Instrumental Achievements

Crystal Structure of 2,5-Dioxa-13,17-diazatricyclo[17.4.0.0^{6,11}]-tricosa-6,8,10,12,17,19,21,23(1)-octaene

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Macrocyclic multidentate Schiff base N_2O_2 and N_2O_3 donor-type ligands have been investigated as complexation agents for alkali, alkaline-earth and transition-metal ion (especially lanthanides) recognition with particular metal-ion binding applications of great interest in environmental, inorganic and coordination chemistry.[1,2] Although a large number of macrocyclic ligand complexes have been extensively examined in order to understand their structural properties of complex formation, there are a few reports about the structures of the free macrocyclic multidentate N_2O_2 and N_2O_3 donor-type ligands.[2–6]

The title compound was prepared from the reaction of 1,2-bis(salicyloxy)ethane (2.70 g, 10.0 mmol) and 1,3-diaminopropane (0.74 g, 10.0 mmol) in dry methanol (100 ml) with argon passing over the reaction mixture. After refluxing for 5 h, the solvent was evaporated and the residue was crystallized from diethylether (m.p., 473 K; yield, 3.00 g, 97 %).

The results of an X-ray structure determination are given in Tables 1 – 4. The two HC=N hydrogen atoms were located by a difference Fourier synthesis, and their positional and thermal parameters were refined. The other hydrogen atoms were located by geometrical calculations.

The title molecule (Fig. 2) consists of a macrocyclic ring containing two imine nitrogens and two etheric oxygens.

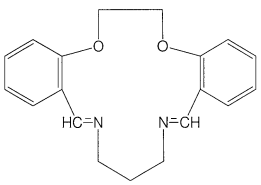

Fig. 1 Chemical diagram.

