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Crystal structures of four inclusion compounds of 2,2'-dithiosalicylic acid and tetraalkylammonium

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ABSTRACT

Herein four inclusion compounds of 2,2'-dithiosalicylic acid $2(CH_3)_4N^+ \cdot C_{14}H_8O_4S_2^{2-} \cdot H_2O_1$ tetraalkylammonium, (1), and $(C_2H_5)_4N^+ \cdot C_{14}H_9O_4S_2^{-1} \cdot 0.25H_2O(2), (n-C_3H_7)_4N^+ \cdot C_{14}H_9O_4S_2^{-1}$ (**3**) and $(n-C_4H_9)_4N+C_{14}H_9O_4S_2^{-}(4)$ are prepared and characterized by X-ray single crystal diffraction. As shown in the results, compounds 1 and 3 belong to orthorhombic crystal system with different space groups of P2₁2₁2₁ and Pca2₁, and **2** and **4** are monoclinic system with similar groups of $P2_1/n$ and $P2_1/c$. The crystallography data are displayed below: **1**: *a* = 10.5903(7) Å, *b* = 10.6651(7) Å, *c* = 21.9476(13) Å, V = 2478.9(3) Å³, Z = 4, $R_1 = 0.0359$; **2**: a = 8.13340(1) Å, b = 22.0741(3)Å, c = 13.2143(2)Å, $\beta =$ 101.6360(1) °, V = 2323.70(6) Å³, Z = 1, R_1 = 0.0385; **3**: a = 15.7857(2) Å, b = 8.24830(1) Å, c = 20.2599(2) Å, V = 2637.94(5) Å³, Z = 4, R₁ = 0.0308_{dearee}4: a = 11.7476(2) Å, b = 17.1346(1) Å, c = 16.3583(3)Å, $\beta = 109.4560(1)$ °, V = 3104.74(9)Å³, Z = 4, R_1 = 0.0562. Interestingly, although the carbon chains of the guest templates vary from methyl group to butyl group, the host molecules of 2,2'-dithiosalicylic acid all construct the similar 2D hydrogen-bonded host layers with or without the existence of water molecules to contain the guest templates to yield analogous sandwich-like inclusion compounds. Obviously, although the guest templates will have certain effects on the ultimate formation of these crystal structures, the host molecule of 2,2'-dithiosalicylic acid is a controlling factor to form these four inclusion compounds.

KEYWORDS

Crystal structure; hydrogen bond; inclusion compounds

Introduction

One of the most important problems of crystal engineering is crystal structure prediction (CSP) [1]. It's a tough task to predict the crystal structure from the original organic molecule due to many reasons such as temperature, solvent, pH value, molecular configuration, weak interaction and so on. Thus, if some variables can be fixed during the formation of the crystals and only one or two variables are adjusted, it is very possible to obtain beneficial results to provide useful information for CSP.

In our systematic research of crystal structures of inclusion compounds, one host molecule with special configuration was often adopted to interact with the guest

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template of tetraalkylammonium to understand various weak interactions in the hostguest system and the infection of varied carbon chains of the guest templates [2]. And 2,2'-dithiosalicylic acid (DTSA) came into our eyes because it can generate hydrogen bonds with its COOH groups and it also can freely rotate with its S-S bond to get a relatively flexible configuration. As a multi-carboxyl multi-ring aromatic host molecule with 'L' configuration, DTSA is usually applied as the ligand of different MOFs [3] and its metal derivatives have special medicinal values [4]. As we know, the crystal structure of DTSA has been reported before [5] and it shows DTSA indeed displays good ability to form hydrogen bonds with its functional groups. At the same time, the two central S atoms, to some degree, make the two terminal rigid benzene rings rotate with each other to obtain abundant hydrogen-bonded linking modes and various packing patterns. Searching in CSD database [6], DTSA can interact with many compounds, such as methyltriethylammonium chloride [7], pyridine [8], hexamethylenetetramine [9], isoniazid [10], 1,4,10,14-tetraoxa-7,16-dizazcyclo-octadecane [11], bipyridine [12], bipyridine derivatives [13], tetrahydrofuran [14], 1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-aminium [15], aminopyridine [16], 1,1'-(p-phenylenedimethylidene)diimidazol-3-ium [17], sulfanylbenzoic acid [18], azanium [19] and iminodiethanaminium [20], to yield a plenty of interesting cocrystals, in which the molecules of **DTSA** emerge as the 'L' configuration along the central S-S axis with the interplanar angles between two terminal benzene rings being near to 90° and the S \leftarrow O hypervalent bonds existed between S atoms and the neighboring O atoms also consolidate the special shape of **DTSA** molecules [13]. Therefore, **DTSA** can be thought of as a potential host molecule that is a rigid aromatic molecule with relative flexibility.

