Self-Organized Anionic Networks in Quaternary Ammonium and Phosphonium Salts of Mellitate

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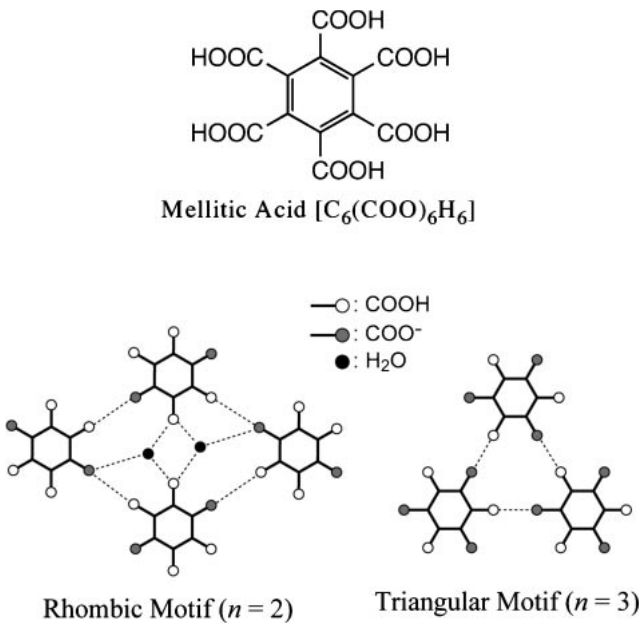
Mellitate is a unique anion that can form hydrogen-bonding anionic networks. In this study, crystal structures of the salts with quaternary ammonium and phosphonium cations that bear no hydrogen-bonding functional groups are investigated. When the number of deprotonation (n) from the parent mellitic acid is one, two kinds of networks, a two-dimensional sheet and a three-dimensional network containing helical chains, have been obtained. Both networks involve a common network motif, and this variation arises from the difference in the connection sequence of the motif. When $n = 2$, a rhombic motif that frequently occurs in the salts with proton-donating cations is also found to form. However, the vacant proton accepting sites of the anions are occupied by water molecules, and a sheet-like network with corner-sharing connection of the rhombic motifs occurs. For the salt of $n = 3$, a triangular motif that has commonly been found in the other mellitate salts of $n = 3$ with proton-donating cations is also involved in the network. Because the charge density in the simple two-dimensional sheet composed solely of the triangular motif is rather high, the network is divided into one-dimensional belts.

Mellitic acid (benzenehexacarboxylic acid; Scheme 1) has six radially arranged carboxy groups, and is known to form a two-dimensional sheet-like network by typical paired hydrogen bonds.[1] On the other hand, partially deprotonated mellitate anions also form self-organized anionic networks by strong carboxy–carboxylato hydrogen bonds.[2] Although relatively many structures of metal cordination compounds of mellitate are known,[3] there have been only a few reports about the structure of mellitate salts with organic cations.[4] Therefore, we first studied the network structures in salts made by acid–base reaction through proton transfer, in order to know the ability of network formation.[5,6] In this system, since protonated bases also have hydrogen-bonding functionality, we can see whether the self-aggregated network formation of mellitate preferentially occurs or not. As a result, when the number of deprotonation (n in $[C_6(COO)_6H_{6-n}]^{n-}$) is in a range of 2–4, infinite mellitate network formation was found to take precedence when mellitic acid was reacted with relatively small organic bases, although some exceptional structures were found in recent studies of the combination with complicated organic cations.[7] It was also found in our study that there were some common motifs in the anion–anion connection, and that the sequences of the motif made infinite networks varying from one-dimension to three-dimension. Two of the representatives are shown in Scheme 1.



Scheme 1.

The above results indicated that it might be possible to regulate the arrangement of the cationic components in the crystal using anionic mellitate networks. Indeed, when mellitate was combined with π-radical cations of the TTF (TTF = tetrathiafulvalene) derivatives, unique cationic arrangements dictated by the conformation of the anionic networks were found to form.[2,8–10] In this case, the cationic components have no hydrogen-bonding functionality, and mellitate is supposed to form self-consistent hydrogen-bonding networks. This situation is rather different from the above cases in which the cationic components finally bound to the peripheries of the anionic networks.

In order to utilize the mellitate networks for regulation of cationic arrangements, it is necessary to know how mellitate forms anionic networks when it is combined with non-

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hydrogen-bonding cationic components. Especially, it is expected that the size and shape of the cation seriously affect the network structure. For this purpose, structures of mellitate salts with quaternary ammoniums and phosphonium have been studied.

Mellitic acid deprotonates in six steps. In combination with organic amines, the number of deprotonation is governed by the equilibrium conditions in the solution rather than the simple stoichiometry of acid and base. On the other hand, in the combination with hydroxide of quaternary ammonium, the number of deprotonation is simply controlled by the stoichiometry. Also, cation exchange of the alkali metal salt prepared in a similar way will give the salt with a fixed number of deprotonation. In this paper, crystal structures of five quaternary ammonium and phosphonium salts with mellitate prepared by these methods and of a salt closely related to this systematic study (Scheme 2) will be described, especially noting the mellitate network structures, the number of deprotonation, and inter-anionic connecting patterns.

Experimental

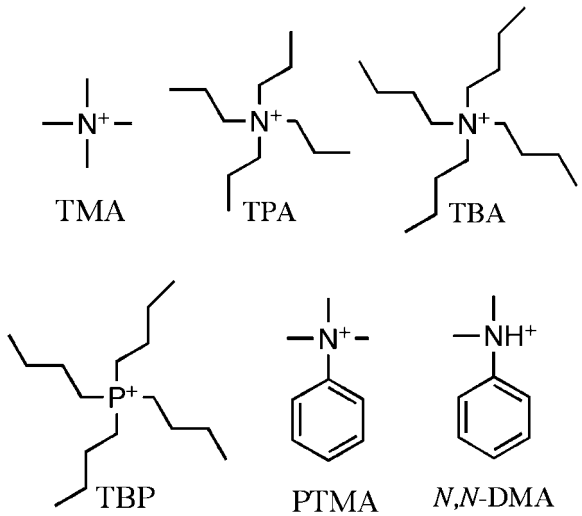
Preparation of the Salt Crystals. The salt crystals were prepared by the following two methods.

