

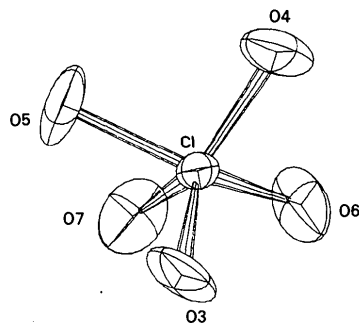
Table 3. Equations of mean planes and distances of the atoms from the planes (Å)

(a) $0.7684x - 0.2101y + 0.6044z = 6.1808$

N(1)	-0.021	C(3)	0.017
N(2)	-0.013	C(4)	0.006
C(7)	0.011	C(5)	0.007
O(2)	0.004	C(6)	-0.015
C(1)	0.001	N(3)	-0.030
C(2)	-0.011	Cu	0.000

(b) $0.8912x + 0.1242y + 0.4361z = 7.6704$

C(8)	0.002	C(10)	-0.004
N(4)	-0.008	C(11)	-0.003
C(9)	0.009	C(12)	0.003

Fig. 2. Disordered positions in the ClO₄⁻ anion.

to the elongated form of the thermal ellipsoids; the oxygen atoms O(5), O(6) and O(7) are refined respectively with 0.75, 0.75 and 0.5 occupancy factors; see Fig. 2.

The whole crystal structure can be described by alternative layers of [Cu(odp)₂(H₂O)₂]²⁺ and ClO₄⁻, probably linked by hydrogen bonds of the type O(1)⋯O(5) = 2.64 Å.

The mononuclear complex in [Cu(odp)₂(H₂O)₂](ClO₄)₂ will be used to initiate an interesting structural study of a new polynuclear complex family.

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Structures of Chromium(III) Cyclam Complexes. 2. Structure of *trans*-Dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) Bromide

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Abstract. [CrBr₂(C₁₀H₂₄N₄)]Br, *M_r* = 492.0, tetragonal, *P*4₂/*m*, *a* = 7.860 (1), *c* = 13.507 (2) Å, *V* = 834.5 (3) Å³, *Z* = 2, *D_x* = 1.96 g cm⁻³, λ(Cu *K*α) = 1.54184 Å, μ = 119.4 cm⁻¹, *F*(000) = 483.96, room temperature, *R* = 0.0722 for 637 observed reflections. The cyclam moiety exists in a chair conformation with exact 2/*m* symmetry. The twofold axis passes through Cr and bisects the C(1)—C(1') and C(1'')—C(1'') bonds of the five-membered chelate

rings; the mirror plane also passes through Cr and contains atoms C(4) and C(4') of the cyclam moiety. The Br⋯Br' vector is tilted by 2.4° from the perpendicular to the CrN₄ plane.

Introduction. Quadrate complexes (*i.e.* *MBA*₂) of metals with *B* = quadridentate cyclic ligand have been extensively studied because they essentially have a stable four-donor-atom plane allowing for kinetic, photochemical and spectroscopic evaluation of the *A*₂ ligands. When the effective crystal field is

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assumed to be D_{4h} then the spectra can be described by three parameters D_q , D_s and D_r . This makes it possible to test the crystal field theory.

Tetraaza cyclic ligands can present a simple model for more complex, naturally occurring porphyrins. Manganese porphyrin complexes have been prepared and studied by Zaleski (1904) and Taylor (1940), for example.

Increasing interest has been shown recently in the chromium complexes of cyclic ligands. Although several workers have prepared and studied *trans*-dibromo complexes of Ru, Co, Cu and Cr with 5,6,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, preparation of the corresponding *trans*-dibromo cyclam complex is not known. The title complex has now been prepared in the pure form and crystallized. It is particularly interesting because components of all three spin-forbidden electronic transitions have been located and assigned (Gazi, 1988).