Herein, **DTSA** was adopted as the host molecule to react with four tetraalkylammonium hydroxides with varied carbon chains to get four inclusion compounds with the same solvents of $H_2O/EtOH$ (v:v = 2:1): $2(CH_3)_4N^+ \cdot C_{14}H_8O_4S_2^{-2-} \cdot H_2O$ (1), $(C_2H_5)_4N^+ \cdot C_{14}H_9O_4S_2^{--} \cdot 0.25H_2O$ (2), $(n-C_3H_7)_4N^+ \cdot C_{14}H_9O_4S_2^{--}$ (3) and $(n-C_4H_9)_4N^+ \cdot C_{14}H_9O_4S_2^{--}$ (4). Analyzing these crystal structures, in compound 1, **DTSA**²⁻ anion links the only water molecule with O-H ...O interactions to yield the 2D waving host layers to contain two tetramethylammonium cations to form the sandwich-like structure, and **DTSA**⁻ anions of compounds 2–4 generate long hydrogen-bonded chains by themselves with O-H ...O contacts to yield the layer host lattices, in which different guest cations are accommodated between the layers to construct the ultimate crystal structures. Interestingly, although different guest cations with varied carbon chains were used in the experiments, the final crystal packing modes all show similar layer host lattices and sandwich-like structures. From here, we can see that the host molecule of **DTSA** is a more significant factor to control the final crystal structures during the formation of these four inclusion compounds.

Experimental

Synthesis of inclusion compounds

DTSA (98%, A. R.) was purchased from Alfa Company and tetraalkylammonium hydroxides (25% aqueous solution, A. R.) were from Aladdin company. **DTSA** and the corresponding tetraalkylammonium hydroxides were dissolved in small quantities of water/ethanol (100/50 v/v) with a 1: 2 molar ratio. The mixtures were stirred for about half an hour and set aside to crystallize, finally yielding yellow block crystals suitable for single crystal X-ray diffraction after 15 days.

X-ray data collection and structure determination

Crystals of four compounds were mounted on glass fibers for geometry and intensity data collection with a Bruker SMART Apex II CCD area detector [21] at room temperatures. The structures were solved with the direct methods and refined by full matrix least square methods based on F^2 , using the structure determination and graphics package SHELXTL [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all H atoms bonded to C atoms were introduced in idealized dispositions. The H atoms bonded to O atoms were located in the difference maps and refined with the riding model with the fixed distance of 0.86 Å. The crystallography information was tabulated in Table 1 and selected bond lengths and angles were in Table 2.

Results and discussion

Crystal structure description

Crystal structure of $12(CH_3)_4N^+ \cdot C_{14}H_8O_4S_2^{2-} \cdot H_2O$

Compound 1 belongs to orthorhombic system, in which there are one $DTSA^{2-}$ anion, two tetramethylammonium cations and one independent water molecule in its asymmetric unit. Observing the configuration of $DTSA^{2-}$ anion, the interplanar angle between two terminal benzene rings that are coplanar (the mean deviation values from the least-square planes are 0.0060 Å and 0.0104 Å) is 76.5° and the related dihedral angles between two deprotonated carboxyl groups and the neighboring rings are 43.6° and 25.1° separately. Obviously, two carboxyl groups retort to some degree, which is inconsistent with the normal planar conjugate structure of benzoate, and it can be concluded that the interactions between water molecule and $DTSA^{2-}$ anion result in the distortion mentioned above to adapt the needs during the crystal packing. Additionally, S \leftarrow O hypervalent bonds of the host anion are 2.835 Å and 2.634 Å, in which the weaker one can be attributed to the carboxyl group that has a smaller retorting angle and the stronger one is the carboxyl group of greater torsion angle.

