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A novel binucleating macrocyclic ligand with two alcohol pendants

De-Xi Yang, Shu-An Li, Dong-Feng Li and Wen-Xia Tang*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: wxtang@netra.nju.edu.cn

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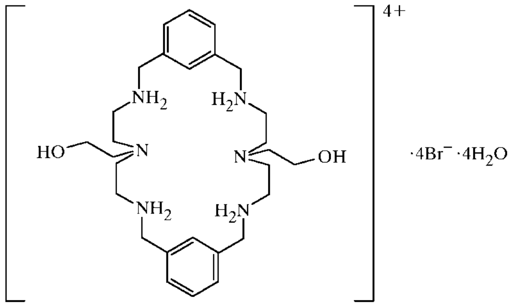
A novel binucleating 24-membered macrocyclic ligand, 6,20-bis(2-hydroxyethyl)-3,6,9,17,20,23-hexazatricyclo[23.3.1.1^{11,15}]-triaconta-1(29),11(30),12,14,25,27-hexaene (*L*), was synthesized and crystallized as the tetrahydrobromide salt, *i.e.* 6,20-bis(2-hydroxyethyl)-6,20-diaza-3,9,17,23-hexaazoniatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25,27-hexaene tetrabromide tetrahydrate, $C_{28}H_{50}N_6O_2^{4+}\cdot 4Br^-\cdot 4H_2O$. A crystallographic inversion center is located in the macrocyclic cavity and the two hydroxyethyl pendants are on opposite sides of the macrocyclic plane. The benzene rings of the macrocycle are parallel to each other and a π–π-stacking interaction exists between the benzene rings of adjacent macrocycles, which are separated by 3.791 (9) Å. An infinite intermolecular hydrogen-bond network stabilizes the crystal.

Comment

The design and synthesis of new macrocyclic polyaza ligands are of great current interest. The cavity, rigidity and donor type of a macrocycle are all important in governing the host–guest interaction, the selectivity of metal ions and the construction of model compounds of the active site of enzymes (Shangguan *et al.*, 2000; Lu *et al.*, 1995). In particular, the incorporation of functionalized pendant coordinating arms on macrocyclic polyaza compounds can provide additional coordinating functions and hence enhance the complexing stability. A few macrocycles with pendants have been reported previously. However, the synthesis of binucleating macrocyclic ligands with hydroxyethyl pendants is rare (Kimura & Kikuta, 2000; Bazzicalupi *et al.*, 1999). In this article, we report the structure of a novel 24-membered macrocyclic ligand with two hydroxyethyl pendants as its tetrahydrated tetrahydrobromide salt, *i.e.* 6,20-bis(2-hydroxyethyl)-6,20-diaza-3,9,17,23-hexaazoniatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,-25,27-hexaene tetrabromide tetrahydrate, $(H_4L)Br_4\cdot 4H_2O$, (I).



(I)

The macrocycle adopts a chair conformation with a crystallographic inversion center located in the macrocyclic cavity (Fig. 1). The four secondary N atoms are coplanar, while the tertiary N atoms deviate by 0.379 (8) Å from the macrocyclic plane, one up and one down. The benzene rings are tilted at angles of 36.9 (2)° to the macrocyclic least-squares plane and are parallel to one another, at a distance of 8.835 (9) Å. The two hydroxyethyl pendants appear on opposite sides of the macrocyclic plane and the distance between the two O atoms is 10.57 (1) Å. The structure of this compound is quite different from that of the hexahydrobromide salt of a similar macrocyclic compound, *viz*. BMXD, which is *L* without the hydroxyethyl pendants (Nation *et al.*, 1996). In $H_6BMXDBr_6\cdot 7H_2O$, the six N atoms are approximately planar and the three N atoms of each diethylenetriamine unit are in a linear arrangement. The difference is due to the the incorporation of the two hydroxyethyl pendants into the macrocycle in (I). Furthermore, the two tertiary amine N atoms of $(H_4L)^{4+}$ are not protonated and the distance between them is 9.686 (9) Å, which is much longer than the distance of 6.35 (2) Å between the two secondary amine N atoms in $H_6BMXDBr_6\cdot 7H_2O$.