Experimental. Crystals of the title compound were grown from a saturated green solution that was slowly evaporated over sodium hydroxide. Bright-green square platy crystal $0.30 \times 0.30 \times 0.14$ mm used for data collection, preliminary Weissenberg photographs yielded approximate cell dimensions and showed tetragonal ($4/m$) Laue symmetry. Space group $P4_2$ or $P4_2/m$ indicated from systematic absences ($00l$: $l = 2n + 1$); $P4_2/m$ confirmed by structure analysis.

Enraf-Nonius CAD-4 diffractometer; 25 high-angle reflections ($20^\circ < \theta < 40^\circ$) used to obtain accurate cell dimensions by least-squares fit. ω - 2θ scan width ($0.90 + 0.14 \tan \theta$) in ω , vertical aperture 6 mm. 4992 reflections measured ($-6 \leq h \leq 6$, $0 \leq k \leq 8$, $-15 \leq l \leq 15$) ($0 < \theta < 60^\circ$); three intensity standards (233, 524, 524) monitored at intervals of 100 reflections showed no significant variations during data collection; intensity data corrected for Lorentz-polarization factors; empirical absorption correction (North, Phillips & Mathews, 1968) based on φ scan for a reflection near $\chi = 90^\circ$ measured at 10° intervals from $\varphi = 0^\circ$ to $\varphi = 360^\circ$, normalized transmission factors 1.000 to 0.472. Space group $P4_2$ was assumed initially. Merging equivalent reflections gave 1219 unique intensities, 1216 with $I > 3\sigma(I)$ with $R_{int} = 0.039$. The structure was solved by Patterson 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 C—N—C 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

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

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Br(1)	0.2466 (1)	1.1914 (1)	0.5	0.040 (1)
Cr(1)	0.5	1.0	0.5	0.023 (1)
Br(2)	0.5	0.5	0.25	0.041 (1)
C(1)	0.4137 (9)	0.9559 (7)	0.7037 (3)	0.038 (1)
N(2)	0.4025 (6)	0.8526 (5)	0.6121 (3)	0.034 (1)
C(3)	0.2310 (8)	0.7810 (7)	0.5980 (6)	0.044 (1)
C(4)	0.2236 (12)	0.6772 (11)	0.5	0.047 (1)

To complete the 14 atoms in the cyclam ring: twofold axis at $(\frac{1}{2}, 1, z)$ generates ' atoms *via* operation $(1 - x, 2 - y, z)$; m plane at $z = \frac{1}{2}$ generates '' atoms *via* operation $(x, y, 1 - z)$; $\bar{1}$ at $(\frac{1}{2}, 1, \frac{1}{2})$ generates ''' atoms *via* operation $(1 - x, 2 - y, 1 - z)$.

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) with *e.s.d.'s* in parentheses

Cr(1)—Br(1)	2.496 (1)	C(1)—N(2)	1.483 (6)
N(2)—Cr(1)	2.055 (4)	N(2)—C(3)	1.473 (8)
C(1)—C(1')	1.523 (12)	C(3)—C(4)	1.555 (9)
N(2)—Cr(1)—Br(1)	92.4 (1)	C(3)—N(2)—C(1)	111.8 (4)
N(2)—Cr(1)—Br(1)	87.6 (1)	C(4)—C(3)—N(2)	110.2 (5)
N(2)—Cr(1)—N(2')	85.1 (3)	C(3)—C(4)—C(3')	116.6 (7)
C(1)—N(2)—Cr(1)	106.5 (3)	C(1')—C(1)—N(2)	107.6 (8)
C(3)—N(2)—Cr(1)	117.5 (4)	N(2)—Cr(1)—N(2')	94.9 (1)
N(2)—C(1')—C(1)—N(2)	57.8 (8)	C(1)—N(2)—C(3)—C(4)	178.7 (5)
C(1')—C(1)—N(2)—C(3)	-172.0 (9)	N(2)—C(3)—C(4)—C(3')	-70.6 (8)

parameter. This method enabled completion of the structure to be carried out during the least-squares analysis without recourse to a more lengthy graphical confirmation.* Correct assignment of the nitrogen H atoms was subsequently confirmed by graphics plots. A geometrically acceptable model for the cyclam moiety was obtained initially only when C—C and C—N bond lengths were restrained within tolerable limits. Release of the restraints on the refined model subsequently gave a geometrically acceptable structure in space group $P4_2$, with $R = 0.0752$, 92 parameters.