Due to the total deprotonation, $DTSA^{2-}$ anion can just act as the proton donor to interact with some proton acceptor such as water molecule. From the hydrogen-bonded linking diagram of compound 1 (Fig. 1b), $DTSA^{2-}$ anion connects with water molecule by O-H ...O hydrogen bonds to generate the long waving anionic chain along the b axis and two neighboring 2₁-related chains fit each other to yield undulating double hydrogen-bonded layers that are repeatedly assigned along the a axis, then two guest cations are orderly accommodated between the double layers to form the stable sandwich-like structure as shown in Fig. 1a.

Clearly, water molecule is a very important linking unit in this structure. It is these two O-H ...O hydrogen bonds of water and $DTSA^{2-}$ anion that lead to the formation of the long anionic chain which is the elementary unit of forming the host layers of compound **1**.

Crystal structure of 2 $(C_2H_5)_4N^+ \cdot C_{14}O_4H_9S_2^- \cdot 0.25H_2O$

Compound 2 crystallizes in monoclinic system. Its asymmetric unit contain one independent DTSA⁻ ion, one tetraethylammonium ion and one position-disordered water molecule with the occupancy of 0.25. Compared with compound 1, the dihedral angle of two benzene rings (the mean deviation values of the rings are 0.0024 Å and 0.0094 Å) is also 76.5°, but the torsion angles of two carboxyl groups related to their rings are very different with the corresponding values of 3.7° and 3.6°. That is to say, two carboxyl groups of the host anion in this compound are almost coplanar with the abut rings. By calculation, S \leftarrow O distance existing between S

Table 1. Crystallographic data.				
Compound	Compound 1	Compound 2	Compound 3	Compound 4
Formula	2(CH ₂), _A N ⁺ ·C, _A H ₈ O ₄ S, ²⁻ ·H,O	(C, H _E), N ⁺ · C, H _o O, S, ⁻ · 0.25H, O	(<i>n</i> -C, H,), N ⁺ .C,, H, O, S, ⁻	(<i>n</i> -C, H _o), N ⁺ ·C, H _o O, S, ⁻
CCDC No.	1427025	1427118 7 2 2	1427119	1427026
Crystal color	yellow	yellow	yellow	yellow
Crystal shape	block	block	block	block
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2,2,2,	P2,/n	Pca2,	P2,/c
Crystal size/mm	$0.24 \times 0.19 \times 0.18$	$0.31 \times 0.26 \times 0.20$	0.51 imes 0.49 imes 0.20	0.55 imes 0.42 imes 0.20
a/Å	10.5903	8.13340	15.7857	11.7476
b/Å	10.6651	22.0741	8.24830	17.1346
c/Å	21.9476	13.2143	20.2599	16.3583
BP	06	101.6360	60	109.4560
V/Å ³	2478.9(3)	2323.70(6)	2637.94(5)	3104.74(9)
Z	4		4	4
Dc/(mg·cm ⁻³)	1.261	1.258	1.238	1.172
µ/mm ⁻¹	0.248	0.257	0.233	0.204
heta range for data collection	2.12 to <i>27.5</i> 9	1.82 to 27.63	2.58 to 27.70	2.19 to 27.65
Reflection number	8221	14243	13382	17856
Independent reflections	5473	5360	5847	7184
$R_{\eta}wR_{2}[l > 2\sigma(l)]$	0.0359,0.0891	0.0385,0.1096	0.0308,0.0817	0.0562,0.1493
S.	1.025	1.012	1.043	1.021