Method A: Mellitic acid and quaternary ammonium hydroxide with a desired molar ratio were mixed in methanol/H_2O (TPA and TBA) or in methanol/*t*-butyl alcohol (TMA) with mild heating. The solution was left standing at room temperature with slow evaporation of the solvent.

Method B: Mellitic acid was first reacted with KOH of a desired molar ratio in water, and the potassium salt was obtained after evaporating water. Then, the ammonium or phosphonium salt crystal was precipitated by metathesis of the potassium salt with the bromide salt (PTMA and TBP) in water.

The *N*,*N*-DMA salt was obtained by the method A using the PTMA hydroxide in methanol. During the crystal growth, PTMA was found to convert to *N*,*N*-DMA. The obtained salt crystals were the TPA salt (TPA[$C_6(COO)_6H_5^-$]·3H_2O, $n = 1$), TBA salt (TBA[$C_6(COO)_6H_5^-$]·2H_2O, $n = 1$), TBP salt (TBP[$C_6(COO)_6H_5^-$]·2H_2O, $n = 1$), PTMA salt ([PTMA]$_2$-[$C_6(COO)_6H_4^{2-}$]·4H_2O, $n = 2$), TMA salt ([TMA]$_3$[C_6-$(COO)_6H_3^{3-}$]·4H_2O, $n = 3$), and *N*,*N*-DMA salt ([*N*,*N*-DMA]$_2$[$C_6(COO)_6H_4^{2-}$]·2H_2O, $n = 2$).

X-ray Structure Analyses. Diffraction data were recorded on a Rigaku R-AXIS Rapid imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The crystal data are summarized in Table 1. The structures were solved using direct methods (SIR-92,[11] SHELX97,[12]



Scheme 2.

Table 1. Crystal Data and Structural Refinement Parameters

	TPA salt ($n = 1$)	TBA salt ($n = 1$)	TBP salt ($n = 1$)	PTMA salt ($n = 2$)	TMA salt ($n = 3$)	*N*,*N*-DMA salt ($n = 2$)
Formula	$C_{24}H_{39}NO_{15}$	$C_{28}H_{45}NO_{14}$	$C_{28}H_{45}O_{14}P$	$C_{30}H_{40}N_2O_{16}$	$C_{24}H_{47}N_3O_{16}$	$C_{28}H_{32}N_2O_{14}$
Formula weight	581.57	619.66	636.63	684.65	633.65	620.56
Crystal system	orthorhombic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$C222_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a/Å	14.010(15)	9.677(9)	9.599(1)	10.699(1)	9.541(1)	9.798(1)
b/Å	13.249(16)	9.680(9)	9.721(1)	19.428(2)	9.716(1)	15.352(2)
c/Å	31.07(4)	19.00(2)	18.592(3)	15.780(2)	33.187(2)	10.047(1)
α/°	—	84.30(4)	99.42(1)	—	—	—
β/°	—	76.63(4)	101.94(1)	98.57(1)	—	71.17(1)
γ/°	—	74.67(3)	100.58(1)	—	—	—
V/Å^3	5767(11)	1669(3)	1631.3(4)	3243.3(6)	3076.3(4)	1430.3(3)
Z	8	2	2	4	4	2
D_x/g cm^{-3}	1.340	1.233	1.296	1.402	1.368	1.441
μ(Mo Kα)/cm^{-1}	1.118	0.986	1.488	1.144	1.148	1.167
$2\theta_{max}$	55.0	55.0	55.0	55.0	55.0	55.0
Temp. of data collection/K	110	118	153	123	120	273
No. of unique reflections	3636	7507	7406	7429	3991	3257
R_{int}	0.058	0.092	0.025	0.030	0.031	0.051
No. of variables	450	446	445	503	435	215
$R1$ [$I > 2.0\sigma(I)$]	0.060	0.066	0.053	0.038	0.035	0.052
R_w (F^2, all data)	0.147	0.137	0.134	0.113	0.091	0.118
GOF indicator	0.918	1.019	1.185	1.339	0.926	0.879

or SIR2002[13]) and refined with all data on F^2 using the CrystalStructure program package.[14] Full-matrix least-squares refinements were performed for non-hydrogen atoms with anisotropic thermal parameters.

The hydrogen positions in the O–H···O hydrogen bonds of mellitate (except for the paired hydrogen bond) were determined by applying the geometric features as follows.[5] The deprotonation from a carboxy group was determined from the ratio ($r = a/b$) of lengths of two C–O bonds (a and b; $a \geq b$). An r value larger than 1.07, and an O–H···O hydrogen-bond distance longer than about 2.5 Å is characteristic of a carboxy group. Deprotonation occurs in a species with an r value smaller than 1.03 and an O···O distance longer than about 2.5 Å. When $1.03 < r < 1.07$ and the hydrogen-bond distance is very short (O···O < 2.5 Å), the proton is thought to be equally shared by the two O atoms (deprotonation number is 0.5). For the carboxy···carboxy paired hydrogen bond, the above relation cannot be applied. However, it is easy to recognize the formation from the molecular arrangement; two COO groups are arranged to form two pairs of short O···O contacts (typically around 2.6 Å). Structural data of paired hydrogen bonds in various compounds revealed that the r value of the carboxy group in a paired hydrogen bond became much smaller than those of normal carboxy groups.[15] The atom to which the hydrogen is attached was determined from the geometric features, and the position was finally determined by the difference Fourier maps or assigned at the midpoint of the hydrogen bond (*N*,*N*-DMA salt) due to the broad electron density peak (fixed position with isotropic thermal parameters). The hydrogen positions of water molecules were also determined from the difference Fourier maps except those of the TPA salt for which hydrogen atoms of water were not included in the refinement. The other hydrogen atoms were placed at the ideal positions, and included in the refinement with a riding model. Disorder of alkyl chains and water found in the TPA salt was treated as two overlapped moieties with 0.5 occupancies.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-763024–763029 for the six compounds. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results

The charge of mellitate (n) in the quaternary ammonium and phosphonium salts can simply be determined from the anion/cation ratio in the composition. The n values thus derived were found to be consistent with those determined independently from the geometries of the carboxy/carboxylato groups as shown below. The r values of the carboxy/carboxylato groups for the determination of n are summarized in Table 2. Also, the O···O distances in hydrogen bonds found between mellitates are listed in Table 3.

