CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200903134

Controlled Aggregation of Multiple Guanidinium Ions through a Hydrogen-Bonded Network Assembly with Deprotonated Forms of Kemp's Triacid

Jie Han, Shuang-Quan Zang, and Thomas C. W. Mak*[a]

In memory of Dr. Richard K. McMullan (1929–2002)

Abstract: A series of five complexes that incorporate the guanidinium ion and various deprotonated forms of Kemp's triacid (H_3KTA) have been synthesized and characterized by single-crystal X-ray analysis. The complex $[C(NH_2)_3^+]\cdot[H_2KTA^-]$ (**1**) exhibits a sinusoidal layer structure with a centrosymmetric pseudo-rosette motif composed of two ion pairs. The fully deprotonated Kemp's triacid moiety in $3[C(NH_2)_3^+]\cdot[KTA^{3-}]$ (**2**) forms a record number of eighteen acceptor hydrogen bonds, thus leading to a closely knit three-dimensional network. The KTA^{3-} anion adopts an uncommon twist conformation in $[(CH_3)_4N^+]\cdot 2[C(NH_2)_3^+]\cdot[KTA^{3-}]\cdot 2H_2O$ (**3**). The crystal structure of $[(nC_3H_7)_4N^+]\cdot 2[C(NH_2)_3^+]\cdot[KTA^{3-}]$ (**4**) features a tetrahedral aggregate of four guanidinium ions stabilized by an outer shell that comprises six equatorial carboxylate groups that belong to separate $[KTA^{3-}]$ anions. In $3[(C_2H_5)_4N^+]\cdot 20[C(NH_2)_3^+]\cdot 11[HKTA^{2-}]\cdot[H_2KTA^-]\cdot 17H_2O$ (**5**), an even larger centrosymmetric inner core composed of eight guanidinium ions and six bridging water molecules is enclosed by a crust composed of eighteen axial carboxyl/carboxylate groups from six $HKTA^{2-}$ anions.

Keywords: crystal engineering · guanidinium · hydrogen bonds · Kemp's triacid · supramolecular chemistry

Introduction

In the realm of crystal engineering,[1] the guanidinium cation is one of the most versatile building blocks for the designed construction of two- and three-dimensional hydrogen-bonded networks. In particular, novel frameworks that exhibit the rosette layer[2,3] and rosette ribbon[4] motifs have been assembled with the guanidinium ion and a variety of neutral and anionic C_3-symmetric molecular species.

In the crystal structure of $[(C_2H_5)_4N^+]\cdot 7[C(NH_2)_3^+]\cdot 3CO_3^{2-}\cdot[C_3N_2H_2(COO^-)_2]$[3b] there exists a tetrahedral aggregate of four proximal guanidinium ions that is stabilized by charge-assisted hydrogen bonding[5] with the surrounding anions (Figure 1a). Its size can be gauged by the separation $d_{GC\cdots GC}$ between the carbon atoms of each pair of guanidinium ions, which lies in the range 4.06–4.83 Å. A search of the Cambridge Structural Database (Version 5.30) yielded only two other crystal structures with four guanidinium ions arranged in a similar tetrahedral fashion: tetraguanidinium 3,3′,3″-phosphinetriyltris(4,6-dimethylbenzenesulfonate) chloride[6] (Figure 1b) and dodecaguanidinium cyclododecaphosphate hexahydrate[7] (Figure 1c) with $d_{GC\cdots GC}$ of 3.82–4.27 and 4.53–4.58 Å, respectively. In the context of organic crystal engineering, we considered it worthwhile to devise a general strategy for the entrapment of a closely packed, nonbonded aggregate of multiple guanidinium ions in a crystalline environment using a centripetal converging system of hydrogen-bond acceptors.

Kemp's triacid (*cis*,*cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid, $C_6H_6(CH_3)_3(COOH)_3$, henceforth represented by H_3KTA)[8] is a nonplanar structural analogue of trimesic acid (1,3,5-benzenetricarboxylic acid).[9] It has a flexible cyclohexane ring skeleton that can exist in several distinct conformations (Scheme 1). The crystal structures of its neat and acetonitrile-solvate forms have been determined by Rebek et al.[10] and Chan et al.,[11] respectively. In both solution[12] and the solid state,[10,11,13] Kemp's triacid takes the chair conformation with three axial carboxyl groups, and

[a] Dr. J. Han, Dr. S.-Q. Zang, Prof. Dr. T. C. W. Mak
Department of Chemistry and Center of Novel Functional Molecules
The Chinese University of Hong Kong, Shatin, New Territories
Hong Kong SAR (P.R. China)
Fax: (+852) 2603-5057
E-mail: tcwmak@cuhk.edu.hk

Supporting information for this article (including colored versions of all the figures to facilitate better visualization of the structural details) is available on the WWW under http://dx.doi.org/10.1002/chem.200903134.

WILEY InterScience DISCOVER SOMETHING GREAT
© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

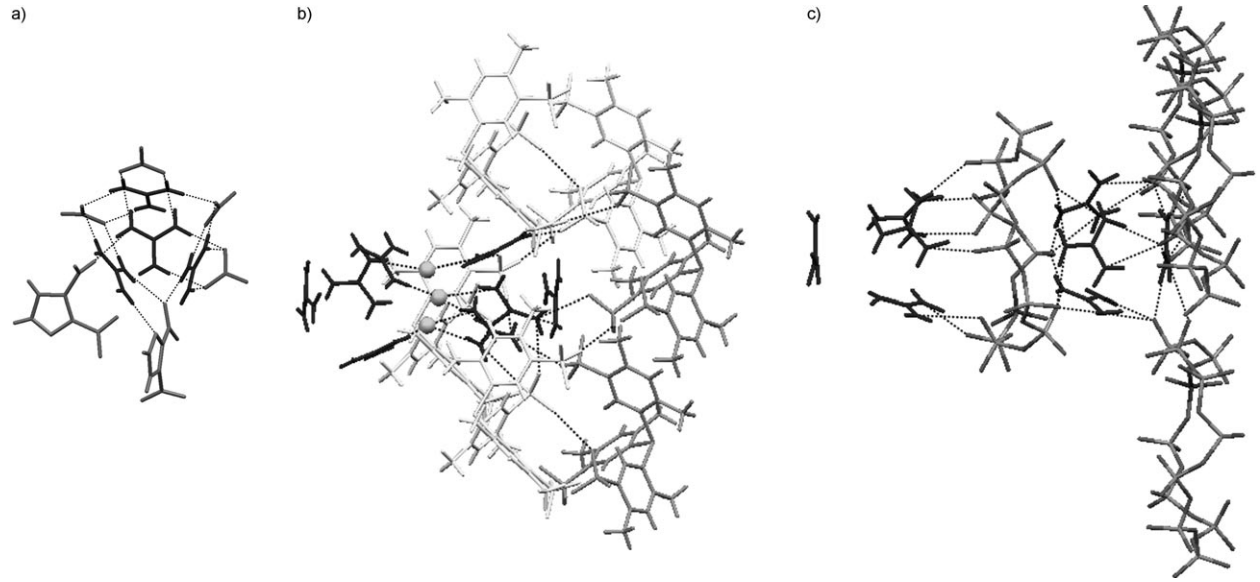
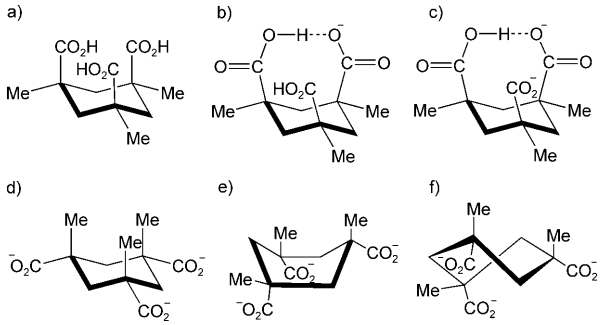


Figure 1. Tetrahedral aggregation of four guanidinium ions in a) $[(C_2H_5)_4N^+]\cdot 7[C(NH_2)_3^+]\cdot 3\,CO_3^{2-}\cdot[C_3N_2H_2(COO^-)_2]$, b) tetraguanidinium 3,3′,3″-phosphinetriyltris(4,6-dimethylbenzenesulfonate) chloride, and c) dodecaguanidinium cyclododecaphosphate hexahydrate. Note that in (b) the tetrahedral aggregates are bridged by chloride ions, and in (c) the tetrahedral aggregates are located in layers.



