the now well documented participation of chromium(III) complexes in biological processes.

The ring size of cyclic ligands is a parameter of great importance for the behaviour of metal complexes. It has thus been demonstrated for cobalt(III) complexes of a series of saturated cyclic tetraamines that larger ring sizes favour faster ligand substitution reactions and ease the reduction to cobalt(II). For the sixteen membered 1,5,9,13-tetraazacyclohexadecane ring, cycnt, cf. Fig. 1, this last feature is so pronounced that oxidation of the cobalt(II) amine complex was unsuccessful in aqueous solution and could only be performed in a nonaqueous solvent. Such complications may be some of the reasons why complexes of this ligand have been very little investigated despite the similarity to many naturally occurring unsaturated systems.

Chromium(III) is much more difficult to reduce than cobalt(III) and is therefore a good candidate for investigating cyctn ligand complexes without extra complications from redox reactions. Also the substitution kinetic behaviour of cobalt(III) complexes is different from that of most other trivalent robust transition metal ions, and the present work was initiated with the intention to attempt to assess to which extent conclusions on the kinetic behaviour of macrocyclic complexes, based upon data for cobalt(III), are valid also for other systems.

Fig. 1. 1,5,9,13-Tetraazacyclohexadecane.
RESULTS AND DISCUSSION

Two rather general synthetic procedures for the preparation of chromium(III) amine complexes involve reacting the free amine with either anhydrous chromium(III) chloride or with suitable salts of the trans-difluoridotetrakis(pyridine)chromium(III) cation in a poorly coordinating solvent. Both methods work satisfactorily for the cysctn ligand. The first method gives a yellowish green solid, which can be purified as a perchlorate salt. This was identified as trans-[Cr(cycn)Cl_2]ClO_4 by its visible absorption spectrum and analytical data. The second method gives significant amounts of a red violet solid and a much smaller yield of a violet substance. Visible absorption spectra, cf. Fig. 2, and analytical data identified these two compounds as cis- and trans-[Cr(cycn)F_2]I, respectively.

cis-[Cr(cycn)F_2]I can be reacted with hydrochloric acid to give a green compound. Analytical data and the colour suggest a formulation as trans-[Cr(cycn)Cl_2]I. However, the visible absorption spectra of the cation of this compound and of that of the perchlorate salt are different, cf. Fig. 3. Both are characteristic of trans complexes, however. Prolonged heating of a solution of the iodide salt in hydrochloric acid converts the dichlorido isomer of this salt into that of the above perchlorate salt, which is therefore the more stable isomer. In accordance with this, these two trans isomers are referred to below as (u)- and (s)-trans-[Cr(cycn)Cl_2]^+, the prefixes being derived from unstable and stable, respectively.

In the trans-Cr(cycn) moiety the tetraamine can have four different conformations, as shown in Fig. 4. For cobalt(III) a brown and a green trans-dichlorido isomer have been obtained. The modes of formation of these isomers can be summarized as:

\[
\text{cis-[Co(cycn)(O_2CO])^+} \rightarrow \text{(green)trans-[Co(cycn)Cl_2]^+} \rightarrow \text{(brown)trans-[Co(cycn)Cl_2]^+}
\]

Fig. 4. Possible amine ligand conformations in octahedral trans-M(cycn)X_2 complexes. Nitrogen bound hydrogen atom positions above and below the MN_4-plane are indicated by + and −, respectively. Conformer names are constructed by considering the nitrogen bound hydrogen atom pairs on the four six membered chelate rings cyclically using c and t prefixes for cis and trans hydrogens, respectively.

compared with

cis-[Cr(cyctn)F₂]⁺ →
  (u)-trans-[Cr(cyctn)Cl₂]⁺  
  (s)-trans-[Cr(cyctn)Cl₂]⁺

for the chromium(III) system. Spectrochemically the pairs of isomers for cobalt(III) and for chromium(III) behave similarly, cf. Fig. 3 and Ref. 1. A comparison of Δ-values for the cyctn ligand thus shows:

Co(III): Δ[(brown)trans]<Δ[(green)trans]  
Cr(III): Δ[(s)-trans]<Δ[(u)-trans]

Both the modes of formation and spectral characteristics make it therefore likely that the tetraamine ligand conformation of the brown cobalt complex is the same as that of the stable chromium complex, and also that the green cobalt complex has the tetraamine configuration of the unstable chromium isomer.

