

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- $\mu$ -methoxy-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<sup>III</sup> 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). Corre-

sponding 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.* **C41**, 899–902.  
 CLEGG, W. (1985). *Acta Cryst.* **C41**, 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.* **C42**, 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.* **C46**, 396–399.  
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.  
 ROBERTS, P. & SHELDRIK, 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.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1992). **C48**, 1756–1759

## 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

BY T. K. CHATTOPADHYAY AND R. A. PALMER\*

*Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England*

J. N. LISGARTEN AND L. WYNS

*Department of Ultrastructure, Instituut voor Moleculaire Biologie, Vrije Universiteit Brussel, Paardenstraat 65, B-1640 Sint-Genesius Rode, Belgium*

AND D. M. GAZI

*Department of Chemistry, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England*

(Received 14 October 1991; accepted 30 March 1992)

**Abstract.** [CrBrCl(C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>)]Br,  $M_r = 447.7$ , tetragonal,  $P4_2/m$ ,  $a = 7.775$  (1),  $c = 13.686$  (2) Å,  $V = 827.2$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.81$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 7.7$  cm<sup>-1</sup>,  $F(000) = 446.0$ , room temperature,  $R = 0.030$  for 658 observed reflections and 63 parameters. The *trans*-bromochloro(cyclam)-chromium(III) bromide complex is almost isostruc-

tural 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  $[x \frac{1}{4} 0]$ .

\* Correspondence to this author.

**Introduction.** We recently reported the structure of *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten, Palmer & Gazi, 1990). The title complex was of interest because the electronic origins of non-centrosymmetric complexes are expected to gain electric dipole intensity and this should facilitate locating them. The similarities in the  $\sigma$ - and  $\pi$ -donor properties of the Br and Cl ions should therefore allow a comparison of the spectra of *trans*-bromochloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide with those of the centrosymmetric pair *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride and *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide. Any significant departure from tetragonal symmetry for the complex ion will invalidate this comparison.

**Experimental.** The *trans*-bromochloro(cyclam)chromium(III) bromide complex was crystallized by slow evaporation of an aqueous solution of the salt. Dark green prismatic crystal  $0.24 \times 0.24 \times 0.50$  mm used for data collection; preliminary Weissenberg photographs yielded approximate cell dimensions and showed tetragonal ( $4/m$ ) Laue symmetry. Space group  $P4_2/m$  indicated from systematic absences ( $00l: l = 2n + 1$ );  $P4_2/m$  confirmed by structure analysis.

Intensity data were collected on an Enraf-Nonius FAST diffractometer. One hemisphere of data was collected with a detector swing angle of  $18^\circ$  and a crystal-to-detector distance of 40 mm. This corresponds to a minimum  $\theta_{\max}$  value of  $24^\circ$ ; additional data with a non-spherical distribution, due to the geometry of the flat-plate system, were also collected and included. Data were corrected for Lorentz-polarization factors and absorption. Space group  $P4_2/m$  was assumed. Merging equivalent reflections gave 812 unique intensities, 658 with  $I > 3\sigma(I)$  with  $R_{\text{int}} = 0.50\%$ . 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 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.

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, Vol. IV) (for  $\text{Cr}^{3+}$ ). Atomic absorption coefficient for Cr from Cromer & Liberman (1970). Dispersion coefficients  $f'$  and  $f''$  for Cr from *International Tables for X-ray Crystallography* (1974, Vol. IV). Function minimized was  $\sum(|F_o| - |F_c|)^2$ .  $R = 0.030$ ,  $wR (= RG) = 0.033$  where  $w = 1/\sigma^2(F_o)$ ,  $R$  (all data) = 0.040, max. (shift/ $\sigma$ ) = 0.014. Final difference electron density synthesis showed electron density  $-0.020$  to  $+0.01$  e  $\text{\AA}^{-3}$ . 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 view 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 Br and Cl ligands an octahedrally coordinated Cr atom. The Cr—N ligand distance is 2.064 (4)  $\text{\AA}$  which is normal, agreeing with many literature values, e.g. for *trans*-amminebis(ethylenediamine)fluorochromium(III) perchlorate (Beveridge, Bushnell & Kirk, 1985), *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten, Palmer & Gazi, 1990) and di- $\mu$ -methoxy-bis[7-amino-4-methyl-5-azahept-3-en-2-onato-*O,N,N'*]aquachromium(III) diperchlorate (Clegg, 1985). The Br(1)—Cr(1)—Cl(1) and N(1)—Cr(1)—N(1'') angles are approximately linear, with values of 4.3 (9) and  $180.0^\circ$ , respectively.

