Chromium(III) Complexes of Macrocyclic Ligands. Reactivity and Structure of Chromium(III) Complexes of 1,5,9,13-Tetraazacyclohexadecane

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Chromium(III) complexes of the title amine ligand, cyctn, exist with a *cis*, an unstable *trans* and a stable *trans* configuration. Configurational changes are unusually rapid for a chromium(III) center and conform to the general scheme:

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

with *trans* configurations labelled (u) and (s) for *u*nstable and *s*table, respectively. (s)-*trans*-[Cr(cyctn)Cl$_2$]ClO$_4$ crystallizes in the orthorhombic space group $Pnam$ with $a = 25.354(11)$, $b = 7.513(4)$ and $c = 10.045(5)$ Å. Data for 1219 observed reflections [$F^2 > 2\sigma(F^2)$] were refined to give R ≈ 0.046. The amine ligand is coordinated to give two neighbouring *chair* and two *twist* conformations of the six-membered rings, and inequivalent axial ligands.

The cyclic sixteen-membered tetraamine ligand 1,5,9,13-tetraazacyclohexadecane, cyctn, shown in Fig. 1, forms complexes with chromium(III),
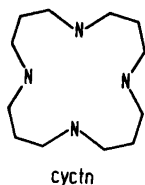

cyctn

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

and derivatives of one *cis* and two *trans* configurations have been characterized.[1] The *trans* complexes were labelled (u) and (s) for *u*nstable and *s*table, respectively, as the interconversion reactions took place according to the simplified scheme

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

The identification of two *trans*-[Cr(cyctn)Cl (OH$_2$)]$^{2+}$ isomers, which apparently both had the

stable *trans* conformation of the amine, led to the tentative assignment of this conformation as that with three of the four nitrogen-bound hydrogens on one side of the plane of the four ligand nitrogen atoms. This was not in agreement with strain energy calculations on similar complexes of cobalt(III).[2]

This work describes further stoichiometric studies of the stereochemical rearrangement processes, and reports the crystal and molecular structure of (s)-*trans*-[Cr(cyctn)Cl$_2$]ClO$_4$.

Results and discussion

Stoichiometric studies. *cis*-[Cr(cyctn)F$_2$]$^+$ reacts initially in acidic and basic solution to give products in which aquation of one fluoride ligand has occurred. The products, which are complicated mixtures of tetraaminechromium(III) complexes, were investigated by ion exchange chromatography, acid-base titration and spectrophotometric measurements.

Reactions in basic solution. Heating basic solutions of *cis*-[Cr(cyctn)F$_2$]$^+$ at 100 °C for longer than a few minutes results in the formation of chromium(III) hydroxide. With shorter reaction times or at lower temperatures solutions remain homogeneous, however, and most of the stoichiometric studies in basic solution were carried out with solutions 0.25 M in NaOH which had been heated at 80 °C for about 2 min. Ion exchange chromatography of acidified reaction mixtures shows four bands of which the first and the last two were identified as *cis*-[Cr(cyctn)F$_2$]$^+$, and *trans*- and *cis*-[Cr(cyctn)(OH$_2$)$_2$]$^{3+}$, respectively. The second band showed elution behaviour typical of dipositive cations and had uniform spectral characteristics. The chromium(III)-containing species could be titrated as a monovalent acid with an acid dissociation constant given by $-\log(K_{1A}/M) \approx 5.65 \pm 0.02$ at 25.0 °C for a 1.00 M NaClO$_4$ solution. Visible absorption spectra in acidic and basic solution accord with a *cis*-tetraamine structure, so that the initial aquation and anation reactions are stereoretentive substitution reactions (Scheme 1). These are fol-

$$OH_2(OH^-):$$

$$\textit{cis-}[Cr(cyctn)F_2]^+ \rightleftarrows \textit{cis-}[Cr(cyctn)F(OH)]^+$$
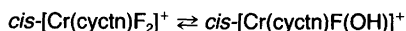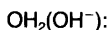
Scheme 1.

lowed by further loss of coordinated fluoride, and competition between isomerization to more robust *trans* complexes and precipitation of chromium(III) hydroxide.