Scheme 1. Possible conformations of neutral and deprotonated forms of Kemp's triacid: a) H_3KTA chair form; b) chair H_2KTA^-; c) chair $HKTA^{2-}$; d) chair KTA^{3-} with carboxylate groups in equatorial positions; e) boat KTA^{3-}; and f) twist KTA^{3-}.

the crystal packing involves intermolecular head-to-tail cyclic hydrogen-bonded units, with two at the head and one at the tail. Thus far it has been established that the chair conformation and triaxial orientation of the carboxyl/carboxylate groups in Kemp's triacid are retained after mono- and di-deprotonation, and the resulting H_2KTA^- and $HKTA^{2-}$ anions are each stabilized by an intramolecular charge-assisted hydrogen bond. However, the trianion KTA^{3-} is the lone exception with its carboxylate groups occupying equatorial positions due to mutual electrostatic repulsion.[14]

Since the deprotonated forms of Kemp's triacid possess distinct hydrophobic and hydrophilic sides with multiple sites for acceptor hydrogen bonding, we decided to exploit the possibility of employing them for the entrapment and stabilization of positively charged molecular aggregates that comprise four or even more guanidinium ions.

Several H_2KTA^-[13a,b,15] and $HKTA^{2-}$[12b,16] salts of nitrogen heterocycle bases have been elucidated by single-crystal X-ray analysis, but there is as yet no reported isolation of any crystalline KTA^{3-} salt. The structural analogy between KTA^{3-} and the trimesate ion prompted us to conduct a systematic investigation of the synthesis and structural characterization of complexes formed by the guanidinium ion and all deprotonated forms of Kemp's triacid. In conducting the synthetic procedures, we also introduced various tetraalkylammonium ions as additional guest components for space filling and charge balance in the generation of stable anionic host networks.

In the present work, we report the synthesis and structural characterization of new crystalline compounds **1–5** constructed with various deprotonated forms of Kemp's triacid:

$[C(NH_2)_3^+]\cdot[C_6H_6(CH_3)_3(COOH)_2(COO^-)]$ **1**

$3\,[C(NH_2)_3^+]\cdot[C_6H_6(CH_3)_3(COO^-)_3]$ **2**

$[(CH_3)_4N^+]\cdot 2\,[C(NH_2)_3^+]\cdot[C_6H_6(CH_3)_3(COO^-)_3]\cdot 2\,H_2O$ **3**

$[(nC_3H_7)_4N^+]\cdot 2\,[C(NH_2)_3^+]\cdot[C_6H_6(CH_3)_3(COO^-)_3]$ **4**

$3\,[(C_2H_5)_4N^+]\cdot 20\,[C(NH_2)_3^+]\cdot 11\,[C_6H_6(CH_3)_3(COOH)(COO^-)_2]\cdot$
$[C_6H_6(CH_3)_3(COOH)_2(COO^-)]\cdot 17\,H_2O$ **5**

Results and Discussion

Structural description: In previous reports of hydrogen-bonded networks that exhibit the rosette motif, the hydrogen carbonate dimer $(HCO_3^-)_2$ or the nitrate ion was connected with guanidinium ions to generate a hexagonal as-

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

sembly of six molecular components, which may be designated as $\{(HCO_3^-)_2\cdots[C(NH_2)_3^+]\}_2$[4] or $\{(NO_3^-)\cdots[C(NH_2)_3^+]\}_3$,[17] respectively. In the complex **1**, Kemp's triacid monoanion H_2KTA^- forms a cyclic dimer held by a very strong intramolecular O–H···O hydrogen bond of 2.41 Å, and the dihedral angle between the carboxyl and carboxylate groups is about 40°. Hydrogen-bonding interaction of such dimers with adjacent guanidinium ions generates a corrugated layer that exhibits motifs labeled as **A**, **B**, **C**, and **D**, as illustrated in Figure 2.

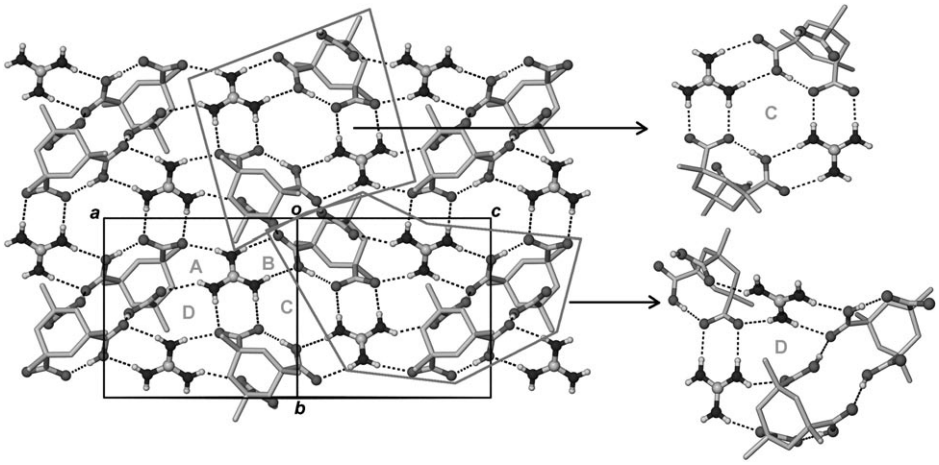


Figure 2. Layer structure of **1** projected along the [101] direction showing centrosymmetric pseudo-rosette motif **C** that comprises four molecular moieties, which may be compared with unsymmetric motif **D** built of five molecular components. For clarity, hydrogen atoms of methylene and methyl groups are omitted.

Notably, the "pseudo-rosette" motif **C** is composed of a centrosymmetric cyclic assembly of four molecular components, which may be represented as $\{(H_2KTA^-)\cdots[C(NH_2)_3^+]\}_2$, in which intramolecular hydrogen bonding between one carboxyl group and the carboxylate group of H_2KTA^- gives a substructure that mimics the hydrogen carbonate dimer in the $\{(HCO_3^-)_2\cdots[C(NH_2)_3^+]\}_2$ rosette motif. In contrast, unsymmetric motif **D** is built up from a $(H_2KTA^-)_2$ dimer, a H_2KTA^- anion, and two guanidinium cations. The crystal structure of **1** consists of a packing of corrugated layers (Figure 3).

The simple salt **2** crystallizes in the trigonal space group *R*3*c*; the guanidinium ion occupies a general position, whereas the trianion KTA^{3-} is located at a special position of site symmetry 3. In the crystal structure, nine symmetry-related guanidinium ions are arranged around one KTA^{3-} to form a total of eighteen donor hydrogen bonds (Figure 4). In turn, the guanidinium ions are arranged around a 3_1 axis, each being surrounded by three KTA^{3-} anions (Figures 4 and 5).

In the crystal packing of **2**, the KTA^{3-} and guanidinium ions are cross-linked to form a closely knit, three-dimensional hydrogen-bonded network (Figure 5).

In the crystal structure of **3**, fully deprotonated Kemp's triacid KTA^{3-} shows an unusual twist conformation; the torsion angles around the cyclohexane carbon skeleton in cyclic order, starting from C1-C2-C3-C4, take the values +59.5, −26.6, −34.2, +62.1, −26.7, and −29.4° (Figure 6a). The KTA^{3-} ion and independent bridging water molecules O1w and O2w form a centrosymmetric cyclic hexamer with endocyclic methyl groups (Figure 6b). These $(KTA^{3-}\cdot 2H_2O)_2$ moieties are interconnected by two independent guanidinium ions: one (designated by its carbon atom **C13** in boldface type) orientated nearly parallel to [001] and the other (**C14**) at a slant to form a wide ribbon (Figure 7). Such ribbons are further cross-linked by guanidinium **C14** and KTA^{3-} ions to from a three-dimensional network (Figure 8). The well-ordered tetramethylammonium cations are located in channels between the wide ribbons.

The tetra-*n*-propylammonium ion serves as a structure-inducing agent in generating the complex **4**. Four independent guanidinium cations approach close together to form a tetrahedral central core despite the expected electrostatic repulsion between them; their carbon atoms occupy the vertices of the tetrahedron, with edge lengths lying in the range of

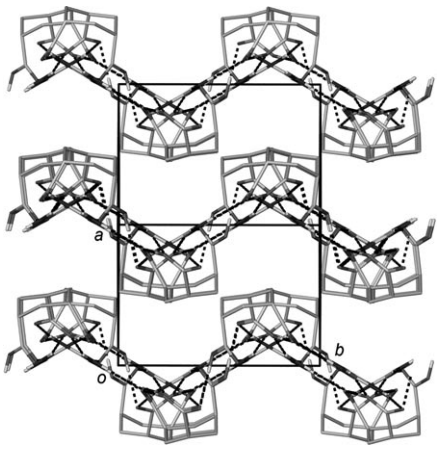


Figure 3. Sinusoidal layer structure of complex **1** viewed along the [101] direction. Hydrogen atoms of methylene and methyl groups of H_2KTA^- are omitted for clarity.