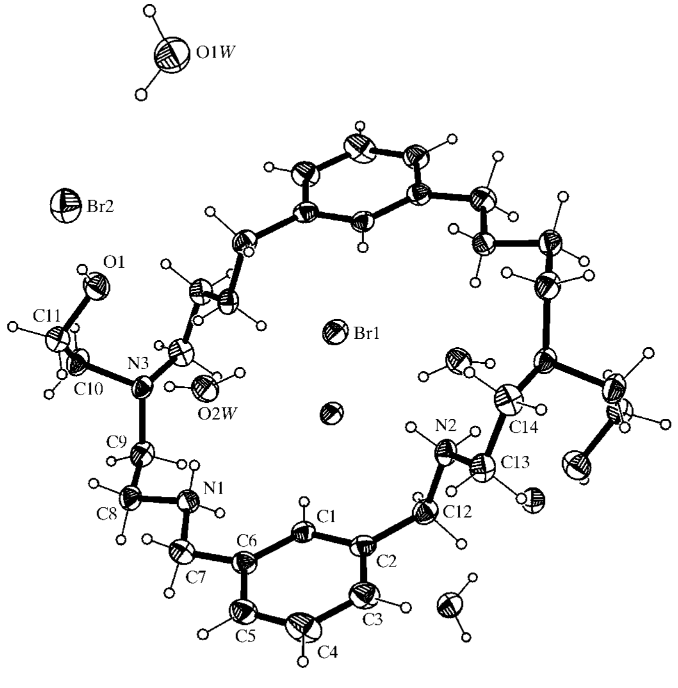


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids.

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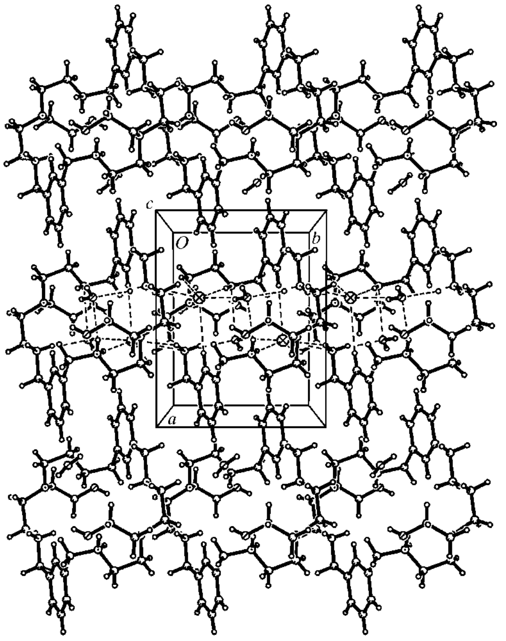

Figure 2
A view of the one-dimensional quasi-chain structure formed through hydrogen bonds along the *b* axis.

The four secondary amine N atoms in the macrocycle in (I) are protonated. The tertiary amine N atoms are not protonated, indicating that they are of weak basicity. The four bromide counter-ions and the four water molecules are bound to the protonated amine N and hydroxyethyl O atoms through hydrogen bonds (Table 1). Only two bromide counter-ions and two water molecules are encapsulated in the macrocyclic cavity. Inside each macrocycle, O2*W* forms hydrogen bonds with N1 and N2, and the hydroxyethyl O1 atom forms a hydrogen bond with N2. The Br1 atom forms hydrogen bonds separately with N1 and N2 of two adjacent macrocyclic rings, and simultaneously forms a hydrogen bond with O2*W*, which is responsible for the formation of a one-dimensional quasi-chain structure along the *b* axis, as shown in Fig. 2. The hydrogen bond between Br2 and the hydroxyethyl O1 atom, together with that between Br2 and O1*W*, links the chains into a two-dimensional network, as shown in Fig. 3. In addition, Fig. 2 also reveals that the two-dimensional structures are connected into an infinite three-dimensional structure (Fig. 3) through π–π-stacking interactions between the adjacent benzene rings of two one-dimensional quasi-chain elements, with a nearest distance of 3.791 (9) Å. All the Br$\cdots$N and Br$\cdots$O distances in all contacts are typical of hydrogen-bonding interactions and range from 2.756 (7) to 3.358 (5) Å.