Reactions in acidic solution. *cis*-[Cr(cyctn)F$_2$]$^+$ rapidly loses one fluoride ligand in 1.0 M perchloric acid at 100 °C. Thus, ion exchange fractionation experiments on solutions held at this temperature for between a few minutes to more than one hour show only a band of dipositive cations, which, however, from the fractionation behaviour and titration with base contains more than one aquafluorido species. Successive treatment of the mixture with base and then acid changes the spectral characteristics of the eluate of divalent cations to those of a mixtrue of *cis*-[Cr(cyctn)F(OH$_2$)]$^{2+}$ and that *trans* isomer which is produced either by aquation of *trans*-[Cr(cyctn)F$_2$]$^+$ or by fluoride ion anation of *trans*-[Cr(cyctn)(OH$_2$)$_2$]$^{3+}$. Comparative spectral studies indicate this latter isomer to be the (s)-*trans*-[Cr(cyctn)F(OH$_2$)]$^{2+}$. Since isomerization from the (u)-*trans* to the (s)-*trans* configuration is rapid in base, the (u)-*trans*-[Cr(cyctn)F(OH$_2$)]$^{2+}$ is probably an initial reaction product of the acid hydrolysis of the *cis*-difluorido complex. Fig. 2 shows the absorption spectrum of this isomer calculated by assuming that only the *cis*- and (u)-*trans*-aquafluorido isomers are initially formed, and that the (u)-*trans* to (s)-*trans* isomerization is quantitative in base. The relative transition energies and absorption band intensities support the proposed structural assignments (cf. Ref. 1). The initial behaviour of *cis*-[Cr(cyctn)F$_2$]$^+$ in acidic solution is therefore a relatively rapid competitive stereoretentive and stereomobile reaction, followed by a significantly slower transformation into stable *trans* isomers (Scheme 2).
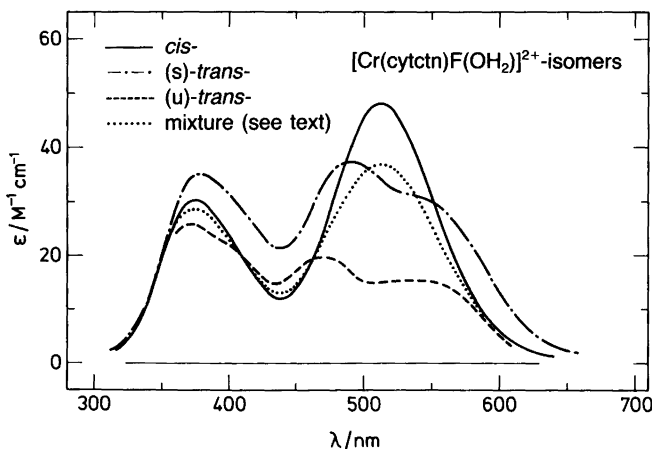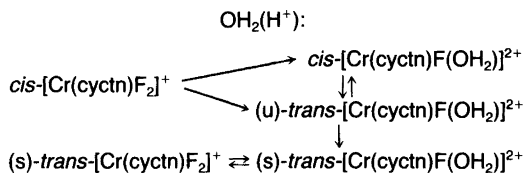

Fig. 2. Visible absorption spectrum of [Cr(cyctn)F(OH$_2$)]$^{2+}$ isomers in 1.0 M (Na,H)ClO$_4$.

$OH_2(H^+)$:

$$cis\text{-}[Cr(cyctn)F_2]^+ \rightarrow cis\text{-}[Cr(cyctn)F(OH_2)]^{2+}$$
$$\updownarrow$$
$$(u)\text{-}trans\text{-}[Cr(cyctn)F(OH_2)]^{2+}$$
$$\downarrow$$
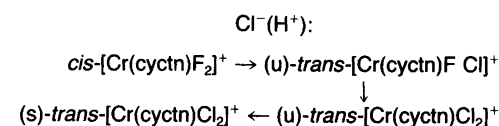$$(s)\text{-}trans\text{-}[Cr(cyctn)F_2]^+ \rightleftarrows (s)\text{-}trans\text{-}[Cr(cyctn)F(OH_2)]^{2+}$$

Scheme 2.

