

# The Crystal Structure of *trans*-Difluoro(1,4,8,11-tetraazaundecane)-chromium(III) Perchlorate

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The complex ion in *trans*-[Cr(1,4,8,11-tetraazaundecane) $F_2$ ] $ClO_4$  was determined from X-ray diffraction to be of the *meso*-type having an *R,S*-configuration of the two inner asymmetric nitrogen ligators. The crystals are monoclinic, space group *Cc* or *C2/c*,  $a = 21.86(3)$ ,  $b = 5.618(4)$ ,  $c = 28.39(3)$  Å,  $\beta = 126.84(3)^\circ$ ,  $Z = 8$ . After isotropic refinement the final *R* value was 0.13. The oxygen atoms of the perchlorate ions are disordered. The *R,S*-configuration is consistent with the chemical properties.

In their thorough and pioneering studies of cobalt(III) complexes of 1,4,7,10-tetraazadecane (2,2,2-tet), Sargeson and coworkers<sup>1–2</sup> showed that this linear tetradentate ligand has a pronounced tendency to form *cis*-octahedral complexes. The homologous ligands 1,4,8,11-tetraazaundecane (2,3,2-tet) and 1,5,8,12-tetraazadodecane (3,2,3-tet) show an increased preference to form *trans*-complexes. A large number of cobalt(III)<sup>3–8</sup> and a few chromium(III)<sup>7–11</sup> and rhodium(III)<sup>7,8,12</sup> complexes have been studied. The potential of the two inner nitrogen atoms to introduce dissymmetry close to the metal ion has been an important aspect in these investigations. During our studies of such chromium(III) complexes in the late sixties we encountered the present *trans*-complex which resisted optical resolution.

## EXPERIMENTAL

The orange-red crystals were prepared as reported earlier.<sup>10</sup> They occur prismatic with parallel extinc-

tion and the *b* axes in the length of the crystal, or rhombohedral with diagonal extinction on the large face (100). Weissenberg and precession photographs showed the possible space groups to be *Cc* or *C2/c*. Intensity data were collected on a Picker FACS-1 diffractometer with graphite monochromated  $CuK\alpha$  radiation. ( $\lambda = 1.5405$  Å). The copper radiation was preferred to the molybdenum on account of the long axes of the unit cell. The data collection was performed in the  $\theta - 2\theta$  mode. The scan rate was  $1^\circ/\text{min}$ , the scan range was  $1.5^\circ$  and increasing with  $2\theta$ . The background counts were made for 20 s at each end of the scan range.

Only reflections from two octants were collected. 1756 independent reflections were recorded, but only 696 had  $I/\sigma(I) > 3.0$ . The crystal size was  $0.12 \times 0.05 \times 0.03$  mm<sup>3</sup>. No correction for absorption was applied. The anisotropic temperature factors found later in the refinement showed the influence of absorption to be of minor importance for the gross features of the structure. The cell dimensions were refined from powder diagrams obtained from a Hägg-Guinier camera and  $CuK\alpha$  radiation. The X-ray system<sup>13</sup> was used in the crystal structure analysis, and the Ortep II<sup>14</sup> for the illustrations.

## CRYSTAL DATA

[Cr(C<sub>7</sub>H<sub>20</sub>N<sub>4</sub>)F<sub>2</sub>] $ClO_4$ . Space group *C2/c* (No. 15) or *Cc* (No. 9).  $a = 21.86(3)$ ,  $b = 5.618(4)$ ,  $c = 28.39(3)$  Å,  $\beta = 126.8(3)^\circ$ ,  $Z = 8$ ,  $D_m = 1.66$  g cm<sup>-3</sup>,  $D_x = 1.67$  g cm<sup>-3</sup>,  $\mu(CuK\alpha) = 97$  cm<sup>-1</sup> (See Fig. 1).

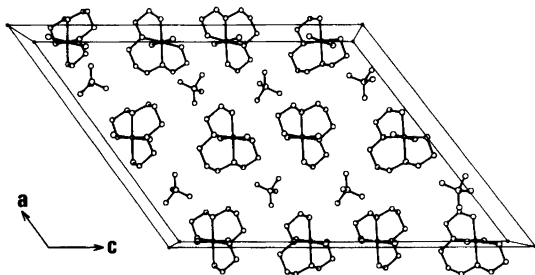


Fig. 1. View of the unit cell along the *b*-axis.

