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### *cis*-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) Chloride

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**Abstract.**  $[\text{CrCl}_2(\text{C}_{10}\text{H}_{24}\text{N}_4)]\text{Cl}$ ,  $M_r = 358.7$ , monoclinic,  $P2_1/a$ ,  $a = 14.709$  (2),  $b = 14.514$  (2),  $c = 7.542$  (1) Å,  $\beta = 102.6$  (1)°,  $V = 1571.3$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.516$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 12.3$  cm<sup>-1</sup>,  $F(000) = 748$ ,  $T = 295$  K.  $R = 0.025$  for 2228 unique observed reflections. The X-ray analysis indicates that this is the *RRRR(SSSS)* *cis* species with the uncoordinated chloride anion in a position where it can be hydrogen-bonded by the amine H atoms. The four N atoms of the macrocyclic ligand coordinate to the Cr atom in adjacent octahedral sites with the two Cl atoms occupying the two remaining positions.

**Introduction.** As part of an examination of the way in which the sensitivity of an octahedral acido amine complex depends upon the nature of the central atom we have examined the complexes of the type  $[M(\text{cyclam})\text{Cl}_2]^+$  where  $M = \text{Co}, \text{Cr}, \text{Ru}, \text{Rh}$  (Sosa, 1983; Lichtig, Sosa & Tobe, 1984) (cyclam is 1,4,8,11-tetraazacyclotetradecane). In addition to the geometric (*trans-cis*) isomerism in which the ligand is flat or folded, it is necessary to take into account further isomerism arising from the configuration of the coordinated amine N atoms. In the case of the diamagnetic substrate ( $M = \text{Co}^{\text{II}}$ ), it is possible to infer the type of

isomerism from the <sup>1</sup>H NMR spectrum, but this was not possible for  $\text{Cr}^{\text{III}}$  and the structure of the substance used has had to be determined by single-crystal X-ray diffraction analysis. In this paper we report the structure of the *cis* isomer. After this work had been finished, the structure of (–)-*cis*-(*RRRR*)- $[\text{CrCl}_2(\text{cyclam})]\text{ClO}_4$  (House & McKee, 1984) was published. The effect of changing the anion from chloride to perchlorate is quite important in determining the crystal packing and the two structures are compared in this paper.

**Experimental.** Dark-red crystals of *cis*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride prepared as reported (Ferguson & Tobe, 1970).

Needle crystals 0.24 × 0.12 × 0.36 mm; Philips PW 1100 automatic four-circle diffractometer, Mo *K*α radiation, graphite-monochromated; lattice parameters refined by least squares from 25 reflections with  $7 \leq \theta \leq 12^\circ$ . Two standard reflections 841 and  $\bar{2}52$  measured at 3 h intervals, no significant fluctuations in intensities other than those expected from Poisson statistics. Intensities measured up to  $2\theta = 52^\circ$ ;  $\theta/2\theta$  scan technique, scan width  $1.20^\circ$  in  $\theta$ , scan speed  $1.8^\circ \text{ min}^{-1}$ . Intensities corrected for Lorentz and

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\times 10^3$ ) with e.s.d.'s in parentheses

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cr	8974.3 (4)	2608.3 (4)	3036.9 (8)	25.3 (2)
Cl(1)	8362 (1)	3596 (1)	4906 (1)	43.3 (4)
Cl(2)	8166 (1)	1374 (1)	3942 (2)	50.2 (4)
Cl(3)	5814 (1)	2112 (1)	-644 (1)	39.4 (4)
N(1)	10206 (2)	2391 (2)	4996 (4)	30 (1)
C(1)	10568 (3)	1427 (3)	5310 (6)	43 (2)
C(2)	10771 (3)	975 (3)	3630 (6)	48 (2)
C(3)	9932 (3)	822 (3)	2105 (6)	48 (2)
N(2)	9479 (2)	1694 (2)	1318 (4)	32 (1)
C(4)	8682 (3)	1487 (3)	-231 (6)	45 (2)
C(5)	8211 (3)	2380 (3)	-886 (6)	42 (2)
N(3)	7952 (2)	2867 (2)	679 (4)	33 (1)
C(6)	7676 (3)	3840 (3)	206 (6)	41 (2)
C(7)	8481 (3)	4453 (3)	-50 (6)	41 (2)
C(8)	9223 (3)	4593 (3)	1674 (6)	35 (2)
N(4)	9733 (2)	3725 (2)	2317 (4)	26 (1)
C(9)	10493 (3)	3923 (3)	3938 (5)	37 (2)
C(10)	10941 (3)	3029 (3)	4638 (6)	36 (1)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j).$$

polarization effects; empirical absorption correction using  $\psi$  scans (North, Phillips & Mathews, 1968) applied; 3084 reflections measured, 2745 unique reflections,  $R_{int} = 0.01$ , 2228 with  $I \geq 3\sigma(I)$ ; index range  $-18 \leq h \leq 17$ ,  $0 \leq k \leq 17$ ,  $0 \leq l \leq 7$ .