Computations of differences in conformational energies have been the basis for tentatively assigning:

(brown)trans ≡ (cict)−trans

and

(green)trans ≡ (ccct)−trans

cf. Fig. 4, for the cobalt complexes.¹

The present trans-dichlorochromium(III) isomers are much more robust than the corresponding cobalt(III) isomers, which have half-lives of about 0.3 s at 25 °C for aquation of the first chloride ligand in both isomers.² The analogous chromium(III) complexes can be kept in acid solution for extended periods of time without measurable chloride ligand aquation, and can be boiled in strongly basic solution for several minutes without aquation of the amine ligand. This robustness makes the chromium complexes amenable for detailed studies. In Fig. 5 a summary is given of the experiments conducted, in an attempt to further clarify the conditions for the stereochemical transformations. Configurational change around the chromium center is seen to be the preferred reaction in acid solution, whereas in basic solution the stereochemical reactivity is dominated by configurational changes around coordinated nitrogen atoms. Two trans isomers have only been obtained for the dichloro species. Reactivities and spectral characteristics of the remaining trans isomers, particularly the similarity in intensities and positions of the high energy component of the “first” spin-allowed absorption bands, make it most likely that these are all complexes, which have the stable tetraamine configuration. One other observation is of stereochemical significance: aquation of (s)-trans-[Cr(cyctn)Cl₂]⁺ and anation of trans-[Cr(cyctn)(OH₂)₂]³⁺ with Cl⁻ gives mixtures which contain two aquachlorido isomers. They can be partly separated by ion exchange chromatography and both give trans-[Cr(cyctn)-(OH₂)₂]³⁺ by treatment with mercury(II). The mercury(II) induced aquation of (u)-trans-[Cr(cyctn)Cl₂]⁺ gives cis-[Cr(cyctn)(OH₂)₂]³⁺, cf. Fig. 5, and both aquachlorido isomers therefore most likely have the stable trans conforma-

Fig. 5. Summary of reactions of Cr(cyctn) complexes, see also the text.
tion which consequently must be unsymmetrical with respect to axial coordination. The (ccct)-trans or (ccct)-trans, cf. Fig. 4, are therefore the most likely conformations of the stable trans complexes. This result is not in agreement with conclusions from molecular mechanics computations on cobalt(III) complexes, if the comparison between the cobalt(III)- and chromium(III) isomers is valid.

It may be concluded from the above that tetraaminechromium(III) complexes of the cyctn ligand show a behaviour much more normal within chromium(III) chemistry than does the cobalt(III) cyctn complexes within tetraaminecobalt(III) systems. This latter feature has been rationalized on the basis of an ill fitting ring size for a cobalt(III) center, but the behaviour of the present chromium(III) complexes makes this hypothesis less attractive as the only contributing factor.

A detailed mechanism for configurational and conformational changes must at present be speculative. Work is in progress, however, both on the further characterization of the intermediates of the reactions described in Fig. 5, and also on the preparation of solid compounds suitable for direct structural investigations.

EXPERIMENTAL

Chemicals. 1,5,9,13-Tetraazacyclohexadecane, cyctn, and trans-difluoridotetrakis(pyridine)-chronium(III) iodide, trans-[Cr(py)₂F₂]I₂ were prepared according to literature methods. All other chemicals were commercial products.

