

***cis*-(Carbonato- $\kappa^2$ O,O')(rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4$ N)-chromium(III) bromide monohydrate**

Liliana Dobrzańska

Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

Correspondence e-mail: lianger@sun.ac.za

**Key indicators**

Single-crystal X-ray study

 $T = 100$  KMean  $\sigma(\text{C}-\text{C}) = 0.005$  Å $R$  factor = 0.050 $wR$  factor = 0.117

Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $[\text{Cr}(\text{CO}_3)(\text{C}_{16}\text{H}_{36}\text{N}_4)]\text{Br}\cdot\text{H}_2\text{O}$ , the chromium cation has a distorted octahedral geometry with ligation provided by the four N atoms of the 'folded' macrocyclic ligand and by two O atoms of the bidentate carbonate anion. Two neighbouring chromium complexes are bridged by two strong  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to form dimeric units which, in turn, are constituents of infinite chains formed by virtue of three other types of hydrogen bonds ( $\text{N}-\text{H}\cdots\text{Br}$ ,  $\text{N}-\text{H}\cdots\text{Ow}$  and  $\text{Ow}-\text{H}\cdots\text{Br}$ ).

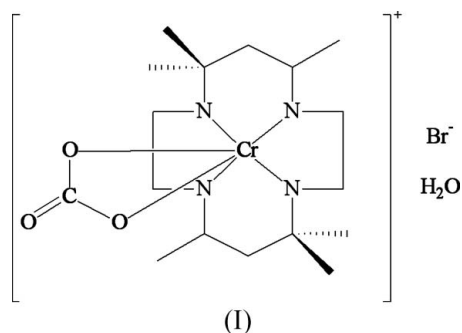
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**Comment**

Macrocyclic chromium complexes have been the subject of structural studies aimed at improved understanding of the magnetic behaviour and catalytic properties of such systems (Goodson *et al.*, 1994, 2001; Bang *et al.*, 1994). In the previously reported structures  $[\text{Cr}(\text{cycb})Lx]^{n+}$  (cycb is *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), two coordination sites  $L$  are occupied by mono- ( $x = 2$ ) or bidentate ( $x = 1$ ) ligands. These chromium complexes are then held together by intermolecular hydrogen bonds to form different types of aggregates. Our attempt at applying a ditopic N,N-ligand to form a coordination polymeric network failed, yielding instead the 'monomeric' species *cis*- $[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]\text{Br}\cdot\text{H}_2\text{O}$  (I), which is an analogue of the previously described *cis*- $[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]_2\text{S}_2\text{O}_6\cdot 4\text{H}_2\text{O}$  (Bang & Mønsted, 1984).



In (I), the central  $\text{Cr}^{\text{III}}$  atom is pseudooctahedrally coordinated by the four N atoms of the ligand and two O atoms from the carbonate anion (Table 1). The complex cation adopts the *cis*-geometry in which atoms N11 and N4 of the macrocyclic ligand are mutually *trans* (Fig. 1). Slight tetrahedral distortion of the  $\text{CrN}_2\text{O}_2$  plane is observed with atoms O1, O2, N8 and N1 situated at distances of 0.105 (2),  $-0.106$  (1), 0.069 (1) and  $-0.074$  (1) Å, respectively, from the plane. Ligand 'folding' parameters  $\delta$  and  $\alpha$  [where  $\delta$  is the distance between the Cr

atom and the centroid ( $M^*$ ) of the *trans* N–N atoms and  $\alpha$  is the fold angle defined by  $N_{cis}-M^*-N_{cis}$  are 0.195 Å and 108.55°, respectively. These values are similar to those calculated for the previously reported  $[Cr(cycb)(O_2CO)]^+$  cationic complex, where  $\delta = 0.189$  Å and  $\alpha = 107.64^\circ$ .

Strong hydrogen-bonded interactions present in (I) between the chromium complexes, solvent water molecules and bromide anions account for the most significant difference between the two *cis*- $[Cr(cycb)(O_2CO)]^+$  structures. Two symmetry-related N–H...O bridges between amino groups of macrocyclic ligands and carbonate anions from neighbouring chromium cations facilitate the formation of dimeric units. The dimers are further connected to one another by three other types of hydrogen bonds to form infinite chains (Fig. 2). In contrast, two parallel rows of separate mononuclear units are held together by chains of interacting water molecules and dithionate ions in the previously reported structure. It is interesting to note that one of the NH groups of the ligand does not participate in hydrogen bonding, presumably because of steric constraints.

### Experimental

The N,N-ditopic ligand was added to a methanol solution of *cis*- $[Cr(cycb)(H_2O)_2]Br_3 \cdot 2.5H_2O$  [obtained according to the procedure of Eriksen & Mønsted (1983)] in a 2:1 molar ratio. Violet prisms suitable for single-crystal X-ray diffraction analysis were obtained by slow evaporation. The presence of the  $CO_3^{2-}$  anion in the coordination sphere is attributed to slight contamination of the N,N-ligand by  $K_2CO_3$ .