Cr-atom parameters found by direct methods with *SHELX76* (Sheldrick, 1976); all other non-H atoms located in subsequent difference Fourier synthesis; function minimized in full-matrix least-squares refinement  $\sum w(\Delta F)^2$ ;  $w = 6.2399 [\sigma^2(F_o) + 0.00057 (F_o)^2]^{-1}$ ; all non-H atoms refined anisotropically; H atoms on N atoms included at positions indicated by difference Fourier synthesis, those on C atoms included at calculated positions (C-H = 0.95 Å); H atoms riding on their bonded atoms refined with a fixed isotropic temperature factor  $U = 0.05 \text{ \AA}^2$ ; final  $R = 0.0252$ ,  $wR = 0.0251$  for 164 variable parameters;  $(\Delta/\sigma)_{max} = 0.96$ ;  $\Delta\rho$  in final difference map within  $-0.24$  and  $0.28 \text{ e \AA}^{-3}$ ,  $S = 1.05$ . Scattering factors and anomalous-dispersion terms for Cr from *International Tables for X-ray Crystallography* (1974), for other atoms factors from *SHELX76*.

Other programs used: *PARST* (Nardelli, 1983) and *PLUTO* (Motherwell & Clegg, 1978) for figure drawing.

**Discussion.** Atomic coordinates are given in Table 1, bond lengths and bond angles in Table 2.\* The stereochemical arrangement of the complex cation with the atom numbering is shown in Fig. 1 while Fig. 2 shows the molecular packing.

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42714 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Cr—Cl(1)	2.325 (2)	Cr—Cl(2)	2.333 (2)
Cr—N(1)	2.097 (4)	Cr—N(2)	2.101 (4)
Cr—N(3)	2.097 (4)	Cr—N(4)	2.105 (4)
N(1)—C(1)	1.497 (5)	N(1)—C(10)	1.492 (6)
C(1)—C(2)	1.513 (7)	C(2)—C(3)	1.509 (6)
N(2)—C(3)	1.492 (5)	N(2)—C(4)	1.494 (5)
C(4)—C(5)	1.502 (6)		
N(3)—C(5)	1.495 (6)	N(3)—C(6)	1.491 (5)
C(6)—C(7)	1.527 (7)	C(7)—C(8)	1.518 (6)
N(4)—C(8)	1.492 (5)	N(4)—C(9)	1.494 (5)
C(19)—C(10)	1.498 (6)		
Cl(1)—Cr—Cl(2)	90.4 (1)	Cl(1)—Cr—N(4)	88.8 (1)
N(4)—Cr—N(2)	92.8 (2)	N(2)—Cr—Cl(2)	88.1 (1)
N(3)—Cr—N(1)	166.9 (2)	N(4)—Cr—Cl(2)	177.9 (1)
N(2)—Cr—Cl(1)	177.9 (2)		
Cr—N(1)—C(1)	118.3 (3)	N(1)—C(1)—C(2)	113.6 (4)
C(1)—C(2)—C(3)	115.1 (5)	C(2)—C(3)—N(2)	113.5 (4)
C(3)—N(2)—Cr	118.5 (2)	N(1)—Cr—N(2)	88.4 (2)
Cr—N(2)—C(4)	116.7 (3)	C(3)—N(2)—C(4)	110.3 (4)
N(2)—C(4)—C(5)	108.1 (4)	C(4)—C(5)—N(3)	109.1 (4)
C(5)—N(3)—Cr	109.0 (3)	N(3)—Cr—N(2)	82.8 (1)
Cr—N(3)—C(6)	118.7 (3)	N(3)—C(6)—C(7)	113.8 (5)
C(6)—C(7)—C(8)	113.7 (4)	C(7)—C(8)—N(4)	112.4 (4)
C(8)—N(4)—Cr	118.5 (4)	N(4)—Cr—N(1)	82.7 (2)
Cr—N(4)—C(9)	106.3 (2)	N(4)—C(9)—C(10)	108.4 (4)
C(9)—C(10)—N(1)	108.7 (5)	C(10)—N(1)—Cr	109.1 (3)

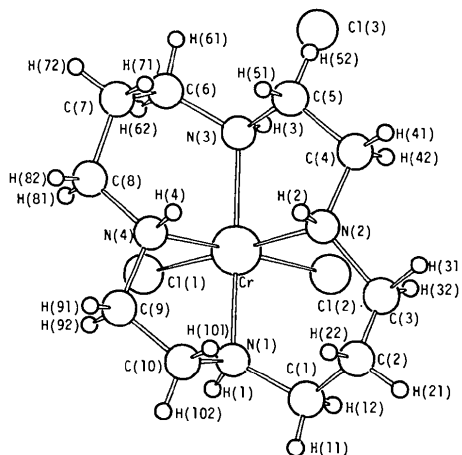


Fig. 1. Perspective view of the complex cation.