The cyclam moiety has normal geometry and assumes a chair conformation with exact  $2/m$  symmetry. The least-squares-planes equation for the  $\text{Cr}^{\text{III}}$  ion and the four nitrogen ligands is  $0.573x' - 0.820y' - 2.226z' = 0$ , where  $x'$ ,  $y'$  and  $z'$  are the coordinates in  $\text{\AA}$  with respect to the orthonormal axes (Rollett, 1965). These equatorial ligands are coplanar. The axial Br and Cl ligands are related through the centre of symmetry at  $(\frac{1}{2}, 0, 0)$ , each ion being assigned half-occupancy. 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

\* 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 55047 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0039]

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

$$U_{eq} = (U_1 U_2 U_3)^{1/3}$$

	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
Br(1)	0.3012 (10)	0.2466 (8)	0.0	0.042 (1)
Cr(1)	0.5	0.0	0.0	0.024 (1)
Cl(1)	0.3258 (29)	0.2526 (21)	0.0	0.039 (1)
N(1)	0.6470 (4)	0.1027 (5)	-0.1113 (3)	0.039 (1)
C(2)	0.5425 (6)	0.0878 (7)	-0.2009 (3)	0.036 (2)
C(3)	0.7174 (6)	0.2783 (6)	-0.0944 (4)	0.049 (3)
C(4)	0.8167 (10)	0.2893 (9)	0.0	0.051 (3)
Br(2)	0.0	0.0	0.25	0.052 (5)

To complete the 14 atoms in the cyclam ring: twofold axis at  $(\frac{1}{2}0z)$  generates primed atoms *via* symmetry operation  $1 - x, -y, z$ ;  $m$  plane at  $z = 0$  generates double-primed atoms *via* symmetry operation  $x, y, -z$ ;  $\bar{1}$  at  $(\frac{1}{2}00)$  generates triple-primed atoms *via* symmetry operation  $1 - x, -y, -z$ .

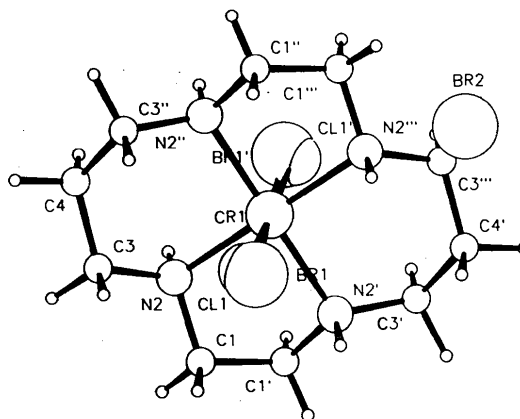


Fig. 1. Minimum-overlap view of the molecule.

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

Cr(1)—Cl(1)	2.385 (5)	C(2)—N(1)	1.476 (6)
Cr(1)—Br(1)	2.463 (2)	C(3)—N(1)	1.489 (6)
Cr(1)—N(1)	2.064 (4)	C(3)—C(4)	1.507 (6)
C(2)—C(2')	1.517 (11)		
N(1)—Cr(1)—Br(1)	96.6 (2)	C(3)—N(1)—Cr(1)	116.3 (3)
N(1)—Cr(1)—Cl(1)	89.8 (4)	C(2)—N(1)—C(3)	113.8 (4)
Cl(1)—Cr(1)—Br(1)	4.3 (9)	C(2)—N(1)—Cr(1)	106.2 (3)
N(1)—Cr(1)—N(1')	85.0 (2)	C(3)—C(4)—C(3')	117.9 (6)
N(1)—Cr(1)—N(1'')	95.0 (2)		
N(1)—C(2)—C(2)—N(1)	58.1 (8)	C(2)—N(1)—C(3)—C(4)	117.5 (6)
C(2)—C(2)—N(1)—C(3)	-171.5 (8)	N(1)—C(3)—C(4)—C(3')	-69.9 (8)

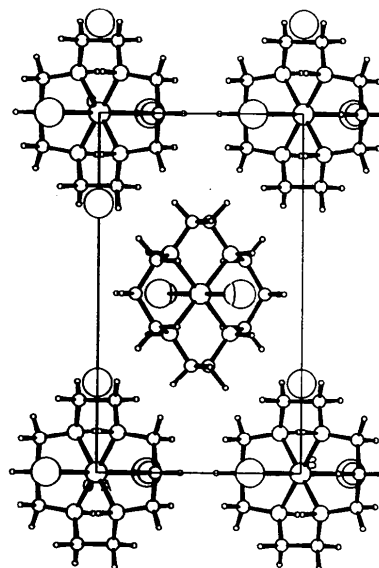


Fig. 2. Packing diagram viewed along *a*.

within 0.048 (8) Å, bond angles within 2.0 (7)°. *trans*-Bromochloro(1,4,8,11-tetraazacyclotetradecane)-chromium(III) bromide was found to be almost isostructural with *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten *et al.*, 1990) which crystallizes in  $P4_2/m$  with  $a = 7.860$  (1),  $c = 13.507$  (2) Å. The packing diagrams for the two structures are compared in Fig. 3. In both structures, the Cr<sup>3+</sup> ion lies on a centre of symmetry as does the Br<sup>-</sup> counterion. The only significant difference between these two structures is the relative orientations of the cyclam rings. In the *trans*-bromochloro structure, the cyclam moiety is related to the *trans*-dibromo structure by an *a* glide perpendicular to *b* at  $[x\frac{1}{2}0]$ . Since this feature does not appear to be associated with any energetic advantage it is conceivable that the dibromo and bromochloro compounds could both occur in structurally enantiomorphic crystal forms, as yet undiscovered.

