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Structure of the Macrocyclic Ligand Tetrakis(2-hydroxyethyl)cyclam at 123 K

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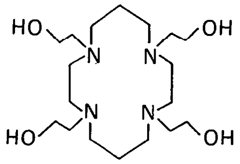
Abstract. 1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane, $C_{18}H_{40}N_4O_4$, $M_r = 376{\cdot}54$, monoclinic, $P2_1/n$, $a = 9{\cdot}945\ (1)$, $b = 9{\cdot}562\ (1)$, $c = 11{\cdot}116\ (1)$ Å, $\beta = 100{\cdot}03\ (1)^\circ$, $V = 1040{\cdot}9\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}201$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·079 mm^{-1}, $F(000) = 416$, $T = 123\ (2)$ K, $R = 0{\cdot}041$ for 1513 unique reflections. The macrocyclic ligand crystallizes in the *RSSR* (*trans* IV) configuration on a crystallographic centre of symmetry, with the electron pairs on 1,8-related N atoms directed away from the centre of the ring. Thus it is not possible from this structure to determine accurately the dimensions of the metal ion binding cavity. Intramolecular hydrogen bonding brings together 1,4-related hydroxyl groups in an association which also involves the N atoms to which they are appended. There is no indication of significant intermolecular hydrogen bonding.

Experimental. Suitable crystals of the title compound, (1), were obtained from the reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam) with excess oxirane in ethanol (Madeyski, Michael & Hancock, 1984) followed by recrystallization of the crude product at 279 K from a $10^{-2}M$ solution in propan-2-ol. The data crystal was a colourless prism 0·21 × 0·25 × 0·23 mm. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$-scan mode. Unit-cell parameters from 25 accurately centred reflections ($12{\cdot}6 \le \theta \le 18{\cdot}8^\circ$). 3225 reflections measured with $\theta \le 23^\circ$, 494 with $\sigma(I)/I \le 1{\cdot}0$ rejected on fast scan, range $-10 \le h \le 11$, $0 \le k \le 10$, $-12 \le l \le 12$. Three standard reflections (111, $\bar{1}0\bar{5}$, $\bar{2}20$) measured periodically showed no significant variation. Data merged to give 1513 unique reflections, R_{int} = 1·7%, 37 with $I \le 0$.



(1)

The *XTAL System of Crystallographic Programs* (Hall & Stewart, 1989) was used for all computer calculations. Structure was solved by direct methods, H atoms located in difference map. Refined by full-matrix least squares of 198 parameters based on F^2 using *SFLSX* (Hall, Spadaccini, Olthof-Hazekamp & Dreissig, 1989). Scale factor, positional parameters for all atoms, anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms refined. On F^2, final $R = 0{\cdot}054$, $wR = 0{\cdot}058$, $w = 1{\cdot}0/[\sigma(F^2)]^2$ where $\sigma(F^2) = \sigma(I)/(2{\cdot}0|F|)$, $S = 2{\cdot}32$. A structure factor calculation after the

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Table 1. *Atomic coordinates and isotropic thermal parameters*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U^*(Å^2)
N(1)	−0·0108 (1)	0·2007 (1)	0·1379 (1)	0·0167 (6)
C(2)	0·0046 (2)	0·2925 (2)	0·0358 (1)	0·0193 (8)
C(3)	0·1513 (2)	0·3049 (2)	0·0145 (1)	0·0182 (8)
N(4)	0·2272 (1)	0·1717 (1)	0·0249 (1)	0·0159 (6)
C(5)	0·1711 (2)	0·0743 (2)	−0·0740 (1)	0·0181 (8)
C(6)	0·2256 (2)	−0·0737 (2)	−0·0502 (1)	0·0215 (8)
C(7)	0·1549 (2)	−0·1774 (2)	−0·1452 (1)	0·0213 (8)
C(8)	0·3726 (2)	0·2034 (2)	0·0238 (1)	0·0209 (8)
C(9)	0·4528 (2)	0·2337 (2)	0·1503 (1)	0·0244 (8)
O(10)	0·4826 (1)	0·1096 (1)	0·2210 (1)	0·0325 (7)
C(11)	0·0668 (2)	0·2486 (2)	0·2560 (1)	0·0193 (8)
C(12)	0·1267 (2)	0·1224 (2)	0·3277 (1)	0·0226 (8)
O(13)	0·2173 (1)	0·0495 (1)	0·2626 (1)	0·0261 (6)
H(1)	0·411 (2)	0·087 (2)	0·249 (2)	0·051 (6)
H(2)	0·202 (2)	0·078 (2)	0·190 (2)	0·055 (6)
H(21)	−0·052 (1)	0·255 (2)	−0·038 (1)	0·024 (4)
H(22)	−0·030 (1)	0·391 (2)	0·047 (1)	0·023 (4)
H(31)	0·152 (1)	0·348 (1)	−0·067 (1)	0·014 (4)
H(32)	0·201 (1)	0·371 (1)	0·076 (1)	0·011 (4)
H(51)	0·071 (2)	0·072 (1)	−0·079 (1)	0·016 (4)
H(52)	0·188 (1)	0·109 (1)	−0·157 (1)	0·019 (4)
H(61)	0·323 (1)	−0·077 (1)	−0·057 (1)	0·021 (4)
H(62)	0·212 (1)	−0·104 (1)	0·033 (1)	0·023 (4)
H(71)	0·206 (1)	−0·269 (2)	−0·135 (1)	0·019 (4)
H(72)	0·159 (1)	−0·138 (1)	−0·228 (1)	0·015 (4)
H(81)	0·415 (1)	0·120 (1)	−0·010 (1)	0·013 (4)
H(82)	0·379 (1)	0·290 (2)	−0·033 (1)	0·026 (4)
H(91)	0·545 (2)	0·277 (2)	0·140 (1)	0·027 (4)
H(92)	0·402 (1)	0·305 (1)	0·194 (1)	0·020 (4)
H(111)	0·145 (1)	0·310 (1)	0·243 (1)	0·018 (4)
H(112)	0·006 (1)	0·302 (1)	0·303 (1)	0·021 (4)
H(121)	0·181 (1)	0·151 (2)	0·408 (1)	0·022 (4)
H(122)	0·051 (2)	0·057 (2)	0·343 (1)	0·025 (4)

