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Bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium chloride monohydrate, an anion receptor complex

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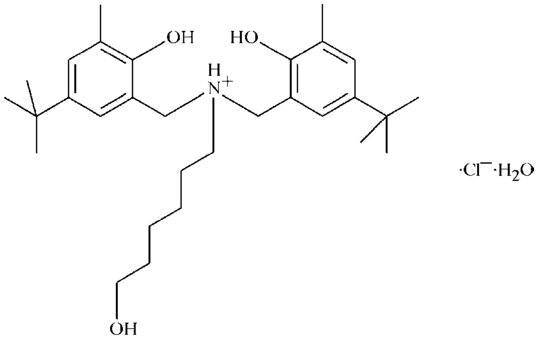
In the title compound, $C_{30}H_{48}NO_3^+\cdot Cl^-\cdot H_2O$, the cation acts with a water molecule as a chloride ion receptor. The chloride ion forms three strong intramolecular hydrogen bonds. The water molecule forms both an intramolecular bridge between one phenol H atom and the chloride ion, and an intermolecular link to the aliphatic alcohol O atom. Weak intermolecular C—H···Cl and C—H ···O hydrogen bonds provide additional packing interactions.

Comment

Studies of anion and cation receptors have gained increasing attention lately owing to their importance in biological, environmental and supramolecular chemistry (Amendola *et al.*, 2006; Bianchi *et al.*, 1997; Cormode *et al.*, 2006; Gale *et al.*, 2006). For instance, a large majority of substrates and cofactors engaged in biological processes are anions; among them, phosphate and chloride ions are of special interest because of their ubiquitous presence in biological systems. Indeed, this focus has led to a new branch of chemistry defined as anion coordination chemistry (Bowman-James, 2005). A significant difference between anion and cation bond formation is that cations usually involve strong coordinate bonds. Conversely, anion binding is significantly weaker, often involving multiple hydrogen-bond formation acting in concert with electrostatic interactions (Amendola *et al.*, 2006; Goetz *et al.*, 2006; Wichmann *et al.*, 2006).

The selectivity of an anion receptor is an important factor. Inorganic anions can, in principle, be discriminated on the basis of geometrical parameters, *viz.* size and shape (Bianchi *et al.*, 1997). Generally, an anion receptor can be either positively charged or a neutral molecule; in the former case, the interaction is based mainly on electrostatic forces and in the latter case on hydrogen bonds (Amendola *et al.*, 2006). Very high selectivity towards anions can be achieved with proteins, which form strong and selective bonds to the anions even in a highly competitive aqueous medium. Thus, amides are used as model receptors for anions (Chmielewski *et al.*, 2006). Many molecular topologies based on amine and phenol functions as building blocks of the molecular system have been synthesized for selective anion or cation binding (Ambrosi *et al.*, 2006; Wichmann *et al.*, 2006). However, only a few cationic aminoalkylbisphenols and aminotrisphenols have been shown to form salt-like structures with anions; examples are those in which the phosphates and carbonates act as anions (Chandrasekaran *et al.*, 1999, 2003). To our knowledge, no structural studies of aminoalcoholbisphenols or their hydrochlorides have been reported.



(I)

In light of the factors mentioned above we introduce the compound 6-[bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)-amino]hexan-1-ol, which as an ammonium cation serves as a chloride ion receptor. The compound was prepared as part of our search for new low molecular weight organic molecules for uranyl ion complexation and extraction (Sopo *et al.*, 2007). During the purification process, the ligand was transformed to a hydrochloride, which was extracted in chloroform; the

