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# Structures of Chromium(III) Cyclam Complexes. 1. Structure of *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

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**Abstract.** $[Cr(CN)_2(C_{10}H_{24}N_4)]ClO_4$, $M_r = 403{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}874\,(2)$, $b = 13{\cdot}506\,(1)$, $c = 19{\cdot}222\,(2)$ Å, $V = 1784{\cdot}6\,(4)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}50$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 7{\cdot}7$ cm$^{-1}$, $F(000) = 834{\cdot}97$, room temperature, $R = 0{\cdot}036$ for 4186 observed reflections. The cyclam moiety exists in a chair conformation. The equatorial nitrogen ligands and the central chromium ion are approximately coplanar. The Cr–C(cyano) vectors lie 1·3 and 1·9° respectively from the normal to the $CrN_4$ plane.

**Introduction.** The cyclam ligand has been used in the preparation of transition-metal complexes for kinetic (Ferguson & Tobe, 1970; Eriksen & Monsted, 1983), photochemical (Maguire, Crippen & Miller, 1983) and spectroscopic (Forster & Monsted, 1986) studies where it is desirable to maintain a rigid four-coordinate plane in order to investigate the properties of the two remaining ligands (*i.e.* in six-coordinate complexes).

It has been suggested that macrocyclic complexes of transition metals have similar properties to biologically important systems (Christensen, Eatough & Izatt, 1974). Cyclam structures resemble porphyrins in that both systems are cyclic tetradentate nitrogen donor ligands. A crystal structure has been reported for a copper complex where the tetrathia analogue of cyclam was used as a ligand (Glick, Gavel, Diadoarrio & Robarbacher, 1976). We report here the crystal-structure determination of the *trans*-dicyano chromium(III) complex.

The compound is of interest because it displays unusual phosphorescence behaviour in solution. It has also been described as exhibiting unusual behaviour in its visible emission spectrum (Kane-Maguire, 1983). Luminescence of the chromium(III) complex is thought to arise from the lowest component of the $^2T_{1g}$ $(O_h)$ electronic state. Solid-state absorption and emission spectra for spin-forbidden transitions have also been measured (Flint & Gazi, 1989). However, the complete and detailed assignments of these spectra will depend on some knowledge of the crystal structure of the complex

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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*

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

| | $x$ | $y$ | $z$ | $U_{\mathrm{eq}}$ (Å$^2$) |
|---|---|---|---|---|
| Cr | −1·22988 (5) | −0·02387 (2) | −1·12826 (2) | 0·022 (2) |
| N(1) | −1·2398 (3) | 0·0515 (2) | −1·0347 (1) | 0·033 (10) |
| C(2) | −1·0811 (4) | 0·0076 (3) | −0·9912 (2) | 0·041 (13) |
| C(3) | −1·0823 (5) | −0·1032 (3) | −1·0014 (2) | 0·043 (16) |
| N(4) | −1·0553 (3) | −0·1224 (2) | −1·0765 (1) | 0·031 (11) |
| C(5) | −1·0829 (5) | −0·2294 (2) | −1·0944 (2) | 0·043 (16) |
| C(6) | −1·0575 (6) | −0·2465 (2) | −1·1727 (2) | 0·045 (17) |
| C(7) | −1·2222 (5) | −0·2073 (2) | −1·2190 (2) | 0·041 (14) |
| N(8) | −1·2218 (3) | −0·0973 (2) | −1·2221 (1) | 0·065 (9) |
| C(9) | −1·3848 (4) | −0·0559 (2) | −1·2644 (1) | 0·038 (44) |
| C(10) | −1·3860 (5) | 0·0547 (2) | −1·2554 (1) | 0·039 (14) |
| N(11) | −1·4013 (3) | 0·0777 (2) | −1·1799 (1) | 0·027 (10) |
| C(12) | −1·3649 (4) | 0·1833 (2) | 1·1624 (2) | 0·035 (15) |
| C(13) | −1·3918 (5) | 0·2028 (2) | −1·0858 (2) | 0·043 (17) |
| C(14) | −1·2350 (5) | 0·1616 (2) | −1·0386 (2) | 0·044 (14) |
| C(21) | −1·4807 (3) | −0·1015 (2) | −1·0992 (1) | 0·030 (12) |
| N(23) | −1·6223 (4) | −0·1393 (2) | −1·0832 (2) | 0·018 (16) |
| C(22) | −0·9772 (4) | 0·0517 (2) | −0·1563 (1) | 0·030 (12) |
| N(24) | −0·8318 (4) | 0·0875 (2) | −1·1702 (2) | 0·046 (15) |
| Cl | −0·60408 (10) | 0·03976 (6) | −0·88343 (4) | 0·041 (3) |
| O(1) | −0·4291 (4) | −0·0172 (2) | −0·8813 (2) | 0·064 (17) |
| O(2) | −0·7665 (4) | −0·0278 (3) | −0·8763 (2) | 0·073 (20) |
| O(3) | −0·6043 (7) | 0·1090 (3) | −0·8275 (2) | 0·102 (32) |
| O(4) | −0·6202 (5) | 0·0893 (3) | −0·9498 (2) | 0·063 (19) |