We thank NATO for grant No. 900270 to enable this work to be carried and Dr M. A. Mazid of the SERC Crystallography Service, School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, for collection of the intensity data.

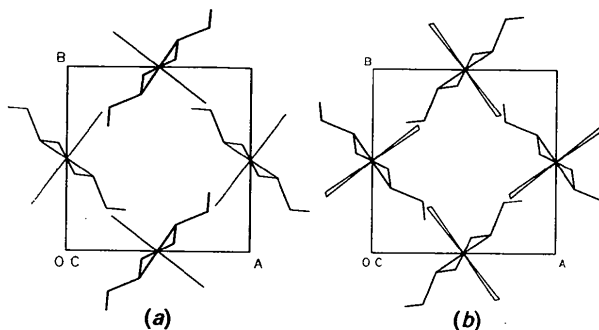


Fig. 3. Packing diagrams viewed along *c*. (a) *trans*-Dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten *et al.*, 1990) and (b) present structure.

## References

- BEVERIDGE, K. A., BUSHNELL, G. W. & KIRK, A. D. (1985). *Acta Cryst.* **C41**, 899–902.
- CLEGG, W. (1985). *Acta Cryst.* **C41**, 1830–1831.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Phys. Chem.* **53**, 1891–1898.
- LISGARTEN, J. N., PALMER, R. A. & GAZZI, D. M. (1990). *Acta Cryst.* **C46**, 396–399.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- ROBERTS, P. & SHELDRIK, 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.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1992). **C48**, 1759–1761

## Structure of a Tetrahedral Niobium Oxo Compound [Nb(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>(O)]

BY JOYCE S. YU, PHILIP E. FANWICK AND IAN P. ROTHWELL\*

*Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393, USA*

(Received 4 October 1991; accepted 5 February 1992)

**Abstract.** Tris(2,6-diphenylphenoxy)oxoniobium(V), [Nb(C<sub>18</sub>H<sub>13</sub>O)<sub>3</sub>O],  $M_r = 844.82$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.704$  (1),  $b = 19.562$  (3),  $c = 19.823$  (3) Å,  $V = 4150$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.35$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 3.22$  cm<sup>-1</sup>,  $F(000) = 1744.0$ ,  $T = 293.15$  K,  $R = 0.054$  for 1680 reflections with  $I > 3.0\sigma(I)$ . A tetrahedral geometry is seen to be adopted around the Nb-metal center with three aryl oxide O atoms and one terminal oxo group. Nb—O(terminal oxo group) = 1.685 (9) Å; Nb—O(aryl oxide) = 1.896 Å (av.).

**Introduction.** Recent years have seen a dramatic increase in the study of the synthesis, structure and reactivity of transition-metal compounds containing a terminal oxo group (Nugent & Mayer, 1987). We report here the isolation and structural characterization of a mononuclear aryl oxide compound of niobium(V) containing a terminal oxo group, [Nb(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>(O)] (OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6 = 2,6-diphenylphenoxy).

**Experimental.** The compound Nb(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>(O) was obtained in low yield during the room-temperature reduction of toluene solutions of the dichloride Nb(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub> (Chesnut, Durfee, Fanwick, Rothwell, Folting & Huffman, 1987) with sodium amalgam. This oxo compound was either formed during the reaction, by traces of water, or else was present in the original sample of the dichloride.

A yellow crystal of [Nb(OC<sub>6</sub>H<sub>3</sub>Ph<sub>2</sub>-2,6)<sub>3</sub>(O)], having approximate dimensions 0.28 × 0.25 ×

0.22 mm, was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo  $K\alpha$  radiation on an Enraf–Nonius CAD-4 computer-controlled  $\kappa$ -axis diffractometer equipped with a graphite-crystal incident-beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range  $9 < \theta < 15^\circ$ , measured by the computer-controlled diagonal-slit method of centering.

The data were collected at a temperature of 293 K using the  $\omega$ - $2\theta$  scan technique. The scan rate varied from 2 to 20° min<sup>-1</sup> (in  $\omega$ ). The variable scan rate allows rapid data collection for intense reflections (where a fast scan rate is used) and assures good counting statistics for weak reflections (where a slow scan rate is used). Data were collected in a  $2\theta$  range of 4.00–45.00° with  $hkl$  limits of 0 to 11, 0 to 21 and 0 to 21, respectively. Systematic absences of  $h00$ ,  $h = 2n$ ;  $0k0$ ,  $k = 2n$ ;  $00l$ ,  $l = 2n$ , and subsequent least-squares refinement, indicated space group  $P2_12_12_1$ . The scan range (°) was determined as a function of  $\theta$  to correct for the separation of the  $K\alpha$  doublet (*CAD-4 Operations Manual*, 1977); the scan width was calculated as  $\omega$ -scan width =  $(0.83 + 0.350 \tan \theta)^\circ$ . Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of  $\theta$ . The horizontal aperture width ranged from 2.0 to 2.4 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident-beam collimator was 0.7 mm and the crystal to detector

\* Author to whom correspondence should be addressed.