Preparations. Most Cr(cyctn) complexes are readily soluble in a variety of solvents. This in combination with an apparently lower stability of the cyctn complexes than is usual for chromium(III) amines under preparative conditions, limits the yields from the following preparations. More material than reported containing the Cr(cyctn) moiety may, however, be obtained by evaporating the mother liquors at 50 °C in vacuum and treating the residue with hot 4 M hydrochloric acid. Addition of excess ClO₄⁻ to these solutions gives (u,s)-trans-[Cr(cyctn)Cl₂]ClO₄, analyses Cr, Cl, N, C, H, and it usually brings the total yield of material containing the Cr(cyctn) moiety by the following preparations up around 70%.

1. (s)-trans-[Cr(cyctn)Cl₂]ClO₄. 1.75 g CrCl₃ is warmed with about 10 mg of Zn-powder in 10 ml N,N-dimethylformamide until it dissolves. A solution of 2.5 g cyctn in 5 ml N,N-dimethylformamide is added, and the mixture is kept at 120 °C for 30 min. This produces a yellowish green compound. The mixture is cooled in ice after which the precipitate is filtered off and washed twice with acetone. Yield 2.3 g. The crude product is dissolved in 30 ml 0.1 M HCl at room temperature, and this solution is filtered to remove traces of chromium(III) hydroxide. Slow addition of 5 ml saturated NaClO₄ solution and cooling in ice gives a yellowish green precipitate. This is filtered off and washed twice with cold acetone. Yield 1.9 g (38%). Analyses Cr, Cl, N, C, H.

2. cis-[Cr(cyctn)F₂]I₂·2H₂O. 9.4 g trans-[Cr(py)₂F₂]I₂ is dissolved in 40 ml warm methoxyethanol. 4.0 g cyctn is added to this solution which is then refluxed for 1 h. During this treatment a red violet precipitate is slowly formed. The resulting mixture is cooled in ice after which the precipitate is filtered off and washed twice with cold acetone. Yield 4.7 g (51%) of the anhydrous compound. The mother liquor is left overnight. This produces a small amount, ≤0.2 g, of violet trans-[Cr(cyctn)F₂]I₂, which is filtered off and washed with acetone. Analyses Cr, I, N, C, H. The cis compound is recrystallized by dissolving 4.7 g of the anhydrous compound in 35 ml water at 100 °C. The solution is filtered while hot and left to crystallize at 0 °C. Yield 2.3 g of the dihydrate. Analyses Cr, I, N, C, H.

3. (u)-trans-[Cr(cyctn)Cl₂]I₂. 2.8 g cis-[Cr(cyctn)F₂]I₂·2H₂O is treated with 10 ml 4 M HCl. The mixture is kept at 100 °C for 10 min and then cooled in ice. The green precipitate is filtered off and washed twice with cold acetone. Yield 2.1 g (76%). Analyses Cr, I, Cl, N, C, H. This compound contains the pure (u)-trans isomer as judged from the fact that it produces pure cis-[Cr(cyctn)(OH₂)₂]³⁺ when reacted with excess Hg₂⁺, see later. The mother liquor contains the (u)-trans and the (s)-trans isomer, and both may be precipitated by adding excess I⁻ or ClO₄⁻. Longer reaction times at 100 °C than about 10 min produces more of the (s)-trans isomer, and at shorter reaction times mixtures containing trans-[Cr(cyctn)ClF]I are obtained.