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

| | | | | | |
|---|---|---|---|---|---|
| Cr | N(1) | 2·067 (2) | Cr | N(4) | 2·067 (2) |
| Cr | N(8) | 2·059 (2) | Cr | N(11) | 2·063 (2) |
| Cr | C(21) | 2·093 (2) | Cr | C(22) | 2·085 (3) |
| C(21) | N(23) | 1·142 (4) | C(22) | N(24) | 1·142 (4) |
| N(1) | C(2) | 1·498 (4) | C(2) | C(3) | 1·508 (5) |
| C(3) | N(4) | 1·483 (4) | N(4) | C(5) | 1·472 (4) |
| C(5) | C(6) | 1·532 (5) | C(6) | C(7) | 1·534 (5) |
| C(7) | N(8) | 1·486 (3) | N(8) | C(9) | 1·494 (4) |
| C(9) | C(10) | 1·503 (5) | C(10) | N(11) | 1·488 (4) |
| N(11) | C(12) | 1·486 (4) | C(12) | C(13) | 1·507 (5) |
| C(13) | C(14) | 1·514 (5) | C(14) | N(1) | 1·489 (4) |
| Cl | O(1) | 1·428 (3) | Cl | O(2) | 1·449 (3) |
| Cl | O(3) | 1·425 (3) | Cl | O(4) | 1·445 (3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N(1) | Cr | N(4) | 85·6 (1) | N(4) | Cr | N(8) | 95·1 (1) |
| N(8) | Cr | N(11) | 85·1 (1) | N(11) | Cr | N(1) | 94·1 (1) |
| C(21) | Cr | C(22) | 179·0 (1) | N(1) | C(2) | C(3) | 108·4 (2) |
| C(2) | C(3) | N(4) | 108·5 (2) | C(3) | N(4) | C(5) | 113·4 (2) |
| N(4) | C(5) | C(6) | 111·1 (3) | C(5) | C(6) | C(7) | 115·7 (3) |
| C(6) | C(7) | N(8) | 111·5 (2) | C(7) | N(8) | C(9) | 113·3 (2) |
| N(8) | C(9) | C(10) | 108·3 (2) | C(9) | C(10) | N(11) | 108·7 (2) |
| C(10) | N(11) | C(12) | 114·2 (2) | N(11) | C(12) | C(13) | 111·6 (2) |
| C(12) | C(13) | C(14) | 115·7 (2) | C(13) | C(14) | N(1) | 112·4 (2) |
| C(14) | N(1) | C(2) | 114·1 (3) | N(23) | C(21) | Cr | 175·5 (3) |
| N(24) | C(22) | Cr | 175·3 (3) | O(1) | Cl | O(2) | 107·8 (2) |
| O(2) | Cl | O(3) | 110·0 (3) | O(34) | Cl | P(4) | 111·2 (2) |
| O(4) | Cl | O(1) | 108·7 (2) | O(1) | Cl | O(3) | 109·8 (2) |
| O(2) | Cl | O(4) | 108·4 (2) | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | C(2) | C(3) | N(4) | −59·1 (4) | N(8) | C(9) | C(10) | N(11) | 56·6 (3) |
| C(2) | C(3) | N(4) | C(5) | 172·5 (1) | C(9) | C(10) | N(11) | C(12) | −169·3 (1) |
| C(3) | N(4) | C(5) | C(6) | −177·2 (1) | C(10) | N(11) | C(12) | C(13) | 177·0 (1) |
| N(4) | C(5) | C(6) | C(7) | 70·6 (5) | N(11) | C(12) | C(13) | C(14) | −72·7 (4) |
| C(5) | C(6) | C(7) | N(8) | −70·2 (5) | C(12) | C(13) | C(14) | N(1) | 70·9 (4) |
| C(6) | C(7) | N(8) | C(9) | 175·7 (1) | C(13) | C(14) | N(1) | C(2) | −177·0 (1) |
| C(7) | N(8) | C(9) | C(10) | −178·8 (1) | C(14) | N(1) | C(2) | C(3) | 170·9 (1) |

