Sheldrick, G. M. (1990). *SHELXTL-PC. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Germany.
Truter, M. R. (1967). *Acta Cryst.* **22**, 556–559.
Wang, S. & Fackler, J. P. Jr (1990). *Organometallics*, **9**, 111–115.
Wang, S., Fackler, J. P. Jr, King, C. & Wang, J. C. (1988). *J. Am. Chem. Soc.* **110**, 3308–3310.

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Structures of Chromium(III) Cyclam Complexes. 3. Structure of *trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) Bromide

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Abstract. [CrCl$_2$(C$_{10}$H$_{24}$N$_4$)]Br, $M_r = 403.1$, triclinic, $A\bar{1}$, $a = 6.440$ (3), $b = 16.608$ (1), $c = 7.641$ (2) Å, $\alpha = 86.61$ (2), $\beta = 89.21$ (2), $\gamma = 105.13$ (3)°, $V = 787.4$ (3) Å^3, $Z = 2$, $D_x = 1.70$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 122.3$ cm^{-1}, $F(000) = 410$, room temperature, $R = 0.032$ for 1461 observed reflections and 113 parameters. The X-ray analysis indicates that the cyclam moiety exists in a chair conformation located on a crystallographic centre of symmetry. The equatorial nitrogen ligands and the central Cr ion are coplanar.

Introduction. A number of salts of the complex ion *trans*-[Cr(cyclam)Cl$_2$]$^+$, where cyclam = 1,4,8,11-tetraazacyclotetradecane, have been prepared. The electronic spectra of these compounds should be similar especially in the region around 200–600 cm^{-1} from the electronic origin where the intramolecular vibrational modes are expected. In practice, the electronic spectra that have been measured for different salts differ in detail and spectral resolution. The complexity of some of the spectra would seem to indicate the existence of multiple sites. We present the structure of *trans*-[Cr(cyclam)Cl$_2$]Br as part of our investigation into the roles of exact site symmetry and the field due to neighbouring counterions in determining the form of the electronic spectra of these compounds. Structures bearing *cis* forms of the cations of the title compound have been reported by House & McKee (1984) and Forsellini, Parasassi, Bombieri, Tobe & Sosa (1986): (−)-*cis*-dichloro-[(*R*,*R*,*R*,*R*)-1,4,8,11-tetraazacyclotetradecane]chromium(III) perchlorate and *cis*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride, respectively.

Experimental. Crystals from slowly cooled warm methanolic solution. Red rectangular prisms 0.42 × 0.10 × 0.21 mm used for data collection. Preliminary Weissenberg and precession photographs yielded approximate cell dimensions. Space group $A1$ or $A\bar{1}$ indicated from systematic absences (hkl, $k + l = 2n$), $A\bar{1}$ confirmed by structure analysis. Enraf–Nonius CAD-4 diffractometer; 25 high-angle reflections ($20 < \theta < 40°$) used to obtain accurate cell dimensions by least-squares fit. ω–2θ scan width $(0.85 + 0.14\tan\theta)°$ in ω, vertical aperture 4 mm; 3250 reflections measured ($-7 \leq h \leq 7$, $-20 \leq k \leq 20$, $0 \leq l \leq 9$; $0 < \theta < 70°$); three intensity standards ($0\bar{5}1$, 002, $0\bar{4}0$) monitored at intervals of 100 reflections showed no significant variations during data collection; intensity data corrected for Lorentz–polarization factors. Merging equivalent reflections gave 1491 unique intensities, 1461 with $I > 3\sigma(I)$ with $R_{\text{int}} = 0.024$. The

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Table 1. *Atomic positional parameters and equivalent isotropic temperature factors for the non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_1U_2U_3)^{1/3}$.

	x	y	z	U_{eq}(Å^2)
Br(1)	0.5	0.25	0.25	0.020 (3)
Cr(1)*	0.0	0.0	0.0	0.030 (3)
Cl(1)	−0.2594 (1)	0.0102	−0.2039 (1)	0.041 (3)
N(1)	−0.2143 (3)	0.0111 (1)	0.1946 (2)	0.028 (10)
C(2)	−0.1379 (5)	0.0977 (2)	0.2545 (3)	0.039 (14)
C(3)	−0.0636 (5)	0.1565 (2)	0.0940 (4)	0.039 (14)
N(4)	0.1069 (3)	0.1287 (1)	−0.0011 (3)	0.027 (10)
C(5)	0.1687 (5)	0.1738 (2)	−0.1755 (4)	0.035 (14)
C(6)	0.3365 (5)	0.1415 (2)	−0.2713 (4)	0.037 (14)
C(7)	−0.2607 (5)	−0.0549 (2)	0.3398 (3)	0.039 (15)

