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Structural Relationships among Methyl-, Dimethyl-, and Trimethylammonium Phosphododecatungstates

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Crystals of $(CH_3NH_3)_3[PW_{12}O_{40}]\cdot 2H_2O$ (**1**), $[(CH_3)_2NH_2]_3[PW_{12}O_{40}]$ (**2**), and $[(CH_3)_3NH]_3[PW_{12}O_{40}]$ (**3**) exhibit a similar packing of cations and anions, although they crystallize into different space group types, namely $P\bar{1}$, $R\bar{3}m$, and $R\bar{3}$, respectively. Their structures were interpreted in terms of supergroup–subgroup relationships, revealing that the basic arrangements of cations and anions are primarily dominated by electrostatic interactions on which hydrogen bonds exert influences.

Phosphododecatungstate is one of the best characterized polyoxometalate cluster anions.[1] Since Keggin first determined the structure of its α-isomer,[2,3] its structure has been repeatedly analyzed.[4,5] A Keggin polyoxometalate is considered to be a large, practically spherical unit with an equal charge distribution over its surface.[3,6] This even distribution of negative charge challenges us to predict the attainable topology when Keggin anions interact with other chemical substances, especially with organic molecules. While the crystal structures of Keggin anions with inorganic cations were classified by Evans,[4] the structural relationships among the crystals of Keggin anions with organic cations have not been extensively explored. We have focused our attention on the balance between the electrostatic and the hydrogen-bond interactions in the crystals of Keggin anions. The former interaction is the most prominent interaction in ionic crystals and the latter interaction is prevalent in many molecular crystals. In the present study, methyl-, dimethyl-, and trimethylammonium cations were selected to crystallize α-Keggin-type phosphododecatungstate anions in order to observe the effect of the number of hydrogen bond donors of the cations. These cations are the simplest and smallest examples of primary, secondary, and tertiary alkylammonium cations that provide three, two, and one hydrogen bond donors, respectively. Their small sizes minimize the distances between the cations and the anions and maximize the electrostatic interactions. Here, we report the crystal structures of methyl-, dimethyl-, and trimethylammonium salts of phosphododecatungstates **1**, **2**, and **3** and discuss their structural relationships.

Experimental

Reagents and General Procedure. The following were purchased from commercial sources and used without further purification: 99% $NaH_2PO_4\cdot 2H_2O$, 99% $Na_2WO_4\cdot 2H_2O$, 35%–37% hydrochloric acid, 98% $CH_3NH_2\cdot HCl$, 98% $(CH_3)_2NH\cdot HCl$, 99.5% acetone, and 99.5% diethyl ether (Wako); 95% $(CH_3)_3N\cdot HCl$ (Kanto); and 99.5% acetonitrile (Nacalai Tesque). Infrared absorption spectra were recorded as KBr pellets on a JASCO FT/IR-460 spectrometer (250–4000 cm^{-1}). Elemental analyses of C, H, and N were carried out in our department. Powder X-ray diffraction patterns were measured using a Bruker D8 Advance/L diffractometer at ambient temperature.

Sample Preparations. **$[CH_3NH_3]_3[PW_{12}O_{40}]\cdot 2H_2O$ (1):** Trihydrogen phosphododecatungstate was obtained by following a procedure described by Bailar.[7] $Na_2WO_4\cdot 2H_2O$ (50.00 g) and $NaH_2PO_4\cdot 2H_2O$ (7.01 g) were dissolved in 75 mL of boiling water. The heteropolyacid was extracted with Et_2O after the addition of concentrated HCl (40 mL). The etherate was allowed to stand for two days, when colorless crystals of trihydrogen phosphododecatungstate (18.50 g) were obtained. A 2.00 g sample of trihydrogen phosphododecatungstate was dissolved in 20 mL of water. The solution was precipitated by adding 0.16 g of $CH_3NH_2\cdot HCl$. The resulting white powder (1.44 g) was collected by filtration. The powder (0.15 g) was recrystallized from acetone/water (1:1 v/v, 10 mL) by concentrating the solution under controlled evaporation rate. After four weeks, colorless crystals (0.07 g) of **1** were obtained. ν/cm^{-1} 1078m, 977s, 890m, 803vs, and 387m. Anal. Found: C, 1.41; H, 0.70; N, 1.31%. Calcd for $C_3H_{22}N_3O_{42}PW_{12}$: C, 1.20; H, 0.74; N, 1.40%.

