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# 1,14-Dioxa-5,10-diaza-2,3:12,13-dibenzocyclooctadeca-2,12-diene monohydrate

**Tuncer Hökelek,[a]* Elif Ece Kaya[b] and Zeynel Kılıç[b]**

[a]Hacettepe University, Department of Physics, 06800 Beytepe, Ankara, Turkey, and [b]Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey
Correspondence e-mail: merzifon@hacettepe.edu.tr

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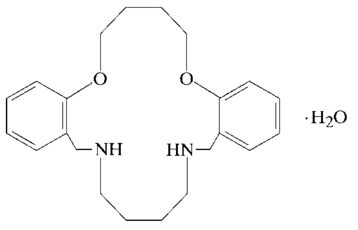
The title compound, $C_{22}H_{30}N_2O_2\cdot H_2O$, is an 18-membered diaza-crown ether ligand containing two ether O and two aza N atoms. In the macrocyclic ring, the mean N···O distance is 4.526 (4) Å. The macrocyclic inner-hole size, estimated as twice the mean distance of the donor atoms from their centroid, is ~2.29 Å.

## Comment

Macrocyclic multidentate ligands, such as the 16-, 17-, 18- and 19-membered rings containing the $O_xN_y$-donor type (where $x = 2$ and 3, and $y = 2$ and 3), have been the subject of structural studies as potential metal-ion selective reagents for transition-metal-ion recognition (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Lindoy, 1987; Lindoy *et al.*, 1993; Esteban *et al.*, 2000). Particular metal-ion binding applications (*e.g.* selective extraction of heavy and precious metals) are of great interest in environmental, inorganic, organic, bio- and coordination chemistry (Lindoy, 1997; Hayvalı *et al.*, 1999; Esteban *et al.*, 2000; Vicente *et al.*, 2000; Hökelek, Kaya & Kılıç, 2001).

Some of the macrocyclic ligands may act as capping ligands, favouring both the blocking of transition-metal coordination sites and the formation of discrete metal complexes in inorganic chemistry (Blake & Schröder, 1990; Blake *et al.*, 2000; Nunes *et al.*, 2003). On the other hand, azamacrocycles, crown ethers and cryptates also play a part in forming host–guest-type inclusion complexes with neutral polar molecules and onium salts (Newcomb *et al.*, 1977; Lehn, 1985; Byriel *et al.*, 2003).

Many investigations have been devoted to the synthetic, thermodynamic and/or structural properties of selective complex formation for a range of transition-metal ions and neutral molecules (Adam *et al.*, 1979, 1994; Fenton *et al.*, 1987). However, there are only a limited number of reports concerning the structures of the free macrocyclic multidentate $N_2O_2$- and $N_2O_3$-donor-type ligands and neutral molecular complexes (Hökelek *et al.*, 1999*a*,*b*, 2000, 2001*a*,*b*, 2002, 2003; Hökelek, Bilge *et al.*, 2001; Hökelek, Kaya & Kılıç, 2001). The title compound, (I), may be a potential cation-selective reagent for transition-metal ions. Its dionium salt may also be a potential anion-selective reagent. The structure determination of (I) was carried out in order to estimate the macrocyclic ring hole size.



(I)

Fig. 1 shows the molecular structure of (I), with the atomic numbering scheme. The macrocyclic ring contains two ether O and two aza N atoms and crystallizes with one water molecule. The ligand cavity plays an important role in metal-ion selectivity. The intramolecular O2···N15 [6.877 (3) Å], O7···N20 [5.113 (4) Å], O2···C14 [6.988 (3) Å], O7···C21 [6.118 (4) Å], C3···C16 [7.611 (4) Å] C5···C18 [4.109 (3) Å] and C13···C22 [8.711 (4) Å] distances may indicate the hole size of the macrocyclic ring. When only the N and O atoms are taken into account, the average value of the four N···O distances in the ring is 4.526 (4) Å [O2···N20 = 2.985 (4) Å and O7···N15 = 3.130 (4) Å]. The deviations from the least-squares plane defined by atoms O2, O7, N15 and N20 are −0.009 (2) Å (O2), 0.012 (2) Å (O7), −0.021 (2) Å (N15) and 0.017 (2) Å (N20).

The macrocyclic inner-hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 2.29 Å, using the 'modified covalent radii' of the $Nsp^2$ (0.66 Å) and $Osp^3$ (0.76 Å) atoms (Drummond *et al.*, 1982; Goodwin *et al.*, 1982; Adam *et al.*, 1983). The inner-hole size of (I) (2.29 Å), which is an 18-membered macrocycle, can be compared with the 16- (1.57 Å; Hökelek *et al.*, 2000), 17- [1.29 Å (Hökelek *et al.*, 2003) and 2.08 Å (Hökelek, Kaya & Kılıç, 2001)], 18- [1.63 and 1.87 Å (Hökelek *et al.*, 2001*a*), 2.15 Å (Hökelek *et al.*, 2001*b*), and 2.28 Å (Hökelek, Bilge *et al.*, 2001)] and 19-membered (2.53 Å; Hökelek *et al.*, 1999*b*) multidentate-ligand hole sizes. The 15- and 17-membered rings containing the $N_2O_2$- and $N_3O_2$-donor-type ligands afford the $Ni^{II}$ and $Pd^{II}$ complexes (Bilge *et al.*, 2004). The title ligand may also give similar complexes with $Ni^{II}$, $Pd^{II}$ and other transition-metal cations.

In (I), the intermolecular O—H···N hydrogen bonds (Table 2) between the water molecule and atoms N15 and N20 of the macrocycle, and the intramolecular N—H···O close contacts, seem to affect the macrocyclic ring conformation and, therefore, the macrocyclic inner-hole size. The conformation of the macrocyclic ring is given by the torsion angles. The optimum values of the torsion angles in the macrocyclic ring are 180 (*anti*) or 60° (*gauche*), and in (I), 11 are *anti* and five are *gauche* (Table 1). As shown in the packing diagram

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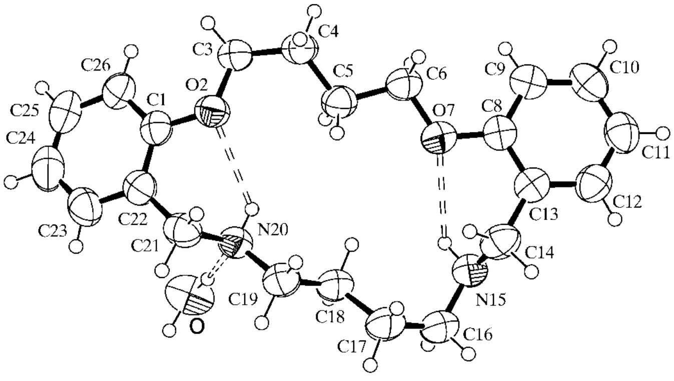

**Figure 1**
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The broken bonds indicate hydrogen bonds.

(Fig. 2), the macrocyclic ligands are elongated approximately parallel to the *c* axis and are stacked along the *a* axis. The intermolecular hydrogen bonds between the water molecules and the N atoms of the macrocycles result in the formation of zigzag polymeric chains (supramolecules; Lindoy & Atkinson, 2000) parallel to the *c* axis.

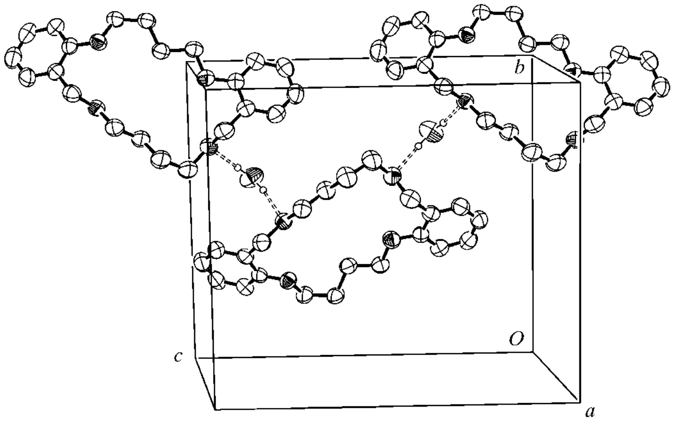

**Figure 2**
The crystal packing of (I). The broken bonds indicate hydrogen bonds.

## Experimental

Compound (I) was obtained from the reaction of 1,4-bis(salicyloxy)butane (0.5 g, 1.65 mmol; Hökelek, Kaya & Kılıç, 2001) in methanol (100 ml) and 1,4-diaminobutane (0.26 ml, 2.47 mmol) in methanol (50 ml). Argon was passed over the reaction mixture and the mixture was refluxed for 1 h, after which excess amounts of borax (2.51 g, 6.60 mmol) and sodium borohydride (0.25 g, 6.60 mmol) were added. The reduction was complete after 2 h. The solvent was then evaporated under reduced pressure. The residue was dissolved in chloroform and extracted with water, and the chloroform layers were collected and evaporated under reduced pressure. The oily residue was crystallized from *n*-heptane (yield 0.58 g, 56%; m.p. 352 K).

### *Crystal data*

$C_{22}H_{30}N_2O_2{\cdot}H_2O$
$M_r = 372.50$
Monoclinic, $P2_1/c$
$a = 8.6247$ (12) Å
$b = 14.7854$ (10) Å
$c = 16.6181$ (14) Å
$\beta = 99.352$ (12)°
$V = 2091.0$ (4) Å$^3$
$Z = 4$
$D_x = 1.183$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 0.08$ mm$^{-1}$
$T = 293$ (2) K
Block, colourless
0.40 × 0.25 × 0.25 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega$ scans
4475 measured reflections
4190 independent reflections
2237 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 26.3°$
$h = 0 \rightarrow 10$
$k = -18 \rightarrow 0$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 1%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.158$
$S = 1.01$
4190 reflections
356 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.5446P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.41$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.19$ e Å$^{-3}$

**Table 1**
Selected torsion angles (°).

| | | | |
|---|---|---|---|
| C6—O7—C8—C13 | 165.3 (2) | O7—C6—C5—C4 | 164.3 (2) |
| C14—C13—C8—O7 | −2.2 (3) | N20—C19—C18—C17 | 179.2 (2) |
| C3—O2—C1—C22 | 168.4 (2) | C19—C18—C17—C16 | −176.2 (3) |
| O2—C1—C22—C21 | −1.7 (3) | C18—C17—C16—N15 | 59.9 (4) |
| C8—O7—C6—C5 | −178.0 (2) | C14—N15—C16—C17 | 67.9 (4) |
| C19—N20—C21—C22 | 175.0 (2) | O2—C3—C4—C5 | 53.4 (4) |
| C1—C22—C21—N20 | −68.7 (3) | C6—C5—C4—C3 | 155.0 (3) |
| C21—N20—C19—C18 | −173.5 (2) | C16—N15—C14—C13 | 178.7 (2) |
| C1—O2—C3—C4 | −173.3 (2) | C8—C13—C14—N15 | 77.8 (3) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O—H1···N15$^{\rm i}$ | 0.96 (3) | 1.98 (3) | 2.940 (3) | 179 (3) |
| O—H2···N20 | 0.89 (4) | 1.99 (4) | 2.868 (3) | 170 (4) |
| N15—H15···O7 | 0.92 (3) | 2.57 (3) | 3.130 (3) | 120 (2) |
| N20—H20···O2 | 0.87 (2) | 2.43 (2) | 2.985 (3) | 122 (2) |

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

Atoms H16*A*, H16*B*, H17*A* and H17*B* were positioned geometrically at distances of 0.97 Å ($CH_2$) from the parent C atoms; a riding model was used during the refinement process, with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(carrier atom). All other H atoms were located in difference syntheses and refined isotropically [C—H = 0.91 (3)–1.04 (3) Å, N—H = 0.87 (2) and 0.92 (3) Å, and O—H = 0.89 (4) and 0.96 (3) Å].

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1170). Services for accessing these data are described at the back of the journal.

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