Reactions in hydrochloric acid. The reactivity of cis-[Cr(cyctn)F_2]^+ in hydrochloric acid is significantly affected by chloride ions. From concentrated solutions a greyish green precipitate of the chloridofluorido isomer can be isolated which usually contains some (u)-trans-[Cr(cyctn)Cl_2]^+. This product reacts with base and with mercury(II) according to Scheme 3, and a comparison

$$[Cr(cyctn)FCl]^+ \xrightarrow{Hg^{2+}} cis\text{-}[Cr(cyctn)F(OH_2)]^{2+}$$
$$\xrightarrow{OH^-} trans\text{-}[Cr(cyctn)F(OH)]^+$$
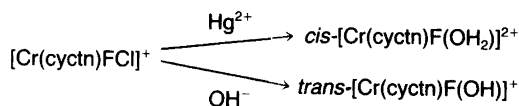
Scheme 3.

with the reactivity of the (u)-trans-[Cr(cyctn)Cl_2]^+ isomer[1] strongly indicates the former product to have the *u*nstable *trans*-configuration. The initial reaction between the cis-fluorido isomer and chloride therefore occurs with change of configuration according to Scheme 4.

$$Cl^-(H^+):$$
$$cis\text{-}[Cr(cyctn)F_2]^+ \rightarrow (u)\text{-}trans\text{-}[Cr(cyctn)F\ Cl]^+$$
$$\downarrow$$
$$(s)\text{-}trans\text{-}[Cr(cyctn)Cl_2]^+ \leftarrow (u)\text{-}trans\text{-}[Cr(cyctn)Cl_2]^+$$

Scheme 4.

Structure of (s)-trans-[Cr(cyctn)Cl_2]ClO_4. The stable dichloro chromium(III) complex crystallizes as an anhydrous perchlorate in the orthorhombic spacegroup *P n a m* (see Experimental). The chromium atom, the two chloride ligands and two nitrogen ligators of the macrocyclic ligand lie in a mirror plane and have the Cl–Cl axis of the complex tilted an angle of 40° to the *b* axis. The perchlorate ion is disordered around the mirror plane. This arrangement explains the strong pleochroism of the crystals. Furthermore, about 20 % of the cations are disordered by 90° rotations around the Cl–Cr–Cl axis. The macrocyclic

amine ligand is coordinated so that 3 of the 4 nitrogen-bound hydrogens are on the same side of the CrN_4 plane. This gives two neighbouring six-membered chelate rings with chair conformations and two with twist conformations, as demonstrated in Fig. 3. A summary of bond lengths and angles is given in Table 1. The crystals are held together in two dimensions by hydrogen bonds between nitrogen-bound hydrogens and perchlorate ions, as demonstrated by the simplified cell packing in Fig. 4.

The free cyctn ligand,[3] as well as complexes of cadmium(II), mercury(II) and lead(II)[4] have previously been characterized structurally. A comparison of the data for the free ligand with those for the present chromium(III) complex reveals the normal increase in intraligand carbon-nitrogen bond lengths upon coordination, viz. from 1.457(2) Å in the free ligand to 1.46(1)–1.51(1) in the coordinated ligand. The ligand conformation in the present chromium(III) complex is different from those of the previously characterized cadmium(II), mercury(II) and lead(II) compounds. In all the latter complexes the ligand is coordinated to give chair conformations to all the six-membered chelate rings, which are distorted to a greater or lesser degree. This is accompanied by significantly longer metal-nitrogen bond lengths than in the chromium(III) complex: $d(Cd\text{-}N) \approx 2.33$ Å, $d(Hg\text{-}N) \approx 2.38$ Å and $d(Pb\text{-}N) \approx 2.54$ Å.

Stereochemistry of structural changes. In the *trans*-Cr(cyctn) moiety the tetraamine ligand can have four different conformations, as shown in Fig. 5. Strain energy calculations have indicated that the $(ctct)$ conformation should be slightly more stable than the $(cctt)$ conformation[2] in *trans*-[Co(cyctn)Cl_2]^+. This result is apparently not valid for chromium(III), as the stable *trans* isomers have the $(cctt)$ conformation of the amine, with inequivalent axial ligands, as tentatively proposed earlier on the basis of stoichiometric studies.

The facile transformation between the cis and the *u*nstable *trans* configurations makes it likely that the 'folding' and 'unfolding' of the MN_4 unit takes place along an N–M–N axis with nitrogen-bound hydrogens pointing in the same direction. This clearly excludes the $(ctct)$ conformation as a possible candidate for the structure of the *u*nstable *trans* complexes. The heavy-metal com-
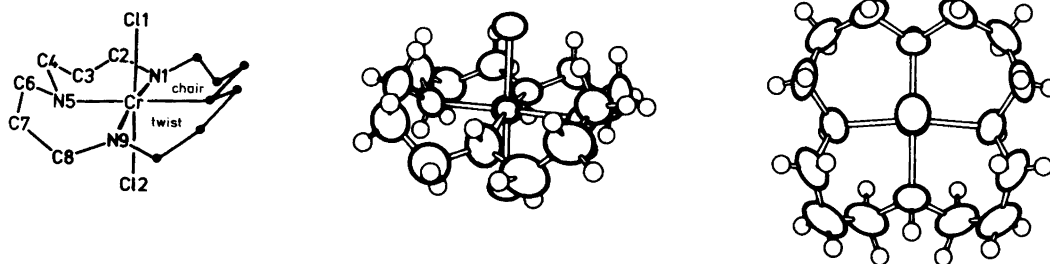
Fig. 3. Numbering scheme and two views of the (s)-*trans*-[Cr(cyctn)Cl₂]⁺ cation. Hydrogen atoms are drawn as spheres with a radius equivalent to 0.23 Å, and the remaining atoms as 50 % probability ellipsoids. The figure furthest to the right is seen from the Cl1 ligand.
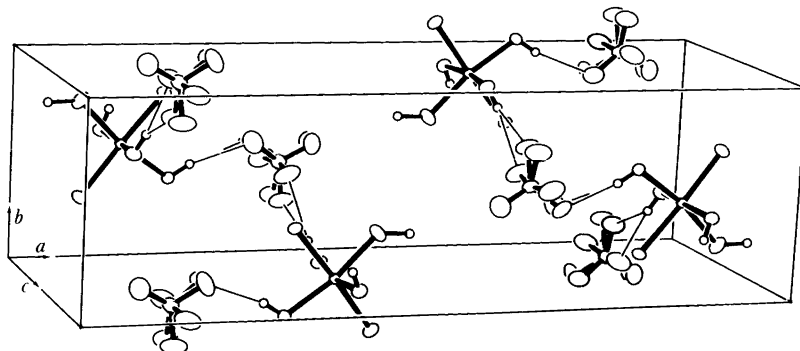

Fig. 4. Simplified cell packing and hydrogen bonds in (s)-*trans*-[Cr(cyctn)Cl₂]ClO₄. All carbon atoms and carbon-bound hydrogen atoms are omitted. Both perchlorate ion orientations, but only the dominant cation orientation are shown. Hydrogen atoms are drawn as spheres with a radius equivalent for 0.10 Å, and the remaining atoms as 35 % probability ellipsoids.

Table 1. Summary of structural data for (s)-*trans*-[Cr(cyctn)Cl₂]ClO₄.