$[(CH_3)_2NH_2]_3[PW_{12}O_{40}]$ (2): A 1.00 g sample of trihydrogen phosphododecatungstate was dissolved in 10 mL of water. The solution was precipitated by adding 0.09 g of $(CH_3)_2NH\cdot HCl$. The resulting white powder (0.50 g) was collected by filtration. The powder (0.15 g) was recrystallized from acetone/water (8:7 v/v, 15 mL) by concentrating the solution under controlled evaporation rate. Colorless crystals (0.11 g) of **2** were obtained after three months. ν/cm^{-1} 1078s, 982s, 890m, 815vs, and 386m. Anal. Found: C, 2.63; H, 0.93; N, 1.38%. Calcd for $C_6H_{24}N_3O_{40}PW_{12}$: C, 2.39; H, 0.80; N, 1.39%.

$[(CH_3)_3NH]_3[PW_{12}O_{40}]$ (3): A 1.00 g sample of trihydrogen phosphododecatungstate was dissolved in 10 mL of water. The solution was precipitated by adding a 0.10 g sample of $(CH_3)_3N\cdot HCl$. The white powder (0.84 g) was collected by filtration. The powder (0.15 g) was recrystallized from acetonitrile/water (1:1 v/v, 10 mL) by concentrating the solution under controlled evaporation rate. Colorless crystals (0.12 g) of **3** were obtained after three weeks. ν/cm^{-1} 1079s, 982s, 887m, 801vs, and 385s. Anal. Found: C, 3.75; H, 1.05; N, 1.32%. Calcd for

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Table 1. Crystal Data and Experimental Conditions of Compounds **1**–**3**

	1	**2**	**3**
Chemical formula	$C_3H_{22}N_3PW_{12}O_{42}$	$C_6H_{24}N_3PW_{12}O_{40}$	$C_9H_{30}N_3PW_{12}O_{40}$
Formula weight	3009.4	3015.5	3057.5
Crystal system	Triclinic	Trigonal	Trigonal
Space group (No.)	$P\bar{1}$ (2)	$R\bar{3}m$ (166)	$R\bar{3}$ (148)
a/Å	13.0234(2)	16.4347(2)	17.7906(3)
b/Å	13.3341(2)		
c/Å	13.3508(3)	25.2744(4)	23.8397(4)
α/°	86.758(2)		
β/°	81.586(1)		
γ/°	88.179(2)		
V/Å^3	2289.16(7)	5912.01(12)	6534.50(16)
Z	2	6	6
T/K	123	123	298
μ(Mo Kα)/mm^{-1}	30.15	35.02	31.69
Crystal size/mm^3	0.10 × 0.06 × 0.05	0.10 × 0.10 × 0.10	0.14 × 0.10 × 0.10
Number of measured/ independent reflections	21299/12014	18012/1955	20054/3910
R_{int}	0.042	0.066	0.048
$R1(F_O)$ for observed data/ $wR2(F_O{}^2)$ for all data	0.043/0.122	0.033/0.086	0.030/0.078

$C_9H_{30}N_3O_{40}PW_{12}$: C, 3.54; H, 0.99; N, 1.37%.

Crystal Structure Determinations. Single-crystal X-ray diffraction data for **1**, **2**, and **3** were collected using a Rigaku Mercury CCD diffractometer. Each structure was determined by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELX-97 program suite.[8] For the structure of **1**, the W, P, and O atoms constituting the phosphododecatungstate framework and the O atoms of water molecules were refined using anisotropic displacement parameters. Methylammonium cations were found to be disordered. Hydrogen atoms in the cations and water molecules were not included. For **2** and **3**, all the non-hydrogen atoms were refined anisotropically. In both these compounds, hydrogen atoms in the ammonium cations were included using the riding model. Selected experimental parameters and crystal data are summarized in Table 1. Table 2 lists the geometrical parameters of hydrogen bonds. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-743538, CCDC-743539, and CCDC-743540 for compounds **1**, **2**, and **3**, respectively. 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 and Discussion

The structures for **1**–**3** illustrate that the variation in the number of hydrogen bond donors of alkylammonium cations results in the crystallization of $PW_{12}O_{40}{}^{3-}$ anion into different space group types, the relationships among which will be discussed below. The unit cell dimensions and the space group types of **2** and **3** clearly show that these two structures are closely related. A closer inspection reveals that the crystal structures of **1** and $(NH_4)_3PW_{12}O_{40}$[9,10] can also be interpreted to be analogous to those of **2** and **3**. Since the atomic coordinates of $(NH_4)_3PW_{12}O_{40}$ have not been published, in this section we compare the structures of **1**, **2**, and **3** with that of $K_3PW_{12}O_{40}$ (**4**),[11] which is isomorphous to $(NH_4)_3PW_{12}O_{40}$.

