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

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Chromium(III) reacts in anhydrous solvents with the title cyclic tetraamine, cyctn, 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:

$cis \rightleftarrows$ (u)-*trans* $\rightarrow$ (s)-*trans*

with the *trans* configurations labelled (u) and (s) for *u*nstable and *s*table, 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).[1,2] For the sixteen membered 1,5,9,13-tetraazacyclohexadecane ring, cyctn, *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.[1] 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),[2] are valid also for other systems.

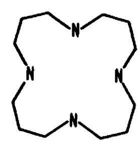

Fig. 1. 1,5,9,13-tetraazacyclohexadecane.

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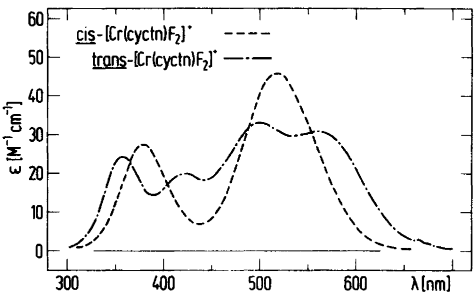

Fig. 2. Visible absorption spectra of *cis-* and *trans*-$[Cr(cyctn)F_2]^+$ in 1.0 M $NaClO_4$.

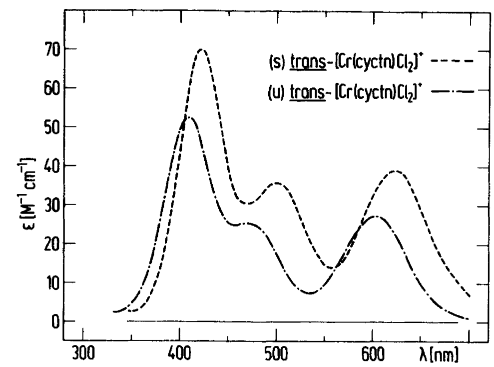

Fig. 3. Visible absorption spectra of (u)-*trans-* and (s)-*trans*-$[Cr(cyctn)Cl_2]^+$ in 0.1 M HCl+0.9 M NaCl.

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 cyctn ligand. The first method gives a yellowish green solid, which can be purified as a perchlorate salt. This was identified as *trans*-$[Cr(cyctn)Cl_2]ClO_4$ 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*-$[Cr(cyctn)F_2]I$, respectively.

cis-$[Cr(cyctn)F_2]I$ can be reacted with hydrochloric acid to give a green compound. Analytical data and the colour suggest a formulation as *trans*-$[Cr(cyctn)Cl_2]I$. 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*-$[Cr(cyctn)Cl_2]^+$, the prefixes being derived from *u*nstable and *s*table, respectively.

In the *trans*-Cr(cyctn) 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.[1] The modes of formation of these isomers can be summarized as:

cis-$[Co(cyctn)(O_2CO)]^+ \rightarrow$
(green)*trans*-$[Co(cyctn)Cl_2]^+ \rightarrow$
(brown)*trans*-$[Co(cyctn)Cl_2]^+$

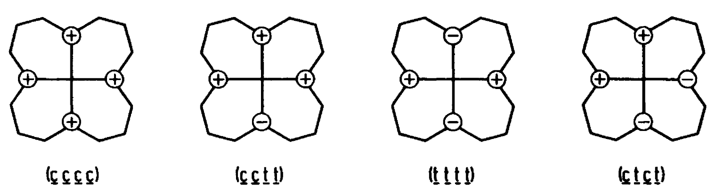

Fig. 4. Possible amine ligand conformations in octahedral *trans*-$M(cyctn)X_2$ complexes. Nitrogen bound hydrogen atom positions above and below the MN_4-plane are indicated by + and −, respectively. Conformer names are constructed by considering the nitrogen bound hydrogen atom pairs on the four six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

compared with

cis-[Cr(cyctn)F_2]$^+$ →
(u)-$trans$-[Cr(cyctn)Cl_2]$^+$ →
(s)-$trans$-[Cr(cyctn)Cl_2]$^+$

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 *s*table chromium complex, and also that the *green* cobalt complex has the tetraamine configuration of the *u*nstable chromium isomer.