TPA Salt ($n = 1$). The geometries of six independent carboxy/carboxylato groups (A to F in Figure 1a) are summarized in Table 2. From the r values, C, D, E, and F can be assigned as carboxy groups. The r value of B is close to the boundary between the carboxylato and intermediate regions.

Table 2. C–O Bond Lengths and r in Mellitate Anions

	Carboxy/carboxylato group	a/Å	b/Å	r	Assignment[a)]
TPA salt	A	1.264(5)	1.226(5)	1.03	carboxylato
($n = 1$)	B	1.278(5)	1.230(5)	1.04	paired
	C	1.312(5)	1.201(5)	1.09	carboxy
	D	1.302(5)	1.211(5)	1.08	carboxy
	E	1.325(5)	1.195(5)	1.10	carboxy
	F	1.314(5)	1.212(5)	1.08	carboxy
TBA salt	A	1.272(3)	1.241(3)	1.02	carboxylato
($n = 1$)	B	1.279(3)	1.270(3)	1.01	paired
	C	1.313(3)	1.221(4)	1.08	carboxy
	D	1.313(4)	1.226(3)	1.07	carboxy
	E	1.307(4)	1.264(4)	1.03	paired
	F	1.328(4)	1.214(3)	1.09	carboxy
TBP salt	A	1.279(2)	1.231(2)	1.04	carboxylato
($n = 1$)	B	1.297(2)	1.229(2)	1.06	carboxy
	C	1.306(2)	1.209(2)	1.08	carboxy
	D	1.288(2)	1.222(2)	1.05	carboxy
	E	1.307(2)	1.222(2)	1.07	carboxy
	F	1.309(2)	1.215(2)	1.08	carboxy
PTMA salt	A	1.262(1)	1.247(1)	1.01	carboxylato
($n = 2$)	B	1.318(1)	1.214(1)	1.09	carboxy
	C	1.266(1)	1.238(1)	1.02	carboxylato
	D	1.312(1)	1.212(1)	1.08	carboxy
	E	1.300(1)	1.222(1)	1.06	carboxy
	F	1.308(1)	1.221(1)	1.07	carboxy
TMA salt	A	1.263(2)	1.236(2)	1.02	carboxylato
($n = 3$)	B	1.320(2)	1.210(2)	1.09	carboxy
	C	1.275(2)	1.241(2)	1.03	carboxylato
	D	1.297(2)	1.222(2)	1.06	carboxy
	E	1.273(2)	1.233(2)	1.03	carboxylato
	F	1.290(2)	1.226(2)	1.05	carboxy
N,*N*-DMA	A	1.309(2)	1.205(2)	1.09	carboxy
salt	B	1.271(2)	1.218(2)	1.04	shared
($n = 2$)	C	1.275(2)	1.228(2)	1.04	shared

a) Paired: forming a paired hydrogen bond with itself (carboxy group), shared: one proton is shared with another carboxylato group (intermediate between carboxy and carboxylato group).

However, this group can be assigned as a carboxy, since it forms a paired hydrogen bond with the same group of the neighboring anion related by twofold rotation symmetry. Indeed, the difference Fourier map clearly indicates electron densities corresponding to a paired hydrogen bond between B and B^{ii} (symmetry operation; $-x, y, -z + 1/2$). The r value of A indicates that this is a carboxylato group. This assignment is supported by the fact that A forms a single hydrogen bond with carboxy D. Consequently, n becomes one, which is consistent with the composition.

In this crystal, direct inter-anionic hydrogen bonds are only A···D (single hydrogen bond) and B···B (paired hydrogen bond). However, there are many crystal water molecules, and all of them are bound to the anions by strong hydrogen bonds as shown in Figure 1. The total anionic network including water becomes a complicated 3-D conformation. The unique

Table 3. Selected Hydrogen Bonds between Carboxy/Carboxylato Groups

	Groups	O···O distance/Å	Symmetry operation
TPA salt ($n = 1$)	A···D^{i}	2.486(4)	$x - 1/2, y + 1/2, z$
	B···B^{ii}	2.603(4)	$-x, y, -z + 1/2$
TBA salt ($n = 1$)	B···B^{ii}	2.644(2)	$-x, -y + 1, -z + 1$
	D···A^{iii}	2.502(2)	$x + 1. y, z$
	E···E^{i}	2.621(2)	$-x + 1, -y + 1, -z$
TBP salt ($n = 1$)	B···B^{i}	2.639(2)	$-x + 1. -y + 2, -z + 1$
	E···E^{ii}	2.644(2)	$-x, -y + 1, -z$
	A···D^{iii}	2.459(2)	$x, y + 1, z$
PTMA salt ($n = 2$)	A···D^{i}	2.587(1)	$-x + 3/2, y - 1/2, -z + 1/2$
	C···E^{v}	2.463(1)	$x + 1/2, -y + 1/2, z + 1/2$
	D···A^{iv}	2.587(1)	$-x + 3/2, y + 1/2, -z + 1/2$
	E···C^{iii}	2.463(1)	$x - 1/2, -y + 1/2, -z - 1/2$
TMA salt ($n = 3$)	C···F^{i}	2.497(2)	$x, y - 1, z$
	D···E^{ii}	2.515(2)	$-x, y - 1/2, -z + 1/2$
N,*N*-DMA salt ($n = 2$)	B···C^{ii}	2.480(2)	$x - 1/2, -y + 1/2, z + 1/2$

fragment in this network may be an infinite helical chain as depicted in Figure 1b. The TPA cations are entangled in the mellitate network; a single pitch of the helix accommodates two TPA cations, while a space between the helical chains accommodates two other TPA cations (Figure 1c).

