

# 1,15-Diaza-3,4:12,13-dibenzo-5,8,11-trioxacycloheptadecane hemihydrate

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

$R$  factor = 0.052

$wR$  factor = 0.169

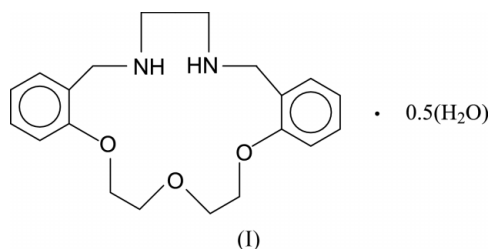
Data-to-parameter ratio = 13.1

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

The title compound,  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ , contains a 17-membered diaza-crown ether ligand with three ether O and two N atoms. It consists of the macrocyclic ligand and one half water molecule; the latter possesses crystallographically imposed  $C_2$  symmetry. In the macrocyclic ring, the mean  $\text{N} \cdots \text{O}$  distance is  $3.995(4)\text{ \AA}$ . The macrocyclic inner hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately  $1.29\text{ \AA}$ .

## Comment

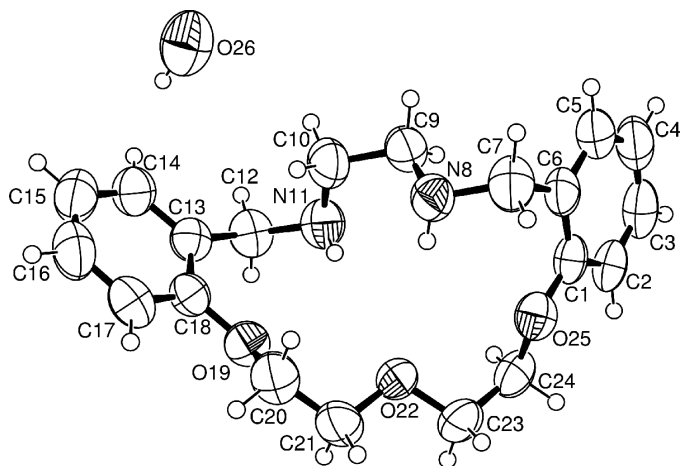
During the last three decades, macrocyclic multidentate ligands, such as 16- and 18-membered rings composed of the  $-\text{N}_x\text{O}_y$  donor type (where  $x = 2,3$  and  $y = 2,3$ ) have been investigated as potential metal-ion selective reagents (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Lindoy, 1987; Lindoy *et al.*, 1993; Esteban *et al.*, 2000). A series of these investigations have involved the synthetic, thermodynamic and/or structural properties of selective complex formation of a number of transition metal ions (Adam *et al.*, 1979, 1994; Fenton *et al.*, 1987).



Macrocycles have been widely studied as complexation agents for alkali, alkaline-earth and transition-metal ion (especially lanthanides) recognition with particular metal-ion binding applications (*e.g.* selective extraction of heavy and precious metals) of great interest, and are of fundamental importance to broad areas of environmental, inorganic, coordination, organic and biochemistry (Lindoy, 1997; Hayvalı *et al.*, 1999; Vicente *et al.*, 2000).

In the literature, there is only a very limited number of reports concerning the structures of the free macrocyclic multidentate  $\text{N}_2\text{O}_2$  and  $\text{N}_2\text{O}_3$  donor-type ligands (Chia *et al.*, 1991; Hökelek *et al.*, 1999*a,b*; Hökelek *et al.*, 2000, 2001*a,b*; Hökelek, Bilge *et al.*, 2001; Hökelek, Kaya & Kılıç, 2001).

