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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gsch20</u>

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Published online: 18 Nov 2013.

To cite this article: Md. Najbul Hoque, Arghya Basu & Gopal Das (2014) Structural insight into the anion-water cluster: stabilised by alcohol and carboxylic acid containing tripodal ligand, Supramolecular Chemistry, 26:5-6, 392-402, DOI: <u>10.1080/10610278.2013.844811</u>

To link to this article: <u>http://dx.doi.org/10.1080/10610278.2013.844811</u>

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Structural insight into the anion-water cluster: stabilised by alcohol and carboxylic acid containing tripodal ligand

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(Received 13 June 2013; accepted 6 September 2013)

A new flexible N-bridged, unsymmetrical, water-soluble tripodal ligand (L) bearing alcohol and carboxylic acid groups has been synthesised and its solid-state interaction with anions has been investigated. The fully deprotonated ligand encapsulates a sodium cation in a half cryptand bowl-shaped cavity (1). The chloride complex 2, contains a cyclohexane-like water cluster incorporating ligand OH groups. However, complexes with bromide and nitrate (3 and 4) are dimeric. Tetrahedral clusters containing two water molecules and two anions were found in complexes 3 and 4. Perchlorate complex 5 forms perchlorate– methanol adducts. Complex 1 forms a hydrophilic cation–water channel and complexes 2-4 form anion–water channels between the hydrophobic layers of the naphthalene moieties. Complexes 2, 5 and 3, 4 are isostructural in nature having similar packing structures.

Keywords: water soluble tripodal ligand; sodium encapsulation; tetrahedral anion-water cluster; crystal structure; species distribution curve

Introduction

H-bonded supramolecular self-assembly, anion-water, water-water interactions are phenomena relevant to the structural properties of water or anion-water clusters. The roles of these clusters in different chemical and biochemical processes are well documented. Indeed, a plethora of reports including theoretical (1) and experimental (2) studies have been discussed to reveal the role of water or anion-water clusters in protein foldingunfolding, protein function and mobility of anions. Living systems exploit the varied H-bond motifs around different anions during their transportation between cellular systems. The structural characterisation of water cluster or anion-water cluster is also important to restore the knowledge about crystallisation of proteins, interaction of water with enzymes (3), stabilisation and functions of biomolecules, (4) solvation chemistry, mobility of anions in water-membrane interfaces and electrical phenomena in ionosphere and troposphere. Hence, scientists investigated hydrated anionic clusters (5) as the species play a key role in signal transduction (6) and in atmospheric chemistry (7), biochemistry and biology (8). Recent advances in supramolecular chemistry have allowed the study of self-assembled ion-water clusters through electrostatic, π -stacking and Van der Waals interactions. Recently, Bowman-James (9) reported the nature of binding modes for different anions in a pragmatic way which helps in the design of the supramolecular architecture required for the self-assembly of anions with host molecules. However, the challenges in the anion coordination chemistry can be attributed to the various geometries, properties of anions and high solvation energies (10). Most recently, Bowman-James et al. reported a tetrahedral molecule that encapsulated a tetrahedron of water molecules which in turn holds a small guest (water or fluoride ion), and few other reports also explain waterwater and water-anion interactions (11). In our continuing effort (12) to explore the structural significance of anionwater clusters, herein we demonstrate the formation of anion-water cluster of varying geometries as well as the encapsulation of a sodium ion in the cleft of a tripodal ligand and the formation of sodium-water channels. Consequently, we are able to explain the interaction patterns of different anions such as spherical chloride and bromide anions, planar nitrate and tetrahedral perchlorate anion with water and tripodal host. Higher solubility in polar solvent is assisted by -OH and -COOH groups in the ligand and these also triggered the formation of water clusters (2b, 13).

Results and discussion

Crystal structure studies

$[LNa_2 \cdot 6H_2O](1)$

Structural elucidation by single crystal X-ray analysis revealed that the sodium salt of the ligand crystallises in monoclinic $P2_1/c$ (Z = 4) to yield the complex

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[LNa₂·6H₂O] (1). Figure 1(a) shows the encapsulation of a sodium ion in the half crypt-like bowl-shaped cavity formed by the tripodal ligand. Sodium ion (Na₂) is encapsulated in the bowl-shaped cavity by six coordination bonds formed by three ethereal oxygen atoms, one water oxygen, one carboxylate oxygen and one apical nitrogen atom. The coordinate bonds between Na₂ and different ethereal oxygen atom and apical nitrogen atom are strong enough for stabilising Na₂ in the cavity. One of the carboxylate groups inclined towards the cavity and interacted strongly with the encapsulated sodium ion (Na₂). The torsion angle for the arm N1-C3-C4-O2

which forms ionic bond with interior sodium ion (Na_2) is little more (65°) than the rest of the two arms with average angle 53°. The ethereal bond distances for O1–O5, O2–O5, O1–O2 are 3.952, 3.606 and 4.560 Å, respectively, and they formed a half crypt-like cavity. The torsion angle and ethereal bond distances are less than the reported value (14), suggesting the folded conformation of the ligand favouring the encapsulation of sodium ion in the bowl-shaped cavity. A detailed structural study showed that a metallacrown-like structure containing Na–O–Na coordinate bond and O···O interaction was observed and is shown Figure 1(b). Crystal packing diagram ascribed in