TBA Salt ($n = 1$). The geometries of six independent carboxy/carboxylato groups (A to F in Figure 2a) are summarized in Table 2. The *r* values clearly indicate that C, D, and F are carboxy groups. On the other hand, the *r* values suggest that A, B, and E are carboxylato groups. However, B and E respectively form paired hydrogen bonds with themselves related by inversion symmetry. Since the Fourier map revealed two electron density peaks in each O···O contact, the refinement was performed by assuming that one hydrogen atom with 0.5 occupancy is attached to each oxygen atom. The remaining A was assigned as a carboxylato group, since it forms a single hydrogen bond with carboxy D. The charge of the anion is thus -1.

Direct inter-anionic hydrogen bonds are A···D (single hydrogen bond), B···B and E···E (paired hydrogen bond). These hydrogen bonds connect one anion to the four neighboring anions, resulting in the formation of a 2-D sheet-like network. The unit motif of the connection quite resembles the rhombic hydrogen bond for mellitate with $n = 2$. Indeed, the water occupation pattern in the rhombic hole is the same. If the paired hydrogen bonds in the present salt are replaced with the single hydrogen bonds, they are completely identical. The TBA cations are sandwiched between the sheets with spreading flat alkyl chains (Figure 2b).

TBP Salt ($n = 1$). The geometries of six independent carboxy/carboxylato groups (A to F in Figure 3a) are summarized in Table 2. Practically, the crystal structure is the same with the TBA salt, although it is not crystallographically isomorphous with the TBA salt. B and E are carboxy groups

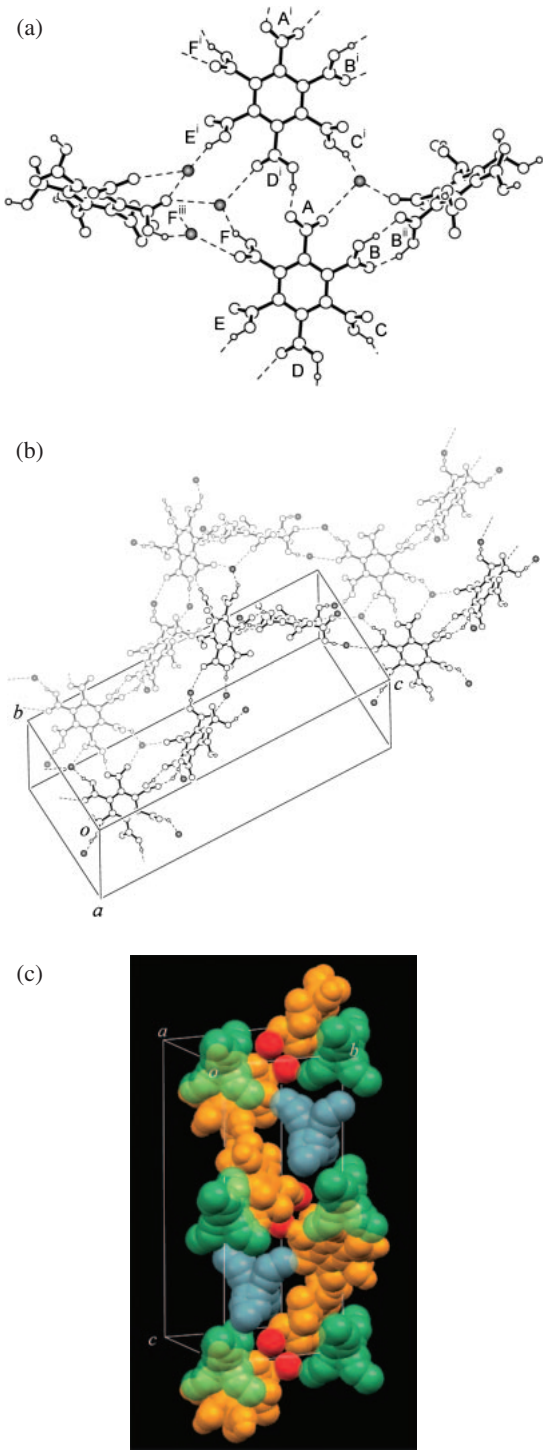


Figure 1. (a) Hydrogen bonds in the mellitate network in the TPA salt. (b) Helical chains in the mellitate network in the TPA salt. (c) Packing of the TPA cations in the mellitate network. Yellow: mellitate, red: water, light blue: TPA accommodated in the helical chain, light green: TPA located between the helical chains.

forming paired hydrogen bonds, and C and F are also carboxy groups hydrogen-bonding with water. The *r* values of A and D which form a single hydrogen bond are both in the intermediate region. Since the Fourier map indicated a hydrogen peak closer to D, D was assigned as a carboxy group and A as carboxylate.