Compound 1			
S(1)-C(1)	1.7875(19)	S(1)-S(2)	2.0522(7)
O(2)-C(7)	1.234(3)	C(1)-C(6)	1.393(3)
O(3)-C(14)	1.253(2)	O(1)-C(7)	1.255(3)
O(4)-C(14)	1.239(2)	C(8)-C(13)	1.396(3)
C(1)-S(1)-S(2)	103.46(6)	C(2)-C(1)-S(1)	118,33(13)
C(6)-C(1)-S(1)	121 28(16)	C(18)-N(1)-C(17)	109 08(19)
C(18)-N(1)-C(15)	109 57(18)	C(16) - N(1) - C(15)	109.8(2)
C(16) - N(1) - C(17)	109.37(10)	$C(8)_{-}S(2)_{-}S(1)$	105.6(2)
O(2) - C(7) - O(1)	176 8(2)	C(0) = S(2) = S(1) C(22) = N(2) = C(21)	110 4(2)
C(2) - C(7) - O(1)	120.0(2)	C(22) - N(2) - C(21) C(22) - N(2) - C(10)	100.4(2)
C(21)-N(2)-C(20) C(20)-N(2)-C(19)	109.3(2)	$C(22)^{-1}V(2)^{-}C(19)$	109.4(2)
Compound 2	100.2(2)		
S(1) = C(8)	17061(16)	S(1)_S(2)	2 0573(6)
O(4) C(14)	1,7,501(10)	C(1) = C(2)	2.03/3(0)
O(4) - C(14)	1.223(2)	C(1) - 3(2)	1.7914(13)
O(1) - C(1)	1.21/(2) 1.772(2)	O(2) - C(7)	1.202(2)
O(3)-C(14)	1.272(2)	C(2)-C(7)	1.492(2)
C(9) - C(14)	1.504(2)	C(1)-S(2)	1.7914(15)
C(2) - C(7)	1.492(2)		101 00(14)
C(8)-S(1)-S(2)	105.28(5)	O(1)-C(2)	121.20(14)
O(2) - C(7) - C(2)	114.20(14)	C(6)-C(1)-S(2)	121.06(12)
O(1)-C(7)-O(2)	124.59(15)	O(4)-C(14)-O(3)	124.98(15)
C(17)-N(1)-C(21)	106./6(15)	C(19)-N(1)-C(21)	110.58(16)
C(17)-N(1)-C(15)	111.26(18)	C(19)-N(1)-C(15)	105.56(15)
Compound 3	1 7000/15)		4 7056 (46)
S(I)-C(I)	1./902(15)	S(2)-C(8)	1./956(16)
S(1)-S(2)	2.0587(6)	O(2)-C(7)	1.226(2)
O(3)-C(14)	1.215(2)	O(4)-C(14)	1.286(2)
O(1)-C(7)	1.2/0(2)	C(2)-C(7)	1.510(2)
C(9)-C(14)	1.505(2)		
C(21)-N(1)-C(24)	111.31(14)	C(24)-N(1)-C(15)	112.03(13)
C(21)-N(1)-C(18)	111.74(13)	C(15)-N(1)-C(18)	111.44(15)
C(6)-C(1)-S(1)	120.85(13)	C(8)-S(2)-S(1)	105.55(5)
C(2)-C(1)-S(1)	120.45(12)	C(8)-S(2)-S(1)	105.55(5)
O(2)-C(7)-O(1)	125.41(16)	O(3)-C(14)-O(4)	125.72(16)
C(8)-C(9)-C(14)	122.00(14)	C(10)-C(9)-C(14)	118.86(15)
C(1)-C(2)-C(7)	124.98(15)	C(3)-C(2)-C(7)	116.65(15)
Compound 4			
N(1)-C(19)	1.514(3)	S(1)-C(1)	1.789(2)
N(1)-C(23)	1.518(4)	S(1)-S(2)	2.0557(9)
N(1)-C(27)	1.522(3)	S(2)-C(8)	1.794(2)
N(1)-C(15)	1.534(3)	O(1)-C(7)	1.263(3)
O(2)-C(7)	1.230(3)	O(4)-C(14)	1.293(3)
C(19)-N(1)-C(23)	109.3(2)	C(23)-N(1)-C(27)	110.9(2)
C(19)-N(1)-C(15)	111.7(2)	C(27)-N(1)-C(15)	107.48(19)
C(1)-S(1)-S(2)	104.21(8)	C(2)-C(1)-S(1)	121.72(19)
C(6)-C(1)-S(1)	119.24(18)	O(3)-C(14)-O(4)	123.3(2)
C(8)-S(2)-S(1)	105.20(8)	O(2)-C(7)-O(1)	124.9(3)
O(2)-C(7)-C(6)	117.0(2)	O(1)-C(7)-C(6)	118.0(2)
O(3)-C(14)-C(13)	122.8(2)	O(4)-C(14)-C(13)	113.8(2)

Table 2. Selected bond lengths (Å) and bong angles (°).

atom and the carbonyl O atom of the COOH group is 2.680 Å, while another S \leftarrow O of the deprotonated COO⁻ group is just 2.611Å. From this, it can be judged that the torsion angle of the related carboxyl group is not the only affecting factor to S \leftarrow O hypervalent bond. It can be imagined that the electron atmosphere of S and O atoms would interact with each other to form S \leftarrow O hypervalent bond. To the deprotonated carboxyl group, its carbonyl O atom should bear dense electron cloud, which may facilitate to get stronger S \leftarrow O hypervalent bond. Thus, it can be explained why S atom and the neighboring carbonyl O atom of the COO⁻ group can produce stronger S \leftarrow O interaction even though the torsion angles of two carboxyl groups are so approximate.



