A Non-Symmetric Water Complex of a Tripod Ligand: The Structure of Tris[(2-methyl-8-quinolyloxy)ethyl]amine Dihydrate

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Abstract. $C_{36}H_{36}N_4O_3.2H_2O$, $M_r = 608\cdot7$, monoclinic, $P2_1/c$, $a = 20\cdot048$ (8), $b = 15\cdot623$ (6), $c = 10\cdot483$ (4) Å, $\beta = 90\cdot72$ (9)°, $Z = 4$, $d_c = 1\cdot231$ Mg m^{-3}, $R = 0\cdot068$, $R_w = 0\cdot051$. One chain of the tripod ligand wraps around a solvent water molecule, whilst the remaining chains are left without obvious interactions. A second water molecule is hydrogen bonded to the first.

Introduction. Tri- and tetrapod organic molecules containing donor atoms may be considered as non-cyclic cryptands. Their complexes with alkali- and alkaline-earth-metal ions are more stable than the respective oligoether and crown-ether complexes (Vögtle, Müller, Wehner & Buhleier, 1977; Heimann, Herzhoff & Vögtle, 1979; Vögtle, Müller, Buhleier & Wehner, 1979). Even water is coordinated by tris[(2-methyl-8-quinolyloxy)ethyl]amine.

Colourless needles of the complex were crystallized from ethyl acetate.

Systematic absences on Weissenberg photographs indicated the space group $P2_1/c$; cell dimensions were obtained by least squares from angle measurements of 20 strong reflexions between $2\theta = 20$ and $25°$ on an automated four-circle diffractometer. Intensities for 6152 reflexions were collected from a crystal $0\cdot5 \times 0\cdot2 \times 0\cdot2$ mm with monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å) up to $2\theta = 50°$. Data were corrected for Lp but not for absorption effects ($\mu = 0\cdot07$ mm^{-1}). After equivalents were averaged, 4016 independent hkl reflexions with $F > 3\sigma(F)$ remained. The structure was solved by multisolution Σ_2 sign refinement. Nearly all the non-hydrogen atoms could be located in the E map based on the most self-consistent set of phases (411 E values > 1·78).

In the final cycles common isotropic temperature factors were employed for chemically equivalent H atoms; the other atoms were refined anisotropically. A riding model was employed for the ligand H atoms. H atoms of the second water molecule could not be located from difference syntheses.