Figure 1. (Colour online) (a) Perspective view of $[LNa_2 \cdot 6H_2O]$ (1) showing the encapsulation of sodium ion in the bowl-shaped cavity within the tripodal platform. (b) Metallacrown-like framework constructed from Na—Ow—Na coordinate bond and O···O interaction. (c) Crystal packing along the *b*-axis depicting sodium-water channel entrapped within hydrophobic environment. (d) Close-up view of zig-zag cation–water channel. (e) Hexa-aqua sodium ion-assisted supramolecular self-assembled architecture.

Table 1. Selected bond distances and bond angles.

D···A	$d(\mathbf{D}\cdots\mathbf{A})$ Å	d(H···A) Å	∠(DHA)/°
$[LNa_2 \cdot 6H_2O]$			
Na1···O8	2.323(4)	-	-
Na1···O9	2.521(4)	-	-
Na1···O10	2.325(4)	-	-
Na1···O11	2.743(6)	-	-
Na1···O12	2.533(5)	-	-
Na2· · ·N1	2.513(3)	-	-
Na2···O1	2.471(4)	-	_
Na2···O2	2.629(3)	-	-
Na2···O4	2.225(4)	-	-
Na2···O5	2.439(3)	-	-
Na2···O13	2.291(4)	-	-
O3···O12	2.929(6)	-	_
0409	2.862(5)	-	-
0608	2.652(6)	-	_
$06 \cdot \cdot \cdot C20^{a}$	3.298(6)	2.397(4)	163.4(3)
07011	2.826(7)	-	_
O7···O12	2.830(5)	-	-
0901	2.860(5)	2.075(3)	160.2(3)
01003	2.798(6)	-	_
01201	2.815(5)	-	-
01308	3009(6)	-	_
01309	2.791(5)		
$[LH_3 \cdot Cl \cdot 3H_2O]$			
Cl1···O1 ^b	3.072(4)	2.271(2)	165.0(0)
$Cl1 \cdots O10(w)^b$	3.247(4)	-	_
$O8(w) \cdots O9(w)$	1.970(1)	_	_
O8(w)···O1	2.970(1)	_	_
O9(w)···O1	2.846(5)	_	_
O9(w)···O7	2.653(7)	_	_
$O9(w) \cdot \cdot \cdot C16^{b}$	3.161(6)	2.831(3)	100.9(1)
O10(w)· · · O4	2.708(5)	1.914(4)	162.4(3)
$C4 \cdots O7^{c}$	3.482(6)	2.515(4)	174.6(2)
$C4 \cdot \cdot \cdot O3^d$	3.381(6)	2.408(6)	177.3(3)
$C16 \cdot \cdot \cdot O3^d$	3.449(5)	2.519(4)	160.8(2)
N1···O6 ^e	2.804(4)	1.980(3)	135.0(2)
$C7 \cdot \cdot \cdot C12^d$	3.763	2.892	156.4(3)
$[LH_3 \cdot Br \cdot 2H_2O]$			
$Br1 \cdots O7^{f}$	3.234(5)	2.4470(7)	160.9(4)
$Br1 \cdots O8(w)^g$	3.329(7)		
$Br1 \cdots C1^{h}$	3.819(5)	3.035(7)	138.9(3)
Br1···C16 ⁱ	3.801(7)	3.0086(8)	139.7(4)
$O9(w) \cdots O8(w)$	2.936(9)	_	
$O9(w) \cdots O1^{j}$	2.684(7)	_	_
$O9(w) \cdots O1^k$	2.794(8)	_	_
$04 \cdot \cdot \cdot C17^{i}$	3.422(8)	2.471(5)	166.7(4)
06···C3	3.425(8)	2.486(5)	162.9(4)
$O6 \cdot \cdot \cdot C17^{f}$	3.379(9)	2.408(6)	179.8(4)
$N1 \cdots O3^{f}$	2.775(7)	2.030(5)	134.0(4)
$[LH_3:NO_3:2H_2O]$			
N1···06 ¹	2.805(5)	2.210(6)	122.0(4)
01012	2.816(7)	2.078(5)	149.5(3)
$O3 \cdot \cdot \cdot C4^m$	3.425(6)	2.461(4)	175.5(3)
$O3 \cdot \cdot \cdot C16^m$	3.440(6)	2.512(4)	161.0(3)
0408	2.685(7)	_	_
O8···O11(w)	2.780(1)	_	_
$08 \cdots C3^{1}$	3.410(1)	2.654(8)	134.8(3)
$09 \cdots C1^n$	3.340(1)	2.580(1)	134.7(4)
$O10 \cdot \cdot \cdot C17^{\circ}$	3.390(1)	2.460(1)	160.1(4)
011012	2.804(9)		_
<u> </u>	2.001())		