4.41–4.73 Å (Figure 9a). This $[C(NH_2)_3^+]_4$ cationic core is consolidated by hydrogen-bonding interaction with a pseudo-octahedral shell of six equatorial carboxylate groups that belong to separate independent KTA^{3-} ions. The center of mass of each centripetal carboxylate group constitutes a vertex of the outer octahedron (Figure 9b), which lies above

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

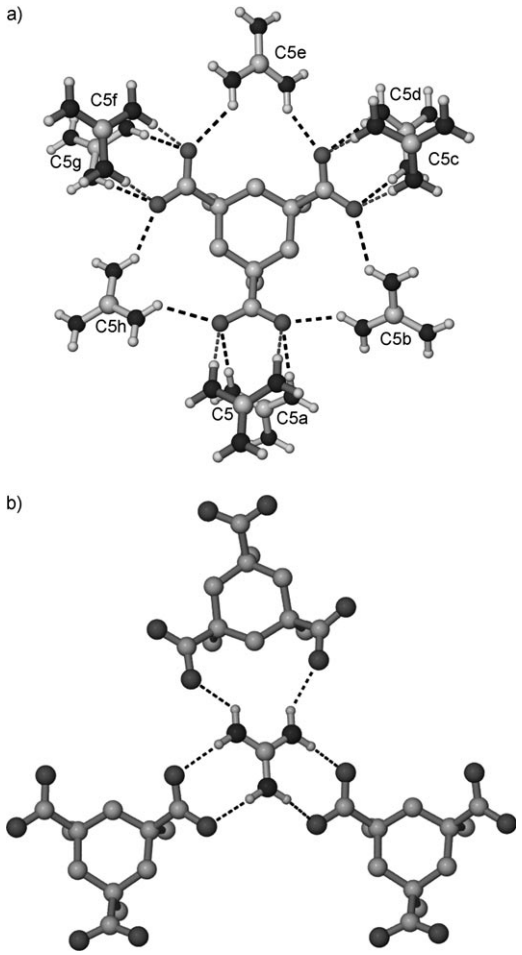


Figure 4. a) Nine guanidinium ions arranged around one trianion in **2** viewed along the *c* axis. Symmetry transformations: a) $^{1}/_{3}-y$, $-^{1}/_{3}+x-y$, $-^{1}/_{3}+z$; b) $-^{1}/_{3}+x$, $-^{2}/_{3}+x-y$, $-^{1}/_{6}+z$; c) $-^{2}/_{3}+y$, $-^{1}/_{3}+y$, $-^{1}/_{3}+z$; d) $-x+y$, $-x$, z; e) $-^{1}/_{3}-y$, $^{1}/_{3}-x$, $-^{2}/_{3}+z$; f) $^{1}/_{3}-x+y$, $^{2}/_{3}-x$, $-^{1}/_{3}+z$; g) $-y$, $x-y$, z; h) $^{2}/_{3}-x+y$, $^{1}/_{3}+y$, $-^{1}/_{6}+z$. b) Hydrogen-bonding environment of the guanidinium ion.

an edge of the inner $[C(NH_2)_3^+]_4$ tetrahedron to form two pairs of acceptor hydrogen bonds (Figure 9c). Each carboxylate group in the shell provides four acceptor sites, so that all twenty-four N–H groups in the core are precisely matched in generating the $[C(NH_2)_3^+]_4[KTA^{3-}]_6$ cluster unit.

Figure 10 shows the three-dimensional network structure of **4** constructed from the assembly of the structural units. The tetra-*n*-propylammonium cations are accommodated in each channel.

The asymmetric unit of **5** contains five guanidinium ions, three Kemp's triacid moieties (two are well-ordered, and the other one exhibits disorder over two slightly different orientations), two tetraethylammonium cations in special positions (**N16** lying on a crystallographic 2-axis, and **N17** occupying a $\bar{4}$ site), together with water molecules including well-ordered O1w, O2w, and O3w; O4w disordered over three general positions (occupancies set at $^{1}/_{2}$, $^{1}/_{4}$, $^{1}/_{4}$); and O5w with $^{1}/_{4}$ occupancy located close to a $\bar{4}$ site. Notably, the lone H_2KTA^- monoanion cannot be distinguished from the $HKTA^{2-}$ dianions, and the total anionic charge is −23 in the stoichiometric formula.

The crystal structure of **5** features a centrosymmetric hydrogen-bonded cluster composed of eight guanidinium ions, six $HKTA^{2-}$ ions (each possessing an intramolecular hydrogen bond) and six water molecules[18] (Figure 11). Unlike the case in **4**, all three axial carboxyl/carboxylate groups of each peripheral anion participate in acceptor hydrogen bonding with the $[C(NH_2)_3^+]_8$ core. The center of mass of the three axial carboxyl/carboxylate groups of each $HKTA^{2-}$ constitutes a vertex of a distorted octahedron of approximate symmetry 3. Three independent guanidinium ions (designated by **C38**, **C40**, and **C41** in boldface type) each lies above a face of the octahedron, and the other independent ion **C39** is located inside it and orientated approximately normal to a face.

The association between guanidinium and $HKTA^{2-}$ ions is consolidated by bridging water molecules O1w, O2w, and O3w, so that the hydrogen-bonded supramolecular assembly can be designated as $[C(NH_2)_3^+]_8[HKTA^{2-}]_6[H_2O]_6$. Figure 12 shows details of the hydrogen-bonding environment of guanidinium ions **C39** and **C41**. Guanidinium **C39** is connected with two carboxylate groups by pairwise donor hydrogen bonds and with bridging water molecule O1w by chelating hydrogen bonds. Guanidinium ion **C41** also forms pairwise hydrogen bonds with two carboxylate groups, but its remaining two donor hydrogen bonds are connected to different carboxylate groups.

Kemp's triacid dianion **O1** (for convenience, it is denoted by the label of an oxygen atom of its carboxyl group with the smallest numbering in boldface type) is hydrogen bonded with guanidinium **C38**, **C39**, **C40**, and **C41** by four pairs of hydrogen bonds (Figure 13a). In contrast, the hydrogen-bonding scheme of anion **O7** does not involve direct pairing of any one of its carboxyl/carboxylate group with a guanidinium ion. As shown in Figure 13b, guanidinium ions **C37**, **C38**, **C40**, and **C41** each donates its hydrogen atoms to different carboxyl/carboxylate groups of **O7**, and guanidinium **C39** is indirectly linked to it through bridging water molecule O1w. The situation in the case of the disordered triacid anion cannot be unambiguously established. In one of the two possible orientations, **O13** is linked with guanidinium **C38**, **C39**, and **C41** by pairwise hydrogen bonds, and with **C37** and **C40** each by a single hydrogen bond (Figure 13c).

Guanidinium **C37** serves as a linker between two adjacent pseudo-octahedral cluster units. The packing diagram of **5** along the *b* axis shows that the two independent $(C_2H_5)_4N^+$ cations are located in different voids: **N16** is accommodated in a cavity of site symmetry 2, whereas **N17** occupies a $\bar{4}$ site (Figure 14).

Discussion

Compounds **1** and **2** are simple guanidinium salts of the corresponding mono- and tri-deprotonated forms of Kemp's tri-

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

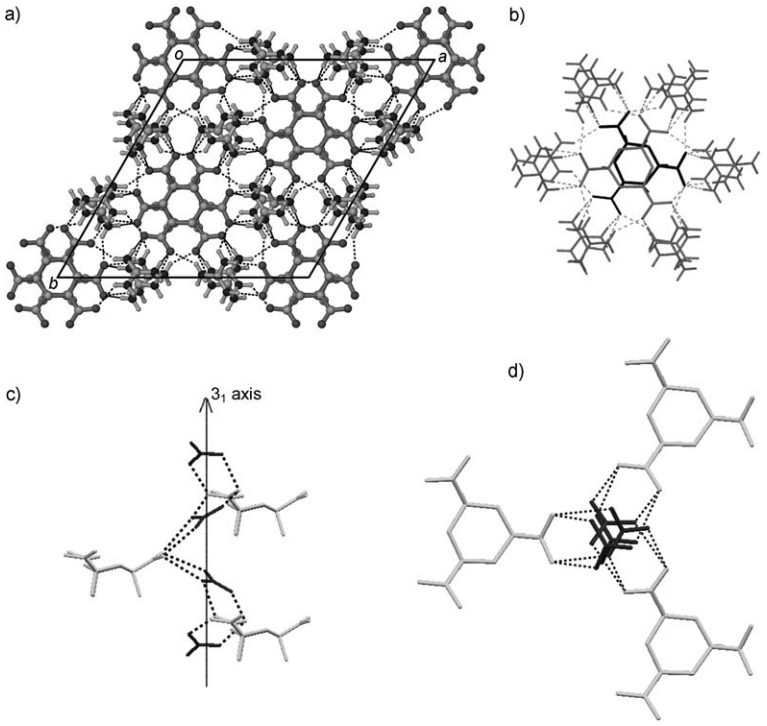


Figure 5. a) Hydrogen-bonded three-dimensional network structure of **2** viewed along the *c* axis. b) Two overlapping but unconnected KTA^{3-} anions, each connected with adjacent guanidinium ions viewed almost along the *c* axis. c) Guanidinium ions related by the 3_1 axis bridged by the carboxylate groups of adjacent KTA^{3-} anions. d) The content of (c) viewed along the *c* axis.