since the splitting of the spin-forbidden states will depend on contributions from spin-orbit coupling and also on the lowering of the point group from a strictly cubic symmetry.

**Experimental.** The *trans*-dicyano(cyclam)chromium(III) perchlorate complex was prepared by the method of Kane-Maguire (1983). Crystals were obtained by slow evaporation of an aqueous solution of the salt at 313 K. Yellow, prismatic crystal 0·23 × 0·28 × 0·50 mm used for data collection, preliminary Weissenberg photographs yielded approximate cell dimensions and showed orthorhombic (*mmm*) Laue symmetry. Space group $P2_12_12_1$, unambiguously determined from systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, 25 high-angle reflections ($1 \le 2\theta \le 25°$) used to obtain accurate cell dimensions by least-squares fit. $\omega$–$2\theta$ scan, width $(0{\cdot}90 + 0{\cdot}34\tan\theta)°$, vertical aperture 3 mm. 5194 unique reflections measured ($-9 \le h \le 9$, $0 \le k \le 19$, $0 \le l \le 27$), 4186 with $I > 3\sigma(I)$ ($1 < 2\theta < 60°$); four intensity standards ($1\bar{2}6$, $1\bar{2}\bar{6}$, $\bar{1}4\bar{3}$ and 143) monitored at intervals of 50 reflections showed no significant variations during data collection; intensity data corrected for Lorentz–polarization factors; empirical absorption correction based on $\varphi$ scans for each of two reflections (North, Phillips & Mathews, 1968) near $\chi = 90°$ measured at 10° intervals from $\varphi = 0°$ to $\varphi = 360°$, normalized transmission factors 0·99 to 0·96. $R_{\mathrm{int}} = 0{\cdot}048$ from merging equivalent reflections. Patterson function and heavy-atom method with initial phases based on position of Cr atom, all remaining non-H-atom positions from electron density synthesis. Refinement by *SHELX76* (Sheldrick, 1976), full-matrix least squares with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms. H-atom positions were fixed geometrically and not refined. Atomic scattering factors from *SHELX76* and *International Tables for X-ray Crystallography* (1974) (for $\mathrm{Cr^{3+}}$). Atomic absorption coefficient for Cr from Cromer & Liberman (1970). Dispersion corrections $f'$ and $f''$ for Cr from *International Tables for X-ray Crystallography* (1974). Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma^2|F| + 0{\cdot}0156|F_o|^2)$, $R^* = 0{\cdot}036$, $wR^* = 0{\cdot}042$, $R$ (all data) $= 0{\cdot}052$, max. (shift/$\sigma$) $= 0{\cdot}136$. Final difference electron density synthesis showed electron density $-0{\cdot}74$ to $+0{\cdot}67$ 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 final atomic coordinates and equivalent isotropic thermal parameters of the non-H

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* Corresponding values for the inverse structure were $R = 0{\cdot}043$ and $wR = 0{\cdot}051$.

atoms are given in Table 1.* Bond distances and angles are listed in Table 2 together with selected torsion angles. Fig. 1 is a view of the molecule showing the numbering scheme. Fig. 2 shows the crystal packing viewed along **a**.