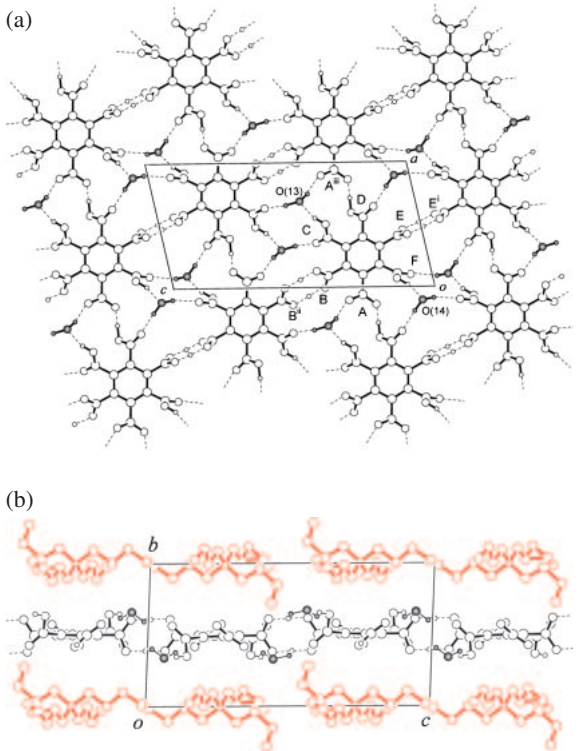


Figure 2. (a) Two-dimensional sheet of mellitate in the TBA salt. (b) Side view of the mellitate sheets and TBA layers. Red fragments are TBA.

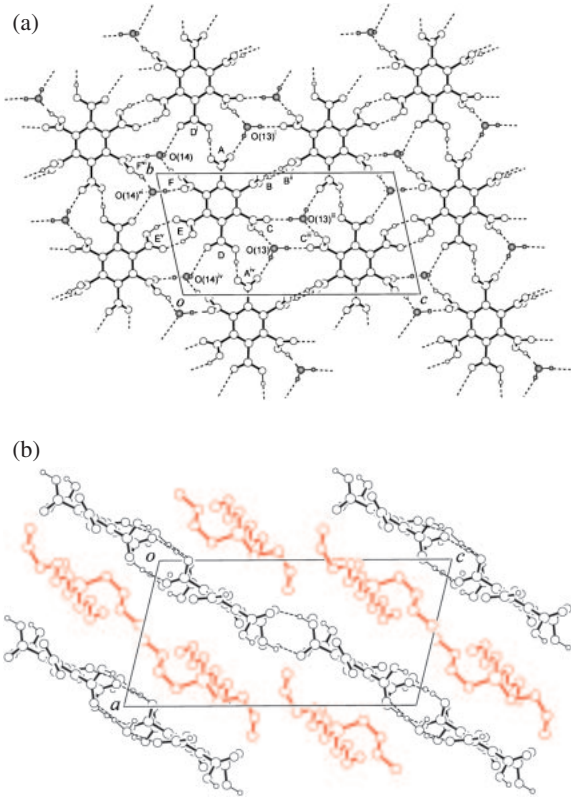


Figure 3. (a) Two-dimensional sheet of mellitate in the TBP salt. (b) Side view of the mellitate sheets and TBP layers. Red fragments are TBP.

The real situation, however, may be such that one proton is shared by A and D, because the O···O distance is extremely short (Table 3). In any case, n should be one that is consistent with the composition.

The anionic sheet-like network is constructed with the rhombic-like motif composed of A···D (single) and B···B and E···E (paired) hydrogen bonds with water molecules (Figure 3a). The conformations of the anionic network and the cation are practically the same as those in the TBA salt (Figure 3b).

PTMA Salt ($n = 2$). The geometries of six independent carboxy/carboxylato groups (A to F in Figure 4a) are summarized in Table 2. The r values clearly indicate that A and C are carboxylato groups and B and D are carboxy groups. Though E and F are near the boundary between the carboxy and intermediate regions, both can be assigned as carboxy groups from the following reasons. First, E forms a single hydrogen bond with carboxylato C. Second, F forms hydrogen bonds with water molecules as shown in Figures 4a and 4b. In this pattern, F has to have a proton donor portion. Assignment of E and F as carboxy is consistent with the Fourier map. The resultant charge, $n = 2$, agrees with the composition.

All of the inter-anionic connections are single hydrogen bonds of A···D and C···E. By these connections, one anion is bound with four anions, forming a 2-D sheet-like network (Figure 4a). The light orange colored rhombus in this figure corresponds to the rhombic hydrogen bond commonly observed in the piperidinium salts.[4] However, in contrast to the 2-D sheet in the piperidinium salts in which the neighboring rhombuses with the same orientation are connected by sharing an edge, the rhombuses in the PTMA salt are connected at the corner since the orientation of the rhombuses changes alternately due to the relation by the 2_1 screw axis. The connection motif surrounded by four orange rhombuses (light blue colored area) contains two water molecules and may be regarded as an analog of the rhombic hydrogen bond. However, water molecules in this motif largely projected from the rhombic plane, and are bound to other water molecules by hydrogen bonds to bridge the neighboring sheets (Figure 4b). As discussed later, it will be seen that this light blue colored motif is inevitable when cations have no proton-donating functional groups. PTMA's are arranged between the anionic sheets with phenyl plane perpendicular to the sheet (Figure 4c).

TMA Salt ($n = 3$). The geometries of six independent carboxy/carboxylato groups (A to F in Figure 5a) are summarized in Table 2. It is not difficult to assign A as a carboxylato group and B as a carboxy group from their r values. The r values of C, D, E, and F are in the intermediate region. These groups form inter-anionic single hydrogen bonds (C···F and D···E). Since the Fourier map clearly indicated electron densities closer to D and F, D and F were assigned as carboxy groups and C and E as carboxylato groups. As a result, the anion is $n = 3$, agreeing with the composition.