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Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U^*
N(1)	340 (1)	−1848 (1)	5409 (2)	89 (1)
C(2)	−252 (2)	−2140 (2)	5063 (3)	107 (2)
C(3)	−854 (2)	−1725 (3)	5354 (3)	134 (2)
C(4)	−833 (2)	−985 (3)	6015 (3)	128 (2)
C(5)	−219 (1)	−621 (2)	6403 (3)	99 (1)
C(6)	−150 (2)	152 (3)	7088 (3)	123 (2)
C(7)	459 (2)	448 (2)	7414 (3)	125 (2)
C(8)	1040 (2)	−1 (2)	7081 (3)	96 (1)
C(9)	985 (1)	−749 (2)	6420 (2)	76 (1)
C(10)	355 (1)	−1098 (2)	6066 (2)	78 (1)
C(11)	−259 (2)	−2956 (2)	4313 (3)	152 (2)
O(12)	1523 (1)	−1217 (1)	6026 (2)	80 (1)
C(13)	2163 (1)	−810 (2)	6048 (2)	74 (1)
C(14)	2643 (1)	−1403 (2)	5403 (2)	65 (1)
N(15)	2598 (1)	−1506 (1)	4013 (2)	60 (1)
N(16)	3402 (1)	−4361 (1)	3904 (2)	69 (1)
C(17)	3931 (1)	−4868 (2)	3838 (2)	81 (1)
C(18)	3943 (2)	−5692 (2)	4379 (3)	97 (2)
C(19)	3397 (2)	−5985 (2)	4972 (3)	102 (1)
C(20)	2819 (2)	−5478 (1)	5067 (2)	80 (1)
C(21)	2223 (2)	−5745 (2)	5639 (3)	102 (1)
C(22)	1691 (2)	−5220 (2)	5688 (3)	96 (1)
C(23)	1713 (1)	−4395 (2)	5178 (2)	78 (1)
C(24)	2288 (1)	−4115 (1)	4608 (2)	63 (1)
C(25)	2849 (1)	−4652 (1)	4522 (2)	64 (1)
C(26)	4525 (1)	−4546 (2)	3137 (3)	115 (2)
O(27)	2359 (1)	−3323 (1)	4080 (1)	71 (1)
C(28)	1809 (1)	−2745 (2)	4163 (3)	76 (1)
C(29)	1990 (1)	−1918 (1)	3530 (3)	72 (1)
N(30)	2889 (1)	1455 (1)	6407 (2)	72 (1)
C(31)	2735 (1)	2025 (2)	7284 (3)	84 (1)
C(32)	3213 (2)	2581 (2)	7851 (3)	103 (1)
C(33)	3856 (2)	2532 (2)	7491 (3)	110 (2)
C(34)	4047 (1)	1948 (2)	6550 (3)	84 (1)
C(35)	4699 (1)	1884 (2)	6086 (3)	103 (1)
C(36)	4850 (2)	1315 (2)	5173 (3)	101 (1)
C(37)	4357 (1)	765 (2)	4658 (3)	81 (1)
C(38)	3720 (1)	815 (1)	5089 (2)	67 (1)
C(39)	3543 (1)	1411 (1)	6034 (2)	68 (1)
C(40)	2019 (1)	2067 (2)	7691 (2)	107 (1)
O(41)	3206 (1)	319 (1)	4636 (1)	71 (1)
C(42)	3341 (1)	−255 (2)	3598 (2)	72 (1)
C(43)	2710 (1)	−724 (1)	3273 (2)	69 (1)
W(1)	3687 (1)	−2586 (1)	3355 (2)	103 (1)
W(2)	4240 (1)	−1735 (2)	1206 (2)	189 (2)
H(W1)	3524 (22)	−3108 (29)	3521 (42)	322 (12)
H′(W1)	3294 (30)	−2140 (33)	3419 (54)	322 (12)

* Equivalent isotropic U calculated from anisotropic U except for H atoms.

Table 2. *Bond lengths* (Å)

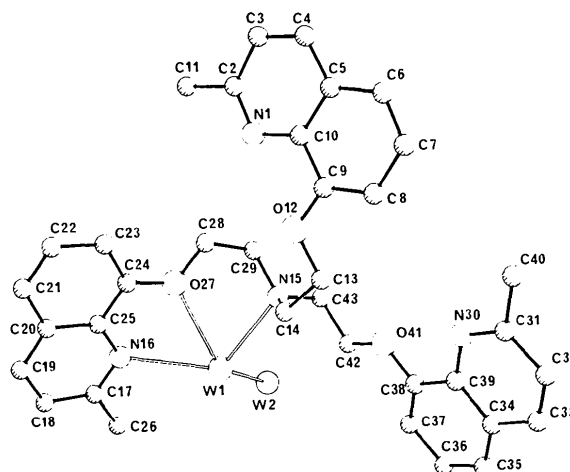|			
C(2)—N(1)	1·319 (5)	C(2)—C(3)	1·406 (7)
C(3)—C(4)	1·347 (7)	C(4)—C(5)	1·412 (6)
C(5)—C(6)	1·411 (6)	C(6)—C(7)	1·346 (7)
C(7)—C(8)	1·407 (7)	C(8)—C(9)	1·363 (5)
C(9)—O(12)	1·369 (4)	C(10)—N(1)	1·359 (4)
C(10)—C(5)	1·420 (5)	C(10)—C(9)	1·421 (5)
C(11)—C(2)	1·498 (6)	C(13)—O(12)	1·433 (4)
C(13)—C(14)	1·503 (5)	C(14)—N(15)	1·467 (4)
C(17)—N(16)	1·325 (5)	C(17)—C(18)	1·405 (5)
C(17)—C(26)	1·495 (5)	C(18)—C(19)	1·346 (6)
C(19)—C(20)	1·408 (6)	C(20)—C(21)	1·408 (6)
C(20)—C(25)	1·413 (4)	C(21)—C(22)	1·346 (6)
C(22)—C(23)	1·396 (5)	C(23)—C(24)	1·376 (5)
C(24)—C(25)	1·407 (4)	C(24)—O(27)	1·363 (4)
C(25)—N(16)	1·370 (4)	C(28)—O(27)	1·429 (4)
C(28)—C(29)	1·500 (5)	C(29)—N(15)	1·462 (4)
C(31)—N(30)	1·318 (4)	C(31)—C(32)	1·420 (6)
C(31)—C(40)	1·503 (5)	C(32)—C(33)	1·351 (7)
C(33)—C(34)	1·400 (5)	C(34)—C(35)	1·405 (5)
C(34)—C(39)	1·416 (5)	C(35)—C(36)	1·343 (6)
C(36)—C(37)	1·412 (5)	C(37)—C(38)	1·363 (5)
C(38)—C(39)	1·408 (4)	C(38)—O(41)	1·369 (4)
C(39)—N(30)	1·375 (4)	C(42)—O(41)	1·438 (4)
C(42)—C(43)	1·498 (5)	C(43)—N(15)	1·466 (4)
H(*W*1)—*W*(1)	0·896 (46)	H'(*W*1)—*W*(1)	1·053 (57)