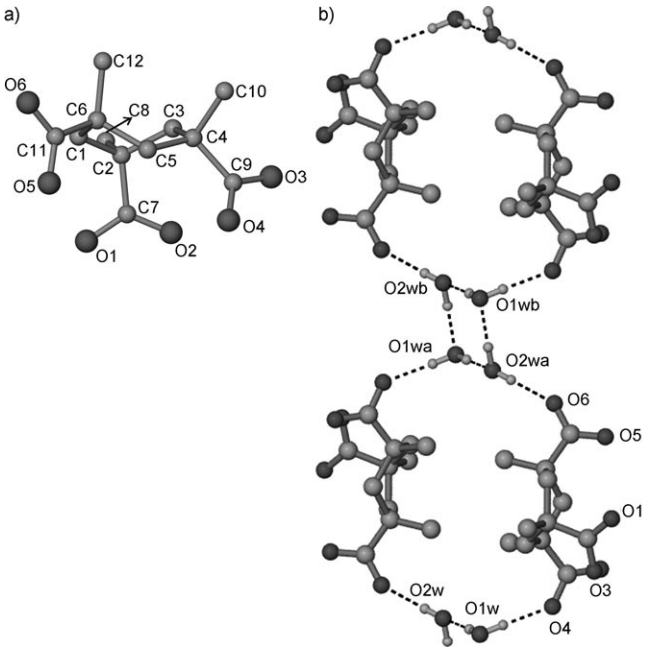


Figure 6. a) Twist formation of KTA^{3-} in **3**. b) Centrosymmetric hydrogen-bonded cyclic hexameric unit formed by KTA^{3-} and two independent water molecules. Symmetry transformations: a) $1-x, 1-y, -z$; b) $x, 1+y, z$.

acid, but the remaining three crystalline complexes also contain different quaternary ammonium ions. The triacid anions take the stable chair conformation in all complexes except **3**, in which KTA^{3-} exhibits the rare twist conformation. The cyclohexane skeletons in all five complexes deviate considerably from their idealized conformations. With reference to the alternating C-C-C-C torsion angles of $\pm 60°$ for the chair form of cyclohexane, the measured C-C-C-C torsion angles are 47, −56, 55, −46, 38, −38° for complex **1**, 46, −46, 46, −46, 46, −46° for **2**, 60, −27, −34, 62, −27, −29° for **3**, 49, −50, 50, −48, 48, −48; 49, −48, 48, −50, 50, −50° for two independent rings in **4**, and 42, −47, 52, −51, 47, −42° for the ordered ring in **5**. In compounds **1** and **5** that contain the monoanion H_2KTA^- and dianion $HKTA^{2-}$, the C···C distances between carbon atoms of axial carboxyl/carboxylate groups lie in the range of 3.2 to 3.8 Å. In the KTA^{3-} complexes **2** and **4**, all three carboxylate groups occupy equatorial positions of the chairlike cyclohexane skeleton, and the corresponding C···C separations are lengthened to approximately 4.9 Å. In complex **3**, the twist conformation of KTA^{3-} accounts for a wide range of C···C distances from 3.4 to 5.0 Å between the carboxylate groups.

The four-component rosette motif $\{(H_2KTA^-)\cdots[C(NH_2)_3^+]\}_2$ in complex **1** is comparable in size to the six-component rosette motif $\{(CO_3^{2-})\cdots[C(NH_2)_3^+]\}_3$ in $[(C_2H_5)_4N^+]\cdot 7[C(NH_2)_3^+]\cdot 3CO_3^{2-}\cdot[C_3N_2H_2(COO^-)_2]$.[3b] The distance between the central carbon atoms of guanidinium ions in each rosette motif is 8.4 and 8.1 Å, respectively. This is a good example of mimicking a known supramolecular synthon with an "equivalent assembly" of molecular components. In the simple guanidinium salt **2**, the trianion of Kemp's triacid forms a record number of eighteen hydrogen bonds involving convergent N–H donor sites from nine guanidinium molecules, thereby yielding a closely fabricated three-dimensional hydrogen-bonded network. Drawing upon our previous experience,[3,4] we made use of globular tetraalkylammonium ions as templates to generate complexes **3**–**5**.

An early NMR spectroscopy solution study and MACROMODEL/molecular dynamics calculations showed that Mg^{2+} ion can convert KTA^{3-} from a chair into a half-chair conformation.[14b] Against this background, X-ray analyses of compounds **2**–**4** provided detailed structural parameters of the KTA^{3-} anion for the first time, and that **3** is the only deprotonated form of Kemp's triacid that takes the twist

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

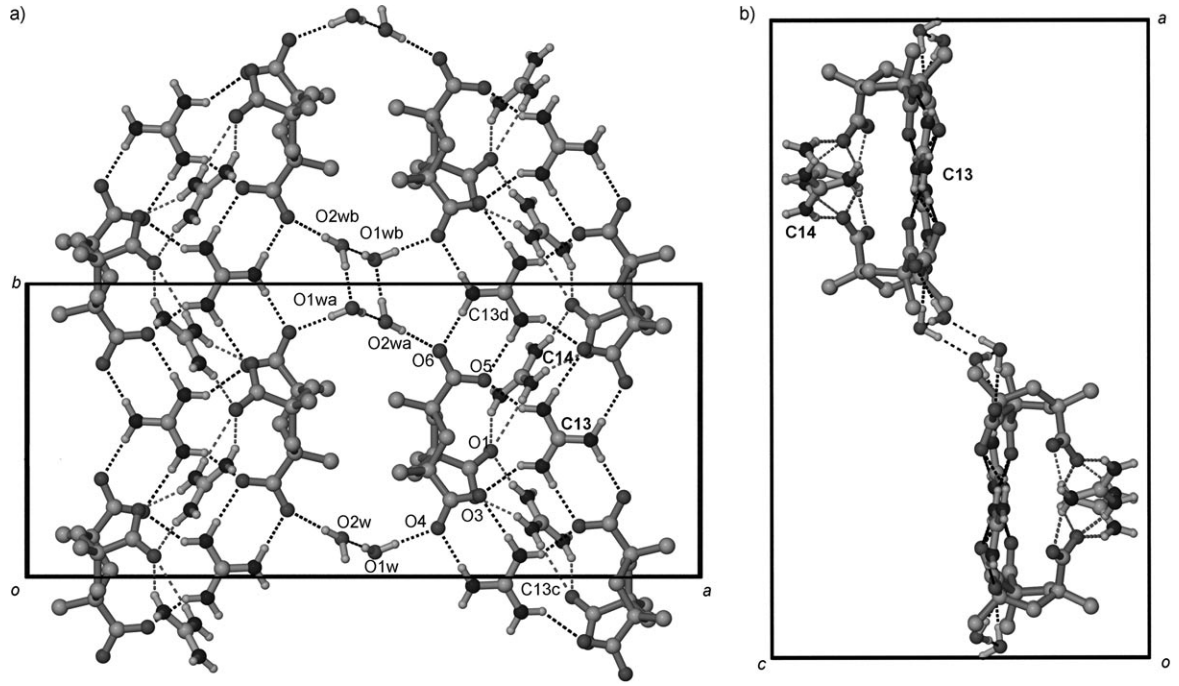


Figure 7. a) Wide ribbon in **3** composed of KTA^{3-}, guanidinium ions (**C13**, **C14**), and water molecules (O1w, O2w) viewed along the *c* axis. Symmetry transformations: a) $1-x, 1-y, -z$; b) $x, 1+y, z$; c) $^3/_2-x, -^1/_2+y, -z$; d) $^3/_2-x, ^1/_2+y, -z$. b) A portion of the wide ribbon viewed along the *b* axis.

