Instrumental Achievements

Crystal Structure of 3,4,6,7,15,16,17,18,19,20,21,27-Dodecahydro-2,5,8-trioxa-16,20-diazatetracyclo[20.4.1.^{16,20}0.0^{9,14}]heptacosa-9,11,13,22,24,26(1)-hexaene

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Macrocyclic multidentate ligands have been examined extensively as potential transition-metal ion selective reagents.[1] Alkaline, alkaline earth and transition-metal ion recognition with particular metal-ion binding applications are of fundamental importance to broad areas of inorganic and coordination chemistry and biochemistry.[2]

The title compound was prepared from the reduction of diimine-crown compound[3] (2.0 g, 5.7 mmol) with borax (1.2 g, 30.0 mmol) and sodium borohydride (1.2 g, 31.0 mmol) in dry methanol (300 ml) and the reaction of the resulting product with formaldehyde (0.18 g, 6.0 mmol) in benzene (50 ml) at 333 K. The compound was crystallized from THF (mp 484 K).

The results of X-ray structure determination are given in Tables 1 – 3. The hydrogen atoms were located by a difference Fourier synthesis and geometrical calculation, parameters of 7 hydrogen atoms (out of 16) being also refined.

The title molecule (Fig. 2) consists of a macrocyclic ring containing three etheric oxygens and two nitrogens, where the nitrogen atoms are linked together by a bridging –CH_2– group. The –CH_2– bridging causes a six-membered ring to form, leading to a bicyclic ring, this is similar to results for cryptand ligands. In the crystal, the molecule has a mirror plane passing through O2, C10 and C12. The ligand cavity plays an important role in the complexation and metal-ion selectivity. The intramolecular C10···O2 [4.145(8)], C12···O2 [5.996(5)], N1···O1 [3.176(5)] and N1···O2 [4.436(6)Å] distances may indicate the hole size of the macrocyclic ring. The relative macrocyclic inner-hole size,[4] estimated as 1.63 Å. As excepted, the calculated inner-hole size for a bicyclic macro-ring is

Table 1 Crystal and experimental data

Formula: $C_{22}H_{28}N_2O_3$	
Formula weight = 368.48	
Crystal system: orthorhombic	
Space group: *C*mc2$_1$	*Z* = 4
a = 15.284(1)Å	
b = 13.855(1)Å	
c = 9.390(1)Å	
V = 1988.5(3)Å^3	
D_X = 1.231 g/cm^3	
μ (Cu K$_\alpha$) = 0.62 mm^{-1}	
T = 293 K	
Colorless	
Crystal size: 0.20 × 0.25 × 0.30 mm	
λ(Cu K$_\alpha$) = 1.54184 Å	
R = 0.056 *wR* = 0.062	
No. of reflections measured = 1124	
No. of reflections used = 841	
[*F* > 3.0 σ(*F*)]	
No. of parameters =151	
Goodness-of-fit = 1.11	
$(\Delta/\sigma)_{max}$ = 0.03	
$(\Delta\rho)_{max}$ = 0.31 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.17 eÅ^{-3}	
$2\theta_{max}$ = 148.7°	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: MolEN	
Refinement: full-matrix least-squares	

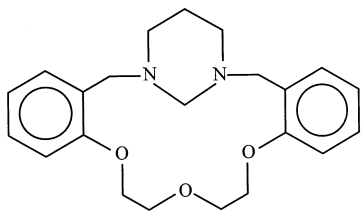

Fig. 1 Chemical diagram.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.3397(2)	0.3997(2)	0.5455(4)	4.27(6)
O2	0.500	0.4695(3)	0.6473(5)	4.6(1)
N1	0.4213(2)	0.2740(3)	0.2958(4)	3.50(7)
C1	0.4231(4)	0.4681(4)	0.7324(6)	5.1(1)
C2	0.3453(3)	0.4822(4)	0.6366(6)	4.7(1)
C3	0.2691(3)	0.3935(3)	0.4550(6)	3.83(9)
C4	0.2021(3)	0.4612(4)	0.4501(6)	4.4(1)
C5	0.1336(3)	0.4460(4)	0.3545(8)	5.5(1)
C6	0.1305(3)	0.3676(4)	0.2705(7)	5.2(1)
C7	0.1989(3)	0.3008(4)	0.2756(6)	4.5(1)
C8	0.2693(3)	0.3122(3)	0.3665(5)	3.74(9)
C9	0.3431(3)	0.2412(3)	0.3738(6)	4.22(9)
C10	0.500	0.2378(4)	0.3681(8)	3.9(1)
C11	0.4184(3)	0.2460(4)	0.1482(5)	4.5(1)
C12	0.500	0.2797(6)	0.0735(7)	4.5(2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

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Table 3 Bond distances (Å) and angles (˚)

N1-C11	1.439(6)	C9-C8	1.497(6)
N1-C9	1.474(6)	O1-C2	1.430(6)
N1-C10	1.470(5)	C1-O2	1.421(6)
C11-C12	1.505(6)	C1-C2	1.504(7)
C3-O1	1.376(6)		
C11-N1-C9	111.8(4)	C3-O1-C2	117.8(3)
C11-N1-C10	112.2(4)	C3-C8-C9	120.2(4)
C9-N1-C10	109.2(4)	N1-C10-N1'	109.9(4)
N1-C11-C12	109.8(4)	C1-O2-C1'	111.6(4)
O1-C3-C8	114.5(4)	O2-C1-C2	108.4(4)
N1-C9-C8	112.6(4)	O1-C2-C1	107.5(4)

smaller than the values (1.87 and 2.15 Å) calculated for monocyclic diaza-crown compound.[5]

The nitrogen atom has a pyramidal configuration around it.

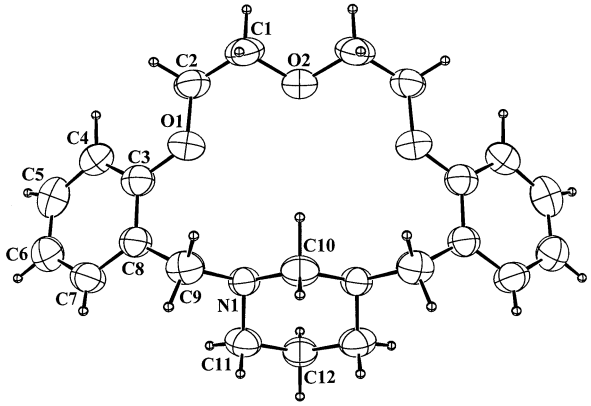

Fig. 2 Molecular structure of the title compound with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

References

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