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

(brown)*trans* ≡ (*ctct*) − *trans*

and

(green)*trans* ≡ (*cctt*) − *trans*

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

The present *trans*-dichloridochromium(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 dichlorido 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)Cl_2]$^+$ and anation of *trans*-[Cr(cyctn)$(OH_2)_2$]$^{3+}$ with Cl^- gives mixtures which contain two aquachlorido isomers. They can be partly separated by ion exchange chromatography and both give *trans*-[Cr(cyctn)-$(OH_2)_2$]$^{3+}$ by treatment with mercury(II). The mercury(II) induced aquation of (u)-*trans*-[Cr(cyctn)Cl_2]$^+$ gives *cis*-[Cr(cyctn)$(OH_2)_2$]$^{3+}$, *cf.* Fig. 5, and both aquachlorido isomers therefore most likely have the stable *trans* conforma-

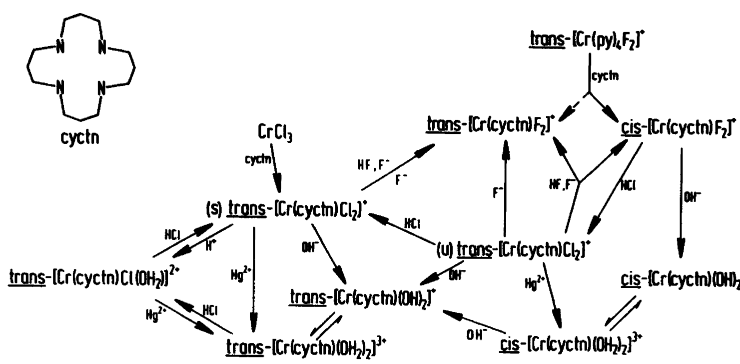

Fig. 5. Summary of reactions of Cr(cyctn) complexes, see also the text.

tion which consequently must be unsymmetrical with respect to axial coordination. The *(cccc)-trans* or *(cctt)-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,[1] 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 tetraamine-cobalt(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,[3] and *trans*-difluoridotetrakis(pyridine)-chromium(III) iodide,[4] *trans*-$[Cr(py)_4F_2]I$, 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 ClO_4^- to these solutions gives (u,s)-*trans*-$[Cr(cyctn)Cl_2]ClO_4$, 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*-$[Cr(cyctn)Cl_2]ClO_4$. 1.75 g $CrCl_3$ 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 $NaClO_4$ 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*-$[Cr(cyctn)F_2]I\cdot 2H_2O$. 9.4 g *trans*-$[Cr(py)_4F_2]I$ 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*-$[Cr(cyctn)F_2]I$, 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*-$[Cr(cyctn)Cl_2]I$. 2.8 g *cis*-$[Cr(cyctn)F_2]I\cdot 2H_2O$ 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*-$[Cr(cyctn)(OH_2)_2]^{3+}$ when reacted with excess Hg^{2+}, see later. The mother liquor contains the (u)-*trans* and the (s)-*trans* isomer, and both may be precipitated by adding excess I^- or ClO_4^-. 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*-$[Cr(cyctn)(OH_2)_2]^{3+}$. Two isomeric tetraaminediaquachromium(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 $NaClO_4$+0.001 M $HClO_4$ as eluent. Both ions show an elution behaviour typical of

Table 1. Acid dissociation constants of some *cis*- and *trans*-tetraaminediaquachromium(III) complexes of macrocyclic tetraamines in 1.00 M $NaClO_4$ at 25 °C.

Complex[a]	$\log(K_1/M)$	$\log(K_2/M)$	Ref.
cis-$[Cr(cyctn)(OH_2)_2]^{3+}$	3.499±0.011	7.099±0.016	This work
cis-$[Cr(cyclam)(OH_2)_2]^{3+}$	4.212±0.013	7.25±0.03	5
cis-$[Cr(cycb)(OH_2)_2]^{3+}$	3.331±0.012	7.019±0.014	5
trans-$[Cr(cyctn)(OH_2)_2]^{3+}$	2.806±0.019	7.133±0.013	This work
trans-$[Cr(cyclam)(OH_2)_2]^{3+}$	3.048±0.011	7.395±0.023	This work

[a] cyclam = 1,4,8,11-tetraazacyclotetradecane; cyc*b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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*-$[Cr(cyctn)Cl_2]I$ is dissolved in 0.5 ml 0.8 M $Hg(ClO_4)_2$-solution. This gives the pure *cis*-$[Cr(cyctn)(OH_2)_2]^{3+}$ isomer, which is separated from Hg(II) by ion exchange chromatography, using 0.1 M NaBr+0.001 M $HClO_4$ to remove the mercury(II). An analogous treatment of (s)-*trans*-$[Cr(cyctn)Cl_2]ClO_4$ gives the pure *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$, and (u,s)-*trans*-$[Cr(cyctn)Cl_2]ClO_4$ gives mixtures containing both diaquaisomers.

Method B: 25 mg (u)-*trans*-$[Cr(cyctn)Cl_2]I$ is dissolved in 2 ml 0.25 M NaOH at 50 °C. The solution is cooled to 0 °C, and made acid by addition of perchloric acid. This gives the pure *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$, which is also obtained by an analogous treatment of (s)-*trans*-$[Cr(cyctn)Cl_2]ClO_4$.

Method C: 50 mg *cis*-$[Cr(cyctn)F_2]I\cdot 2H_2O$ 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*-$[Cr(cyctn)F(OH_2)]^{2+}$ is separated from *cis*-$[Cr(cyctn)(OH_2)_2]^{3+}$ 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.*:

$$cis\text{-}[Cr(cyctn)(OH)_2]^+ \begin{cases} \rightarrow Cr(OH)_3 \\ \rightarrow trans\text{-}[Cr(cyctn)(OH)_2]^+ \end{cases}$$

5. *cis*- and *trans*-$[Cr(cyctn)F_2]^+$. Two tetraaminedifluoridochromium(III) isomers identical to those obtained in the solid iodides, preparation no. 2, can also be generated in solution from the dichlorido isomers. They can be separated on a 15–20 cm Sephadex SP-C-25 filled column using 0.05 M $NaClO_4$+0.001 M $HClO_4$ as eluent, and this separation confirms the isomeric purity of the solid compounds. Solutions containing the difluorido isomers are prepared as follows: Method A: 50 mg (u)-*trans*-$[Cr(cyctn)Cl_2]I$ 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* difluorido isomers. An analogous treatment of the same solid in 0.1 M NaF solution gives *trans*-$[Cr(cyctn)F_2]^+$ exclusively, and this latter isomer is also obtained pure from (s)-*trans*-$[Cr(cyctn)Cl_2]ClO_4$ in both 0.05 M HF+0.05 M NaF and 0.1 M NaF solutions. *cis*-$[Cr(cyctn)F_2]^+$ is stable in 0.1 M NaF solution at the conditions described above, and attempts to prepare difluorido isomers in 0.1 M HF were unsuccessful.

6. *trans*-$[Cr(cyctn)Cl(OH_2)]^{2+}$. Chloride ligand aquation of (s)-*trans*-$[Cr(cyctn)Cl_2]^+$ in 0.1 M CF_3SO_3H and chloride ligand anation of *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$ gives a mixture of two tetraamineaquachloridochromium(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 $NaClO_4$. Base catalyzed hydrolysis of coordinated chloride in macrocyclic 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 $[H^+]\approx 0.01$ M was used. The *trans*-$[Cr(cyctn)Cl(OH_2)]^{2+}$ fractions therefore may contain small amounts of *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$. However, as seen from Fig. 6 spectra of different aquachlorido fractions

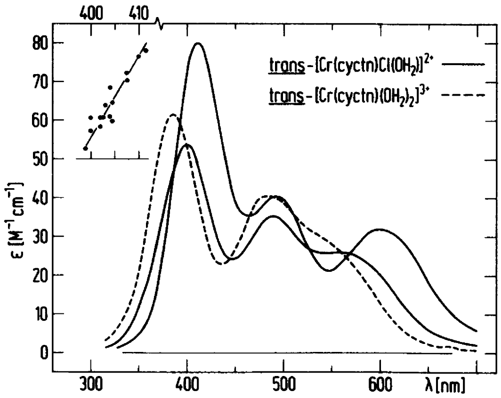

Fig. 6. Visible absorption spectra of *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$ and of two different *trans*-$[Cr(cyctn)Cl(OH_2)]^{2+}$ fractions. The insert shows the correlation between the molar absorption coefficient and the position of the absorption band around 400 nm for various *trans*-$[Cr(cyctn)Cl(OH_2)]^{2+}$ fractions. Fractions with the lower molar absorption coefficient are eluted first. All spectra are measured in solutions with $[ClO_4^-] \approx 1.0$ M and $[H^+] \gtrsim 0.1$ 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 $[H^+] \approx 0.1$ 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_3SO_3H 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 *cis*-$[Cr(cyctn)(OH_2)_2]^{3+}$, *trans*-$[Cr(cyctn)(OH_2)_2]^{3+}$ and *trans*-$[Cr(cyclam)(OH_2)_2]^{3+}$ were performed as previously described.[6]

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