Fig. 1. Perspective plot of the complex showing the numbering scheme. Radii have arbitrary values.

Coordinates of all refined atoms are listed in Table 1;* a plot of the complex showing the numbering scheme is presented in Fig. 1. Bond lengths and angles are given in Tables 2 and 3.

Table 3. *Bond angles* (°)

C(2)—N(1)—C(10)	116·8 (3)	N(1)—C(2)—C(3)	123·5 (4)
N(1)—C(2)—C(11)	116·2 (4)	C(3)—C(2)—C(11)	120·2 (4)
C(2)—C(3)—C(4)	119·1 (5)	C(3)—C(4)—C(5)	121·0 (5)
C(4)—C(5)—C(6)	124·9 (4)	C(4)—C(5)—C(10)	115·0 (4)
C(6)—C(5)—C(10)	120·1 (4)	C(5)—C(6)—C(7)	120·4 (5)
C(6)—C(7)—C(8)	121·1 (5)	C(7)—C(8)—C(9)	119·5 (4)
C(8)—C(9)—C(10)	121·7 (4)	C(8)—C(9)—O(12)	123·6 (4)
C(10)—C(9)—O(12)	114·7 (3)	N(1)—C(10)—C(5)	124·5 (3)
N(1)—C(10)—C(9)	118·4 (3)	C(5)—C(10)—C(9)	117·1 (3)
C(9)—O(12)—C(13)	117·8 (3)	O(12)—C(13)—C(14)	107·3 (3)
C(13)—C(14)—N(15)	118·9 (3)	C(14)—N(15)—C(29)	115·7 (3)
C(14)—N(15)—C(43)	115·2 (3)	C(29)—N(15)—C(43)	108·4 (3)
C(17)—N(16)—C(25)	118·7 (3)	N(16)—C(17)—C(18)	122·4 (4)
N(16)—C(17)—C(26)	117·8 (3)	C(18)—C(17)—C(26)	119·8 (4)
C(17)—C(18)—C(19)	119·1 (4)	C(18)—C(19)—C(20)	121·1 (4)
C(19)—C(20)—C(21)	124·6 (4)	C(19)—C(20)—C(25)	116·5 (4)
C(21)—C(20)—C(25)	118·9 (4)	C(20)—C(21)—C(22)	120·9 (4)
C(21)—C(22)—C(23)	121·2 (4)	C(22)—C(23)—C(24)	119·4 (4)
C(23)—C(24)—C(25)	120·8 (3)	C(23)—C(24)—O(27)	123·9 (3)
C(25)—C(24)—O(27)	115·3 (3)	N(16)—C(25)—C(20)	122·1 (3)
N(16)—C(25)—C(24)	119·1 (3)	C(20)—C(25)—C(24)	118·8 (3)
C(24)—O(27)—C(28)	117·7 (3)	O(27)—C(28)—C(29)	109·0 (3)
N(15)—C(29)—C(28)	115·6 (3)	C(31)—N(30)—C(39)	117·7 (3)
N(30)—C(31)—C(32)	122·9 (4)	N(30)—C(31)—C(40)	117·4 (3)
C(32)—C(31)—C(40)	119·7 (4)	C(31)—C(32)—C(33)	119·3 (4)
C(32)—C(33)—C(34)	120·4 (4)	C(33)—C(34)—C(35)	123·7 (4)
C(33)—C(34)—C(39)	117·0 (4)	C(35)—C(34)—C(39)	119·3 (4)
C(34)—C(35)—C(36)	120·8 (4)	C(35)—C(36)—C(37)	120·9 (4)
C(36)—C(37)—C(38)	119·5 (4)	C(37)—C(38)—C(39)	121·1 (3)
C(37)—C(38)—O(41)	123·8 (3)	C(39)—C(38)—O(41)	115·1 (3)
N(30)—C(39)—C(34)	122·7 (3)	N(30)—C(39)—C(38)	118·9 (3)
C(34)—C(39)—C(38)	118·4 (3)	C(38)—O(41)—C(42)	117·9 (3)
O(41)—C(42)—C(43)	108·1 (3)	N(15)—C(43)—C(42)	114·9 (3)
H(*W*1)—*W*(1)—H'(*W*1)	108 (4)		