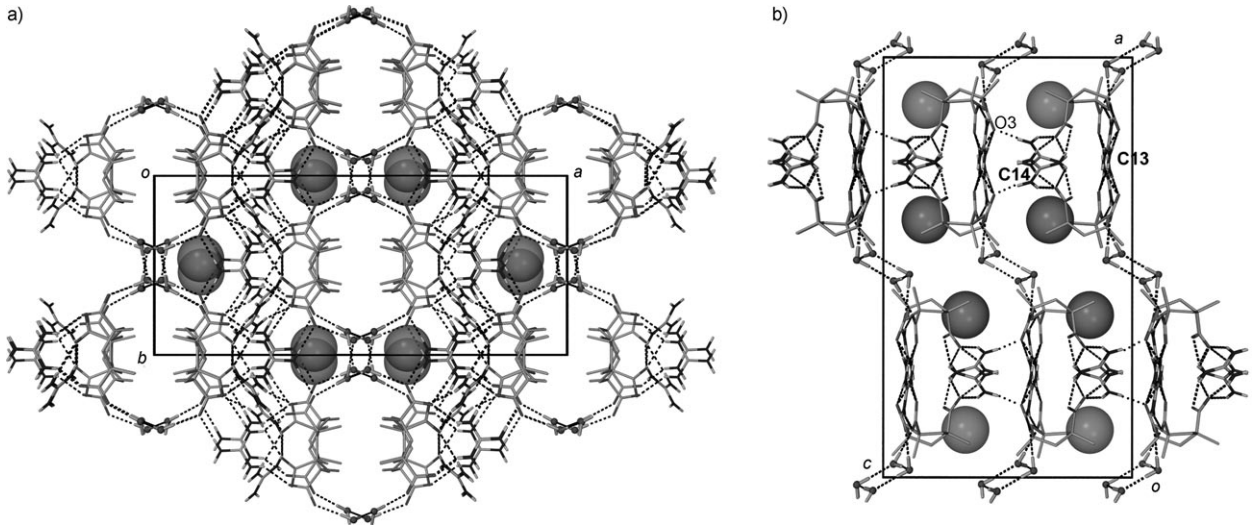


Figure 8. Crystal structure of complex **3** viewed a) along the *c* axis and b) along the *b* axis. Each $(CH_3)_4N^+$ guest species is represented by a large sphere.

conformation, which allows it to interact efficiently with the guanidinium ions to give a three-dimensional host channel structure for the accommodation of $(CH_3)_4N^+$ guest molecules.

The agglomeration of unconnected ions of the same kind is extremely rare in the crystalline state. In complex **4**, four independent guanidinium ions constitute a tetrahedral aggregate that is surrounded and stabilized by a pseudo-octahedral arrangement of six independent KTA^{3-} ions, thus yielding the cluster unit $[C(NH_2)_3^+]_4[KTA^{3-}]_6$. The size of the tetrahedral guanidinium core is similar to that observed in $[(C_2H_5)_4N^+]\cdot 7[C(NH_2)_3^+]\cdot 3\,CO_3^{2-}\cdot[C_3N_2H_2(COO^-)_2]$.[3b] The crystal structure of **5** features a novel $[C(NH_2)_3^+]_8[HKTA^{2-}]_6[H_2O]_6$ supramolecular assembly with a centrosymmetric pseudo-octahedron composed of all carboxyl/carboxylate groups of six peripheral $HKTA^{2-}$ ions surrounding an inner core of eight guanidinium ions, with hydrogen bonding between them consolidated by six bridging water molecules. The separations between proximal carbon atoms in the $[C(NH_2)_3^+]_4$ inner core of **4** are in the range of 4.3 to 4.7 Å, which agree with the range of 3.8 to 4.8 Å found in three previously reported examples. In contrast, the inter-

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

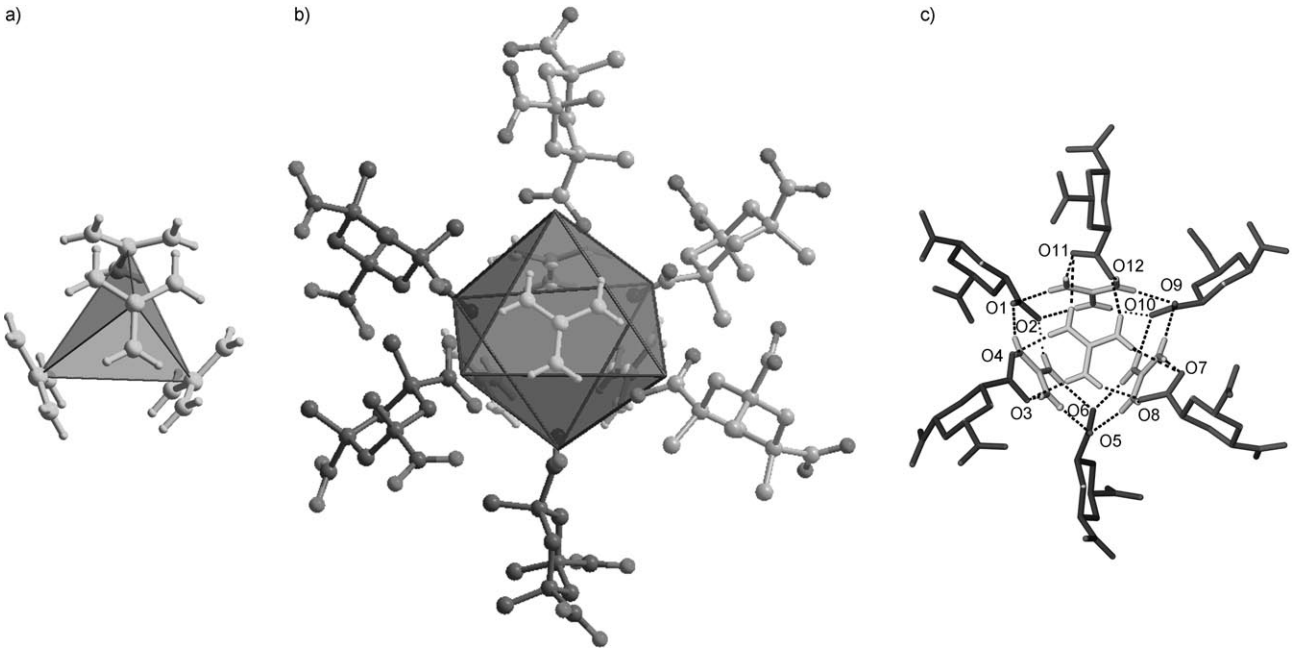


Figure 9. Cluster unit in **4**: a) Four guanidinium cations constitute a tetrahedral $[C(NH_2)_3^+]_4$ central core with a C atom at each vertex; b) arrangement of six KTA^{3-} anions around the tetrahedral central core, with the center of mass of one carboxylate group at each vertex of the pseudo-octahedron; and c) hydrogen-bonding connections between guanidinium and KTA^{3-} ions.

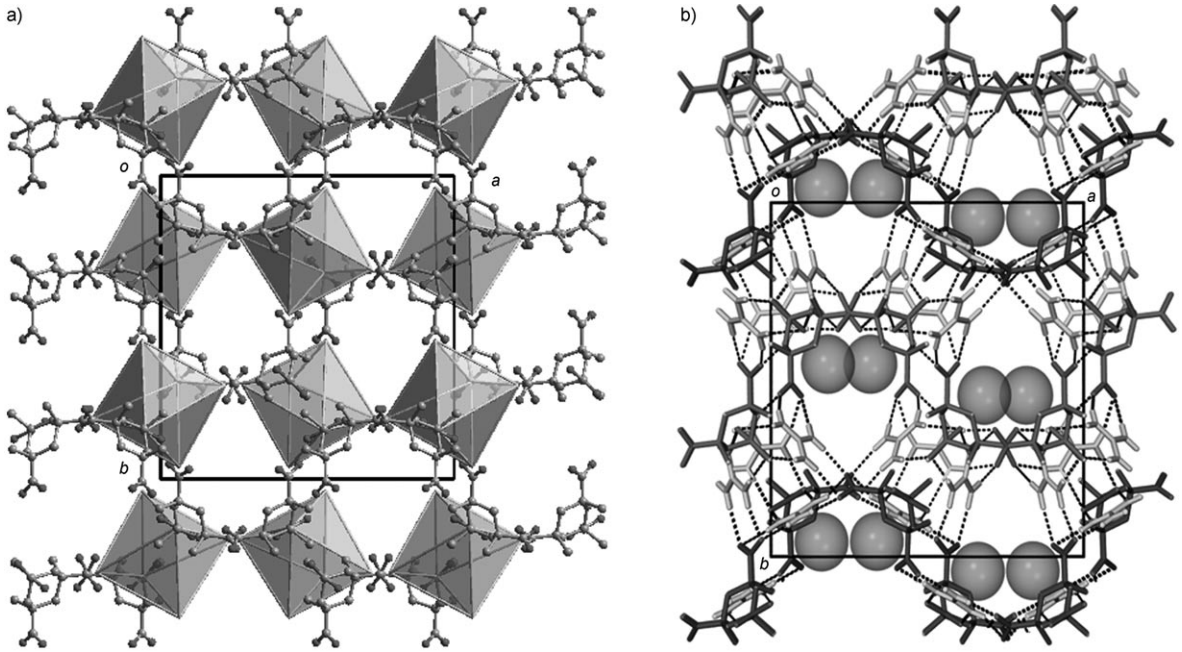


Figure 10. a) Packing of hydrogen-bonded $[C(NH_2)_3^+]_4[KTA^{3-}]_6$ cluster units in complex **4** viewed along the *c* axis and showing the host network with empty channels. b) Crystal structure of **4**, with each $(n\text{Pr})_4N^+$ guest species represented by a large sphere. Hydrogen bonds are represented by broken lines.

atomic distances between carbon atoms in the $[C(NH_2)_3^+]_8$ inner core of **5** vary between 5.6 and 5.8 Å.