(Continued)

Table 1 - continued

D···A	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{A})$ Å	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A}) \ \mathbf{\mathring{A}}$	∠(DHA)/°
01207	2.703(6)	_	_
[LH ₃ ·ClO ₄ ·MeO	[H]		
$O3 \cdot \cdot \cdot C4^p$	3.455(6)	2.485(4)	177.1(3)
$O3 \cdot \cdot \cdot C16^p$	3.534(6)	2.594(4)	163.0(3)
$O7 \cdot \cdot \cdot C4^q$	3.475(6)	2.515(3)	170.6(3)
$O8 \cdots O1^r$	2.858(8)	2.254(6)	130.9(5)
$O8 \cdot \cdot \cdot C16^{s}$	3.578(8)	2.642(6)	162.4(3)
O9···O1	3.131(9)	2.438(6)	142.9(5)
$O11 \cdot \cdot \cdot O4^t$	2.740(1)	1.950(1)	162.4(4)
$O12 \cdot \cdot \cdot O1^{r}$	2.936(8)	2.181(7)	157.8(4)
$O12 \cdot \cdot \cdot O7^{u}$	2.647(5)	1.868(4)	168.3(3)
$a_{x,1/2-y,-1/2} + z;$	${}^{b}x, 1/2-y, -1/2 + z; {}^{c}x,$	$-1 + y_{,z}; \overset{d}{x}, 1.5 - y_{,-}$	$1/2 + z; e^{x}, y, z;$

 $\begin{array}{l} x_1, y_2, y_1, z_2 + z_1, x_1, y_2, y_1, y_2 + y_2, y_3, y_1, y_2 + y_2, y_3, y_1, y_2 + z_1, y_2, y_1, z_1 + z_1, z_1 + y_2, y_1, z_1 + z_1, z_1 + y_2, z_1 + z_1 + y_2, z_1 + z_1 + z_1 + y_2, z_1 + z_1$

Figure 1(c) showed the sodium-water cluster along the crystallographic b-axis where the sodium ion (Na₁) is pseudo-octahedrally arranged by water molecules and away from carboxylate group. The infinite hydrophilic sodiumwater channel propagates in a zig-zag fashion containing Na—Ow—Na linker as shown Figure 1(d). The formation of hydrophobic organic bilayer and hydrophilic hydrated sodium layer is very similar to the 'organic clay' structure reported by Atwood et al. (15). One of the carboxylate groups interacts with the interior sodium ion and oxygen atom of channel water having bond lengths $O3 \cdot O12 = 2.929(6)$ Å and $O3 \cdots O10 = 2.798(6)$ Å, respectively. Other free carboxylate groups linked with the adjacent moiety through C20H $-O_{\text{anionic}}$ and strong H-bond O7 \cdots O11 = 2.826(7) Å with the hydrated sodium ion which stabilises the sodiumwater channel. The axial water molecule of encapsulated sodium (Na₂) offers O13w-O9w-Na1-O8w-O13w nearly square geometry with the hydrated sodium ion (Na₁) of bond length $O13 \cdots O8 = 3.009(6)$ Å and $O13 \cdots O9 = 2.791(6)$ Å. The supramolecular self-assembly that resulted from strong H-bonding among hexa-aqua sodium water cluster and adjacent tripodal molecule is shown in Figure 1(e). In addition, some other weak interactions such as $C-H\cdots\pi$ and $C-H\cdots O_{anionic}$ also play the key role to generate 3D self-assembled architecture. The complete H-bonding interactions are given in Table 1.

$[LH_3 \cdot Cl \cdot 3H_2O]$ (2)

As the tripodal ligand contains several sites suitable for Hbonding and anion coordination, we moved forward to use this features to understand anion-water and water-water interactions. Acidification of **IV** with concentrated HCl yielded colourless crystals of **2** having a monoclinic space group $P2_1/c$ and Z = 4. Chloride ion forms a bridge between water and alcoholic oxygen via sufficiently strong Cl1···O1 = 3.072(5) Å and Cl1···HO1 = 2.271(2) Å interactions. Protonated apical nitrogen forms strong H-bond with two ethereal oxygen and a carboxylic oxygen having distances of N1···O1 = 2.776(4) Å, N1···O6 = 2.862 (4) Å and N1···O5 = 2.862 (4) Å, respectively.