The only known network composed of mellitate with $n = 3$ is a two-dimensional sheet made by triangular hydrogen-bond units.[5,6] In the present salt, a triangle is actually formed by inter-anionic single hydrogen bonds. However, instead of an infinite 2-D sheet, the units form a 1-D belt along the b axis (Figure 5a). Carboxylato A and carboxy B at the hem of the 1-D belt are not

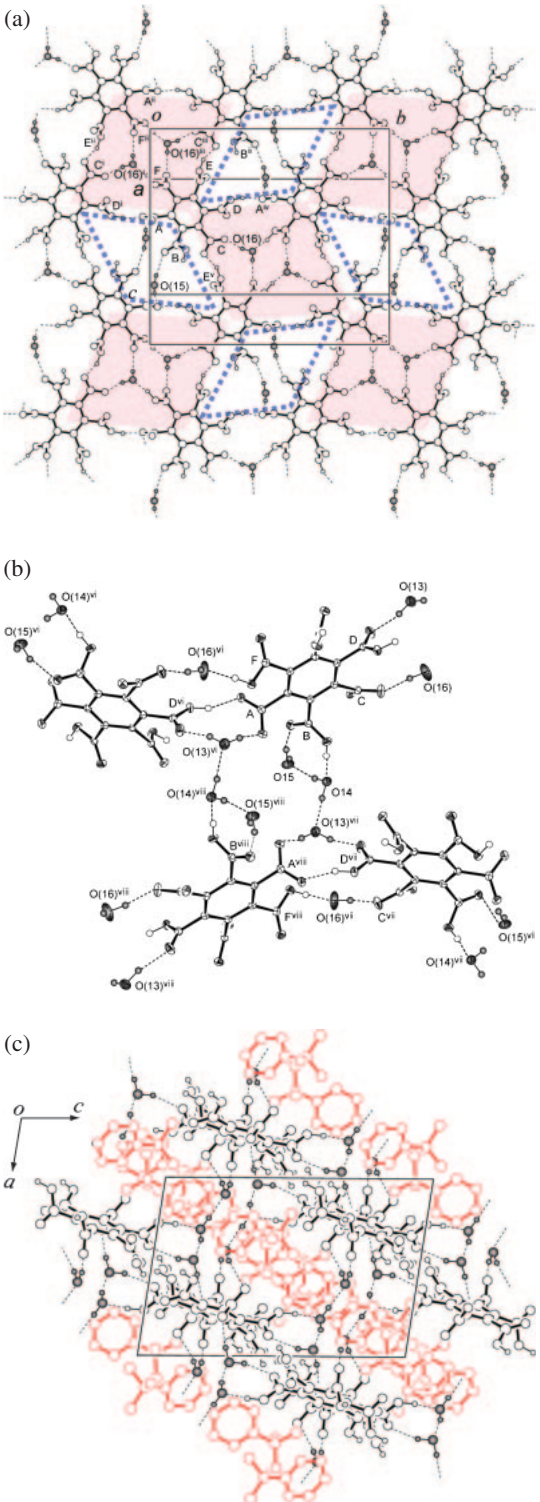


Figure 4. (a) Two-dimensional sheet of mellitate in the PTMA salt. Each orange rhombus indicates the rhombic unit. (b) Hydrogen bonds between the mellitate sheets. (c) Side view of the mellitate sheets and cation layers. Red fragments are PTMA.

bound with the other anions but with water molecules. The hemmed water molecules are further bound with other water molecules so that the 1-D belts are stitched together by the

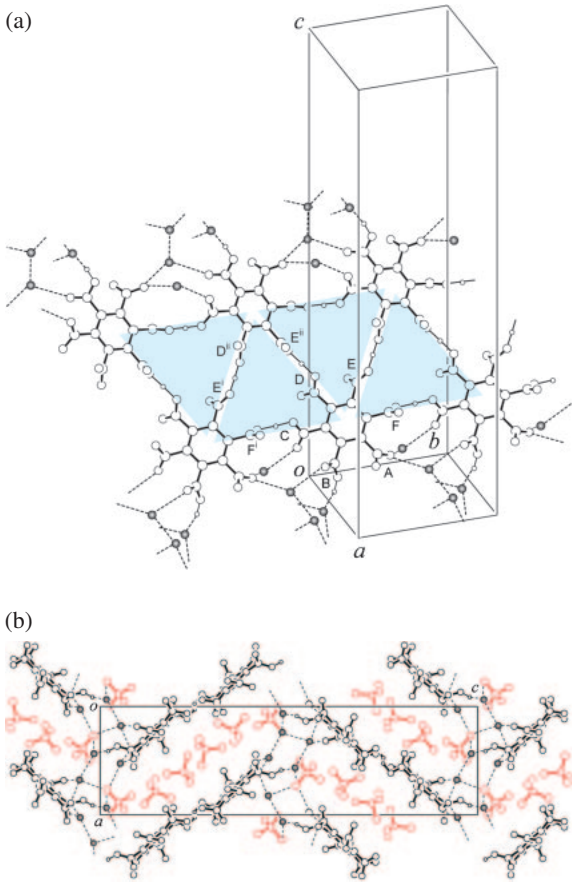


Figure 5. (a) One-dimensional mellitate belt in the TMA salt. Each light-blue triangle indicates the triangular unit. (b) Packing of the mellitate belts and TMA cations. Red fragments are TMA.

water-mediated hydrogen bonds to form a corrugated 2-D sheet-like network as shown in Figure 5b. Most TMA's are packed in the space sandwiched between the 1-D belts.

***N*,*N*-DMA Salt ($n = 2$).** The geometries of three independent carboxy/carboxylato groups (A to C in Figure 6a) are summarized in Table 2. The r value of A clearly indicates that this group is carboxy. Whereas those of B and C are in the intermediate region, these two groups form a single hydrogen bond, and the O···O distance is rather short (Table 3). Therefore, we assumed that one proton was shared by these groups (n for both B and C is 0.5). Indeed, the Fourier map indicates a single broad peak near the center of the hydrogen bond. Since the anion is located at an inversion center, n of the anion becomes 2, and one can conclude that *N*,*N*-dimethylaniline is protonated. The Fourier map actually shows an electron density peak corresponding to the N–H proton of *N*,*N*-DMA.