An anion derived from Kemp's triacid in the triaxial or triequatorial carboxyl/carboxylate conformation can be regarded as a bowl- or saucerlike entity, respectively, which exhibits hydrophilic and hydrophobic properties on the top and bottom sides. In **4** and **5**, the carboxyl/carboxylate groups provide a concave hydrophilic surface with multiple sites for forming acceptor hydrogen bonds with the guanidinium inner core, whereas the hydrophobic methyl groups constitute the periphery of the cluster unit. Both supramolecular assemblies composed of guanidinium cations and

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

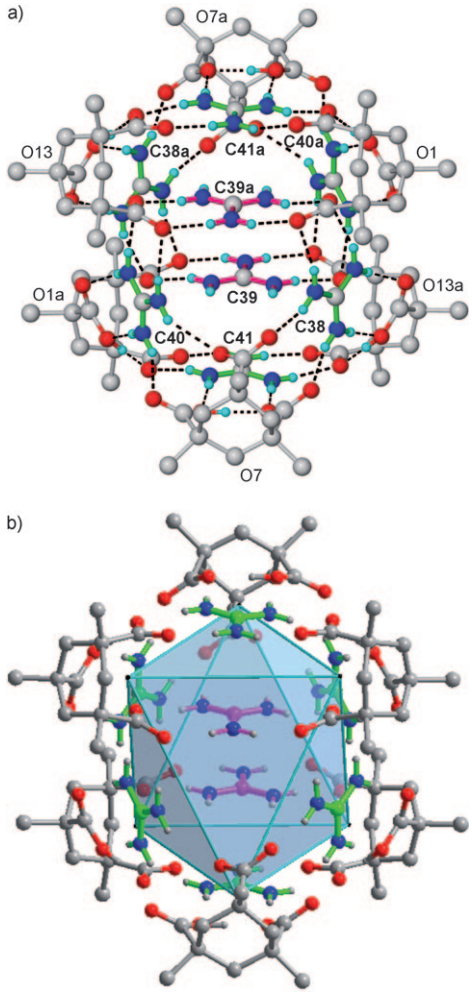


Figure 11. a) Hydrogen-bonded centrosymmetric cluster unit composed of eight guanidinium ions and six Kemp's triacid anions in the crystal structure of **5**. Note that the mono- and dianions are indistinguishable in the crystal structure, and the monoanion is treated as a dianion in the structure description. For clarity, six bridging water molecules that consolidate the cluster unit are not shown. b) Polyhedral representation showing that the center of mass of the triaxial carboxyl/carboxylate groups of each anion constitutes a vertex of a distorted octahedron. Six guanidinium ions that lie above six octahedral faces are shown in green, and two that lie perpendicular to the remaining two faces are colored pink. Symmetry transformations: a) $-x, 1-y, 1-z$.

Kemp's triacid anions in **4** and **5** carry excess negative charge, which accounts for the necessity of incorporating a tetraalkylammonium ion as template and space-filling guest species. The difference in size of the guanidinium cores can be rationalized by the fact that only one of the triequatorial carboxylate groups of each KTA^{3-} binds to the $[C(NH_2)_3^+]_4$ core in **4**, whereas the triaxial carboxyl/carboxylate groups of $HKTA^{2-}$ provide multiple converging acceptor sites for linkage to N–H groups of the $[C(NH_2)_3^+]_8$ core and bridging water molecules in **5** (see Figure 13; compare Figure 9 with Figure 11).

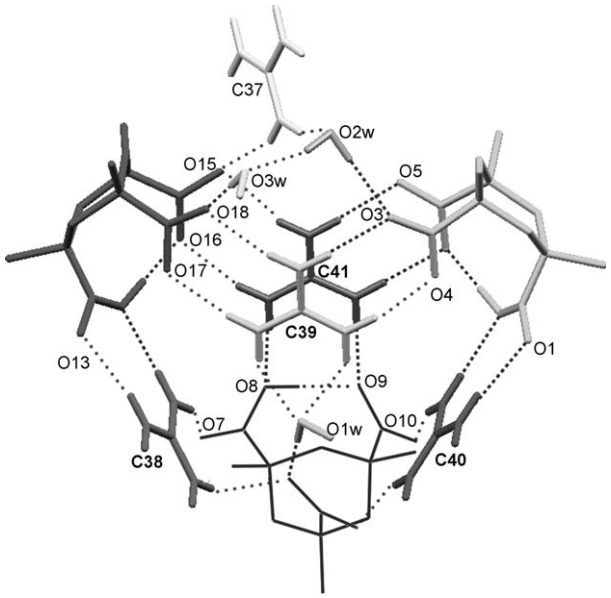


Figure 12. Hydrogen-bonding environment of guanidinium ions (**C39** and **C41**) involving three independent $HKTA^{2-}$ anions and bridging water molecules in **5**.

Conclusion

In summary, we have investigated the crystal structures of a series of five complexes that incorporate the guanidinium ion and various deprotonated forms of Kemp's triacid. The significant results obtained include a sinusoidal layer structure displaying a centrosymmetric pseudo-rosette motif that comprises two pairs of $[C(NH_2)_3^+]$ and H_2KTA^- ions in **1**, a record number of eighteen hydrogen bonds around the KTA^{3-} anion in **2**, an uncommon twist conformation of KTA^{3-} in **3**, and compact $[C(NH_2)_3^+]_4$ and $[C(NH_2)_3^+]_8$ inner cores, each enclosed by a crust composed of KTA^{3-} and $HKTA^{2-}$ in complexes **4** and **5**, respectively. The present finding demonstrates that it is possible to confine multiple molecular ions of the same kind to a small region within a crystalline lattice, and Coulombic repulsion between like charges can be overcome by charge-assisted hydrogen bonding with a shell composed of molecular ions that bear the opposite charge.

Experimental Section

Reagents and instruments: Commercially available guanidinium carbonate (commonly known as guanidine carbonate), Kemp's triacid (*cis*,*cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid), aqueous tetramethylammonium hydroxide, tetraethylammonium hydroxide, and tetra-*n*-propylammonium hydroxide were used as received without further purification.

IR spectra were recorded with KBr pellets using a Nicolet Impact 420 FTIR spectrometer in the region of 4000–400 cm^{-1}. Melting points (uncorrected) were measured using a IA9100 Electrothermal Digital Melting Point apparatus.

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

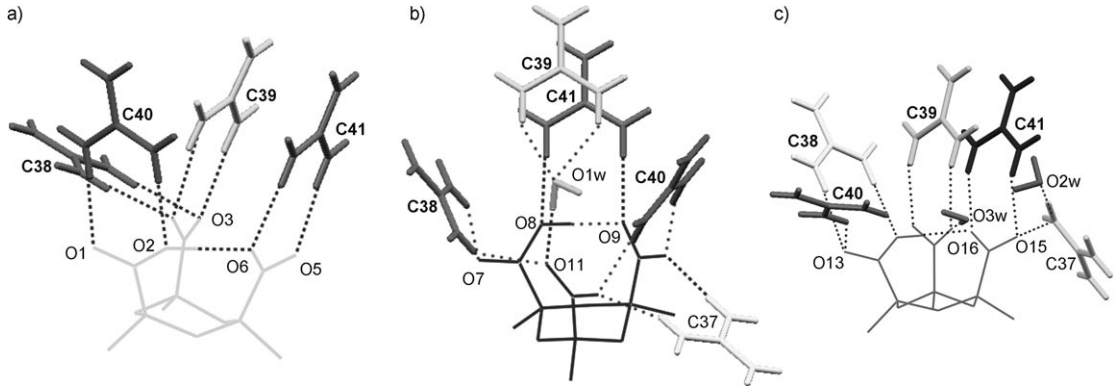


Figure 13. Hydrogen-bonding environments of three independent Kemp's triacid anions in **5**. In (c), the disordered anion is shown in one of its two possible orientations.