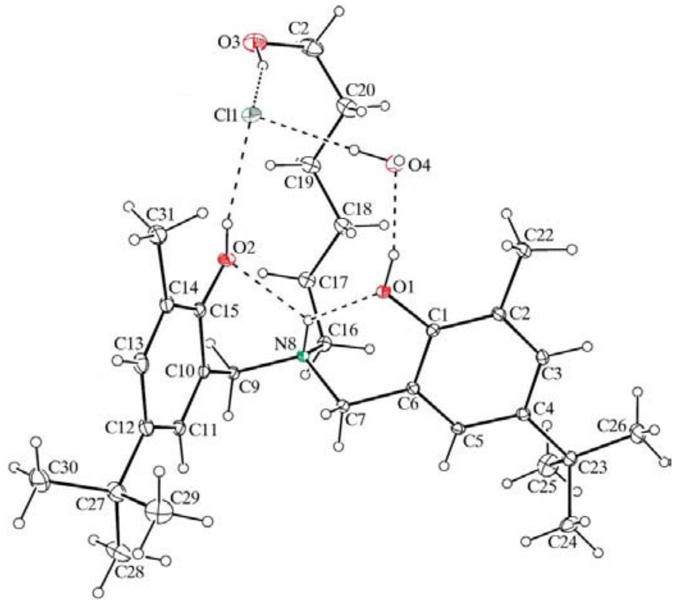


Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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compound crystallized from this as a monohydrate, (I). Although (I) contains a cation and an anion in the solid state, it acts like a molecule with no net charge and thus it dissolves easily into some nonpolar solvents, *e.g.* chloroform. Therefore, we believe the cation of compound (I) either can act as a receptor at interfaces for anions, or is able to solubilize or transport anions into slightly polar or nonpolar organic solvents.

The basic structural unit of (I) consists of an bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium cation, a chloride ion and a water molecule (Fig. 1). Selected bond lengths and angles are presented in Table 1. The chloride ion is surrounded by the OH groups of the phenol groups and the water molecule, and most of the polar part of the compound is located in the polar cavity. The outer surface of the zwitterion is lipophilic, and this allows for an easy transport of the chloride ion into organic solvents. The geometries around phenol atoms O1 and O2 and atom N8 are normal. The symmetry of atom N8 is slightly distorted tetrahedral, with bonding angles in the range 106.6 (13)–112.46 (15)°.

The chloride anion forms three strong intramolecular O—H···Cl1 hydrogen bonds, namely one to phenol atom H2O, one to aliphatic alcohol atom H3O and one to the H atom of the water molecule (H42O) (Table 2). The H···Cl1 interaction lengths of the hydrogen bonds range from 2.15 (2) to 2.29 (2) Å. In addition, the chloride ion forms one intermolecular C—H···Cl hydrogen bond. The coordination number of the chloride ion is 3+1 (three strong and one weak hydrogen bond). The H atom of the ammonium group does not form a hydrogen bond to the chloride ion but forms bifurcated hydrogen bonds to two phenol O atoms and thus stabilizes the conformation of the ligand (Fig. 1). The values of the hydrogen-bond parameters are comparable to literature values (Steiner, 2002; Desiraju & Steiner, 1999).

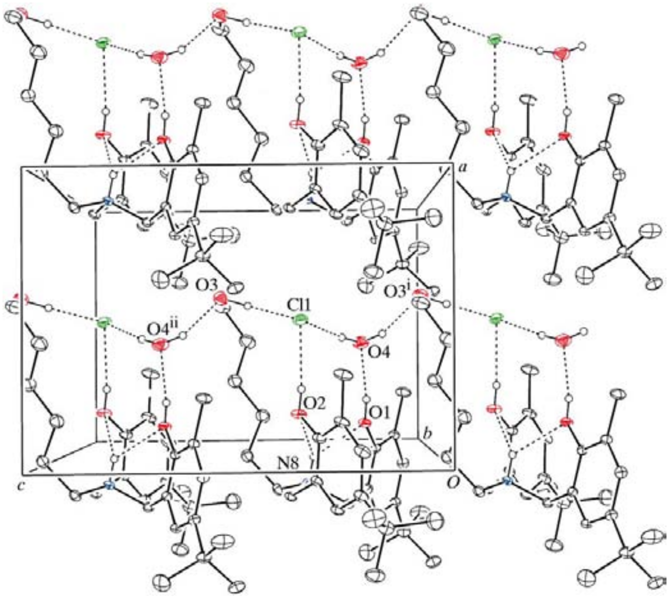

Figure 2
The crystal packing of (I), viewed in the *ac* plane, showing the hydrogen-bonding pattern. Selected O, N and Cl atoms have been labelled. Weak C—H···*X* hydrogen-bond interactions and CH hydrogens have been omitted for clarity. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.]