The alcoholic -OH stays away from protonated NH and finally the tripodal unit became open and lost the bowl-shaped conformation. The torsion angle of two substituted arm is almost comparable with the sodium complex 1, but the torsion angle for the non-substituted arm is remarkably large $(N1-C1-C2-O1 = 157^{\circ})$ giving the open conformation with a greater separation between the ethereal oxygen atom O1 (~ 5.5 Å) and the oxygen atoms of other two arms (O2, O5). The detailed view (Figure 2(a)) showed that the asymmetric unit forms a centro-symmetric dimer consisting of chloride-water Hbonding motif and chair-like cyclohexane conformation. All four water molecules lie on the same plane in the chair structure and offer strong water-water interaction through H-bonding. The third water molecule interacts with chloride ion and carboxylic oxygen atom with bond



Hydrophilic anion-water layer

Figure 2. (Colour online) (a) Perspective view of the dimeric molecular structure bridged with water molecule having chair conformation and formation of water cluster. (b) Crystal packing of the complex 2 along *c*-axis showing hydrophobic layer formation and hydrophilic chloride–water channel which were entrapped between the organic layers.

distances O10···Cl1 = 3.247(4) Å and O10···O4 = 2.708 (5) Å. The packing diagram of the complex **2** along the *c*axis depicted in Figure 2(b) showed the formation of hydrophilic chloride-water channel between the hydrophobic layers. The weak interactions between carbonyl oxygen (O3) and aliphatic hydrogen H18, H8 and aromatic CH··· π also help to grow the molecular assembly.

$[LH_3 \cdot Br \cdot 2H_2O](3)$

We switched to larger spherical Br⁻ anion to understand the formation of anion-water cluster in the same system. The bromide complex $[LH_3 \cdot Br \cdot 2H_2O]$ (3) crystallised in a monoclinic space group C2/c with Z = 4 with two water molecules and exists as a centro-symmetric dimer. A detailed structural view revealed that three water molecules and two Br...OH (-COOH) interactions involved in the dimer formation as shown in Figure 3(a). The interaction between $O9w \cdots O4 = 2.684(7) \text{ Å}$ and $O9w \cdots O1 = 2.794(8) \text{ Å}$ are sufficiently strong to stabilise the dimer. Acidic group forms strong Br1···O7 = 3.234(5) Å and Br1···H-O7 = 2.447(7) A interactions, but alcoholic OH does not participate in H-bonding with Br-. Ethereal oxygen separation with nonsubstituted arm (O1-O2 = 5.606 Å, O1-O5 = 5.488 Å)and torsion angle value (N1-C1-C2-O1 = 153.7°) again suggests the unfolded conformation of 3 like anion complex 2. The *endo*-oriented H-atom of the protonated bridgehead nitrogen offers H-bonding with ethereal oxygen atoms (average distance 2.75 Å) and oxygen of the acid group $N1 \cdots O3 = 2.775(7)$ Å. Unlike the simple linear $Cl \cdots H$ —Ow interaction with the ligand as in complex 2, here we observed a bromide-water tetrahedral motif assigned as $H_2O \cdot \Sigma 2H_2O$, $2Br^-$ illustrated in Figure 3(b). The central water molecule (O8) offers discrete anion coordinating tetrahedron motif having a bond angle between $\angle Br1 - O8w - Br1 = 108.3(3)^{\circ} \text{ and } \angle Br1 - O8w - O9w =$ $107.0(4)^{\circ}$ which is little more than the ideal tetrahedral bond angle of water molecule, whereas ∠O9w-O8w- $O9w = 102.8(4)^{\circ}$ is comparable with the ideal one. The discrete tetrahedron motif is stabilised by relatively strong $O8w \cdots O9w = 2.936(9) \text{ Å}$ and $O8w \cdots Br1 = 3.329(7) \text{ Å}$ interactions. The tetrahedral unit gave two types of tetrahedron edges Ow-Ow, Ow-Br1 with certain distances and angles given in the Table 2. Complex 3 contains a hydrophobic chain of ligand moieties and the bromidewater which are entrapped between the layers along *c*-axis.

$[LH_3 \cdot NO_3 \cdot 2H_2O]$ (4)

At this point of study, we examined the effect of planar ion and its interaction with water. Nitrate complex **4** crystallises in a monoclinic space group C2/c with Z = 4, as the centro-symmetric dimer contains two nitrates and three water molecules like the bromide complex (**3**). The salts **3** and **4** are isostructural in nature and have identical packing motif.



Figure 3. (Colour online) (a) Perspective view depicting $Br \cdots OH$ (acidic) bridged dimeric structure containing pentamer of water and -OH. (b) Discrete tetrahedral bromide–water motif $H_2O \cdot \Sigma 2H_2O$, $2Br^-$. (c) Crystal packing along *c*-axis showing inclusion of bromide– water cluster between hydrophobic layers.