As shown in Figure 6a, one mellitate anion is bound with four neighboring mellitate anions by four inter-anionic B···C single hydrogen bonds, resulting in a 2-D sheet based on the rhombic hydrogen bond that is known as one of the typical inter-anionic connection motifs of mellitate with $n = 2$ (with two water molecules in the rhombic hole).[6] The cations aligned between the sheets with aromatic planes perpendicular to the sheet plane (Figure 6b). There is a N–H···O hydrogen bond between the cation and anion.

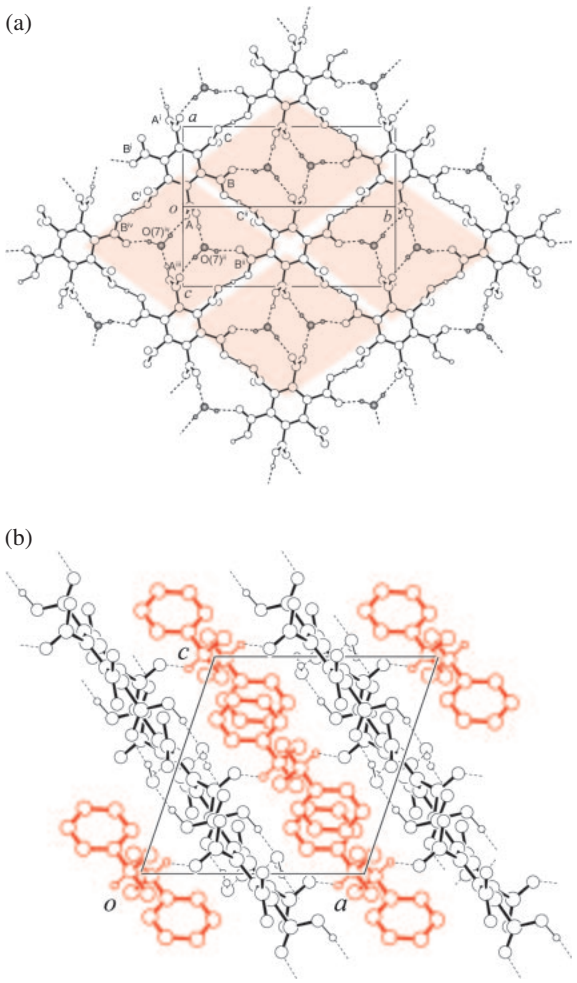


Figure 6. (a) Two-dimensional sheet of mellitate in the *N*,*N*-DMA salt. Each orange rhombus indicates the rhombic unit. (b) Side view of the mellitate sheets and cation layers. Red fragments are *N*,*N*-DMA.

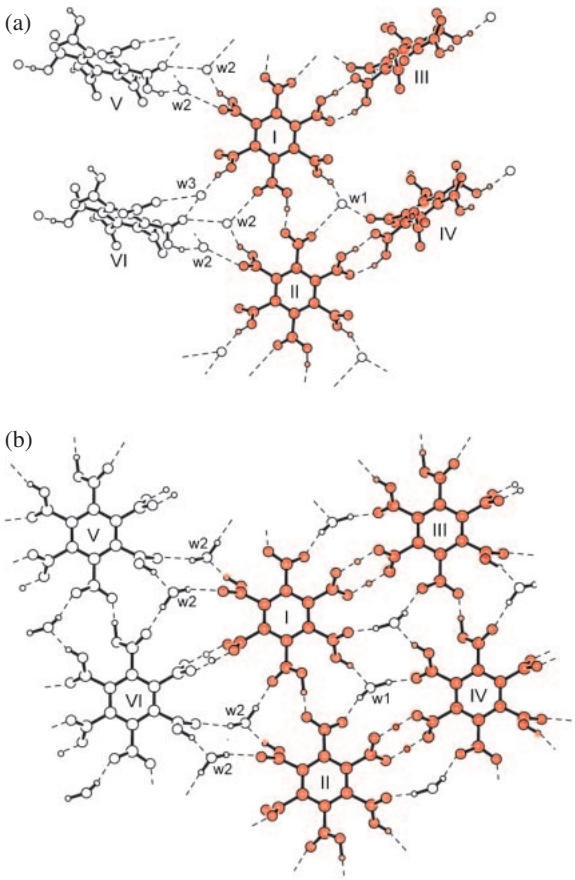


Figure 7. (a) Hydrogen bonds in the mellitate network in the TPA salt. (b) Hydrogen bonds in the mellitate network in the TBA salt.

Discussion

Network of Mellitate with $n = 1$. A network of mellitate with $n = 1$ has not been reported. This is because deprotonation reagents so far used have all been organic amines that mainly induce the anionic species in the range of $n = 2$–4 under the equilibrium conditions. In the present study, deprotonation using strong bases of hydroxides made possible regulation of the n values, yielding three salts with $n = 1$.

The anionic network in the TPA salt looks very different from that in the TBA or TBP salt. However, we found that both networks basically contain a certain common fragment. The fragment is shown in Figure 7. First, mellitate I is connected with translationally related mellitate II by the single hydrogen bond, resulting in formation of a 1-D chain. Mellitate I is further connected with mellitate III by the paired hydrogen bond, and with mellitate V by hydrogen bonds mediated by two water molecules (w2). Mellitate I is also connected with mellitate IV by hydrogen bonds mediated by w1. These features are all common in both TPA and TBA (TBP) salts.

The difference in the total network structure arises from the next step of the connection. For the smaller TPA cation, the neighboring anions (mellitate I and VI) have to be twisted so that the cation is wrapped in the anionic network. For this conformation, mellitate I can be connected with mellitate VI only by water (w3)-mediated hydrogen bonds, forming an anionic network containing helical chains in the TPA salt. On the other hand, for the larger TBA (TBP) cation, planar conformation of the anionic network has enough area to accommodate the cations. As a result, mellitate I is bound directly with coplanar mellitate VI by the paired hydrogen bond, forming a rhombic-like 2-D network.