Cyclam is a tetradentate nitrogen ligand and forms with the two axial cyanide ligands an octahedrally coordinated chromium. The mean Cr—N ligand distance is 2·064 (2) Å which is normal, agreeing with many literature values, *e.g.* *trans*-amminebis(ethylenediamine)fluorochromium(III) perchlorate (Beveridge, Bushnell & Kirk, 1985) and di-$\mu$-methoxo-bis[(7-amino-4-methyl-5-azahept-3-en-2-onato-*O*,*N*,*N'*)aquachromium(III)] diperchlorate (Clegg, 1985). The mean Cr—C distance is 2·089 (3) Å which is also in agreement with literature values [*e.g.* ($\eta^{12}$-[3.3]paracyclophane)chromium(I) triiodide (Blank & Haenel, 1980)]. The perchlorate ion has standard geometry [mean Cl—O distance 1·439 (3) Å, range 1·425 (3) – 1·449 (3) Å, mean O—Cl—O angle 109·4 (3)°, range 107·8 (2) – 111·2 (2)°]. The cyclam moiety has normal geometry and assumes a chair conformation. The least-squares-plane equation for the chromium(III) ion and the four nitrogen ligands is $0\cdot815x' + 0\cdot518y' - 0\cdot259z' + 1\cdot435 = 0$, where $x'$, $y'$ and $z'$ are the coordinates in Å with respect to the orthogonal crystal axes. These equatorial ligands and the central ion were found to be approximately coplanar, the r.m.s. deviation being 0·006 Å for the five atoms. The deviations for Cr, N(1), N(4), N(8) and N(11) are 0·004, 0·005, −0·008, 0·005 and −0·008 Å respectively. The small discrepancies from regular octahedral coordination in the positioning of the axial cyanide ligands relative to the central chromium ion may be due to steric crowding involving the methylene groups at C(13) and C(6). The Cr—C(21) and Cr—C(22) vectors lie 1·3 and 1·9° respectively from the normal to the CrN$_4$ plane. An approximate twofold rotation axis can be found by rotating through 177·3° about the vector (0·373, −0·116, 0·921) and relates the positions of atoms C(3) to C(9) with those of atoms C(2) to C(10) respectively. The r.m.s. atomic deviation after the transformation for seven atom pairs is 0·04 Å. This axis lies 89·7° from the normal to the equatorial CrN$_4$ plane.

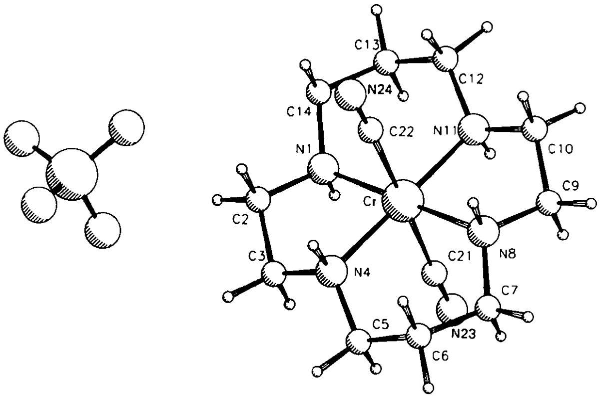

Fig. 1. Minimum-overlap view of the asymmetric unit.

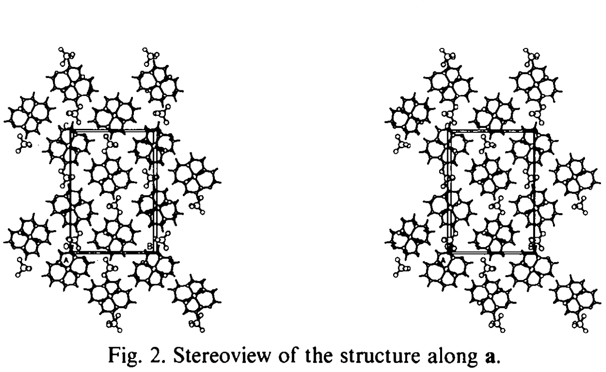

Fig. 2. Stereoview of the structure along **a**.

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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 52191 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.