#### Crystal data

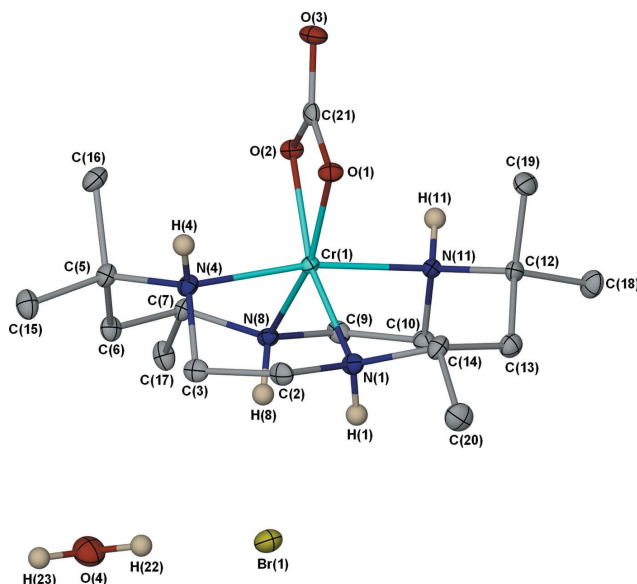
$[Cr(CO_3)(C_{16}H_{36}N_4)]Br \cdot H_2O$	$Z = 2$
$M_r = 494.42$	$D_x = 1.511$ Mg m <sup>-3</sup>
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.633$ (2) Å	Cell parameters from 2358 reflections
$b = 10.924$ (3) Å	$\theta = 2.2$ – $24.4^\circ$
$c = 13.296$ (4) Å	$\mu = 2.39$ mm <sup>-1</sup>
$\alpha = 109.334$ (4)°	$T = 100$ (2) K
$\beta = 90.305$ (5)°	Prism, violet
$\gamma = 111.828$ (4)°	$0.31 \times 0.18 \times 0.15$ mm
$V = 1086.5$ (5) Å <sup>3</sup>	

#### Data collection

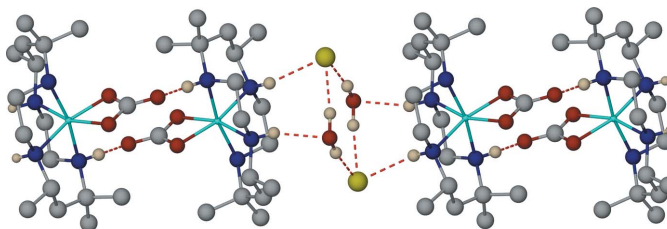
Bruker APEX CCD area-detector diffractometer	4995 independent reflections
$\omega$ scans	3792 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	$R_{int} = 0.047$
$T_{min} = 0.594$ , $T_{max} = 0.695$	$\theta_{max} = 28.3^\circ$
12482 measured reflections	$h = -11 \rightarrow 11$
	$k = -14 \rightarrow 14$
	$l = -17 \rightarrow 17$

#### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4995 reflections	$\Delta\rho_{max} = 2.26$ e Å <sup>-3</sup>
252 parameters	$\Delta\rho_{min} = -0.60$ e Å <sup>-3</sup>



**Figure 1**  
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms bonded to C atoms have been omitted.



**Figure 2**  
Part of the infinite chain in the crystal structure of (I). The hydrogen bonds are shown as dashed lines. H atoms not participating in the hydrogen bonding have been omitted for clarity.

**Table 1**  
Selected geometric parameters (Å, °).

Cr1–O1	1.954 (2)	Cr1–N1	2.096 (3)
Cr1–O2	1.964 (2)	Cr1–N4	2.100 (3)
Cr1–N8	2.093 (3)	Cr1–N11	2.115 (3)
O1–Cr1–O2	67.59 (10)	N8–Cr1–N4	87.74 (11)
O1–Cr1–N1	95.06 (11)	O1–Cr1–N11	99.68 (10)
N8–Cr1–N1	99.92 (11)	N1–Cr1–N11	88.03 (11)
O2–Cr1–N4	99.97 (10)		

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N8–H8...Br1 <sup>i</sup>	0.93	2.55	3.441 (3)	161
N1–H1...O4 <sup>i</sup>	0.93	2.18	3.045 (4)	155
N11–H11...O2 <sup>ii</sup>	0.93	2.46	3.368 (4)	164
N11–H11...O3 <sup>ii</sup>	0.93	2.49	3.168 (4)	130
N4–H4...O3 <sup>iii</sup>	0.93	2.01	2.888 (4)	157
O4–H22...Br1 <sup>iv</sup>	0.99 (4)	2.26 (4)	3.245 (3)	173
O4–H23...Br1 <sup>v</sup>	0.95 (3)	2.46 (2)	3.398 (4)	169

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z$ ; (iii)  $-x + 1, -y + 1, -z$ ; (iv)  $x, y, z$ ; (v)  $-x + 2, -y + 1, -z + 1$ .

The O-bound H atoms were located in a difference map and refined freely [O–H = 0.953 (19)–0.995 (19) Å]. Other H atoms were positioned geometrically [C–H = 0.93 (NH), 1.00 (CH), 0.99 (CH<sub>2</sub>) and 0.98 Å (CH<sub>3</sub>)] and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms]. The largest electron-density peak is located at (0.72,0.38,0.47).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Atwood & Barbour, 2003; Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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