To complete the 14 atoms in the cyclam ring: $\bar{1}$ at (000) generates primed atoms *via* symmetry operation $1 - x$, $1 - y$, $1 - z$.

* Atom fixed to define origin.

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

N(4)—C(3)	1.493 (3)	C(6)—C(5)	1.523 (4)
C(3)—C(2)	1.512 (4)	C(5)—N(4)	1.485 (3)
C(2)—N(1)	1.495 (3)	Cr(1)—N(4)	2.067 (2)
N(1)—C(7)	1.482 (3)	Cr(1)—N(1)	2.064 (2)
C(7′)—C(6)	1.520 (4)	Cr(1)—C(1)	2.332 (1)
N(1)—Cr(1)—N(4)	85.0 (1)	C(7)—C(6′)—C(5′)	116.7 (2)
N(4)—Cr(1)—Cl(1)	91.0 (1)	C(6)—C(5)—N(4)	111.6 (2)
N(1)—Cr(1)—Cl(1)	88.1 (1)	C(5)—N(4)—C(3)	113.2 (2)
N(4)—C(3)—C(2)	108.4 (2)	C(7)—N(1)—Cr(1)	116.6 (2)
C(3)—C(2)—N(1)	107.8 (2)	C(3)—N(4)—Cr(1)	106.0 (2)
C(2)—N(1)—C(7)	113.7 (2)	C(2)—N(1)—Cr(1)	106.8 (1)
N(1)—C(7)—C(6′)	111.4 (2)	C(5)—N(4)—Cr(1)	116.0 (2)
N(1)—C(2)—C(3)—N(4)	−57.1 (4)	C(5′)—C(6′)—C(7)—N(1)	70.7 (4)
C(2)—C(3)—N(4)—C(5)	171.1 (4)	C(6′)—C(7)—N(1)—C(2)	−179.7 (4)
C(3)—N(4)—C(5)—C(6)	−177.8 (4)	C(7)—N(1)—C(2)—C(3)	171.1 (5)
N(4)—C(5)—C(6)—C(7′)	71.1 (3)		

structure was solved using the heavy-atom method with initial phases based on the position of the Cr atom and difference Fourier methods. The pyramidal nitrogen H atoms were positioned unambiguously by refinement of an isotropic thermal parameter for each of the geometrically positioned alternative tetrahedral sites, defined with respect to the CNC moiety, Cr being at too great a distance to be considered by the program for the purposes of this calculation. The incorrect alternative site acquires an unacceptably high value for this parameter. Correct assignment of the nitrogen H atoms was subsequently confirmed by graphics plots. Refinement by *SHELX76* (Sheldrick, 1976), full-matrix least squares with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms. H atoms except for those on N atoms were fixed geometrically and not refined. Atomic scattering factors from *SHELX76* and *International Tables for X-ray Crystallography* (1974, Vol. IV) (for Cr^{3+}). Atomic absorption coefficient for Cr from Cromer & Liberman (1970). Dispersion corrections f' and f'' for Cr from *International Tables for X-ray Crystallography* (1974, Vol. IV). Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1.6395/(\sigma^2|F| + 0.000104|F_o|^2)$, $R = 0.032$, $wR = 0.034$, R (all data) $= 0.035$, max. (shift/σ) $= 0.012$. Final difference electron density synthesis showed electron density $+0.74$ to -0.74 e Å^{-3}. Calculations carried out on Amdahl 470V/8 and VAX 11/750 computers.* Geometrical calculations performed with *XANADU* (Roberts & Sheldrick, 1975). Molecular illustrations were drawn with *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1. Distances and angles are listed in Table 2. Fig. 1 is a minimum-overlap stereoview of the molecule showing the atom numbering. Fig. 2 shows the crystal packing viewed along **a**.