Omission of 16 low-angle reflexions and application of an empirical extinction correction [$x = 2·4$ (1) $\times 10^{-7}$ where $F_c^* = F_c(1 - xF_c^2/\sin \theta)$] led to final $R = 0·068$, $R_w = 0·051$ and $R_G = 0·042$ where $R = \sum \Delta/\sum F_o$, $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$, $R_G = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$, $\Delta = |F_o| - |F_c|$ and $w = 1/\sigma^2(F_o)$.

Discussion. Organic polar molecules or ions such as malononitrile, tetramethylenediammonium or thiourea can replace metal cations in host–guest complexes of cyclic crown ethers (Kaufmann, Knoechel, Kopf, Oehler & Rudolph, 1977; Goldberg, 1977) and also of linear oligoethers (Weber & Saenger, 1980b). Normally, water is only involved in linking ligands, as in the dimeric structure of a complex (Weber & Saenger, 1980a). In the present compound, however, one water molecule is fixed within one loop of the tripod ligand via hydrogen bonds, the geometry of the wrapping chain being close to that of a fragment of 18-crown-6 complexing a suitable metal ion (Dunitz, Dobler, Seiler & Phizackerley, 1974). The O atom of water molecule *W*(1) and the hetero-atoms N(16), O(27) and N(15) are coplanar within 0·12 Å. Angles with *W*(1) as the vertex are about 54 and 59° (Table 4), and the N(16)···O(27) and O(27)···N(15) distances, 2·656 (3) and 2·880 (3) Å, are in the same range as *W*(1)···N(16), 2·891 (3), *W*(1)···O(27), 3·007 (4), and *W*(1)···N(15), 2·851 (4) Å. The respective H···hetero-atom distances and angles (Table 4) indicate one weak O(ether)···H—O and two relatively strong N(aromatic)···H—O hydrogen bonds and a further weak interaction between H(*W*1) and O(27). *W*(1) probably accepts another hydrogen bond from

Table 4. *Interatomic distances (Å) and angles (°) within the system of hydrogen bonds*