Table 2. Hydrogen Bond Parameters in Compounds **1**–**3**

	D(–H)···A$^{a),b)}$	H···A/Å	D···A/Å	D–H···A/°
Compound **1**	N1A···O2W^{ii}		2.92(3)	
	N1A···O31^{i}		3.05(3)	
	N1B···O37		3.20(3)	
	N1C···O24^{iii}		3.19(3)	
	N2A···O37^{ii}		2.88(3)	
	N2B···O40		3.16(3)	
	N2C···O36^{iv}		3.18(3)	
	N3A···O1W^{ii}		3.14(3)	
	N3A···O38		3.25(3)	
	N3B···O1W^{ii}		2.82(3)	
	N3B···O31^{v}		3.07(3)	
	N3B···O38		3.10(3)	
	N3C···O40^{ii}		3.14(3)	
	O29···O2W^{vi}		2.90(1)	
	O30···O1W^{vii}		2.89(1)	
Compound **2**	N1–H1A···O5	2.298	3.120(9)	148.5
	N1–H1A···O10^{viii}	2.219	2.967(5)	129.9
Compound **3**	N1–H1···O5	2.180	3.025(9)	154.2
	N1–H1···O13^{ix}	2.557	3.169(9)	125.1

a) D: hydrogen bond donor atom; A: hydrogen bond acceptor atom. b) Symmetry codes: (i) $x, y, z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $x+1, y, z$; (vi) $x-1, y-1, z$; (vii) $x, y-1, z-1$; (viii) $x-y+1/3, -y+2/3, -z+2/3$; (ix) $-x+1/3, -y+2/3, -z+2/3$.

We also discuss the distances and the network geometries of hydrogen bonds in these compounds.

Compound **1** crystallizes into a triclinic space group $P\bar{1}$ with $Z = 2$. An asymmetric unit of **1** consists of one α-$PW_{12}O_{40}{}^{3-}$ anion, two water molecules of crystallization, and three methylammonium cations. All the methylammonium cations are disordered over three sites. The two water molecules are located close to a crystallographic inversion center and they

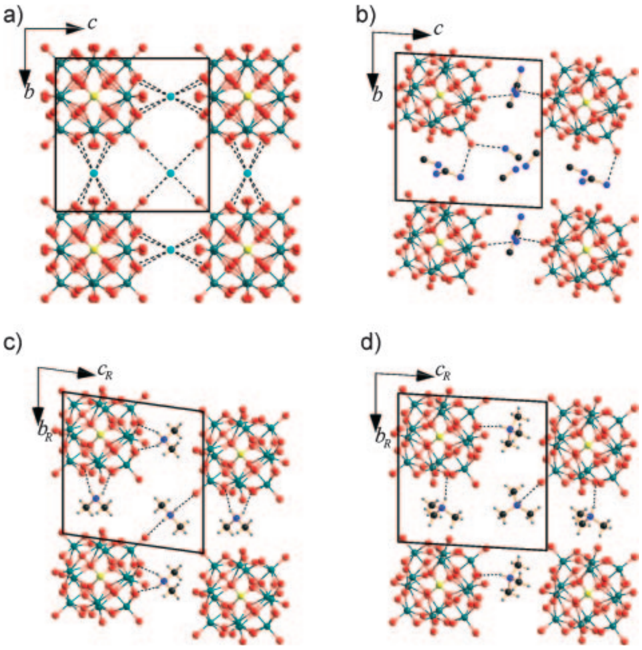

Figure 1. Packing diagrams of compounds (a) **4**, (b) **1**, (c) **2**, and (d) **3** viewed along the *a* axes. Contacts between the K and O atoms and hydrogen bonds are shown as broken lines. Figures (c) and (d) are drawn with respect to their primitive rhombohedral axes to facilitate the comparisons with (a) and (b). Color code: W, greenish blue; K, turquoise; O, red; N, blue; C, dark gray; H, light gray.

form a tetrameric water cluster together with their symmetrically equivalent molecules. Compound **2** crystallizes into a trigonal space group $R\bar{3}m$ with $Z = 6$. This compound is isomorphous with its Mo analog.[12,13] An asymmetric unit of **2** contains one sixth of an α-$PW_{12}O_{40}{}^{3-}$ anion and one half of a dimethylammonium cation. The former is located on a $3m$ site and the latter is located on a mirror plane.[14] Compound **3** crystallizes into a trigonal space group $R\bar{3}$ with $Z = 6$. An asymmetric unit of **3** contains one third of an α-$PW_{12}O_{40}{}^{3-}$ anion and a trimethylammonium cation. The Keggin anion is located on a threefold axis.