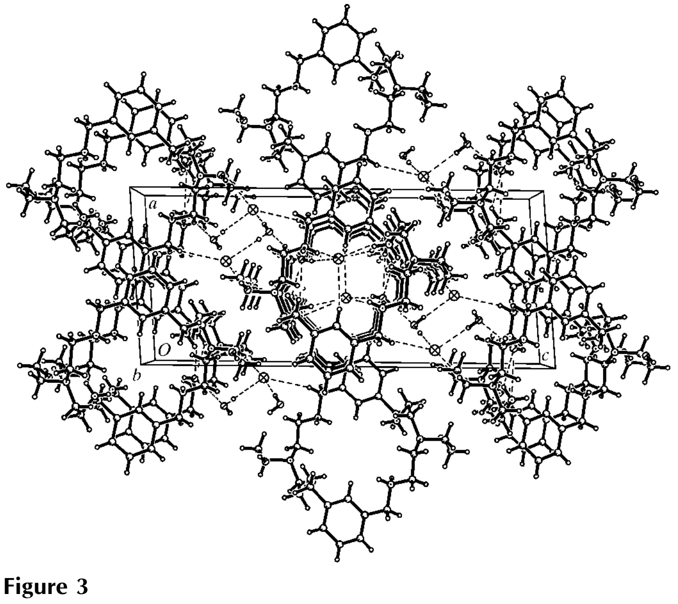

Figure 3
The packing arrangement of $L\cdot 4HBr\cdot 4H_2O$ showing hydrogen bonds and π–π-stacking interactions.

Experimental

A solution of isophthalic aldehyde (0.804 g, 0.006 mol) in CH_3CN (100 ml) was added dropwise to a solution of 2-[bis(2-aminoethyl)-amino]ethanol (0.882 g, 0.006 mol) in CH_3CN (150 ml) under magnetic stirring over a period of 8 h at 273 K and a white suspension appeared. After stirring for another 12 h, a white microcrystalline solid precipitated and was filtered off and washed with ether. The microcrystals were dissolved in EtOH (100 ml) at 318 K and $NaBH_4$ (2.5 g) was added gradually over a period of 3 h with constant stirring. After removing the solvent under reduced pressure, H_2O (5 ml) and CH_2Cl_2 (100 ml) were added sequentially to extract the product. A colorless viscous oil was obtained after removing CH_2Cl_2 from the organic phase. Several hours after the addition of 48% HBr (5 ml) to the product at 273 K, white microcrystals appeared in a yield of 1.61 g (60%). A crystal suitable for X-ray analysis was obtained by evaporation of an aqueous solution of the microcrystal. Elemental analysis, calculated for $L\cdot 4HBr\cdot 4H_2O$ ($C_{28}H_{58}Br_4N_6O_6$): C 37.6, H 6.48, N 9.39%; found: C 37.5, H 6.36, N 9.28%.

Crystal data

$C_{28}H_{50}N_6O_2^{4+}\cdot 4Br^-\cdot 4H_2O$
$M_r = 894.44$
Monoclinic, $P2_1/n$
$a = 10.179$ (4) Å
$b = 7.933$ (2) Å
$c = 23.776$ (6) Å
$\beta = 94.244$ (19)°
$V = 1914.6$ (11) Å^3
$Z = 2$
$D_x = 1.552$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 5.0$–14.3°
$\mu = 4.25$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.3 × 0.3 × 0.2 mm

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1*W*—H1*WA*$\cdots$Br2	0.84	2.46	3.277 (6)	166
N1—H1*A*$\cdots$O2*W*	0.86	1.95	2.804 (6)	172
N1—H1*B*$\cdots$Br1$^{\text{i}}$	0.87 (5)	2.60 (5)	3.358 (5)	146 (5)
O1—H2$\cdots$Br2$^{\text{ii}}$	0.81 (7)	2.48 (7)	3.279 (5)	173 (6)
O1*W*—H1*WB*$\cdots$Br2$^{\text{iii}}$	0.80	2.52	3.294 (5)	165
N2—H2*A*$\cdots$O1$^{\text{iv}}$	0.98 (6)	2.18 (7)	2.886 (7)	127 (5)
N2—H2*A*$\cdots$O2*W*$^{\text{iv}}$	0.98 (6)	2.22 (6)	2.918 (7)	127 (5)
N2—H2*B*$\cdots$Br1	0.82 (7)	2.51 (7)	3.307 (5)	164 (6)
O2*W*—H2*WA*$\cdots$O1*W*$^{\text{i}}$	0.84 (7)	1.93 (7)	2.756 (7)	171 (7)
O2*W*—H2*WB*$\cdots$Br1	0.80 (6)	2.54 (7)	3.332 (5)	173 (6)

Symmetry codes: (i) $x, 1+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, 1-y, 1-z$.

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\min} = 0.292$, $T_{\max} = 0.437$
4531 measured reflections
3335 independent reflections
1991 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.087$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 9$
$l = -28 \rightarrow 28$
3 standard reflections every 97 reflections intensity decay: 14.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.122$
$S = 1.00$
3335 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.6870P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}

All C—H atoms in the macrocycle were fixed geometrically (C—H = 0.93 and 0.97 Å), and N—H and O—H atoms were located according to difference electron-density calculations (see Table 1 for N—H and O—H bond lengths).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1341). Services for accessing these data are described at the back of the journal.

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