W(1)···N(15)	2·851 (4)	H'(W1)···N(15)	1·83 (6)	W(1)–H'(W1)···N(15)	163 (5)	N(15)···W(1)···N(16)	111·5 (2)
W(1)···N(16)	2·891 (3)	H(W1)···N(16)	2·01 (5)	W(1)–H(W1)···N(16)	166 (4)	N(15)···W(1)···O(27)	58·8 (2)
W(1)···O(27)	3·007 (4)	H(W1)···O(27)	2·44 (6)	W(1)–H(W1)···O(27)	122 (5)	N(16)···W(1)···O(27)	53·5 (3)
W(1)···W(2)	2·852 (5)					W(2)···W(1)···N(15)	102·8 (4)
						W(2)···W(1)···N(16)	133·1 (4)
						W(2)···W(1)···O(27)	137·1 (5)

Table 5. *Relevant torsion angles (°)*

N(1)–C(10)–C(9)–O(12)	1·1 (4)	C(9)–O(12)–C(13)–C(14)	−172·0 (3)	C(13)–C(14)–N(15)–C(29)	−66·3 (4)
N(30)–C(39)–C(38)–O(41)	−0·7 (4)	C(38)–O(41)–C(42)–C(43)	−180·0 (3)	C(13)–C(14)–N(15)–C(43)	61·5 (4)
N(16)–C(25)–C(24)–O(27)	−1·8 (4)	C(24)–O(27)–C(28)–C(29)	179·9 (3)	C(14)–N(15)–C(29)–C(28)	−50·3 (4)
C(10)–C(9)–O(12)–C(13)	164·2 (3)	O(12)–C(13)–C(14)–N(15)	72·4 (4)	C(14)–N(15)–C(43)–C(42)	52·4 (4)
C(39)–C(38)–O(41)–C(42)	175·1 (3)	O(41)–C(42)–C(43)–N(15)	−87·0 (3)	C(28)–C(29)–N(15)–C(43)	178·5 (3)
C(25)–C(24)–O(27)–C(28)	−178·8 (3)	O(27)–C(28)–C(29)–N(15)	−55·6 (4)	C(29)–N(15)–C(43)–C(42)	−176·3 (3)

the second water molecule $W(2)$. There are further weak interactions between a symmetry-transformed $W(2)$ $(x, -y - 0·5, 0·5 + z)$ and both $W(1)$ [3·347 (5)] and N(16) [3·387 (4) Å]. The loss of ligand C_3 symmetry is reflected by dihedral and torsion angles: the plane of the 2-methylquinolyl group of the coordinating loop and the planes of the aromatic systems N(1) to C(10) and N(30) to C(39) subtend angles of 57 (2) and 65 (2)° respectively, whilst the latter planes are inclined at 19 (3)° to each other. Torsion angles along N(15)···N(16), N(15)···N(1), and N(15)···N(30) are consistent with one another (see first two columns in Table 5)* but deviations from ideal values, C–C–O–C *trans* and O–C–C–N *gauche* (Truter, 1973), are lowest along the coordinating chain. Torsion angles involving N(15) as an inner atom, however, are in four cases out of six *gauche* instead of the expected *trans*.

Rotation of one non-interacting residue around N(15)–C(14) and the other one around C(42)–C(43) such that only the signs of the respective torsion angles are changed would bring all the hetero-atoms into coordinating positions and make the ligand act as a cryptand. This is actually observed in a complex with K^+ (Weber & Saenger, unpublished). Since mean interatomic distances $K^+ \cdots O$ (*ca* 2·8) and $N \cdots O$ (*ca* 2·9) as well as $O \cdots O$ (*ca* 2·7 Å) are comparable (*International Tables for X-ray Crystallography*, 1968), the spherically symmetric e^--acceptor properties of K^+ as opposed to the directional e^--acceptor

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* A complete list of torsion angles has been deposited. See previous footnote.

properties of water *via* H atoms and the strong $N \cdots H$ bonds must be responsible for this difference. A hexaquo complex with one water molecule in each loop would probably be less stable; models indicate that N(15) would not be able to coordinate all three waters simultaneously, and the O(ether)$\cdots$H interaction can usually be considered weak (Weber & Saenger, 1980b).

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