(a)



Figure 1. (a) The packing diagram of compound **1** (for clarity, tetramethylammonium cations were represented with the big shaded spheres). (b) The projection diagram of the double hydrogen-bonded layer along the *c* axis in compound **1** (all H atoms bonded to C were omitted for simplicity) [A: x, 1 + y, z; B: 1 - x, 1/2 + y, 1 - z].

It can be easily seen that $DTSA^-$ anion utilizes the only independent O-H...O contact to obtain the corresponding long anionic chain along the *b* axis (Fig. 2b), and the adjacent 2₁-related chains are orderly arranged along the *c* axis, which is very similar with the linking mode of compound 1. Comparatively, $DTSA^-$ anion can just be misplaced with each other to yield Z-type hydrogen-bonded layer in compound 2 because the host anion has greater steric effects for the absence of water molecule and cannot fit each other to produce the packing mode just as compound 1. Ultimately, in compound 2, the greater tetraethylammonium ion and the guest water molecule are collectively contained between the Z-type layers to get the sandwich-like crystal structure (Fig. 2a).

Crystal structure of 3 $(n-C_3H_7)_4N^+ \cdot C_{14}H_9O_4S_2^-$

Similar with compound 1, compound 3 also belongs to orthorhombic system with the extra sliding planes. In the asymmetric unit, the content is similar with compound 2 except the



(b)

Figure 2. (a) The packing diagram of compound **2** (for clarity, all H atoms bonded to C atoms and O atoms of water molecules are omitted and the guest cations are represented with big shaded spheres). (b) The hydrogen-bonded linking mode of **DTSA**⁻ anion along the *a* axis (all H atoms bonded to C are omitted for clarity) [A: 3/2 - x, -1/2 + y, 1/2 - z; B: 3/2 - x, 1/2 + y, 1/2 - z; C: 2 - x, 1 - y, 1 - z; D: -1/2 + x, 1/2 - y, 1/2 + z; E: -1/2 + x, 3/2 - y, 1/2 + z].

water molecule. The packing pattern of compound **3** is also approximate to compound **2**, in which the anionic chains of **DTSA**⁻ anion extending along the *c* axis are repeatedly placed to generate the 2D host layers to contain the guest tetrapropylammonium to construct the final structure (Fig. 3).

Comparatively, two benzene rings of **DTSA**⁻ anion deviate their least-square planes with the related values of 0.0045 Å and 0.0061 Å and the interplanar angle is 81.2°. Unexpectedly, S \leftarrow O interaction between S and O derived from COO⁻ group that has a torsion angle of 6.1° is 2.680 Å and another S \leftarrow O involving COOH group (the related torsion angle is 12.1°) is 2.677 Å, which is not accordant with our estimation of the former should bear stronger hypervalent bond and it may be attributed to the





Figure 3. (a) The packing diagram of compound **3** (for clarity, all H atoms bonded to C are omitted and the guest ions are represented with big shaded spheres). (b) The projection diagram of the hydrogen-bonded pattern along the *a* axis in compound **3** (for simplicity, all H atoms bonded to C are eliminated and the purple line represents C-H ... π interaction) [A: 1 – x, 1 – y, 1/2 + z; B: x, 1 + y, z].

greater retorting angle between two terminal benzene rings compared with compounds 1 and 2.

Crystal structure of 4 $(n-C_4H_9)_4N^+ \cdot C_{14}H_9O_4S_2^-$

Compound 4 has the same crystal system as compound 2 and the content of the asymmetric unit is approximate to that of 3, and the hydrogen-bonded pattern and the packing mode of 4 is also similar with compound 3 (Fig. 4). Calculating the parameters of the host DTSA⁻ anion, the dihedral angle between two rings is 87.1°, in which the related deviation values of the rings are 0.0090 Å and 0.0061 Å. The distortion angle of COO⁻ group is just 0.6° and the related S1 \leftarrow O2 bond distance is 2.547 Å, and another torsion angle of COOH is 8.1° and the corresponding S2 \leftarrow O3 is 2.682 Å. It is explicit that the COO⁻ group with smaller torsion angle takes part in the construction of the stronger S \leftarrow O hypervalent bond in compound 4.