The title compound, (I), may be a potential ion-selective reagent for transition metal ions (Lindoy, 1987; Adam *et al.*, 1983). The structure determination of (I) was carried out in order to estimate the macrocyclic ring hole size. Fig. 1 shows the structure of (I), with the atomic numbering scheme. The macrocyclic ring consists of three ether O and two N atoms. It consists of the macrocyclic ligand and one half water molecule,



**Figure 1**  
An ORTEP-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

which possesses crystallographically imposed  $C_2$  symmetry. The ligand cavity plays an important role in metal-ion selectivity. The intramolecular  $C7 \cdots O19$  [5.749 (3) Å],  $C12 \cdots O25$  [5.896 (4) Å],  $N8 \cdots O19$  [4.410 (4) Å],  $N8 \cdots O22$  [3.435 (4) Å],  $N11 \cdots O25$  [4.565 (4) Å] and  $N11 \cdots O22$  [3.569 (4) Å] distances may indicate the hole size of the macrocyclic ring. When only the N and O atoms are taken into account, the mean  $N \cdots O$  distance is 3.995 (4) Å.

The macrocyclic inner hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 1.29 Å, using the 'modified covalent radii' of the  $Nsp^2$  (0.66 Å) and  $Osp^3$  (0.76 Å) atoms as described in the literature (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982). The inner hole size of (I) (1.29 Å), which is a 17-membered macrocycle, can be compared with the 16- (1.57 Å; Hökelek *et al.*, 2000), 17- (2.08 Å; Hökelek, Kaya & Kılıç, 2001), 18- [2.28 Å (Hökelek, Bilge *et al.*, 2001) and 1.63, 1.87 and 2.15 Å (Hökelek *et al.*, 2001*a,b*)] and 19-membered (2.53 Å; Hökelek *et al.*, 1999*b*), multidentate ligand hole sizes.

The multidentate macrocyclic ligand contains intramolecular [ $N8-H8$  0.86 (3) Å,  $H8 \cdots O25$  2.46 (3) Å and  $N8-H8 \cdots O25$  119 (3)°;  $N11-H11$  0.83 (2) Å,  $H11 \cdots O19$  2.45 (4) Å and  $N11-H11 \cdots O19$  120 (2)°] hydrogen bonds and is involved in an intermolecular [ $O26-H26$  0.95 (3) Å,  $H26 \cdots N8^i$  2.72 (3) Å and  $O26-H26 \cdots N8^i$  87.2 (16)°; symmetry code: (i)  $x, y + 1, z$ ] close contact, between the water molecule and atom N8 of the macrocycle, which may play a role in the macrocyclic inner hole size contraction.

The conformation of the macrocyclic ring is defined by the torsion angles (Table 1). As can be seen from the packing diagram (Fig. 2), the macrocyclic ligands are elongated approximately parallel to the  $c$  axis and the water molecules fill the spaces between them. Dipole-dipole and van der Waals interactions are also effective in the molecular packing, as well as the intramolecular hydrogen bonding and intermolecular close contacts between water molecules and macrocyclic ligands.

## Experimental

The title compound, (I), was obtained by a modification of the literature method of Adam *et al.* (1983) [yield 2.77 g, 80%; m.p. 370 K;  $m/z$  342].

### Crystal data

$C_{20}H_{26}N_2O_3 \cdot 0.5H_2O$   
 $M_r = 351.44$   
Monoclinic,  $C2/c$   
 $a = 24.457$  (2) Å  
 $b = 7.5165$  (12) Å  
 $c = 23.865$  (2) Å  
 $\beta = 116.768$  (9)°  
 $V = 3917.0$  (8) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.192$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 10-18^\circ$   
 $\mu = 0.08$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Rod, colourless  
0.40 × 0.25 × 0.15 mm

### Data collection

Enraf-Nonius CAD-4 diffractometer  
Non-profiled  $\omega$  scans  
3856 measured reflections  
3786 independent reflections  
1752 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.022$

$\theta_{max} = 26.0^\circ$   
 $h = 0 \rightarrow 30$   
 $k = 0 \rightarrow 9$   
 $l = -27 \rightarrow 29$   
3 standard reflections  
frequency: 120 min  
intensity decay: 1%

