

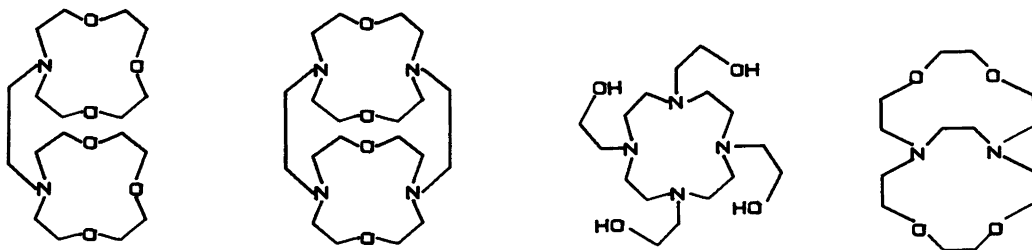
The Crystal Structure of 7,10,19,22-Tetraoxa-1,4,13,16-Tetraazatricyclo[14.8.2.2^{4,13}]-octacosane at -150°C

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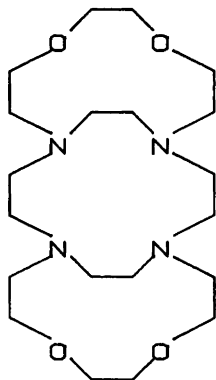
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Aiming for the design of novel ligands with expected selectivity for sodium (and possibly for calcium and lanthanides), synthetic work has

been in progress at this university for some years.¹ Among the ligands investigated are:



Several crystal structure determinations of these ligands and their complexes (especially with Li^+ , Na^+ and K^+) have been carried out in order to obtain precise information about the coordination type and the corresponding ring conformations. Recently the synthesis of a new tricyclic sodium selective ligand has been reported.²



The results of a crystal structure determination of the free ligand are now presented.

The crystals of $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_4$ are monoclinic with cell dimensions $a = 13.705(5)$, $b = 9.241(3)$, $c = 17.149(4)$ Å, $\beta = 93.54(2)^{\circ}$, space group $P2_1/n$ and $Z = 4$ ($D_x = 1.23$ gcm⁻³, $D_m = 1.21$ gcm⁻³). With $2\theta_{\text{max}} = 50^{\circ}$, $\text{MoK}\alpha$ -radiation. 2936 independent reflections ($I > 2.5\sigma(I)$) were recorded on an automatic diffractometer at ca. -150°C . No corrections for absorption or secondary extinction were applied (crystal size $0.4 \times 0.4 \times 0.2$ mm). The structure was solved by direct methods³ and refined by least-squares techniques.⁴ All programs used (except those for phase determination) are given in Ref. 4. Anisotropic temperature factors were introduced for non hydrogen atoms. Weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02 C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N the net count. Hydrogen atom positions were calculated and refined with isotropic temperature factors. The

Table 1. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms.

Atom	X	Y	Z
O1	-0.16164(7)	0.32951(12)	0.24989(5)
O2	-0.11552(8)	0.63302(12)	0.28808(5)
O3	0.39306(8)	0.39609(12)	-0.03079(6)
O4	0.37665(7)	0.08809(12)	0.01769(5)
N1	0.08083(8)	0.55790(13)	0.21645(6)
N2	0.19553(8)	0.46845(13)	0.06170(6)
N3	0.16651(9)	0.13244(13)	0.04820(7)
N4	0.94171(8)	0.21477(13)	0.19558(7)
C1	-0.05484(11)	0.14823(18)	0.20106(9)
C2	-0.13910(12)	0.25178(19)	0.18154(9)
C3	-0.22193(12)	0.45263(19)	0.23194(11)
C4	-0.16244(13)	0.58454(19)	0.21596(9)
C5	-0.03482(12)	0.72754(19)	0.27887(10)
C6	0.06182(12)	0.64754(19)	0.28505(9)
C7	0.13822(11)	0.42879(17)	0.24023(9)
C8	0.07044(12)	0.30704(17)	0.26316(8)
C9	0.12619(12)	0.64529(17)	0.15735(9)
C10	0.12133(12)	0.57833(17)	0.07609(9)
C11	0.29149(11)	0.53373(18)	0.05194(9)
C12	0.37222(12)	0.42209(19)	0.04904(9)
C13	0.46255(13)	0.28249(20)	-0.03923(11)
C14	0.41581(14)	0.13783(20)	-0.05308(10)
C15	0.30349(12)	-0.01085(19)	0.00530(10)
C16	0.20351(12)	0.04561(20)	-0.01535(9)
C17	0.10282(11)	0.25018(17)	0.01746(9)
C18	0.16257(12)	0.37974(18)	-0.00611(8)
C19	0.11998(12)	0.03994(18)	0.10419(9)
C20	0.11753(12)	0.10537(18)	0.18558(9)