Comparison of the Anionic Networks in the PTMA and *N*,*N*-DMA Salts. In these salts, mellitate with $n = 2$ forms a 2-D network containing the rhombic hydrogen bond unit in common. The size and shape of the cation are also similar in these salts. However, there are two distinct features in the network structure; the first is the arrangement of the rhombic units and the second is the existence of the water-mediated hydrogen-bonding connection between the anionic sheets. As shown below, we discuss these points by closing-up the rhombic units.

The rhombic unit moieties in these salts are shown in Figure 8. The arrows in Figure 8a of the *N*,*N*-DMA salt indicate the oxygen atoms which hydrogen-bond with the proton of the cation. As a result, all of the remaining hydrogen-bonding functional sites are occupied by the cationic coordination. On the other hand, in the PTMA salt, water molecules

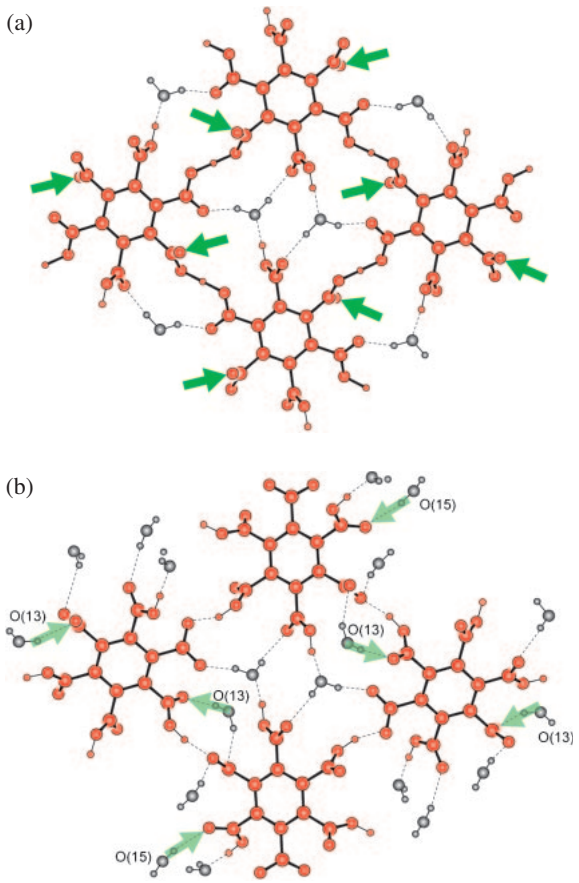


Figure 8. Hydrogen-bonding networks in the *N*,*N*-DMA salt (a) and PTMA salt (b). Arrows in (a) indicate the oxygen atoms that form hydrogen bonds with *N*,*N*-DMA. In (b), most of the corresponding sites (indicated by arrows) are occupied by hydrogen bonds with water.

occupy these hydrogen-bonding functional sites, since the cation has no hydrogen-bonding functional group. Furthermore, since the proton-accepting sites of these water molecules are still accessible, the other water molecules can be bound with these sites and bridge the anionic sheets (Figure 4b). By such modification of the peripheral structure of the rhombic unit, it is no longer possible to be arranged by edge-shared connection, and the network becomes corner-shared connection.

The present study has confirmed that mellitate with $n = 2$ has strong tendency to form the rhombic hydrogen bond unit. However, it has also been found that the infinite network formed by this unit strongly depends on the presence of the proton-donating site in the cation.

Triangular Hydrogen Bond of Mellitate with $n = 3$. The TMA salt contains networks composed of mellitate with $n = 3$. For this anion, only 2-D sheet-like network made by the triangular hydrogen bonds has been known.[5,6] In the TMA salt, the triangular hydrogen bond unit is actually formed. However, the connection is only along the 1-D direction. The peripheries of the belt are coordinated by water molecules, and they bridge the neighboring belts. Most of the TMA cations are accommodated between the belts, but some are crowded out of the space (Figure 5b). Since the area of the unit charge of the anion is apparently incompatible with the cationic size, the space between the simple 2-D anionic sheets based only on the triangular hydrogen bond unit cannot accommodate the required number of the cations. Therefore, bridging water molecules need to participate to increase the area of the network par unit charge.

Conclusion

In this study, crystal structures of the mellitate salts with non-hydrogen-bonding cations of quaternary ammonium and phosphonium have been examined. It has been found that mellitate with $n = 1$ forms two types of networks, a 2-D sheet and a 3-D network containing helical chains, but both networks involve a common network motif and this variation arises from the difference in the connection sequence of the motif according to the cationic size. When $n = 2$, a rhombic motif that frequently occurs in the salts with proton-donating cations is also found to form. However, it has been found from the comparison of the anionic networks in the PTMA and *N*,*N*-DMA salts that the unoccupied proton accepting sites of the anion are occupied by water molecules in the PTMA, leading to a modification of the connection of the rhombic motifs. For the salt of $n = 3$, a triangular motif that has commonly been found in other mellitate salts of $n = 3$ with proton-donating cations is also involved in the network. Because the charge density in the simple two-dimensional sheet composed solely of the triangular motif is rather high, the network is divided into one-dimensional belts bridged by water to reduce the charge density in the anionic network.

In all the crystals, the anionic network is found to involve crystal water, and in some cases, the network is divided by water. The fundamental common motifs determined by n can be found in all the salts. The number of deprotonation, n, determines the number of cations that should be accommodated at the same time. In some cases, unit size per charge in the anionic network simply connected by infinite sequence of the fundamental unit is incompatible with the cationic size. Thus, water molecules play roles of glue and insertion between the fundamental units to help the anionic networks to be modified. In addition, a majority of the cations in this study do not have hydrogen-bonding ability. A part of the hydrogen-bonding functional sites of the anion that do not participate in the inter-anionic hydrogen bonds are thus left unoccupied. These sites are preferentially inhabited with water molecules, stabilizing the overall structure. Due to this situation, all the crystals combined with cations without hydrogen-bonding ability are surmised to be unable to crystallize without crystal water.

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