### Refinement

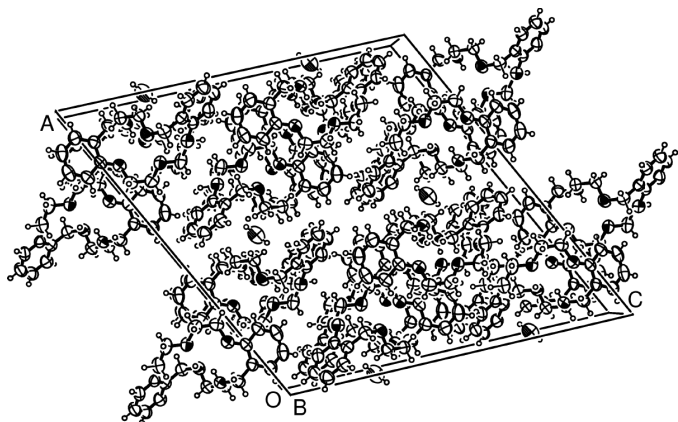
Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.169$   
 $S = 1.02$   
3163 reflections  
242 parameters  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 0.1096P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.51$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.24$  e Å<sup>-3</sup>  
Extinction correction: *SHELXL97*  
Extinction coefficient: 0.0019 (5)

**Table 1**

Selected geometric parameters (Å, °).

O19—C18	1.387 (3)	N8—C7	1.470 (4)
O19—C20	1.425 (3)	C6—C1	1.392 (4)
O22—C21	1.406 (3)	C6—C7	1.506 (4)
O22—C23	1.424 (4)	C13—C18	1.380 (4)
O25—C1	1.363 (3)	C13—C12	1.516 (4)
O25—C24	1.427 (4)	C23—C24	1.490 (4)
N11—C10	1.422 (4)	C20—C21	1.475 (5)
N11—C12	1.475 (4)	C9—C10	1.525 (4)
N8—C9	1.443 (4)		
C18—O19—C20	117.5 (2)	O22—C23—C24	110.1 (2)
C21—O22—C23	111.6 (2)	N11—C12—C13	116.5 (2)
C1—O25—C24	118.2 (2)	O25—C24—C23	108.7 (2)
C10—N11—C12	111.8 (2)	O19—C20—C21	108.4 (3)
C9—N8—C7	113.5 (3)	O22—C21—C20	110.9 (2)
C1—C6—C7	119.3 (3)	N8—C7—C6	113.9 (2)
O25—C1—C6	115.4 (2)	N8—C9—C10	113.5 (3)
C18—C13—C12	120.7 (3)	N11—C10—C9	112.4 (3)
C13—C18—O19	115.6 (2)		
C24—O25—C1—C6	-27.1 (3)	C1—O25—C24—C23	-164.8 (2)
C24—O25—C1—C6	152.2 (2)	O22—C23—C24—O25	60.9 (3)
C5—C6—C1—O25	-179.7 (2)	C18—O19—C20—C21	-175.8 (2)
C7—C6—C1—O25	-3.7 (4)	C23—O22—C21—C20	172.5 (3)
C12—C13—C18—O19	-3.3 (4)	O19—C20—C21—O22	66.6 (3)
C20—O19—C18—C13	146.5 (3)	C9—N8—C7—C6	-59.7 (4)
C20—O19—C18—C17	-35.6 (4)	C5—C6—C7—N8	109.5 (3)
C21—O22—C23—C24	174.9 (2)	C1—C6—C7—N8	-66.2 (4)
C10—N11—C12—C13	-55.5 (4)	C7—N8—C9—C10	179.9 (2)
C18—C13—C12—N11	-59.3 (4)	C12—N11—C10—C9	-176.9 (3)
C14—C13—C12—N11	119.8 (3)	N8—C9—C10—N11	-76.5 (4)



**Figure 2**  
Packing diagram, viewed down the *b* axis.

The large difference between numbers of independent and refined reflections is probably due the fact that most of the reflections were weak, probably due to the crystal quality. Atoms H2, H8, H11 and H26 were located in a difference synthesis and refined isotropically [ $C-H = 0.94$  (3),  $N-H = 0.829$  (17)- $0.86$  (3),  $O-H = 0.95$  (3) Å]. The remaining H atoms were positioned geometrically at distances of 0.97 (CH<sub>2</sub>) and 0.93 Å (CH) from the parent C atoms; a riding model was used during the refinement process [ $U_{iso}(H) = 1.2$  times  $U_{eq}(\text{parent atom})$ ].

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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