Structure of 2. First, the structure of **2**, which exhibits the highest symmetry among **1**–**3**, is compared with that of **4**. In **4**, the Keggin and K^+ ions occupy the $2a$ ($\bar{4}3m$ or T_d symmetry) and $6d$ ($\bar{4}2m$ or D_{2d} symmetry) sites of $Pn\bar{3}m$, respectively. Replacement of the isotropic K^+ cation by the less symmetric dimethylammonium cation ($mm2$ or C_{2v} symmetry) requires the lowering of the symmetry of the resultant crystal. The dimensions of the primitive rhombohedral lattice of **2**, which measure $a = 12.689$ Å and $\alpha = 80.72°$, prompted us to relate the structure of **2** to that of **4** (primitive cubic lattice with $a = 11.6020$ Å) by trigonal distortion. The fractional atomic coordinates of **2** with respect to its primitive rhombohedral axes are comparable to those of **4** (Figure 1 and Table S1), which justifies our interpretation of the structural relationship between **2** and **4**. The prolate distortion can be attributed to the hydrogen bonds that link six dimethylammonium and six Keggin ions into a hexagonal motif around the $1a$ site ($\bar{3}m$ symmetry), as shown in Figure 2. PLATON[15] CALC SOLV routine located a solvent accessible void with the volume of 43 Å^3 on this site, which we concluded to be left vacant judging from its hydrophobic environment and the analysis of the final difference Fourier synthesis.

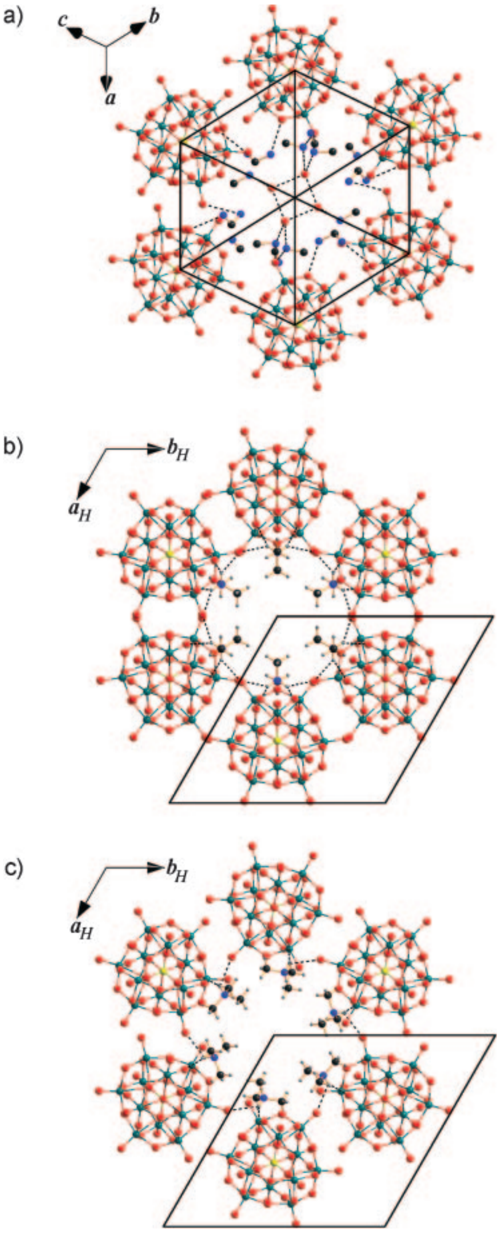

Figure 2. Hydrogen-bond network motifs observed in (a) **1** viewed along $a + b + c$ and (b) **2** and, (c) **3** viewed along their threefold axes. Color code is as in Figure 1.

It is interesting to note that $R\bar{3}m$ is the only *translationengleiche* maximal non-isomorphic subgroup of $Pn\bar{3}m$ where the site derived from the $6d$ site of $Pn\bar{3}m$ ($6h$ site of $R\bar{3}m$ with m or C_s symmetry) is capable of accommodating a $(CH_3)_2NH_2{}^+$ cation without disorder. In the other four subgroups ($P\bar{4}3m$, $P4_232$, $Pn\bar{3}$, and $P4_2/nnm$), corresponding sites show higher symmetry of $\bar{4}2m$ (D_{2d}) or 222 (D_2), and therefore, the $(CH_3)_2NH_2{}^+$ cations would be inevitably disordered. The dimethylammonium cation is located on the $6h$ site of $R\bar{3}m$ so that the plane defined by its C and N atoms coincides with the crystallographic mirror plane. Two N–H hydrogen bond donor