The inverse structure yielded identical refinement criteria, suggesting $P4_2/m$ to be the correct structure as also indicated by the approximate $2/m$ symmetry of the cyclam moiety. The $P4_2/m$ model based on 637 unique reflections with $I > 3\sigma(I)$ again required initial geometrical restraints which were then released to give the final structure with acceptable geometry, having 51 parameters [anisotropic displacement parameters for non-H atoms; H atoms positioned geometrically, fixed H parameters except for U_{iso} of H(2)]. An extinction parameter ε was included having a final value of 0.021 (5). Atomic

* The authors wish to thank Professor M. B. Hursthouse for endorsing this simple but effective method of placing the H atoms on the pyramidal N atoms, the correctness of which can be seen in Fig. 1.

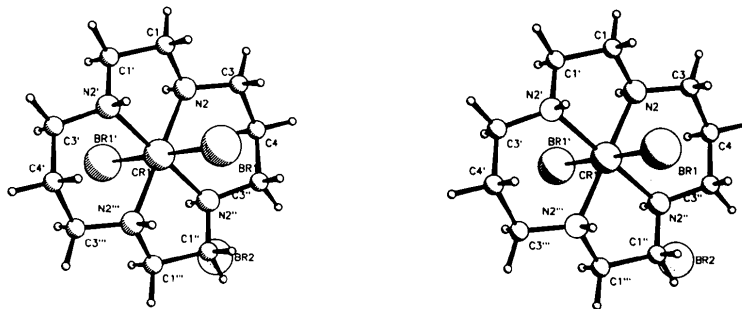


Fig. 1. Minimum-overlap view of the molecule and counter Br⁻ ion.

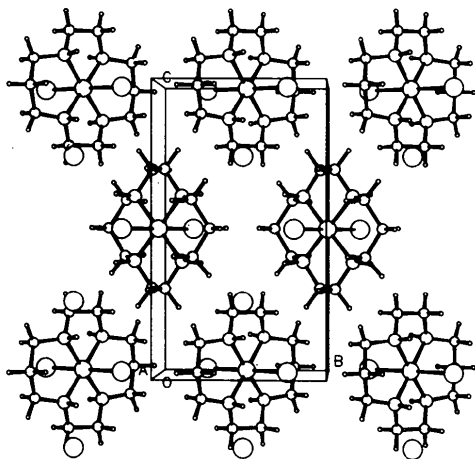


Fig. 2. Packing viewed along a.

scattering factors from *SHELX76* (Sheldrick, 1976) and *International Tables for X-ray Crystallography* (1974). 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 $\sum w(|F_o| - |F_c^*|)^2$, where $|F_c^*| = F(1 - \epsilon|F_c|/\sin\theta)$, $w = (\sigma^2|F_o| + 0.004895|F_o|^2)^{-1}$, $R = 0.0722$, $wR = 0.0822$, max. (shift/ σ) = 0.521. Final difference synthesis showed residual electron density -0.9 to $+0.7$ e \AA^{-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 atoms are given in Table 1.† Distances and angles are listed in Table 2. Fig. 1 is a minimum-overlap

† 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 52397 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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, forming with the two axial bromine ligands an octahedrally coordinated chromium. The Cr—N ligand distance is 2.055 (4) Å which is normal, agreeing with many literature values, e.g. *trans*-dicyano(1,4,8,11-tetraazacyclotetradecane)-chromium(III) perchlorate (Hemmings, Lisgarten, Palmer & Gazi, 1990), *trans*-aminebis(ethylene-diamine)fluorochromium(III) perchlorate (Beveridge, Bushnell & Kirk, 1985) and di- μ -methoxy-bis-[7-amino-4-methyl-5-azahept-3-en-2-onato-*O,N,N'*]-aquachromium(III) diperchlorate (Clegg, 1985). The Br—Cr—Br' and N(2)—Cr—N(2''') angles are exactly linear, due to symmetry requirements.