The crystal structure showed that nitrate complex also formed a pentameric motif containing water and -OH like complex **3**, which is mainly stabilised by several H-bonding as depicted in Figure 4(a). The structure is constructed via the formation of several strong H-bonds such as $O11w\cdots O12w = 2.804(9)$ Å, $O1\cdots O12w = 2.816(7)$ Å and $O7\cdots O12w = 2.703(6)$ Å. The crystal structure revealed that one water molecule is surrounded by another two water molecules and two nitrate ions to form anion coordinated tetrahedral water motif of formula $H_2O\cdot\Sigma 2H_2O$, $2NO_3^-$. The tetrahedron motif having an angle between nitrate and water, $\angle O12w-O11w-O8_{NO_3} = 125.1(5)^\circ$, two nitrates \angle

 $O8_{NO_3}$ —O11w—O8_{NO_3} = 120.3(5)° and two water molecules $\angle O12w$ —O11w—O12w = 112.2(5)° is greater than the bromide–water and water–water bond angle obtained from complex **3** (Figure 4(b)). The nitrate ion of the tetrahedral unit forms strong H-bond (O₂NO···OH = 2.695 (7) Å) with the acid group and the overall tetrahedron motif leads to the building of the molecular assembly. This assembly is stabilised by aliphatic hydrogen and nitrate ion of bond length C1···O9 = 3.340(1) Å and C3···O8 = 3.410 (1) Å with inclusion of tetrahedral motif (Figure 4(c)). There are several weak interactions that resulted from the carbonyl oxygen and aliphatic hydrogen namely O3 with H9, H11 and

Table 2. Dimensions (length, Å; angle, °) of the water-anion tetrahedron.

$H_2O\cdot\Sigma 2H_2O, 2Br^{-}(3)$	Distance (Å)	H_2O · $\Sigma 2H_2O$, $2NO_3^-(4)$	Distance (Å)
09w-09w	09w 4.59 012w-012w		4.668
O9w—Br1 ^a	5.042	$O12w-ONO_2^a$	3.910
O9w-Br1 ^a	5.317	$O12w - ONO_2^{a}$	4.953
Br1-Br1	5.395	O ₂ NO-ONO ₂	
	Angle (°)		Angle (°)
09w-08w-09w	102.81	O12w-O11w-O12w	112.16
O9w-O8w-Br1 ^a	116.00	$O12w-O11w-ONO_2^a$	88.92
Br1–O8w– O9w ^a	107.01	$O12w - O11w - ONO_2^a$	125.06
Br1-O8w-Br1	108.26	ONO ₂ —O11w—ONO ₂	120.30

^aEach contains two equal measurements.



Figure 4. (a) Structure depicting formation of H-bond-assisted pentamer containing water and -OH. (b) Close-up view of tetrahedral building block formulated as $H_2O \Sigma 2H_2O$, $2NO_3^-$. (c) Nitrate ion interacts with acid group and water molecules. (d) Crystal packing along *c*-axis shows the existence of nitrate–water cluster between hydrophobic layers.

C—H··· π interaction (C7···C12g = 3.777, C20···Cg = 3.718) which also play a role in building the supramolecular architecture. The inclusion of the nitrate–water cluster between the hydrophobic layers of aromatic ring produced hydrophilic nitrate–water channel along the crystallographic *c*-axis (Figure 4(d)), which is quite similar to the packing structure of bromide salt **3** showing the isostructural behaviour.

[LH₃•ClO₄•MeOH] (5)

To explore the role of tetrahedral anion, we prepared the complex (5) from IV on treatment with perchloric acid which crystallises in a monoclinic space group $P2_1/c$ with

Z = 4. On the basis of unit cell comparison, we found that it is isostructural with the complex **2** with similar structural arrangement. Instead of water, it contains methanol as a solvent in the crystal structure. The *endo*-oriented hydrogen atom on apical nitrogen forms strong N—H···O H-bonds with two ethereal O-atoms and a carbonyl oxygen of bond lengths 2.819(5), 2.804(5) and 2.785(6) Å, respectively. Methanol forms H-bonds with tripodal ligand through alcoholic part of the complex (Figure 5(a)). The oxygen atoms of the perchlorate ion also interact with both —OH and —COOH simultaneously. The oxygen O8 is bifurcated, while O9 and O11 are mono-furcated giving a four-point attachment with a tripodal ligand, whereas one oxygen atom does not participate in any interaction. The



Figure 5. (Colour online) (a) Depiction of the H-bonding interactions of tetrahedral perchlorate anion in the solid state. (b) Crystal packing of complex **5** exhibiting perchlorate-methanol adducts propagating through the bilayer.

