Instrumental Achievements

Crystal Structure of 3,4,6,7,15,16,17,18,19,20,21-Undecahydro-2,5,6-trioxa-16,20-diazatricyclo[20.4.0.0^{9,14}]hexacosa-9,11,13,22,24,26(1)-hexaene

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A large number of macrocyclic Schiff-base ligands involving the synthetic, thermodynamic and/or structural properties of complex formation of a range of transition metal ions[1] were investigated previously as potential metal-ion-selective reagents.[2] Since the title compound has two N- and three O-donor atoms in the macrocyclic ring, it may be a potential metal-ion-selective reagent for transition, alkaline and alkaline earth metal ions.

The title compound was prepared from the reduction of a 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). The mixture was refluxed for 4 h. Later, methanol was evaporated and the residue was extracted with diethylether.

The organic layer was dried with magnesium sulfate, evaporated and crystallized from diethylether (mp 357 K). The results of an X-ray structure determination are given in Tables 1 – 3. The hydrogen atoms were located by a difference Fourier synthesis and a geometrical calculation, with the parameters of 16 hydrogen atoms (out of 56) also being refined.

The crystal has two molecules (Fig. 2) in an asymmetric unit. The conformations of the two independent molecules in the asymmetric unit are not considerably different from each other. The ligand cavity plays an important role in the complexation and metal-ion selectivity. The intramolecular C19···O2 [5.658(5)], N1···O1 [5.591(6)], N1···O2 [4.829(6)], N2···O2 [4.059(6)], N2···O3 [4.737(5)Å] (molecule A) and C40···O5 [4.666(6)], N3···O5 [4.198(5)], N3···O6 [4.891(5)], N4···O4 [6.534(6)] N4···O5 [5.898(5)Å] (molecule B) distances may indicate the hole sizes of the macrocyclic rings. The relative macrocyclic inner-hole sizes, estimated as being twice the mean

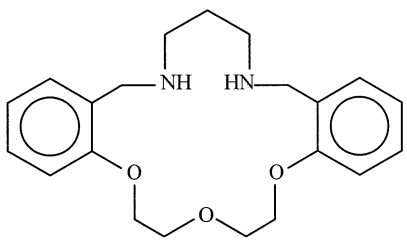

Fig. 1 Chemical diagram.

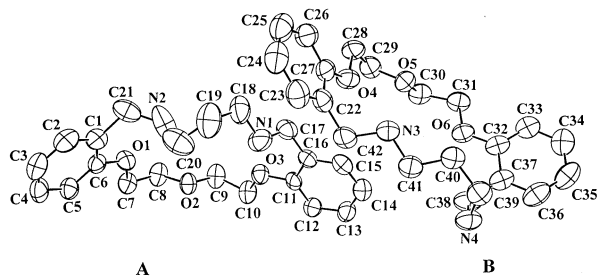

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula: $C_{21}H_{28}N_2O_3$
Formula weight = 356.47
Crystal system: monoclinic
Space group: $P2_1$ $Z = 4$
a = 14.633(1)Å
b = 8.586(2)Å
c = 15.621(1)Å
β = 94.80(1)°
V = 1955.71(4)Å^3
D_x = 1.211 g/cm^3
μ(Cu K$_\alpha$) = 0.61 mm^{-1}
T = 293 K
Colorless
Crystal size: 0.20 × 0.25 × 0.30 mm
λ(Cu K$_\alpha$) = 1.54184 Å
R = 0.045 wR = 0.049
No. of reflections measured = 3849
No. of reflections used = 2542
[F >3.0 $\sigma(F)$]
No. of parameters = 532
Goodness-of-fit = 0.71
$(\Delta/\sigma)_{max}$ = 0.01
$(\Delta\rho)_{max}$ = 0.17
$(\Delta\rho)_{min}$ = –0.06
$2\theta_{max}$ = 148.7°
Measurements: Enraf-Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: MolEN
Refinement: full matrix least-squares