The cyclam moiety has normal geometry and assumes a chair conformation with exact $2/m$ symmetry. The least-squares-planes equation for the chromium(III) ion and the four nitrogen ligands is $0.834x' - 0.552y' + 1.059z' = 0$, where x' , y' and z' are the coordinates in Å with respect to the orthonormal axes (Rollett, 1965). These equatorial ligands and the central chromium ion are coplanar. The geometry of the cyclam ring is similar to that found in *trans*-dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) perchlorate (Hemmings *et al.*, 1990). Corresponding bond lengths agree to within 0.048 (10) Å, bond angles to within 2.4 (9)° and torsion angles to within 6.8 (1.2)°.

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Acta Cryst. (1990). **C46**, 399–402

Structures of Triaqua[1,2-benzenedicarboxylato(2-)](1,10-phenanthroline)nickel(II) Monohydrate (I) and Triaqua[1,2-benzenedicarboxylato(2-)](2,2'-dipyridylamine)-nickel(II) Dihydrate (II)*

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Abstract. (I): $[\text{Ni}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, $M_r = 475.10$, monoclinic, $P2_1/n$, $a = 20.157$ (7), $b = 13.632$ (5), $c = 7.529$ (2) Å, $\beta = 97.36$ (4)°, $V = 2052$ (1) Å³, $Z = 4$, $D_x = 1.54$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.996$ mm⁻¹, $F(000) = 984$, $R = 0.062$ for 3362 observed reflexions. (II): $[\text{Ni}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_9\text{N}_3)(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$, $M_r = 484.11$, monoclinic, $P2_1/n$, $a = 8.026$ (2), $b = 19.901$ (4), $c = 13.235$ (1) Å, $\beta = 99.61$ (1)°, $V = 2084.3$ (7) Å³, $Z = 4$, $D_x = 1.54$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.986$ mm⁻¹, $F(000) = 1008$, $R = 0.037$ for 3902 observed reflexions. In both compounds the discrete complex molecules are found to be of very similar shape. The Ni atoms are in a distorted octahedral environment with three molecules of coordinated water in the meridional position. The 1,2-benzenedicarboxylate(2-) anions act as monodentate ligands, while the rest of the carboxylate O atoms, together with water of crystallization form a system of hydrogen bonding. On the basis of photographic data $[\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ is isostructural with the analogous Ni complex.

Introduction. Crystal structures of about fifteen transition metal-phthalate [1,2-benzenedicarboxylate(2-)] complexes have been determined so far. Most of them are Cu^{II} complexes (for a complete list of references see Krstanović, Karanović & Stojaković, 1985), where polydentate, bridging or combined bridging-chelating behaviour of phthalate ion is predominant. No structures of Co^{II} complexes and only two structures of Ni^{II} complexes (Kozlova, Agre, Trunov, Makarevich & Barkhanova, 1982; Endres, 1984) are known. This is not sufficient for a more detailed study of the factors that determine the coordination mode of the phthalate ion.

We have recently prepared some ternary Co^{II} and Ni^{II} complexes with 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) and 2,2'-dipyridylamine (dipya) as a second ligand. This paper reports the structures of two of them. From the preliminary X-ray data it was found that $[\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ is isostructural with (I).

Experimental. Blue (Ni) and pink (Co) monocrystals were prepared by slow evaporation from dilute aqueous solutions containing equimolar amounts of $M(\text{NO}_3)_2$ ($M = \text{Ni}, \text{Co}$), diamine and sodium

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