Disccusion

Compounds 1–4 are prepared with **DTSA** and different tetraalkylammonium hydroxides with the same molar ratio of 1:2 under room temperature. By analyzing the crystallography results, it can be seen that compounds 1 and 3 belong to orthorhombic system with high symmetry



Figure 4. (a) The packing diagram of compound **4** (for clarity, all H atoms bonded to C are omitted and tetrabutylammonium is represented with the big shaded circle). (b) The projection diagram of the hydrogenbonded pattern along the *b* axis in compound **4** (for simplicity, all H atoms bonded to C are eliminated and the purple line represents C-H ... π interaction) [A: 1/2+x,1/2-y,-1/2-z; B: -1/2+x,1/2-y,1/2+z; C: 1/2+x,1/2-y,1/2+z].

and 2 and 4 are monoclinic system. Noticeably, S←O hypervalent bond is a three-center fourelectron bond to effectively stabilize the configuration of DTSA. As reported in the literatures, the distance of S \leftarrow O varies from 2.561Å to 2.787Å [6], and the related values in the title compounds are 2.547 Å~2.835 Å. In compound 1, S←O bonds are 2.634 Å and 2.835Å, and the stronger bond belongs to the COO⁻ group with a smaller torsion angle of 25.1°; in compound 2, S←O distances are 2.680 Å and 2.611 Å, in which two torsion angles of the related carboxyl groups are very approximate to 4° and the interplanar angle between two rings is the same as that in compound 1, and the stronger $S \leftarrow O$ is also generated by the COO⁻ group; in compound 4, S \leftarrow O values are 2.547Å and 2.682Å, and the stronger S \leftarrow O also exists in the COO^{-} group with smaller torsion angle of 0.6°. Only in compound 3, the hypervalent bonds 2.677 Å and 2.680 Å, which may be attributed to the larger interplanar angle of two rings and the larger torsion angles of two carboxyl groups. However, in the cases of DTSA, the hypervalent bond generated between S atom and the deprotonated carboxyl group should be stronger and if two protons are both eliminated, the torsion angle between the carboxyl group and the neighboring ring should be another crucial factor to affect the S \leftarrow O interaction. Analyzing the corresponding data of 38 organic crystals of DTSA found in CSD database [6], between



Figure 5.	After	optimization	of the	DTSA ²⁻	anion	structure.

	Distance(Å)	WBI	OWBO	NLMO
S1…O3	2.835	0.068	0.037	0.041
S4…O9	2.634	0.077	0.050	0.042

Table 3. WBI, OWBO and NLMO are three different bond orders.

S atoms and the neighboring COO⁻ groups, the shortest distance is 2.561 Å and the related torsion angle is 3.7° and the longest one is 2.787 Å and the angle is 33.5°; between S atoms and the adjacent COOH groups, the shortest value is 2.567 Å and the torsion angle is 4.3° and the longest one is 2.759 Å and the angle is 21°. From this, we can see that, due to complicated interactions among the crystals, the weakest $S \leftarrow O$ contact occurs in COO⁻ group unexpectedly, but from the data mentioned above, we also can conclude that if the COO⁻ group in DTSA anion has a smaller torsion angle, then the related S \leftarrow O interaction should be stronger under normal conditions. Interestingly, analysising structure of four crystals shows that the configuration of the host molecules are very similar, we found that $C_{14}H_{10}O_4S_2$ stably exist with special structure, and a certain interaction between the carboxyl oxygen and sulfur atoms in the same benzene ring connected in a certain condition meta-position. As an example, we optimize the molecular structure of compound 1 (Fig 5.). The molecule was optimized using BP86 method, SVP basis set, and compute the key stage (Table 3: WBI, OWBO and NLMO are three different key level) and orbit interaction (Table 4: LP-lone pair orbital, BD*anti-bonding orbital, SOIE-second-order orbital interaction energy) of S1 ... O3 and S4 ... O9. There are three key stage results show that S1...O3 and S4...O9 becoming the weak force, respectively. The results of the analysis showed that, O3 or O9 lone electron pair have the interaction between anti-bonding orbital of S1 and S4, this result show that S1...O3 and S4...O9 becoming the weak force, too. Whether it is from the key level or orbit interaction, it has an effect between O and S.