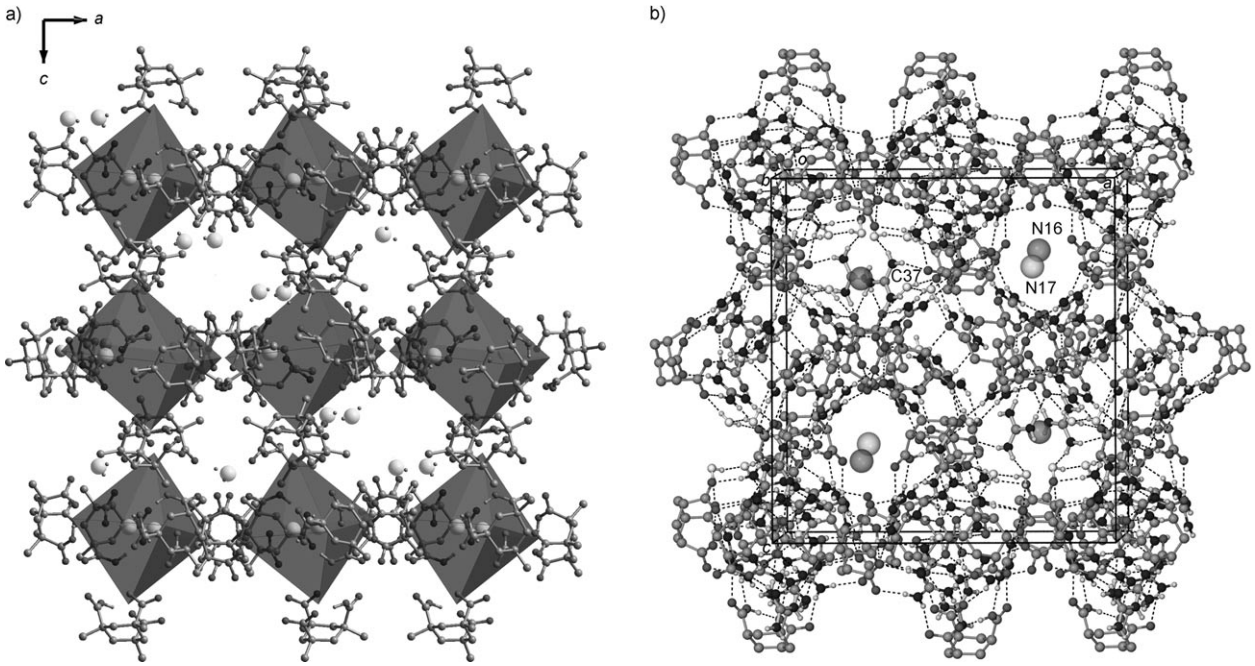


Figure 14. a) Packing of hydrogen-bonded guanidinium–triacid anion cluster units in complex **5** viewed along the *b* axis and showing empty channels for the accommodation of $(C_2H_5)_4N^+$ cations and disordered water molecules. b) Hydrogen-bonded host–guest structure of **5**. Guest cation **N16** is accommodated in a cavity of site symmetry 2, whereas **N17** occupies a $\bar{4}$ site. For clarity, the methyl group of Kemp's triacid anions and disordered water molecules have been omitted.

Synthesis of 1: Guanidinium carbonate (36 mg, 0.2 mmol) was added into an aqueous solution of Kemp's triacid (52 mg, 0.2 mmol) in a 1:1 molar ratio. The solution was stirred for about 5 min and then filtered. The colorless filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Compound **1** was obtained as colorless blocklike crystals in nearly quantitative yield over a period of several weeks. M.p. 257.5–258.2 °C; IR (KBr): $\tilde{\nu}$ = 3391, 3066, 2991, 2980, 1720, 1687, 1662, 1546, 1470, 1444, 1422, 1402, 1358, 1336, 1309, 1208, 1171, 1091, 1002, 978, 902, 888, 865, 832, 788, 704, 637, 564 cm^{-1}.

Synthesis of 2: Kemp's triacid (52 mg, 0.2 mmol) was slowly added into an aqueous solution of guanidinium carbonate (180 mg, 1.0 mmol). The solution was stirred for about 20 min with slight heating at 40 °C and then filtered. The colorless filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Compound **2** was obtained as colorless blocklike crystals in nearly quantitative yield over a period of several weeks. M.p. 222.6–234.2 °C; IR (KBr): $\tilde{\nu}$ = 3400, 3057, 2980, 2838, 1689, 1664, 1545, 1487, 1471, 1442, 1403, 1357, 1336, 1309, 1220, 1209, 1184, 1173, 1094, 1047, 1002, 888, 866, 830 ,791, 666, 625, 564 cm^{-1}.

Synthesis of 3: Kemp's triacid (52 mg, 0.2 mmol) was neutralized with three molar equivalents of aqueous tetramethylammonium hydroxide (0.6 mmol). Guanidinium carbonate (72 mg, 0.4 mmol) was added into the aqueous solution of Kemp's triacid. The solution was stirred for about 20 min with slight heating at 40 °C and then filtered. The colorless filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Compound **3** was obtained as colorless blocklike crystals in nearly quantitative yield over a period of several weeks. M.p. 280.8–283.5 °C; IR (KBr): $\tilde{\nu}$ = 3360, 3153, 2972, 2940, 1661, 1628, 1508, 1472, 1459, 1394, 1383, 1331, 1174, 1101, 1037, 1107, 1037, 1007, 982, 970, 922, 885, 933, 757, 703, 663, 555 cm^{-1}.

Synthesis of 4: Kemp's triacid (52 mg, 0.2 mmol) was neutralized with three molar equivalents of aqueous tetra-*n*-propylammonium hydroxide

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(0.6 mmol). Guanidinium carbonate (72 mg, 0.4 mmol) was added into an aqueous solution of Kemp's triacid. The solution was stirred for about 20 min with slight heating at 40 °C and then filtered. The colorless filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Compound **4** was obtained as colorless blocklike crystals in nearly quantitative yield over a period of several weeks. M.p. 238.5–239.9 °C; IR (KBr): $\tilde{\nu}$ = 3378, 3058, 2980, 2954, 1688, 1668, 1546, 1487, 1470, 1439, 1403, 1358, 1309, 1220, 1208, 1158, 1093, 1007, 1047, 979, 956, 948, 885, 830, 802, 755, 701, 622, 563 cm^{-1}.

Synthesis of 5: An aqueous solution of Kemp's triacid (52 mg, 0.2 mmol) was neutralized by one half-equivalent of tetraethylammonium hydroxide (0.1 mmol), and then one molar equivalent of guanidinium carbonate (36 mg, 0.2 mmol) was added. Next, additional EtOH (2 mL) was introduced. The solution was stirred for about 30 min and then filtered. The colorless filtrate was subjected to slow evaporation at room temperature in a desiccator charged with anhydrous silica gel. Compound **5** was obtained as colorless blocklike crystals in 70% yield over a period of several weeks. M.p. 278.5–279.2 °C; IR (KBr): $\tilde{\nu}$ = 3384, 3051, 2953, 1680, 1544, 1488, 1470, 1402, 1358, 1338, 1309, 1232, 1208, 1157, 1106, 1047, 1007, 982, 956, 948, 904, 887, 829, 800, 791, 780, 673, 564 cm^{-1}.

X-ray crystallography: The intensity data of compound **1** were collected using a Bruker SMART 1000 CCD diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) at 293 K. Intensities of compound **2**–**4** were collected at 293 K using a Bruker AXS Kappa APEX II CCD diffractometer with $Cu_{K\alpha}$ radiation (λ = 1.54178 Å) from a sealed-tube generator. Reflection data for complex **5** was collected using the Bruker AXS diffractometer with $Cu_{K\alpha}$ radiation (λ = 1.54178 Å) at 173 K using an Oxford Cryostream 700 Plus low-temperature attachment. Data collection and reduction were performed using SMART and SAINT software,[19] and empirical multiscan absorption corrections were applied.[20] All the structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[21] In complex **4**, the alkyl chains of both independent tetra-*n*-proplylammonium cations exhibit twofold orientational disorder, which was handled using models with constrained bond distances and angles. In complex **5**, one of the three independent Kemp's triacid moieties exhibits twofold positional disorder, and water molecule O4w is disordered over three sites.

Most hydrogen atoms in the ordered structures could be located from difference electron-density maps. In other cases, their positions were deduced by considering their surrounding environment on the basis of hydrogen-bonding geometry.

Table 1 contains a detailed assignment of the crystallographic data for compounds **1**–**5**. CCDC-754615 (**1**), 754616 (**2**), 754617 (**3**), 754618 (**4**), and 754619 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for complexes **1** to **5**.