Intramolecular distances/Å		Intramolecular angles/°	
Cr–N1	2.119(6)	Cl1–Cr–Cl2	177.1(3)
Cr–N5	2.137(4)	N1–Cr–N9	168.8(3)
Cr–N9	2.131(8)	N5–Cr–N5'	170.9(2)
Cr–Cl1	2.302(2)		
Cr–Cl2	2.325(2)		
C–N	1.46–1.51		
C–C	1.47–1.52		

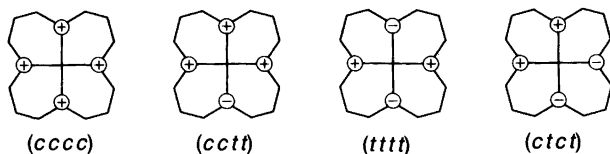| Intermolecular hydrogen-bonds/Å		Distances from "best" plane through (N1,N5,N5', N9)/Å	
N1···O3	3.198(12)	Cr	−0.089
N5···O1	3.007(11)	N1	0.110
N5···O4	3.232(13)	N5,N5'	−0.119
(N)H···O	2.32–2.44	N9	0.128

Fig. 5. 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 *cis* and *trans* hydrogens, respectively.

Table 2. Crystal data for (s)-*trans*-[Cr(cyctn)Cl₂]ClO₄.

Space group	Orthorhombic *Pnam* (no. 62)
a/Å	25.354(11)
b/Å	7.513(4)
c/Å	10.045(5)
Z	4
V/Å³	1913
μ(Mo*K*α)/cm⁻¹	10.4
Crystal size/mm	0.3×0.3×0.4
Total no. of measured refl.	1784
No. of independent obs. refl.	1219
LT[$F^2 < 2\sigma(F^2)$]	352
No. of parameters	210
R	0.046
R_w	0.063

$$w^{-1} = \sigma^2(F) - 0.013|F| + 0.0025\,F^2$$

plexes all have the (*cccc*) conformation, but the metal-nitrogen bond lengths observed here probably cannot be accomodated by a chromium(III) centre. That leaves the (*tttt*) conformation as the most plausible structural candidate for the *un*-stable *trans* complexes. This is further supported by considerations of non-bonded interactions in models of *cis* complexes obtained by folding the possible *trans* configurations. Fig. 6 shows a ten-

tative proposal for the geometrical changes which accompany the configurational interchange processes. Interconversion between the *cis* and the (u)-*trans* configurations is preferred in acid solution and does not require dissociation of nitrogen-bound hydrogen atoms. The relative ease with which these reactions occur is most likely the result of an ill-fitting ring size of the 'macrocyclic' ligand in relation to a chromium(III) center.

With water as the entering ligand there is competition between a stereoretentive and a stereomobile path in acidic solution. With chloride, however, only the stereomobile path is seen. This can be rationalized on the basis of simple electrostatics since the attack of an entering anion may be presumed to occur preferentially *trans* to the displaced anionic ligand.

The (u)-*trans* to (s)-*trans* isomerization is fast in basic solution, and is probably initiated by dissociation of a nitrogen-bound hydrogen atom. This process, which appears to be irreversible for complexes with monodentate ligands, can, however, be reversed by addition of ligands which form chelate complexes, e.g. oxalate.

Experimental

Chemicals, ion exchange chromatography, analyses, spectral measurements and *potentiometric titrations* are all described or referred to in Ref. 1.
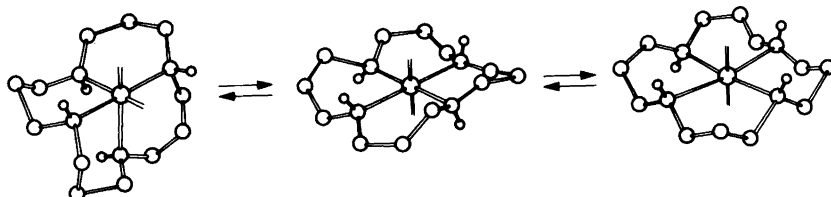

Fig. 6. Proposed geometry of configurational changes: *cis* ⇄ (u)-*trans* ⇄ (s)-*trans*.

Structure determination. Crystals of (s)-*trans*-[Cr(cyctn)Cl₂]ClO₄ suitable for crystallographic work were obtained by suspending 500 mg of the compound in 30 ml of water and boiling this solution until the compound had dissolved. The resulting solution was filtered and kept at 0 °C for a week. This produced 100 mg of dark green crystals.