*U_{eq} for non-H atoms and U_{iso} for H atoms.

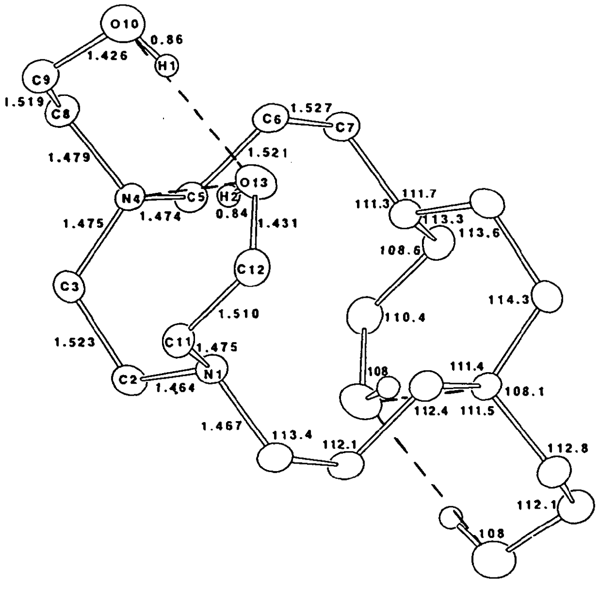

Fig. 1. Molecular structure and atomic numbering for the crystal structure of (1), with thermal ellipsoid boundaries drawn at the 50% probability level. Bond lengths (Å) and angles (°) are shown. E.s.d.'s in bond lengths involving H atoms are 0·02 Å and for others 0·002 Å and the corresponding values for bond angles are 1 and 0·1°. Methylene H atoms omitted for clarity. The intramolecular hydrogen bonds, O10—O13 2·817 (2) Å and O13—N4 2·907 (2) Å, are shown as dashed lines.

refinement gave $R = 0{\cdot}041$. $(\Delta/\sigma)_{\max} = 0{\cdot}001$, $\Delta\rho_{\max} = 0{\cdot}25$ e Å^{-3}. Scattering factors were of the interpolated type from *ADDREF* (Davenport & Hall, 1989). Atomic parameters are given in Table 1,* and the molecular geometry is shown in Fig. 1.

Related literature. This ligand has aroused considerable interest because of the unusually rapid rate, compared to related ligands, at which metal ion incorporation apparently occurs (Madeyski, Michael & Hancock, 1984; Hay, Pujari, Moodie, Craig, Richens, Perotti & Ungaretti, 1987) and is the subject of current investigations directed towards gaining an understanding of this phenomenon (Clarke, Hounslow, Keough, Lincoln & Wainwright, 1990; Clarke, Lincoln & Wainwright, 1991). Crystal structures of complexes formed from the smaller but otherwise similar ligands, 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (Buøen, Dale, Groth & Krane, 1982; Groth, 1983) and 1,4,7,10-tetrakis(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane (Hancock, Shaikjee, Dobson & Boeyens, 1988) which do not show such rapid metal ion incorporation (Duckworth, Laurence, Lincoln, Turonek & Wainwright, 1990; Hancock *et al.*, 1988), have been determined.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54180 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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