Compared with other similar V-shaped molecules that have two terminal hydroxyl groups (or carboxyl groups), the S-S bond in **DTSA** can rotate more flexibly to adjust its molecular configuration to meet different needs. And **DTSA** also can easily lose its protons to generate

donor/acceptor	SOIE (K cal/mol)
LP(O3)/BD*(S1-S4)	3.77
LP(O9)/BD*(S1-S4)	6.24

Table 4. LP-lone pair orbital, BD*-anti-bonding orbital, SOIE-second-order orbital interaction energy.

Hydrogen bonds	OO distance (Å)	Hydrogen bonds	OO distance (Å)
Compound 1			
01W -H01A	2.8517	O1W -HO3	2.8516
C15 -HO2C	3.4368	C19 -HO3D	3.4731
C17- HO4 ^E	3.2523	C22-HO4	3.3825
C17 -HO2 ^F	3.2815	C22 -HO1W ^G	3.4644
C18 -HO4 ^E	3.3786		
C: 1/2+x, 1/2-y, -z; D: 1/2+x, 3/2-y, -	- <i>z</i> ; E: <i>x</i> , -1+ <i>y</i> , <i>z</i> ; F: 1+ <i>x</i> , <i>y</i> , <i>z</i> ; G:	1+ <i>x, y, z</i>	
Compound 2			
02 -H03A	2.449(2)	C21-HO4D	3.256(3)
Compound 3			
O4A -HO1	2.4864		
C15 -HO2C	3.4755	C21 -HO2C	3.4248
C18 -HO3D	3.4312	C24-HO3E	3.3407
C: <i>x</i> , −1+ <i>y</i> , <i>z</i> ; D: − <i>x</i> , 1− <i>y</i> , 1/2+ <i>z</i> ; E: − <i>x</i> ,	1-y, -1/2+z		
Compound 4			
04-H01B	2.4745	C15-HO2D	3.1578
C15-HO1C	3.2704	C23-HO3E	3.4114
D: 3/2- <i>x</i> , -1/2+ <i>y</i> , 1/2- <i>z</i> ; E: 1+ <i>x</i> , <i>y</i> , <i>z</i>			

Table 5. Hydrogen-bonding geometry.

different anions under basic conditions. As shown here, **DTSA**⁻ tends to yield the hydrogenbonded chain and **DTSA**²⁻ needs some hydrogen bond donor (such as water molecule) to participate the construction of the host layer. Obviously, both of the anions display similar linear configuration, which have the tendency of forming 1D hydrogen-bonded chains that can be orderly assigned to obtain 2D host layers without the existence of other ancillary host molecules. It can be imagined that various crystal structures with different packing patterns can be obtained if other auxiliary host molecules that can form varied hydrogen bonds can take part in the formation of the host layers.

In addition, it can be calculated with PLATON [23] that the crystal packing coefficients of compounds 1–4 are 0.681, 0.656, 0.673 and 0.647 sequentially, which means the packing coefficients decrease when the volumes of the guest tetraalkylammonium cations increase. Clearly, guest molecules have concrete affection on the intensity packing of host-guest inclusion compounds. Among the four title compounds, the unique coefficient of compound **2** may be attributed to the occupation of the water molecule that is also regarded as a guest molecule here.

Conclusion

In conclusion, four tetraalkylammonium inclusion compounds with the host molecule of **DTSA** were synthesized and characterized by single X-ray single crystal diffraction. As shown in the results, the host **DTSA** anions of compounds **1–4** all generate long similar hydrogenbonded chains that will produce approximate 2D host layers to accommodate the related guest cations with varied magnitudes to finally form sandwich-like crystal structures. Also, the packing coefficients of **1**, **3** and **4** are decreasing with the increasing of the volumes of the related guest molecules, which show the definite effects of the guest molecules in host-guest system. Interestingly, although the carbon chains of the guest templates are different, the final packing modes of the crystal structures are very approximate, which means the host molecule of **DTSA** is a more important factor during the crystal packing. Additionally, in these four structures, there always exist weak C-H ... O hydrogen bonds between the guest ions and the

host layers, which enforce the interdependence of host-guest system to form the final stable inclusion compounds.

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