maximum r.m.s. amplitudes of thermal vibration range from 0.16 to 0.22 Å. The final *R*-value was 3.5% (*R*_w = 3.4%) for 2936 reflections. Final

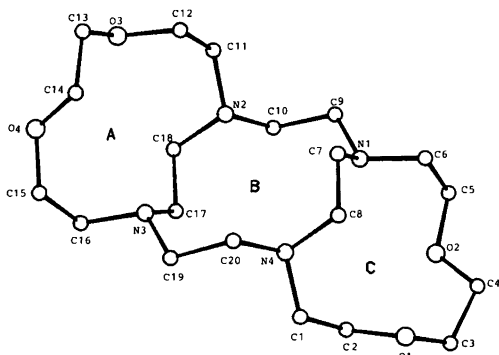


Fig. 1. Perspective drawing of the ligand showing the numbering of atoms.

Table 2. Torsion angles with estimated standard deviations.

Dihedral angle	(°)
C2 - O1 - C3 - C4	-87.6(2)
C3 - O1 - C2 - C1	165.4(1)
C4 - O2 - C5 - C6	-96.8(2)
C5 - O2 - C4 - C3	161.7(1)
C12 - O3 - C13 - C14	92.7(2)
C13 - O3 - C12 - C11	-174.8(1)
C14 - O4 - C15 - C16	-83.7(2)
C15 - O4 - C14 - C13	159.5(1)
C6 - N1 - C7 - C7	86.5(2)
C7 - N1 - C6 - C5	-147.5(1)
C6 - N1 - C9 - C10	-162.6(1)
C9 - N1 - C6 - C5	86.3(2)
C7 - N1 - C9 - C10	72.8(2)
C9 - N1 - C7 - C8	-149.1(1)
C10 - N2 - C11 - C12	171.5(1)
C11 - N2 - C10 - C9	-75.0(2)
C10 - N2 - C18 - C17	-89.0(2)
C18 - N2 - C10 - C9	160.4(1)
C11 - N2 - C118 - C17	156.5(1)
C18 - N2 - C11 - C12	-65.1(2)
C16 - N3 - C17 - C18	-82.5(2)
C17 - N3 - C16 - C15	149.9(1)
C16 - N3 - C19 - C20	156.1(1)
C19 - N3 - C16 - C15	-83.3(2)
C17 - N3 - C19 - C20	78.2(2)
C19 - N3 - C17 - C18	152.2(1)
C1 - N4 - C8 - C7	-150.9(1)
C8 - N4 - C1 - C2	77.5(2)
C1 - N4 - C20 - C19	76.4(2)
C20 - N4 - C1 - C2	-158.7(1)
C8 - N4 - C20 - C19	-157.8(1)
C20 - N4 - C8 - C7	84.1(2)
N4 - C1 - C2 - O1	-87.2(2)
O1 - C3 - C4 - O2	-71.6(2)
O2 - C5 - C6 - N1	73.9(2)
N1 - C7 - C8 - N4	90.9(2)
N1 - C9 - C10 - N2	-81.5(2)
N2 - C11 - C12 - O3	99.5(2)
O3 - C13 - C14 - O4	-72.1(2)
O4 - C15 - C16 - N3	-64.4(2)
N3 - C17 - C18 - N2	-79.9(2)
N3 - C19 - C20 - N4	78.6(2)

fractional coordinates with estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Torsion angles with estimated standard deviations may be found in Table 2. Fig. 1 is a perspective drawing showing the numbering of atoms, and Fig. 2 a stereo view of the free ligand.