-OH of alcohol part forms two hydrogen bonds with the perchlorate oxygen O8 of a bond distance $O1-H\cdots O8 = 2.254(6)$ Å. In addition, the supramolecular self-assembled structure also stabilised by the interaction between carbonyl oxygen and aliphatic hydrogen having an average separation distance of 2.554 Å. The crystal packing along *c*-axis formed a hydrophilic channel enriched with perchlorate-methanol adduct and hydrophobic environment by naphthalene moiety which is shown in Figure 5(b).

Potentiometric study

We performed potentiometric titration to get information about the existence of several species at different pH. The 6×10^{-03} M NaOH solution was added to 1×10^{-03} M solution of complex **2** in water–methanol (3:1) medium in presence of 0.1 M NaCl as a supporting electrolyte (Figure 6). This explains the stability of several protonated and deprotonated species in the pH ranging from 3 to 6. It is clear from the speciation distribution diagram that the triprotonated species LH₃ predominates around pH 4.2. Upon gradual addition of base, it started to release most acidic NH protons to form neutral LH₂ and exists up to pH 4.8. Dissociation of one carboxylic group started around at pH 4.2 and predominates upto pH 5.3. Finally, the complete dissociation started after this pH and the abundance of L^{3-} increased. Deprotonation constants



Figure 6. (Colour online) Species distribution diagram of $[LH_3:Cl:3H_2O]$ (2).

Equilibrium reaction	$\log eta_{\mathrm{i}}^{\mathrm{H}}$	Equilibrium reaction	$\log K_{\rm i}^{\rm H}$	
$LH_3 + OH^- = LH_2$	3.4	$LH_3 + OH^- = LH_2$	3.4	
$LH_3 + 2OH^- = LH^-$	7.27	$LH_3 + OH^- = LH^-$	3.87	
$LH_3 + 3OH^- = L^{2-}$	13.23	$LH_3 + OH^- = L^{2-}$	5.96	

Table 3. Overall $(\log \beta_i^{\rm H})$ and stepwise deprotonation $(\log K_i^{\rm H})$ constant of LH₃^a in H₂O/MeOH (3:1).

^a LH₃ indicates as [LH₃·Cl·3H₂O], T = 298 K, I = 0.10 M in NaCl.

and stability constants were calculated using the HYPE-RQUAD program (16) (Table 3).

Conclusion

In conclusion, we have demonstrated the interaction of a naphthoic acid-based tripodal ligand with cation or anions and have shown the formation of water or anion-water motifs in the solid state. The complete deprotonated ligand at pH \sim 6.0 yields a sodium ion-encapsulated complex 1 where the cation resides within the bowl-shaped tripodal cavity. By way of contrast, the protonated ligand at pH 2.0 forms complexes with various anions. In the solid state, these complexes form different geometries of anion-water motifs. The isostructural behaviour of the two sets of complexes (2 and 5; 3 and 4) with different counter ions gives identical packing. In complexes 3 and 4, discrete anion-water tetrahedra formulated as $H_2O\cdot\Sigma 2H_2O$, $2X^ (X = Br^{-}, NO_{3}^{-})$ were observed. Complex 1 forms hydrophilic sodium-water channels and complexes 2-5 form anion-water or solvent channels adjacent to hydrophobic layers created by a naphthalene moiety and stabilised by C–H··· π and other H-bonding interactions.

Table 4. Crystal data and structure refinement parameters.

Stepwise dissociation of the salt with pH is also confirmed by species distribution curves.

Experimental section

Instrumentation

The IR spectra were recorded on a Perkin Elmer–Spectrum One FT-IR spectrometer with KBr disks in the range 4000– 500 cm^{-1} (PerkinElmer, WA, USA). NMR spectra were recorded on a Varian FT – 400 MHz instrument (Agilent Technology, CA, USA). The chemical shifts were recorded in parts per million (ppm) on the scale using the solvent peak as a reference.

X-ray crystallography

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer (Bruker, Billerica, USA), equipped with a fine focus 1.75 kW sealed tube Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K, with increasing ω (width of 0.3° per frame) at a scan speed of 6 s/frame (Table 4). The SMART software was used for data acquisition. Data integration and reduction were undertaken