The cyclam moiety provides a tetradentate nitrogen ligand, giving with the two axial Cl ligands an octahedrally coordinated Cr atom. The mean Cr—N

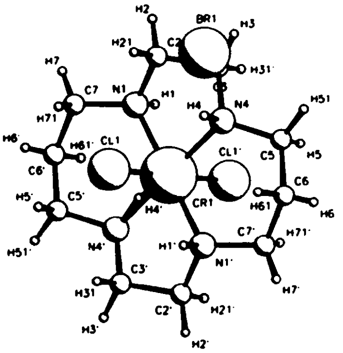

Fig. 1. Minimum-overlap view of the molecule.

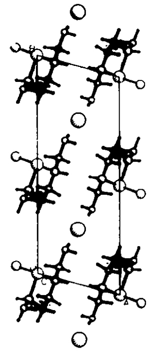

Fig. 2. Crystal packing viewed along **a**.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55046 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0038]

ligand distance is 2.066 (2) Å which is normal, agreeing with many literature values, *e.g.* for *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten, Palmer & Gazi, 1990), di-μ-methoxo-bis[7-amino-4-methyl-5-azahept-3-en-2-onato-*O*,*N*,*N'*)aquachromium(III)] diperchlorate (Clegg, 1985) and *trans*-amminebis(ethylenediamine)-fluorochromium(III) perchlorate (Beveridge, Bushnell & Kirk, 1985). The Cl(1)—Cr(1)—Cl(1') and N(4)—Cr(1)—N(4') angles are exactly linear due to symmetry requirements. The cyclam moiety has normal geometry and assumes a centrosymmetric chair conformation. The least-squares-planes equation for the Cr^{III} ion and the four ligand N atoms is $4.643x' - 3.810y' + 5.33z' = 0$, where x', y' and z' are the coordinates in Å with respect to the orthonormal axes (Rollett, 1965). These equatorial ligand atoms and the central Cr ion are coplanar. The geometry of the cyclam ring is similar to that found in *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten *et al.*, 1990). Corresponding bond lengths agree to within 0.035 (5) Å, bond angles to within 1.9 (3)° and torsion angles to within 1.3 (5)°.

References

BEVERIDGE, K. A., BUSHNELL, G. W. & KIRK, A. D. (1985). *Acta Cryst.* C**41**, 899–902.

CLEGG, W. (1985). *Acta Cryst.* C**41**, 1830–1831.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Phys. Chem.* **53**, 1891–1898.

FORSELLINI, E., PARASASSI, T., BOMBIERI, G., TOBE, M. L. & SOSA, M. (1986). *Acta Cryst.* C**42**, 563–565.

HOUSE, D. A. & MCKEE, V. (1984). *Inorg. Chem.* **23**, 4237–4242.

LISGARTEN, J. N., PALMER, R. A. & GAZI, D. M. (1990). *Acta Cryst.* C**46**, 396–399.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

ROLLETT, J. S. (1965). Editor. *Computing Methods in Crystallography*, p. 22. Oxford: Pergamon Press.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structures of Chromium(III) Cyclam Complexes. 4. Structure of *trans*-Bromochloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) Bromide Displaying Structural Enantiomorphism with the Dibromo Complex

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Abstract. $[CrBrCl(C_{10}H_{24}N_4)]Br$, $M_r = 447.7$, tetragonal, $P4_2/m$, $a = 7.775\ (1)$, $c = 13.686\ (2)$ Å, $V = 827.2\ (3)$ Å^3, $Z = 2$, $D_x = 1.81$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.7$ cm^{-1}, $F(000) = 446.0$, room temperature, $R = 0.030$ for 658 observed reflections and 63 parameters. The *trans*-bromochloro(cyclam)-chromium(III) bromide complex is almost isostructural with the *trans*-dibromo(cyclam)chromium(III) bromide complex with the cation again displaying $2/m$ crystallographic symmetry. Consequently, the Br and Cl axial sites are statistically disordered, each with exactly 50% occupancy of Br and Cl. A further unusual feature of the two structures is that the cyclam moieties are structurally enantiomeric being related by an *a*-glide operator perpendicular to **b** at $[x\ \frac{1}{4}\ 0]$.

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