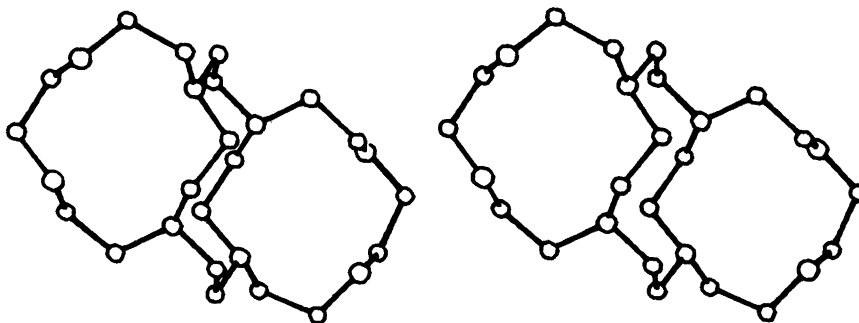
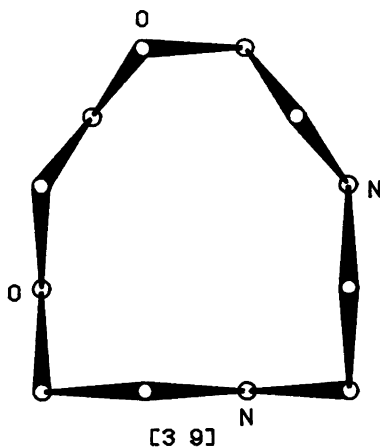
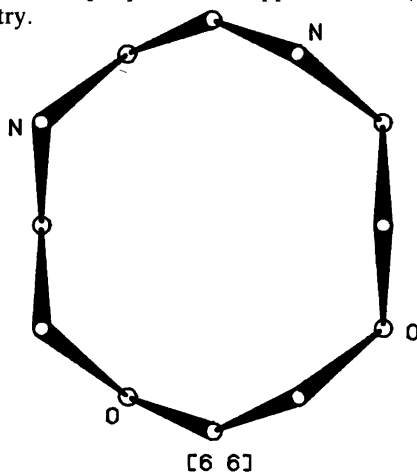


Fig. 2. Stereo view of the ligand.

The dihedral angles shown in Table 2 indicate that one of 12-membered rings (labeled "A" in Fig. 1) adopts the biangular conformation [3 9]⁵ which as been observed earlier,⁶



and that the two others (B and C) prefer a different biangular conformation which may be described as [6 6] with the approximate C_i symmetry.



The [6 6] conformation has also been observed earlier, e.g. in 10,10'-ethylene bis(1,4,7-trioxa-10-azacyclododecane) and in its (1:1) lithium thiocyanate complex.^{7,8} It should, however, be pointed out that although both these conformations are [6 6]-biangular, they are widely different. The ring in the free ligand corresponds to those of the present one, with one "corner" next to the nitrogen. The [6 6]-ring of the complex, adopted in order to offer satisfactory coordination conditions, is not pseudo-centrosymmetric at all, and both corner atoms are situated next to the oxygen atoms.

The bond distances and angles are normal within the estimated limits of error.

Lists of thermal parameters, hydrogen atom parameters, bond distances and angles, and observed and calculated structure factors are available from the author.

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References

1. Dale, J. *Oslo Symposium 1982, Ion Exchange and Solvent Extraction Soc. Chem. Ind. London* (1982).
2. Buøen, S. and Dale, J. *Acta Chem. Scand. B* (B2441).
3. Gilmore, C. J. *J. Appl. Crystallogr.* 17 (1984) 42.
4. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
5. Dale, J. *Acta Chem. Scand.* 27 (1973) 1115.
6. Groth, P. *Acta Chem. Scand.* A39 (1985) 59.
7. Groth, P. *Acta Chem. Scand.* A38 (1984) 342.
8. Groth, P. *Acta Chem. Scand.* A38 (1984) 337.

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