Code name	$[LNa_2 \cdot 6H_2O]$ (1)	$[LH_3 \cdot Cl \cdot 3H_2O] (2)$	$[LH_3 \cdot Br \cdot 2H_2O] (\textbf{3})$	$[LH_3 \cdot NO_3 \cdot 2H_2O]$ (4)	$[LH_3 \cdot ClO_4 \cdot MeOH] (5)$
Empirical formula	C ₂₈ H ₃₇ O ₁₃ NNa ₂	C ₂₈ H ₃₄ O ₁₀ NCl	C ₅₆ H ₆₂ O ₁₇ N ₂ Br ₂	C ₅₆ H ₆₂ O ₂₃ N ₄	C ₂₉ H ₃₂ O ₁₂ NCl
Formula weight	641.59	580.02	1194.89	1159.11	622.01
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	C2/c	$P2_1/c$
a (Å)	17.9123(16)	20.497(15)	41.7832(16)	41.616(2)	20.5072(8)
<i>b</i> (Å)	23.198(2)	9.714(7)	9.6198(4)	9.8238(6)	9.8238(6)
<i>c</i> (Å)	7.4779(9)	14.666(10)	14.3061(5)	14.2763(8)	14.7779(6)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	90.138(7)	97.40(3)	107.947(2)	106.978(4)	98.448(2)
γ (°)	90.00	90.00	90.00	90.00	90.00
$V(Å^3)$	3107.3(5)	2896(4)	5470.5(4)	5582.2(5)	2884.0(2)
Ζ	4	4	4	4	4
P (cal)g/cm ³	1.346	1.316	1.444	1.372	1.433
μ (Mo K α) (mm ⁻¹)	0.130	0.189	1.555	0.108	0.200
<i>T</i> (K)	298(2)	298(2)	298(2)	298(2)	298(2)
R1; wR2 $(I > 2\sigma(I))$	0.0642; 0.2094	0.0768; 0.1348	0.0604; 0.1908	0.1015; 0.210	0.0796; 0.2570
<i>R</i> 1; <i>wR</i> 2 (all)	0.0842; 0.2449	0.2051; 0.1493	0.0848; 0.2118	0.1969; 0.25	0.0967; 0.2789
Residual electron density (e/Å)	0.584/-0.381	0.533/-0.416	0.833/-0.793	0.687/-0.445	0.659/-0.565
Goodness-of-fit	0.839	1.088	1.096	0.984	1.091
Reflection collected	3724	7134	2962	6985	3606
Independent reflection	2763	2150	2142	2861	2679
CCDC No.	857847	857848	857849	857850	857851

with SAINT and XPREP software (17a). Multi-scan empirical absorption corrections were applied to the data using the program SADABS (17b). Structures were solved by direct methods using SHELXS-97 and refined with fullmatrix least-squares on F^2 using SHELXL-97 (17c). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon atoms were geometrically fixed while the hydrogen atoms connected to the tertiary nitrogen atom were located using different Fourier maps and the positional and temperature factors are refined isotropically. However, we are unable to locate hydrogen atoms of the lattice water molecule. Additionally, in complex **2** we have one disordered water molecule. Structural illustrations have been drawn with ORTEP-3 (17d) and MERCURY (17e) Windows.

Materials and methods

All reagents and solvents were obtained from commercial sources and used as received. Tris(2-chloroethyl)amine hydrochloride was prepared by the known literature procedure (18). The tripodal ester was synthesised by modification of the known literature procedure (19).

Ligand design

The designing of molecules to explore the anion-water and water-water interactions in the solid state and solution phase is a great challenge. A considerable progress has been achieved with polyammonium-based receptors (20), azacryptands (21) and cascade complexes (22). In this report, we have designed a molecule that is sufficiently soluble in water and possesses a H-bonding site for anions and a protonation site to generate ionic environment so that we can mimic the water-anion interaction in reality.

Synthesis and characterisation

1-Hydroxy-naphthalene-2-carboxylic acid methylester II

1-Hydroxy-naphthalene-2-carboxylic acid (0.9 g, 5 mM) was dissolved in methanol and 1 ml concentrated H_2SO_4 was added slowly with continuous stirring. The reaction mixture was refluxed at 80°C for 8 h. The solvent was then evaporated under reduced pressure and a brown solid mass was extracted with ethylacetate (3 × 20 ml). The organic layer was washed several times with water and dried over anhydrous Na₂SO₄, and finally the solvent was removed under reduced pressure that gave a brown solid product **II**; yield 80% (Scheme 1).

Tripodal ester (III) and acid (IV)

A mixture of methyl ester II (1.5 g, 7.4 mM) and finely powdered K_2CO_3 (8 g) in 30 ml acetonitrile was refluxed at 80°C for half an hour. Tris(2-chloro-ethyl)amine hydrochloride salt (3.57 g, 14.7 mM) was added in portions over 15 min and the reaction mixture was then refluxed for another 12 h. Then the brown coloured solution was filtered off and the filtrate was evaporated in vacuum to give a brown semi-solid mass III. Tripodal ester III was dissolved in 10 ml methanol, and the methanolic solution of sodium hydroxide (5 N, 40 ml) was added and refluxed for 12 h at 80°C to yield IV. The basic solution of IV was then acidified cautiously with different acids.

Characterisation of the ester II

NMR (400 MHz, CDCl₃) δ (ppm): 3.95 (s, 3H, Me), 8.40– 7.19 (m, 6H, Ar) 11.97 (s, 1 H, OH). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 51.15, 106.09, 118.36, 123.84, 124.85, 125.22, 127.55, 129.27, 137.35, 161.42, 173.77. FT-IR: 1635 cm⁻¹ (-C=O).