The crystals form diamond-shaped plates having (100) as dominant face, with diagonal extinction in the direction of the *b* and *c* axes. The (010) face may occur. The space group could be assigned as either $Pna2_1$ or $Pnam$ on the basis of Weissenberg and precession photographs. Data were collected on a Picker FACS-1 diffracto-

meter with graphite-monochromated Mo$K\alpha$ radiation. No correction for absorption was applied. The crystal data are given in Table 2. The structure was solved by conventional methods. The Patterson function gave the position of the chromium atom and the two coordinated chloride ligands. The rest of the structure was solved using DIRDIF[5] and difference Fourier methods together with the X-Ray system of programs.[6] Disorder was indicated in both space groups. Pseudo-symmetry in the space group $Pna2_1$ led to difficulties in the refinement, and the final refinement was carried out in the space group $Pnam$ with all non-hydrogen atoms having anisotropic temperature factors. Fractional coordinates are given in Table 3. All atoms of the perchlorate ion have populations of 1/2. C8 and C8A have populations of 0.80 and 0.20, respectively. Lists of observed and calculated structure factors as well as anisotropic thermal parameters are available from the authors upon request.

The reduced population of the C8 atom is most likely the result of disorder of the cation by 90° rotations around the Cl–Cr–Cl axis. Fig. 3 shows that, neglecting the C8 atom, there is approximately four-fold symmetry of the macrocyclic ring system. 90° rotations will place C2, C4 or C6 at the position where the C8A atom is found. The C8 atom will simultaneously be placed near either C2, C4 or C6 atoms but with only 1/3 of the C8A population. This was not taken into account in the computations. The fact that the temperature factors are larger than normal for structures of this type may be taken as additional evidence for the suggested disorder of the cation, and it may further be noted from Fig. 4 that the hydrogen bonding pattern is not seriously affected by the disorder.

Table 3. Fractional coordinates for (s)-*trans*-[Cr(cyctn)Cl₂]ClO₄.

Atom	x	y	z
Cr	0.12683(4)	0.59558(12)	0.25000
N1	0.1951(3)	0.4328(8)	0.25000
N5	0.1211(2)	0.6070(6)	0.0380(4)
N9	0.0690(3)	0.8013(11)	0.25000
C2	0.2065(3)	0.3242(8)	0.1306(7)
C3	0.2033(3)	0.4295(10)	0.0040(7)
C4	0.1484(4)	0.4644(11)	−0.0399(7)
C6	0.0655(3)	0.6209(10)	−0.0139(8)
C7	0.0377(4)	0.7898(12)	0.0170(11)
C8	0.0606(5)	0.8960(12)	0.1249(11)
C8A	0.0220(19)	0.766(10)	0.162(7)
Cl1	0.07211(8)	0.3512(2)	0.25000
Cl2	0.18573(7)	0.8328(2)	0.25000
Cl3	0.35277(13)	0.5002(3)	0.242(7)
O1	0.3523(6)	0.3295(14)	0.2984(10)
O2	0.3979(4)	0.5851(15)	0.270(13)
O3	0.3102(4)	0.6017(13)	0.2800(4)
O4	0.3463(6)	0.4790(16)	0.1012(11)
H1	0.225(2)	0.496(9)	0.25000
H2′	0.181(2)	0.222(7)	0.133(5)
H2″	0.244(2)	0.279(8)	0.155(5)
H3′	0.222(3)	0.371(11)	−0.051(9)
H3″	0.220(3)	0.542(10)	0.010(7)
H4′	0.149(3)	0.500(10)	−0.117(8)
H4″	0.120(3)	0.353(11)	−0.027(8)
H5	0.135(2)	0.700(7)	0.014(5)
H6′	0.048(2)	0.512(8)	0.469(6)
H6″	0.067(4)	0.604(12)	−0.094(10)
H7′	0.046(4)	0.867(14)	−0.050(12)
H7″	−0.002(4)	0.772(12)	0.045(9)
H8′	0.109(5)	0.926(15)	0.120(11)
H8″	0.019(4)	0.970(15)	0.170(9)
H9	0.024(4)	0.795(13)	0.25000

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