4. cis- and trans-[Cr(cyctn)(OH₂)₂]³⁺. Two isomeric tetraminediaquachromium(III) complexes containing the cyctn ligand were characterized in solution by their visible absorption spectra, elution behaviour, and acid base properties. Mixtures containing the two isomers could be separated by cation exchange chromatography on 15–20 cm Sephadex SP-C-25 filled columns using 0.5 M NaClO₄+0.001 M HClO₄ as eluent. Both ions show an elution behaviour typical of
Table 1. Acid dissociation constants of some cis- and trans-tetraaminediaqua chromium(III) complexes of macrocyclic tetraamines in 1.00 M NaClO₄ at 25 °C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>log(K₁/M)</th>
<th>log(K₂/M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Cr(cyctn)(OH₂)₂]³⁺</td>
<td>3.499±0.011</td>
<td>7.099±0.016</td>
<td>This work</td>
</tr>
<tr>
<td>cis-[Cr(cyclam)(OH₂)₂]³⁺</td>
<td>4.212±0.013</td>
<td>7.25±0.03</td>
<td>5</td>
</tr>
<tr>
<td>cis-[Cr(cycb)(OH₂)₂]³⁺</td>
<td>3.331±0.012</td>
<td>7.019±0.014</td>
<td>5</td>
</tr>
<tr>
<td>trans-[Cr(cyctn)(OH₂)₂]³⁺</td>
<td>2.806±0.019</td>
<td>7.133±0.013</td>
<td>This work</td>
</tr>
<tr>
<td>trans-[Cr(cyclam)(OH₂)₂]³⁺</td>
<td>3.048±0.011</td>
<td>7.395±0.023</td>
<td>This work</td>
</tr>
</tbody>
</table>

* cyclam = 1,4,8,11-tetraazaacyclotetradecane; cycb = rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazaacyclotetradecane.

Triply charged cations, and the brownish red trans isomer is eluted prior to the red cis isomer. The visible absorption spectra are typical of the cis- and trans configurations and in aqueous solution both can be titrated as divalent acids, with acid dissociation constants of the expected order of magnitude for this type of complexes, cf. Table 1. The isomers may be generated in aqueous solution as follows:

Method A: 25 mg (u)-trans-[Cr(cyctn)Cl₂]I is dissolved in 0.5 ml 0.8 M Hg(ClO₄)₂-solution. This gives the pure cis-[Cr(cyctn)(OH₂)₂]³⁺ isomer, which is separated from Hg(II) by ion exchange chromatography, using 0.1 M NaBr+0.001 M HClO₄ to remove the mercury(II). An analogous treatment of (s)-trans-[Cr(cyctn)Cl₂]ClO₄ gives the pure trans-[Cr(cyctn)(OH₂)₂]³⁺, and (u,s)-trans-[Cr(cyctn)Cl₂]ClO₄ gives mixtures containing both diaquoisomers.

Method B: 25 mg (u)-trans-[Cr(cyctn)Cl₂]I is dissolved in 2 ml 0.25 M NaOH at 50 °C. The solution is then cooled to 0 °C, and made acidic by addition of perchloric acid. This gives the pure trans-[Cr(cyctn)(OH₂)₂]³⁺, which is also obtained by an analogous treatment of (s)-trans-[Cr(cyclam)Cl₂]ClO₄.

Method C: 50 mg cis-[Cr(cyclam)F₂]I·2H₂O is dissolved in 2 ml 0.25 M NaOH and kept at 100 °C for 3 min. The solution is then cooled to 0 °C and traces of chromium(III) hydroxide removed by filtration. The resulting solution is made acid and cis-[Cr(cyclam)F(OH₂)]²⁺ is separated from cis-[Cr(cyclam)(OH₂)₂]³⁺ and small amounts of the trans isomer by ion exchange chromatography. Longer reaction times than 3 min at 100 °C give more of the trans-diaqua isomer, and also more chromium(III) hydroxide, which indicates a competition between unwrapping of the amine and change of configuration, i.e.:

cis-[Cr(cyctn)(OH₂)₂]⁺ → Cr(OH)₃
trans-[Cr(cyclam)(OH₂)₂]⁺ →

5. cis- and trans-[Cr(cyclam)F₂]⁺. Two tetraaminediafluorochromium(III) isomers identical to those obtained in the solid iodides, preparation no. 2, can also be generated in solution from the dichloro isomers. They can be separated on a 15–20 cm Sephadex SP-C-25 filled column using 0.05 M NaClO₄+0.001 M HClO₄ as eluent, and this separation confirms the isomeric purity of the solid compounds. Solutions containing the difluoro isomers are prepared as follows: Method A: 50 mg (u)-trans-[Cr(cyctn)Cl₂]I is kept in 4 ml 0.05 M HF+0.05 M NaF at 100 °C for 1 h. This gives a mixture containing about equal amounts of cis- and trans difluoro isomers. An analogous treatment of the same solid in 0.1 M NaF solution gives trans-[Cr(cyclam)F₂]⁺ exclusively, and this latter isomer is also obtained pure from (s)-trans-[Cr(cyclam)Cl₂]ClO₄ in both 0.05 M HF+0.05 M NaF and 0.1 M NaF solutions. cis-[Cr(cyclam)F₂]⁺ is stable in 0.1 M NaF solution at the conditions described above, and attempts to prepare difluoro isomers in 0.1 M HF were unsuccessful.

6. trans-[Cr(cyctn)Cl(OH₂)]²⁺. Chloride ligand aquation of (s)-trans-[Cr(cyclam)Cl₂]⁺ in 0.1 M CF₃SO₃H and chloride ligand anation of trans-[Cr(cyclam)(OH₂)₂]³⁺ gives a mixture of two tetraaminediaquoacalachlorochromium(III) isomers, both of which are supposed to have the stable trans configuration by the arguments presented in the results section, cf. Fig. 6. They can be separated on Sephadex SP-C-25 using acidified solutions of 0.5 M NaClO₄. Base catalyzed hydrolysis of coordinated chloride in macroring Chromium(III) complexes is very noticeable even at acid concentrations at the millimolar level, and the ion exchange resin is sensitive to much stronger acid concentrations. This clearly dictates a compromise, and [H⁺] ≈ 0.01 M was used. The trans-[Cr(cyclam)Cl(OH₂)]²⁺ fractions therefore may contain small amounts of trans-[Cr(cyclam)(OH₂)₂]³⁺. However, as seen from Fig. 6 spectra of different acualchlorido fractions

Fig. 6. Visible absorption spectra of trans-[Cr(cyctn)(OH$_2$)$_2$]$^{3+}$ and of two different trans-[Cr(cyctn)Cl(OH$_2$)]$^{2+}$ fractions. The insert shows the correlation between the molar absorption coefficient and the position of the absorption band around 400 nm for various trans-[Cr(cyctn)Cl(OH$_2$)]$^{2+}$ fractions. Fractions with the lower molar absorption coefficient are eluted first. All spectra are measured in solutions with [ClO$_4^-$] = 1.0 M and [H$^+$] = 0.1 M.

are so different from each other and from the diaqua spectrum, that the experiments cannot be interpreted solely by assuming one aquachlorido isomer containing varying amounts of diaqua isomer. The experimental conditions for formation of the aquachlorido isomer is as follows:

Anation: 150 mg (s)-trans-[Cr(cyctn)Cl$_2$]ClO$_4$ is dissolved in 5 ml 0.1 M NaOH at 80 °C. This solution is made acid to [H$^+$] = 0.1 M by addition of 1 M hydrochloric acid, and then kept at 100 °C for 1 min. This gives a greyish green solution.

Aquation: 100 mg (s)-trans-[Cr(cyctn)Cl$_2$]ClO$_4$ is dissolved in 10 ml of 0.1 M CF$_3$SO$_3$H and kept at 100 °C for 10 min. This gives a greyish green solution.

**Analyses, spectra, and potentiometric titrations.**

Microanalyses were performed by the analytical sections of the Chemistry Departments I and II of the Institute: I: Cr and II: C, H, N, Cl, I.

Visible absorption spectra were measured on a Cary 118 C spectrophotometer at room temperature, 20–25 °C.

Potentiometric titrations and the processing of these data to give acid dissociation constants for cts-[Cr(cyctn)(OH$_2$)$_2$]$^{3+}$, trans-[Cr(cyctn)-(OH$_2$)$_2$]$^{3+}$ and trans-[Cr(cyctn)(OH$_2$)$_2$]$^{3+}$ were performed as previously described.6

REFERENCES


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