The intermolecular packing of (I) in the *ac* plane is depicted in Fig. 2. Two of the weak intermolecular C—H···Cl1 bonds provide some cohesion between molecules along the *a* axis (these have been omitted from the figure for reasons of clarity). The H atoms of the water molecule form hydrogen bonds to the chloride ion and to aliphatic alcohol atom O3 in an adjacent unit, forming a hydrogen-bond chain along the *c* axis (Fig. 2). Thus, the water molecule plays an important dual (intra- and intermolecular) role by acting as a bridge between the phenol H atom, the aliphatic alcohol O atom and the chloride ion.

Experimental

The title compound was prepared as described by Sopo *et al.* (2007). Crystals suitable for single-crystal X-ray analysis were obtained at room temperature by slow evaporation of the recrystallization solvent (chloroform).

Crystal data

$C_{30}H_{48}NO_3{}^+\cdot Cl^-\cdot H_2O$
$M_r = 524.16$
Monoclinic, $P2_1/c$
$a = 9.3064$ (2) Å
$b = 25.5909$ (9) Å
$c = 13.0271$ (4) Å
$\beta = 90.306$ (2)°
$V = 3102.48$ (16) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.16$ mm^{-1}
$T = 173$ (2) K
0.30 × 0.22 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
10477 measured reflections
6003 independent reflections
4396 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.120$
$S = 1.03$
6003 reflections
351 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.373 (2)	C7—N8	1.510 (2)
O2—C15	1.364 (2)	N8—C16	1.509 (2)
O3—C21	1.431 (3)	N8—C9	1.515 (2)
O1—C1—C2	124.09 (16)	C7—N8—C9	110.41 (14)
O1—C1—C6	115.43 (16)	O2—C15—C10	115.32 (18)
C16—N8—C7	112.46 (15)	O2—C15—C14	124.63 (17)
C16—N8—C9	111.20 (14)	O3—C21—C20	114.2 (2)

H atoms of the OH and NH groups were refined isotropically with fixed displacement parameters (1.2$U_{\rm eq}$ of the host atom). The H3O—O3 distance was refined with a distance restraint of 0.90 (2) Å. H atoms on C atoms were included in calculated positions, with isotropic displacement parameters of 1.2–1.5 times $U_{\rm eq}$ of the host atom.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O$\cdots$O4	0.79 (2)	1.89 (2)	2.672 (2)	166 (2)
O2—H2O$\cdots$Cl1	0.80 (2)	2.29 (2)	3.0686 (15)	162 (2)
O3—H3O$\cdots$Cl1	0.947 (17)	2.146 (18)	3.0663 (18)	164 (2)
O4—H42O$\cdots$Cl1	0.90 (3)	2.19 (3)	3.0773 (19)	172 (2)
O4—H41O$\cdots$O3^{i}	0.84 (3)	1.98 (3)	2.790 (3)	160 (3)
N8—H8$\cdots$O1	0.87 (2)	2.16 (2)	2.803 (2)	130.5 (17)
N8—H8$\cdots$O2	0.87 (2)	2.29 (2)	2.881 (2)	125.2 (17)
C9—H9$B\cdots$Cl1^{iii}	0.99	2.66	3.629 (2)	165
C16—H16$A\cdots$O3^{iii}	0.99	2.60	3.581 (3)	174

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x-1, y, z$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3048). Services for accessing these data are described at the back of the journal.

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