### SOLUTION AND DESCRIPTION OF THE STRUCTURE

Direct methods assuming an acentric structure gave the information which led to the solution of the structure. The many peaks in the Patterson function which could be related to the layer  $u,0,w$  indicated that the space group could possibly be  $C2/c$ , or at least a great number of the atoms were centrosymmetrically arranged. The refinement has been carried out both in  $Cc$  and  $C2/c$  with and without reflections where  $I/\sigma(I) \leq 3.0$  and the value of the calculated structure factor was larger than the  $\sigma(I)$  limit. The resulting structures were almost identical. Anisotropic refinement was carried out for both space groups, but may not be justified as the number of observed intensities is small, and is also small against the number of parameters. Unit weights were used. The results for isotropic refinement in the centrosymmetric case (696 obs. reflections and 545 LT reflections,  $R$  0.13) are given in Tables 1 and 2.

The great number of weak reflections among strong reflections, even for small values of  $\sin \theta$ , can be explained in terms of the positions of some of the atoms. The positions of the cations are such that the chromium, two nitrogen, and two fluorine atoms are close to 0 or  $1/4$ . Furthermore, the vector differences between the chromium and the chlorine atoms are close to  $1/4, 1/4, 0$ .

The two fluorine atoms in the *trans*-positions in the complex, Fig. 2, have the distances 1.85 and 1.90 Å from the chromium atom. This is in agreement with the results for the  $[\text{CrF}_6]^{3-}$  ion as found in  $\text{BaLi}[\text{CrF}_6]$ .<sup>15</sup> The other distances in the complex are Cr–N 2.06–2.08, C–N 1.48–1.56, and C–C 1.51–1.56 Å. The best plane through the Cr, F1, F2, and C4 atoms is very close to being a mirror plane, corresponding to *R* and *S* configurations of

Table 1. Fractional atomic coordinates ( $\times 10^4$ ), isotropic thermal parameters ( $\text{Å}^2 \times 10^2$ ).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Cr	0001(2)	0270(7)	3989(1)	3.4(1)
N1	1176(11)	0078(40)	4482(8)	4.5(5)
N2	4973(10)	2771(34)	1532(8)	2.9(4)
N3	1179(10)	0369(35)	1534(7)	3.1(5)
N4	0087(9)	2620(33)	0501(7)	2.4(4)
F1	0020(7)	2815(24)	3582(5)	4.3(3)
F2	4944(7)	2667(23)	4390(5)	3.4(3)
C1	3620(14)	2760(50)	0694(11)	4.0(5)
C2	4188(13)	2679(46)	1369(10)	3.8(6)
C3	4453(13)	3140(45)	2800(10)	4.2(7)
C4	3628(13)	3097(45)	2612(9)	4.6(6)
C5	1584(14)	0404(50)	2212(11)	4.9(7)
C6	1410(15)	2600(52)	1384(11)	3.5(6)
C7	0901(14)	2616(49)	0701(11)	3.3(5)
Cl	2475(4)	2781(15)	3906(3)	5.2(2)
O1	2441(16)	0178(59)	0947(12)	13(4)
O2	1743(18)	2475(61)	3566(13)	12(3)
O3	2928(18)	1405(61)	4361(14)	12(2)
O4	2791(15)	2519(54)	3620(11)	11(2)

Table 2. Bond lengths (Å) and selected angles (°).

CrF1	1.85(2)	N1CrN2	83.9(9)
CrF2	1.90(2)	N1CrN4	99.2(8)
CrN1	2.06(6)	N2CrN3	93.4(8)
CrN2	2.07(2)	N3CrN4	83.5(8)
CrN3	2.07(6)	N1CrN3	177.3(10)
CrN4	2.05(2)	N2CrN4	175.9(10)
		F1CrF2	178.0(7)
N1C1	1.56(4)		
N2C2	1.49(4)	N1C1C2	105(2)
N2C3	1.54(5)	C1C2N2	108(2)
N3C5	1.57(4)	N2C3C4	110(3)
N3C6	1.51(4)	C3C4C5	113(2)
N4C7	1.51(4)	C4C5N3	109(2)
		N3C6C7	104(2)
C1C2	1.54(6)	C6C7N4	106(2)
C3C4	1.54(5)	C2N2C3	109(2)
C4C5	1.56(4)	C5N3C6	107(2)
C6C7	1.56(4)		

the two asymmetric nitrogen atoms N2 and N3. The three carbon atoms in the trimethylene group and the two nearest carbon atoms in the ethylene groups C2 to C6 are all on the same side of the least squares best plane through the chromium and the four nitrogen atoms. The carbon atom C4 in the middle of the trimethylene group has a shorter