	1	**2**	**3**	**4**	**5**
formula	$[C(NH_2)_3^+]\cdot[H_2KTA^-]$	$3[C(NH_2)_3^+]\cdot[KTA^{3-}]$	$[(CH_3)_4N^+]\cdot2[C(NH_2)_3^+]\cdot[KTA^{3-}]\cdot2H_2O$	$[(nC_3H_7)_4N^+]\cdot2[C(NH_2)_3^+]\cdot[KTA^{3-}]$	$3[(C_2H_5)_4N^+]\cdot20[C(NH_2)_3^+]\cdot11[HKTA^{2-}]\cdot[H_2KTA^-]\cdot17H_2O$
M_r	317.34	435.50	485.59	561.77	4974.77
crystal size [mm]	0.48×0.43×0.39	0.32×0.25×0.20	0.40×0.39×0.38	0.48×0.34×0.31	0.38×0.25×0.18
crystal system	monoclinic	trigonal	orthorhombic	orthorhombic	tetragonal
space group	$P2_1/n$	$R3c$	$Pbcn$	$Pca2_1$	$P4_2/n$
a [Å]	12.720(7)	18.156(2)	27.246(4)	17.9871(3)	23.0829(1)
b [Å]	10.051(5)	18.156(2)	11.833(2)	18.5681(3)	23.0829(1)
c [Å]	13.118(7)	11.980(2)	16.125(4)	19.2007(2)	24.5301(2)
α [°]	90	90	90	90	90
β [°]	114.182(7)	90	90	90	90
γ [°]	90	120	90	90	90
V [Å]	1530(2)	3420.0(7)	5199(2)	6412.8(2)	13070.2(1)
Z	4	6	8	8	2
F(000)	680	1404	2112	2464	5376
ρ_{calcd} [g cm^{-1}]	1.378	1.269	1.241	1.164	1.264
θ range [°]	1.88–28.34	4.87–67.80	4.07–67.82	3.42–67.80	3.25–66.60
measured reflns	10312	14720	96411	35400	86255
index ranges	$-9\le h\le16$ $-13\le k\le13$ $-17\le l\le16$	$-21\le h\le17$ $-20\le k\le21$ $-13\le l\le14$	$-32\le h\le32$ $-14\le k\le14$ $-15\le l\le19$	$-14\le h\le321$ $-22\le k\le22$ $-22\le l\le21$	$-27\le h\le327$ $-26\le k\le324$ $-28\le l\le26$
indep reflns (R_{int})	3791 (0.0360)	1364 (0.0237)	4679 (0.0483)	10699 (0.0503)	11435 (0.0587)
obsd reflns	2823	1352	3997	7184	8189
transmission factor	0.530	0.806	0.671	0.781	0.792
data/restraints/params	3791/0/199	1364/1/92	4679/0/299	10699/6/915	11435/9/874
$R1$ (obsd)[a]	0.0468	0.0288	0.0460	0.0713	0.0629
$wR2$ (obsd)[a]	0.1244	0.0846	0.1312	0.1844	0.1607
$R1$ (all data)[a]	0.0659	0.0289	0.0530	0.1012	0.0915
$wR2$ (all data)[a]	0.1388	0.0848	0.1384	0.2144	0.1820
GOF	1.016	1.089	1.038	1.005	1.030
max./min diff. peak [e $Å^{-3}$]	0.335, −0.326	0.185, −0.095	0.381, −0.278	0.513, −0.189	0.853, −0.390

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Acknowledgements

We acknowledge financial support by the Hong Kong Research Council (GRF CUHK 402206), the Wei Lun Foundation, and The Chinese University of Hong Kong for Research Fellowships awarded to the first two co-authors.

[1] a) *Crystal Design: Structure and Function* (Ed.: G. R. Desiraju), Wiley, New York, **2003**; b) *Frontiers in Crystal Engineering, Vol. 1* (Eds.: E. R. T. Tiekink, J. J. Vittal), Wiley, New York, **2006**; c) G. R. Desiraju *Angew. Chem.* **2007**, *119, 8492–8508; Angew. Chem. Int. Ed.* **2007**, 46, 8342–8356; *Angew. Chem. Int. Ed.* **2007**, *46*, 8342–8356; d) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; e) M. D. Hollingsworth, *Science* **2002**, *295*, 2410–2413.

[2] a) K. T. Holman, A. M. Pivovar, M. D. Ward, *Science* **2001**, *294*, 1907–1911; b) K. T. Holman, S. M. Martin, D. P. Parker, M. D. Ward, *J. Am. Chem. Soc.* **2001**, *123*, 4421–4431; c) M. A. Horner, K. T. Holman, M. D. Ward, *J. Am. Chem. Soc.* **2007**, *129*, 14640–14660.

[3] a) C.-K. Lam, F. Xue, J. P. Zhang, X. M. Chen, T. C. W. Mak, *J. Am. Chem. Soc.* **2005**, *127*, 11536–11537; b) J. Han, C.-W. Yau, C.-K. Lam, T. C. W. Mak, *J. Am. Chem. Soc.* **2008**, *130*, 10315–10326.

[4] T. C. W. Mak, F. Xue, *J. Am. Chem. Soc.* **2000**, *122*, 9860–9861.

[5] a) V. A. Russell, M. C. Etter, M. D. Ward, *J. Am. Chem. Soc.* **1994**, *116*, 1941–1952; b) C.-K. Lam, T. C. W. Mak, *Chem. Commun.* **2001**, 1568–1569; c) V. Bertolasi, L. Pretto, P. Gilli, V. Ferretti, G. Gilli, *New J. Chem.* **2002**, *26*, 1559–1566; d) G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory*, Oxford University Press, New York, **2009**; e) M. D. Ward, *Struct. Bonding* **2009**, *132*, 1–23.

[6] H. Gulyás, A. C. Benyei, J. Bakos, *Inorg. Chim. Acta* **2004**, *357*, 3094–3098.

[7] U. Schulke, M. T. Z. Averbuch-Pouchot, *Z. Anorg. Allg. Chem.* **1995**, 621, 1232–1236.

[8] D. S. Kemp, K. S. Petrakis, *J. Org. Chem.* **1981**, *46*, 5140–5143.

[9] D. J. Duchamp, R. E. Marsh, *Acta Crystallogr. Sect. A* **1969**, *25*, 5–19.

[10] J. Rebek, Jr., L. Marshall, R. Wolak, K. Parris, M. Killoran, B. Askew, D. Nameth, N. Islam, *J. Am. Chem. Soc.* **1985**, *107*, 7476–7481.

[11] T.-L. Chan, Y.-X. Cui, T. C. W. Mak, R.-J. Wang, H. N. C. Wong, *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 297–303.

[12] a) J. Rebek, Jr., *Acc. Chem. Res.* **1990**, *23*, 399–404, and references therein; b) A. Bencini, A. Bianchi, M. I. Burguete, P. Dapporto, A. Doménech, E. García-España, S. V. Luis, P. Paoli, J. A. Ramírez, *J. Chem. Soc. Perkin Trans. 2* **1994**, 569–577.

[13] a) G. Smith, U. D. Wermuth, J. M. White, *Chem. Commun.* **2000**, 2349–2350; b) G. Smith, R. C. Bott, U. D. Wermuth, *Acta Crystallogr. Sect. C* **2000**, *56*, 1505–1506; c) A. Hazell, H. Toftlund, *Acta Crystallogr. Sect. C* **1999**, *55*, IUC9900079; d) S. L. Childs, K. S. Hagen, *CrystEngComm* **2002**, *4*, 265–270; e) T. Hirose, B. W. Baldwin, Z.-H. Wang, C. H. L. Kennard, *Acta Crystallogr. Sect. C* **1998**, *54*, 1143–1144.

[14] a) P. Thuéry, M. Nierlich, B. W. Baldwin, Y. Aoki, T. J. Hirose, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2077–2082; b) F. M. Menger, P. A. Chicklo, M. J. Sherrod, *Tetrahedron Lett.* **1989**, *30*, 6943–6946.

[15] a) A. Huczyński, M. Ratajczak-Sitarz, A. Katrusiak, B. Brzezinski, *J. Mol. Struct.* **2008**, *888*, 84–91; b) A. Huczyński, M. Ratajczak-Sitarz, A. Katrusiak, B. Brzezinski, *J. Mol. Struct.* **2008**, *889*, 64–71; c) A. Huczyński, M. Ratajczak-Sitarz, A. Katrusiak, B. Brzezinski, *J. Mol. Struct.* **2008**, *892*, 414–419.

[16] A. Huczyński, J. Janczak, B. Brzezinski, *J. Mol. Struct.* **2009**, *922*, 77–82.

[17] A. Katrusiak, M. Szafrański, *Acta Crystallogr. Sect. C* **1994**, *50*, 1161–1163.

[18] To simplify the discussion, the lone H_2KTA^- ion is treated as equivalent to the other $HKTA^{2-}$ ions.

[19] Bruker SMART 5.0 and SAINT 4.0 for Windows NT: Area Detector Control and Intergration Software, Bruker Analytical X-ray Systems, Inc.: Madison, Wisconsin, **1998**.

[20] SADABS: Program for Empirical Absorption Correction of Area Detector Data, G. M. Sheldrick, University of Göttingen, Göttingen, **1996**.

[21] SHELXTL 5.10 for Windows NT: Structure Determination Software Programs, G. M. Sheldrick, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, **1998**.

Received: November 16, 2009
Published online: March 25, 2010

 © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim