

2,7-Dioxa-15,19-diazatricyclo[19,4,0,0^{8,13}]pentacos-8,10,12,21,23,25(1)-hexaeneTuncer Hökelek,^{a*} Elif Ece Kaya^b
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.036
wR factor = 0.106
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title molecule, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$, is a macrocyclic multidentate Schiff base ligand containing two imine N and two ether O atoms which has a crystallographic twofold axis. The macrocyclic inner-hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 2.08 Å.

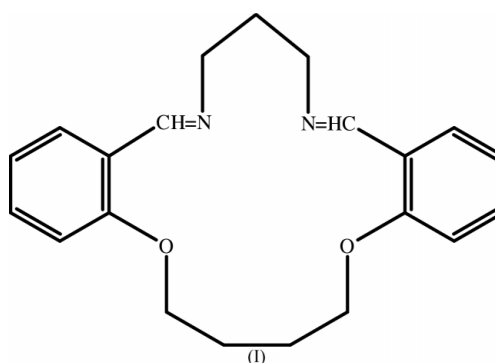
Comment

Over the last two decades, macrocyclic multidentate Schiff base N_xO_y (where $x = 2,3$ and $y = 2,3$) donor-type ligands have been investigated as potential metal-ion-selective ionophores (Lindoy *et al.*, 1993; Esteban *et al.*, 2000). In particular, 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 in environmental, inorganic and coordination chemistry (Lindoy, 1997; Hayvalı *et al.*, 1999; Vicente *et al.*, 2000). Some Schiff base complexes have also been used in catalytic reduction reactions (Tafesh & Weiguny, 1996). In addition, a series of investigations has also involved the synthetic, thermodynamic and structural properties of selective complex formation of a number of transition metal ions (Fenton *et al.*, 1987; Adam, Clarkson *et al.*, 1994). In the literature, there are only a very limited number of reports concerning the structures of the free macrocyclic multidentate N_2O_2

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and N_2O_3 donor-type ligands (Chia *et al.*, 1991; Hökelek *et al.*, 1999*a,b*; Hökelek, Akduran, Kaya & Kılıç, 2000). In 1994, Adam and co-workers synthesized the reduction product (the multidentate diamine, N_2O_2) from the reaction of 1,4-bis-(salicyloxy)butane, 1,3-diaminopropane and sodium borohydride, without isolating the title compound (Adam, Lindoy *et al.*, 1994). The title compound, (I), may be a potential metal-ion selective reagent for lanthanides, alkali and alkaline-earth metal ions. The structure determination of (I) was carried out in order to estimate the macrocyclic ring hole size and to

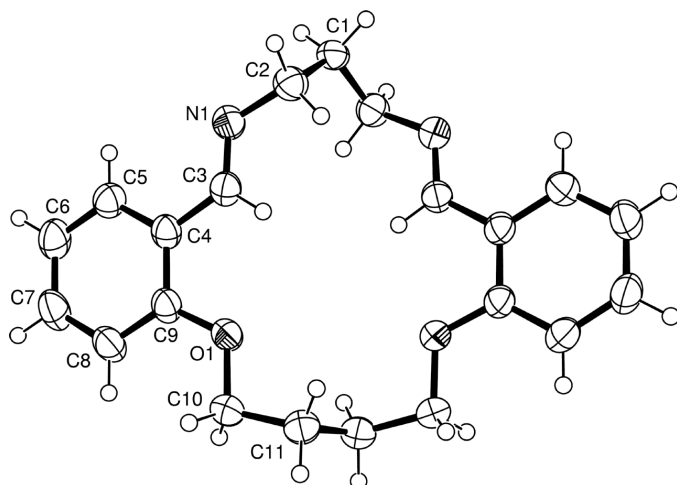


Figure 1
An ORTEPII (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

understand the effects of the macrocyclic ring on the C=N imine bond and C–N=C bond angle.

As shown in Fig. 1, molecule (I) has a crystallographic twofold axis. The intramolecular C1···C11 [7.219 (3) Å], N1···N1ⁱ [3.978 (2) Å], O1···O1ⁱ [3.894 (3) Å] and N1···O1ⁱ [5.580 (3) Å] distances may indicate the hole size of the ligand cavity [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. The C1···C11 distance is larger than the N···N distance in the potassium complex of substituted diaza-18-crown-6 (6.253 Å; Gandour *et al.*, 1986). The macrocyclic inner hole size, estimated as twice the mean distance of the donor atoms from their centroid, is approximately 2.08 Å, using the ‘modified covalent radii’ of the Nsp² (0.66 Å) and Osp³ (0.76 Å) atoms as in the literature method (Goodwin *et al.*, 1982; Adam *et al.*, 1983; Drummond *et al.*, 1982). The inner hole size of (I) (2.08 Å), which is a 17-membered macro-ring, can be compared with the 16- (1.57 Å) and 19-membered (2.53 Å) multidentate ligand hole sizes (Hökelek, Akduran, Kaya & Kılıç, 2000).

The C=N imine bond length [1.2607 (14) Å] and C–N=C imine bond angle [117.71 (10)°] are smaller than the corresponding values in salicylaldehyde and naphthaldimine Schiff base ligands (Yıldız *et al.*, 1998; Hökelek *et al.*, 2001). In naphthaldimine and salicylaldehyde Schiff bases, intramolecular hydrogen bonding is observed, which causes a lengthening of the C=N imine bond and an increase in the C–N=C bond angle (Yıldız *et al.*, 1998; Hökelek, Kılıç, Işıklan & Toy, 2000). C=N imine bond lengthening is also observed in the Schiff base complexes (Fernández-G *et al.*, 1986; Calligaris *et al.*, 1972).

Experimental

1,4-Bis(salicyloxy)butane (m.p. 374 K) was prepared from the reaction of salicylaldehyde (12.2 g, 100 mmol), sodium hydroxide (6.0 g, 150 mmol) and 1,4-dibromobutane (15.3 g, 71 mmol) in boiling ethanol (150 ml). Compound (I) was obtained from the reaction of 1,4-bis(salicyloxy)butane (0.50 g, 1.67 mmol) in ethanol (100 ml) and 1,3-diaminopropane (0.21 ml, 2.45 mmol) in ethanol (50 ml) with

argon passing over the reaction mixture and it was refluxed for 5 h. The solvent was evaporated and the residue was crystallized from ethyl acetate [yield 0.31 g (62%), m.p. 440 K].

Crystal data

C₂₁H₂₄N₂O₂
M_r = 336.43
Monoclinic, C2/c
a = 14.231 (8) Å
b = 15.6630 (14) Å
c = 8.206 (4) Å
β = 103.044 (8)°
V = 1781.9 (13) Å³
Z = 4

D_x = 1.255 Mg m⁻³
Mo Kα radiation
Cell parameters from 25 reflections
θ = 10–18°
μ = 0.08 mm⁻¹
T = 293 (2) K
Block-like, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: ψ scans (MolEN; Fair, 1990)
T_{min} = 0.975, T_{max} = 0.984
3554 measured reflections
1816 independent reflections
1468 reflections with I > 2σ(I)

R_{int} = 0.034
θ_{max} = 26.3°
h = -17 → 17
k = -19 → 19
l = -10 → 0
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.036
wR(F²) = 0.106
S = 1.06
1816 reflections
127 parameters
Only H-atom U's refined

w = 1/[σ²(F_o²) + (0.0488P)² + 0.3494P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.14 e Å⁻³
Δρ_{min} = -0.15 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.063 (3)

Table 1

Selected geometric parameters (Å, °).

O1–C9	1.3629 (14)	C4–C3	1.4724 (16)
O1–C10	1.4350 (13)	C10–C11	1.5069 (18)
N1–C3	1.2607 (14)	C2–C1	1.5181 (14)
N1–C2	1.4587 (15)	C11–C11 ⁱ	1.525 (2)
C9–C4	1.4052 (16)		
C9–O1–C10	118.88 (8)	N1–C3–C4	122.64 (10)
C3–N1–C2	117.71 (10)	O1–C10–C11	106.19 (9)
O1–C9–C8	124.24 (11)	N1–C2–C1	110.72 (9)
O1–C9–C4	115.57 (9)	C10–C11–C11 ⁱ	113.92 (12)
C5–C4–C3	121.09 (10)	C2–C1–C2 ⁱ	113.81 (13)
C9–C4–C3	120.41 (9)		
C2–N1–C3–C4	178.64 (9)	O1–C10–C11–C11 ⁱ	-79.17 (9)
C9–O1–C10–C11	-177.35 (9)	N1–C2–C1–C2 ⁱ	-73.83 (8)
C3–N1–C2–C1	115.50 (11)	C10–C11–C11 ⁱ –C10 ⁱ	151.00 (10)

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

The H atoms were positioned geometrically with C–H distances of 0.96 and 0.93 Å for CH₃ and CH, respectively, and a riding model was used during the refinement.

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: CAD-4 Software; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

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