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.9072(2)	0.234	1.1491(2)	4.25(7)
O2	0.9472(2)	0.1521(4)	0.9788(2)	4.14(6)
O3	0.8769(2)	0.3024(4)	0.8167(2)	4.20(7)
O4	0.5678(2)	0.7890(4)	0.7064(2)	4.69(7)
O5	0.5479(2)	0.6540(4)	0.5396(2)	4.39(7)
O6	0.6467(2)	0.7360(4)	0.3917(2)	4.81(7)
N1	0.7683(3)	0.5918(7)	0.8686(3)	6.4(1)
N2	0.7781(4)	0.4584(7)	1.0849(3)	9.2(1)
N3	0.6644(2)	1.0618(6)	0.6494(2)	4.83(9)
N4	0.8368(3)	1.0715(6)	0.4312(3)	5.4(1)
C1	0.8496(3)	0.4262(6)	1.2369(3)	4.4(1)
C2	0.8594(3)	0.5175(7)	1.3095(3)	5.3(1)
C3	0.9356(4)	0.5070(7)	1.3677(3)	5.5(1)
C4	1.0034(4)	0.4037(7)	1.3539(3)	5.2(1)
C5	0.9972(3)	0.3095(6)	1.2813(3)	4.4(1)
C6	0.9205(3)	0.3221(6)	1.2231(3)	3.87(9)
C7	0.9761(3)	0.1253(6)	1.1304(3)	4.4(1)
C8	0.9449(4)	0.0470(6)	1.0477(3)	4.8(1)
C9	0.9205(4)	0.0776(6)	0.9006(3)	5.1(1)
C10	0.9407(3)	0.1763(6)	0.8257(3)	4.6(1)
C11	0.8724(3)	0.3850(6)	0.7404(2)	3.56(9)
C12	0.9337(3)	0.3663(6)	0.6788(3)	4.1(1)
C13	0.9220(3)	0.4526(7)	0.6033(3)	4.7(1)
C14	0.8505(3)	0.5547(7)	0.5897(3)	4.8(1)
C15	0.7932(3)	0.5735(6)	0.6524(3)	4.5(1)
C16	0.8001(3)	0.4908(6)	0.7291(3)	3.9(1)
C17	0.7327(3)	0.5113(7)	0.7945(3)	5.0(1)
C18	0.6997(4)	0.6201(8)	0.9292(3)	6.8(1)
C19	0.7357(5)	0.6985(8)	1.0069(4)	8.3(2)
C20	0.8069(4)	0.6151(9)	1.0626(5)	8.7(2)
C21	0.7640(3)	0.4315(8)	1.1742(4)	6.5(1)
C22	0.6247(3)	0.9936(6)	0.7950(3)	4.5(1)
C23	0.6184(4)	1.0804(7)	0.8673(3)	6.0(1)
C24	0.5494(4)	1.0640(8)	0.9214(3)	6.6(1)
C25	0.4827(4)	0.9536(8)	0.9023(3)	6.4(1)
C26	0.4872(3)	0.8620(7)	0.8292(3)	5.5(1)
C27	0.5568(3)	0.8803(6)	0.7778(3)	4.3(1)
C28	0.4980(3)	0.6782(6)	0.6819(3)	5.0(1)
C29	0.5314(3)	0.5735(6)	0.6149(3)	5.1(1)
C30	0.5734(3)	0.5525(6)	0.4754(3)	5.0(1)
C31	0.5717(3)	0.6335(6)	0.3905(3)	4.8(1)
C32	0.6585(3)	0.8174(6)	0.3184(3)	4.4(1)
C33	0.5981(3)	0.8114(7)	0.2447(3)	5.2(1)
C34	0.6157(4)	0.8982(7)	0.1728(3)	5.9(1)
C35	0.6933(4)	0.9884(7)	0.1753(3)	6.3(1)
C36	0.7525(4)	0.9940(7)	0.2483(3)	6.2(1)
C37	0.7380(3)	0.9117(6)	0.3199(3)	4.6(1)
C38	0.8048(3)	0.9185(6)	0.4000(4)	5.7(1)
C39	0.7628(3)	1.1810(6)	0.4423(3)	5.3(1)
C40	0.6958(3)	1.1284(6)	0.5047(3)	4.8(1)
C41	0.7362(3)	1.0983(7)	0.5933(3)	5.1(1)
C42	0.7004(3)	1.0152(6)	0.7361(3)	4.9(1)

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

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

O1-C6	1.379(5)	N1-C17	1.409(6)
O1-C7	1.424(5)	N1-C18	1.456(7)
O2-C8	1.408(5)	N2-C20	1.460(9)
O2-C9	1.405(5)	N2-C21	1.447(8)
O3-C10	1.429(6)	N3-C41	1.458(6)
O3-C11	1.384(5)	N3-C42	1.467(6)
O4-C27	1.383(6)	N4-C38	1.464(7)
O4-C28	1.425(6)	N4-C39	1.455(7)
O5-C29	1.403(6)	O6-C31	1.406(6)
O5-C30	1.402(6)	O6-C32	1.364(6)
C6-O1-C7	118.6(3)	C31-O6-C32	117.6(3)
C8-O2-C9	110.5(4)	C17-N1-C18	112.8(4)
C10-O3-C11	117.1(3)	C20-N2-C21	116.4(5)
C27-O4-C28	117.8(3)	C41-N3-C42	113.1(3)
C29-O5-C30	111.6(4)	C38-N4-C39	113.6(4)

distance of the donor atoms from their centroid, are approximately 1.87 (molecule A) and 2.15 Å (molecule B), using the "modified covalent radii" of the N sp^2 (0.66 Å) and O sp^3 (0.76 Å) atoms, as in a literature method.[4] The calculated inner-hole sizes are smaller than the value 2.53 Å given for a diaza-crown compound.[5]

The multidentate macrocyclic ligand contains intramolecular hydrogen bonds [N2–H2 0.88, H2··O1 2.78 and N3–H3 0.87(4), H3··O4 2.29(4)Å], which may be effective on the macrocyclic inner-hole sizes.

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