(a) Conc. H₂SO₄, MeOH, reflux; (b) HCl•N(CH₂CH₂Cl)₃, K₂CO₃, CH₃CN, reflux; (c) NaOH, MeOH, reflux,

(d) crystallization at pH 6, (e) crystallization at pH 2

Scheme 1. Synthesis of the tripodal ligand and different salts.

Characterisation of the tripodal ester III

NMR (400 MHz, CDCl₃) δ (ppm): 7.30–8.40 (m, Ar), 4.80 (t, OCH₂), 3.80 (t, OHCH₂), 4.20 (s, OMe), 3.30 (t, NCH₂). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 42.15, 52.83, 56.91, 63.64, 72.26, 105.64, 118.65, 123.92, 124.30, 125.32, 126.70, 129.45, 137.24, 160.94, 171.47. FT-IR: 1712 cm⁻¹(-C=O).

Preparation of complex 1-5

$[LNa_2 \cdot 6H_2O](1)$

Methanolic solution of **IV** was neutralised to pH ~ 6.0 with slow addition of concentrated HCl in hood to avoid fumes. The solution was afforded white powder after few days. Recrystallisation of the white powder from ethanol–water (1:1) at low temperature gave the colourless crystals suitable for X-ray analysis. All crystals are stable at room temperature. Yield 50%; ¹H NMR (400 MHz, D₂O) δ (ppm): 7.30–8.20 (m, Ar), 4.80 (t, OCH₂), 3.76 (t, HOCH₂), 3.36 (t, NCH₂). FT-IR: 1592 cm⁻¹ v_{as} (-C=O) and 1398 cm⁻¹ v_s (-C=O).

$[LH_3 \cdot Cl \cdot 3H_2O]$ (2)

However, when the pH of the solution of **IV** was maintained at pH ~2.0 by adding concentrated HCl, colourless solid sodium chloride crystals were developed after few days and separated from the solution. Light yellow solid was collected from the remaining solution after removal of sodium chloride crystals, which on recrystallisation from ethanol–water (1:1) at low temperature yielded X-ray quality crystal. All crystals are stable at room temperature. Yield 60%; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.49–8.39 (m, Ar), 4.25 (t, OCH₂), 4.12 (t, HOCH₂), 3.98 (t, NCH₂). FT-IR: 1694 cm⁻¹ for v(-C=-0).

$[LH_3 \cdot Br \cdot 2H_2O]$ (3)

This is a similar experiment like complex **2**, but the use of concentrated HBr for acidification results in colourless single crystal suitable for X-ray analysis. All crystals are stable at room temperature. Yield 55%; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.46–8.37 (m, Ar), 4.15 (t, OCH₂), 4.10 (t, HOCH₂), 3.93 (t, NCH₂). FT-IR: 1703 cm⁻¹ v (-C=O).

$[LH_3 \cdot NO_3 \cdot 2H_2O]$ (4)

This is a similar experiment like complex **2**, but the use of concentrated HNO_3 for acidification results in colourless single crystal suitable for X-ray analysis. All crystals are stable at room temperature. Yield 60%; ¹H NMR

(400 MHz, d_6 -DMSO) δ (ppm): 7.54–8.35 (m, Ar), 4.45 (t, OCH₂), 4.09 (t, HOCH₂), 3.97 (t, NCH₂). FT-IR: 1997 cm⁻¹v(-C=O).

$[LH_3 \cdot ClO_4 \cdot MeOH]$ (5)

This is a similar experiment like complex **2**, but the use of concentrated HClO₄ for acidification (in fume hood) results in colourless single crystal suitable for X-ray analysis. All crystals are stable at room temperature. Yield 55%; ¹H NMR (400 MHz, d_6 -DMSO) δ (ppm): 7.54–8.35 (m, Ar), 4.56 (t, OCH₂), 4.11 (t, HOCH₂), 3.97 (t, NCH₂). FT-IR: 1700 cm⁻¹ v_s (-C=O).

Caution! The perchlorate salts must be handled with care as they form potentially explosive mixtures with organic compounds and they are also hazardous in nature.

Acknowledgements

G.D. gratefully acknowledges the Council of Scientific and Industrial Research (01/2727/13/EMR-II) and Department of Science and Technology (DST), New Delhi, India, for financial support, CIF and IIT Guwahati for providing instrument facility and DST FIST for single crystal X-ray diffraction facility. N.H. and A.B. thank IIT Guwahati for fellowship.

Supporting Information

Electronic supplementary information (ESI) available: X-ray crystallographic file of the structures in CIF format, ORTEP diagram, ¹H NMR, ¹³C NMR and FT-IR Spectra. For ESI and crystallographic data in CIF or other electronic format see DOI.

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