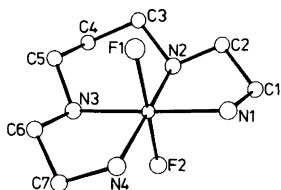


Fig. 2. The chromium complex cation.

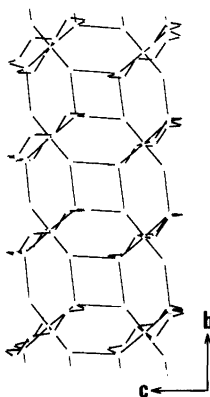


Fig. 3. Contacts formed between complexes in the *bc*-plane along the *b*-axis.

distance, 0.51 Å, than the two others in this group, C3 0.89 Å and C5 0.97 Å. Only C1 and C7 are at the opposite side of the plane, which indicates that the two fluorine atoms are placed in essentially different environments.

The chair configuration of the six-membered ring has also been found in several cobalt(III) complexes.<sup>16-19</sup> In the case of tris(1,3-propanediamine)chromium(III) pentacyanonickelate(II)<sup>20</sup> there are two six-membered rings with the chair configuration whereas the third forms a skew boat.

The complex ions form infinite double-bands in the *bc* plane in the direction of the *b*-axis as shown in Fig. 3. The fluorine-nitrogen intercomplex distances in these bands are 2.80–2.98 Å. Within the complexes these distances are 2.73–2.88 Å. The perchlorate ions are placed between these bands as seen from the view of the unit cell in Fig. 1. Difference syntheses and the large temperature factors indicate disorder of the oxygen atoms in the perchlorate ion. The position of the chlorine excludes the possibility of strong hydrogen bonds from oxygen to nitrogen atoms.

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## CONCLUSIONS

*trans*-[Cr(2,3,2-tet)F<sub>2</sub>]ClO<sub>4</sub> was prepared by a general procedure<sup>10</sup> for preparation of chromium(III) complexes with two fluorine atoms and four nitrogen atoms as ligands. This procedure yields *trans*-complexes unless it is prevented by steric factors as observed for 2,2,2-tet and tris(2-aminoethyl)amine where *cis*-complexes are formed. Visible absorption spectra of the present compound indicated a *trans*-configuration as now finally shown by X-ray analysis. An earlier procedure<sup>3</sup> yielded almost entirely the *cis*-complex with a small amount of *trans*-complex as an impurity.<sup>4</sup>

This indicates the great flexibility of the 2,3,2-tet ligand. In the *trans*-configuration there are two possible isomers having *R,R/S,S* (racemate) or *R,S* configurations on the two inner nitrogen atoms. These isomers would have a skew boat and a chair configuration in the six-membered ring, respectively. The *R,R/S,S* configuration is possible in cobalt(III) complexes<sup>5</sup> as indicated by their optical resolutions. The *R,S*- or *meso*-configuration is observed in the crystal structure<sup>22,23</sup> of a nickel(II) complex of 2,3,2-tet obtained by cyclizing the amine with 1,3-dibromopropane.

The *R,S*-configuration found in the present complex remains intact even in basic aqueous solution. Our attempts to obtain optical resolution by precipitation as  $\alpha$ -bromocamphor- $\pi$ -sulfonates in weakly acid solution failed both before and after treatment with base.

Another chemical evidence for the *R,S*-configuration obtained at an early stage was the observation that during the reaction of the complex in a 5:1 v/v mixture of 12 M hydrochloric acid and 70% w/w perchloric acid the *trans*-[Cr(2,3,2-tet)ClF]<sup>+</sup> ion was easily obtained. Further substitution of the second fluoride ligand was very slow. This is probably related to the position of the fluorine atom which is partly protected in the chair. For the related *trans*-difluoro complexes with ammonia<sup>24</sup> and ethylenediamine it is difficult to isolate the intermediate product.

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