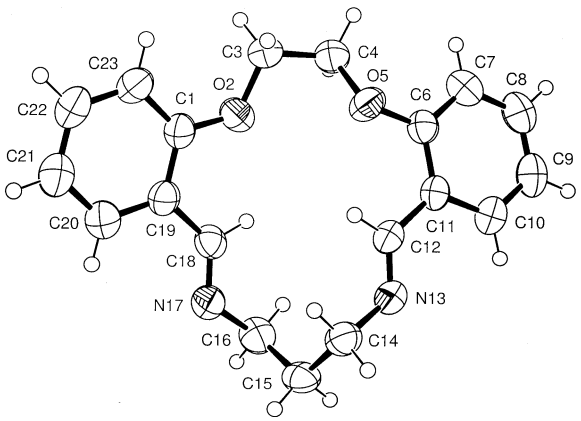

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula: $C_{19}H_{20}N_2O_2$
Formula weight = 308.37
Crystal system: monoclinic
Space group: $P2_1$ $Z = 2$
a = 4.772(1)Å
b = 15.548(2)Å
c = 11.032(1)Å
β = 94.03(1)˚
V = 816.4(2)Å^3
D_x = 1.254 g/cm^3
μ(Mo K$_\alpha$) = 0.082 mm^{-1}
T = 293 K
Colorless
Crystal size: 0.15 × 0.15 × 0.30 mm
λ(Mo K$_\alpha$) = 0.71073 Å
R = 0.043 wR = 0.125
No. of reflections measured = 1840
No. of reflections used = 1405
[$I > 2.0\ \sigma(I)$]
No. of parameters = 217
Goodness-of-fit = 1.04
$(\Delta/\sigma)_{max}$ = 0.001
$(\Delta\rho)_{max}$ = 0.18
$(\Delta\rho)_{min}$ = –0.15
$2\theta_{max}$ = 52.6˚
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*	U_{eq}/Å^2
O2	0.1748(6)	0.3867(1)	-0.0542(2)	0.0707(7)
O5	0.1630(4)	0.2766(2)	0.1335(2)	0.0580(6)
N13	0.4795(5)	0.4527(2)	0.3709(2)	0.0549(6)
N17	0.5067(6)	0.5958(2)	0.0990(2)	0.0587(7)
C1	0.3521(7)	0.4277(2)	-0.1251(3)	0.0541(7)
C3	0.1085(8)	0.2990(2)	-0.0756(3)	0.0610(8)
C4	-0.0353(7)	0.2683(2)	0.0321(3)	0.0628(8)
C6	0.0639(6)	0.2719(2)	0.2472(3)	0.0490(6)
C7	-0.1402(7)	0.2136(2)	0.2761(3)	0.0618(8)
C8	-0.2219(7)	0.2092(2)	0.3936(4)	0.0679(9)
C9	-0.1008(7)	0.2634(3)	0.4815(3)	0.0669(9)
C10	0.0961(7)	0.3225(2)	0.4522(3)	0.0580(8)
C11	0.1862(6)	0.3283(2)	0.3351(2)	0.0461(6)
C12	0.4028(6)	0.3901(2)	0.3028(2)	0.0465(6)
C14	0.7062(6)	0.5063(2)	0.3329(3)	0.0552(7)
C15	0.6188(7)	0.6004(2)	0.3195(3)	0.0571(7)
C16	0.3997(7)	0.6165(2)	0.2156(3)	0.0585(7)
C18	0.3799(7)	0.5362(2)	0.0392(3)	0.0515(7)
C19	0.4654(6)	0.5056(2)	-0.0796(2)	0.0512(7)
C20	0.6453(8)	0.5511(2)	-0.1488(3)	0.0620(8)
C21	0.7191(9)	0.5209(3)	-0.2599(3)	0.0731(9)
C22	0.6071(9)	0.4446(3)	-0.3036(3)	0.0726(9)
C23	0.4324(8)	0.3966(2)	-0.2375(3)	0.0627(8)

$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

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

C1-C19	1.405(5)	C6-C11	1.404(4)
C3-C4	1.491(5)	C15-C14	1.526(5)
C11-C12	1.473(4)	C18-N17	1.266(4)
C15-C16	1.516(5)	C18-C19	1.478(4)
N13-C12	1.268(4)	O2-C1	1.351(4)
N13-C14	1.450(4)	O2-C3	1.416(4)
N17-C16	1.453(4)	O5-C6	1.373(3)
C1-O2-C3	119.9(3)	N13-C12-C11	122.4(2)
C1-C19-C18	118.1(3)	N13-C14-C15	112.0(3)
C12-N13-C14	117.4(2)	N17-C18-C19	123.1(3)
C16-C15-C14	113.6(2)	N17-C16-C15	111.5(3)
C18-N17-C16	116.0(3)	O2-C3-C4	106.6(3)
C6-O5-C4	117.5(2)	O5-C6-C7	122.6(3)
C6-C11-C12	120.3(2)	O5-C6-C11	116.4(2)
		O5-C4-C3	106.3(2)

Table 4 Torsion angles (˚)

C1-O2-C3-C4	167.6(3)	C16-C15-C14-N13	-67.5(3)
C12-N13-C14-C15	122.4(3)	C18-N17-C16-C15	117.9(3)
C14-N13-C12-C11	176.5(3)	C18-C19-C20-C21	-179.5(3)
C14-C15-C16-N17	-63.3(4)	C19-C18-N17-C16	-178.4(3)
		C6-O5-C4-C3	165.0(3)

Although a molecular-structure determination of this compound was already done[6], it was a different polymorph of the title compound.

The macrocyclic ligand cavity plays an important role in the complexation and metal-ion selectivity. The intramolecular N13··O2 4.920(4), N17··O5 5.249(5), C3··C15 6.736(5), C4··C15 6.712(5), N17··O2 3.944(4) and N13··O5 4.010(5)Å distances may indicate the hole size of the macrocyclic ring. The relative macrocyclic inner-hole size,[2,5] which is a 15-membered macro-ring, is estimated to be 1.83 Å, can be compared with 17- (2.08 Å)[2] and 19-membered (2.53 Å)[5] multidentate ligand hole sizes.

The close contacts are H18··O2 2.29(4) [C18–H18 0.96(4)Å] and H12··O5 2.37(4)Å [C12–H12 0.97(4)Å].

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