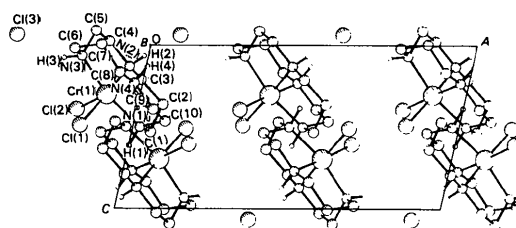


Fig. 2. Unit-cell content as viewed down b.

The structure, which consists of *cis*-[CrCl<sub>2</sub>-(cyclam)]<sup>+</sup> cations and Cl<sup>-</sup> anions, differs from that of (-)-*cis*-(*RRRR*)-[CrCl<sub>2</sub>(cyclam)]ClO<sub>4</sub> (House & McKee, 1984) in that there is no crystallographically imposed C<sub>2</sub> symmetry and the compound crystallizes in a centrosymmetric space group with both the *RRRR* and *SSSS* cations present in the unit cell.

The perchlorate crystals were obtained from a resolved sample and it is not known whether or not the racemic perchlorate crystallizes differently.

The cyclam ligand is folded along the N(1) and N(3) direction with the four N atoms coordinated to the Cr atom in adjacent octahedral sites and the two Cl atoms *cis*-related, occupying the two remaining positions. Within the complex the five-membered ethylenediamine rings adopt a  $\delta$  configuration (Purcell & Kotz, 1977) while the six-membered trimethylenediamine rings are in the chair (*c*) form.

Although the molecular geometries of the cation in the two salts are comparable, there are significant differences in some bond angles and torsional angles as seen for example in the greater folding at N(1) and N(3) [N(1)–Cr–N(3) bond angle 166.9 (1)° (chloride); 169.0 (4)° (perchlorate)] and the N(4)–Cr–N(2) bond angle [92.8 (1)° (chloride); 94.3 (3)° (perchlorate)].

It is likely that the interaction between the hydrogen-bonding system of the amine protons and the counter-anion is the major cause of these differences and of the differences in packing. The chloride anion is within strong hydrogen-bonding distance of the amine protons H(2) and H(4) [H(2)···Cl(3<sup>i</sup>) = 2.27 (3), H(4)···Cl(3<sup>i</sup>) = 2.26 (3) Å] with N–H···Cl angles of nearly 180° [174 (2) and 169 (2)° respectively] [(i) 0.5 + x, 0.5 – y, z] and there is a possible weaker interaction of H(1) and H(3) with other cations [H(3)···Cl(3) = 2.47 (3) Å and N(3)–H(3)···Cl(3) = 147 (2)°, H(1)···Cl(3<sup>ii</sup>) = 2.50 (3) Å and N(1)–H(1)···Cl(3<sup>ii</sup>) = 136 (2)°] [(ii) 0.5 + x, 0.5 – y, 1 + z].

In the perchlorate salt there appears to be, not unsurprisingly, no interaction between the amine

protons and the ClO<sub>4</sub><sup>-</sup> anion, which remains disordered and presumably able to rotate freely; instead the complex cations are linked by significant intermolecular hydrogen-bonding interactions between the coordinated chloride and the amino protons on adjacent cation groups (N···Cl about 3.28 Å). These hydrogen bonds hold the molecules in chains along the twofold axis, while in the chloride salt it is the Cl(3) anion which forms hydrogen bonds with the amine protons of adjacent cations.

All bond lengths and angles within the cations are in the range expected for such compounds (Bang & Mønsted, 1982). The greater length of the Cr–N (mean 2.100 (1) Å than the means 2.080 (6) Å in [CrCl<sub>2</sub>-(cyclam)]<sup>+</sup> (House & McKee, 1984) and 2.083 Å in [CrCl(H<sub>2</sub>O)(hexamethylcyclam)]<sup>2+</sup> (Temple, House & Robinson, 1984) is probably related to the hydrogen-bond system previously described.

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## Structure of Diiodo(1,4,8,11-tetrathiacyclotetradecane)mercury(II)

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**Abstract.** [HgI<sub>2</sub>(C<sub>10</sub>H<sub>20</sub>S<sub>4</sub>)], *M<sub>r</sub>* = 722.90, orthorhombic, *Pnam*, *a* = 10.641 (3), *b* = 8.507 (3), *c* = 20.087 (8) Å, *V* = 1818 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 2.62, *D<sub>x</sub>*

= 2.640 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.7107 Å, μ = 12.25 mm<sup>-1</sup>, *F*(000) = 1320, *T* = 293 K, final *R* = 0.052 for 1726 observed reflections. The structure is

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