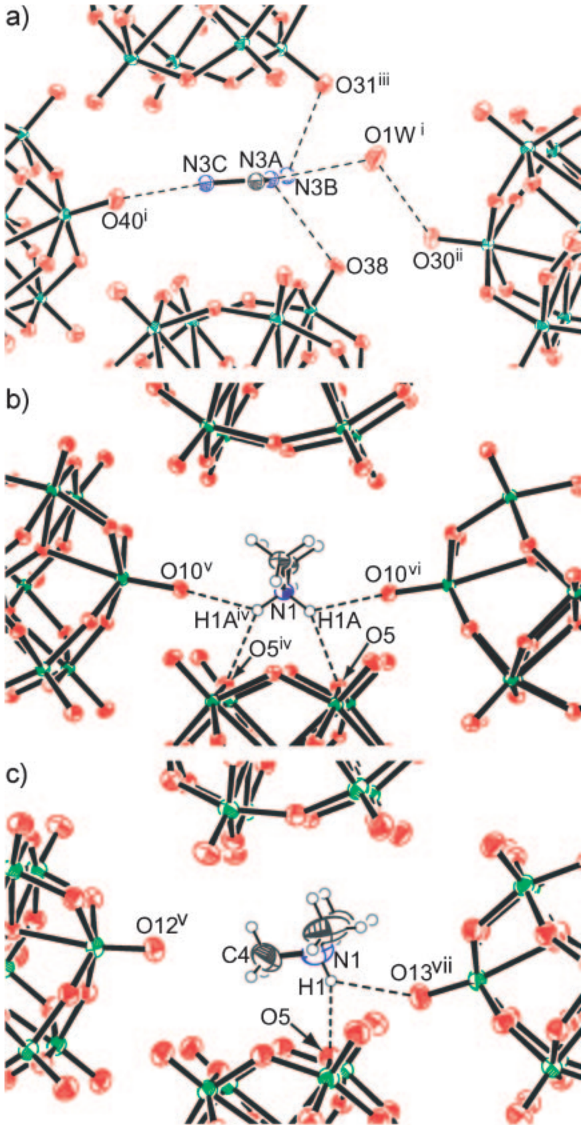

Figure 3. Intermolecular interactions between Keggin anions and (a) methylammonium cations, (b) a dimethylammonium cation, (c) and a trimethylammonium cation. Color code is as in Figure 1. Symmetry codes: (i) $-x+1$, $-y+1$, $-z+1$; (ii) $-x+1$, $-y$, $-z$; (iii) $x+1$, y, z; (iv) x, $x-y$, z; (v) $x-y+1/3$, $x-1/3$, $-z+2/3$; (vi) $x-y+1/3$, $-y+2/3$, $-z+2/3$; (vii) $-x+1/3$, $-y+2/3$, $-z+2/3$.

groups are off the mirror plane and crystallographically equivalent. Each N–H group donates a bifurcated hydrogen bond to two Keggin anions, as shown in Figure 3.

Structure of 3. As shown in Figures 1 and 2, the crystal packing of **3** resembles that of **2**. The fractional atomic coordinates of **3** with respect to its primitive rhombohedral axes are comparable to those of **4** (Table S1). The structure of **3** can be compared to that of **2**, with one of the H atoms of its N–H groups replaced by a methyl group. The replacement breaks the mirror symmetry and therefore the space group symmetry is lowered from $R\bar{3}m$ to $R\bar{3}$. This methyl group (C4) causes a steric repulsion against the O atom of the Keggin anion to which the replaced H atom donated a hydrogen bond (O12$^{\mathrm{v}}$), as shown in Figure 3c. As a result, the trimethylammonium cation is shifted away from the extinct mirror plane and the Keggin anion is rotated around the threefold axis to minimize the steric hindrance and maximize the hydrogen-bond interactions. The steric repulsion caused by the methyl group expands the hexagonal motif of the trimethylammonium and Keggin ions, resulting in a less pronounced prolate trigonal distortion of **3** than that of **2**. The dimensions of the primitive rhombohedral lattice of **3** are $a = 12.987$ Å and $\alpha = 86.47°$. PLATON[15] CALC SOLV routine located a solvent accessible void with the volume of 55 Å^3 at the center of the hexagonal motif ($1a$ site with $\bar{3}$ symmetry), which we also concluded to be left vacant judging from its hydrophobic environment and the analysis of the final difference Fourier synthesis.

Structure of 1. The space group symmetry of **1** is as low as $P\bar{1}$; however, its fractional atomic coordinates are still comparable to those of **4** (Figure 1 and Table S1). Although $P\bar{1}$ can also be derived from $Pn\bar{3}m$ via tetragonal or orthorhombic distortion (through $P4_2/nnm$ or $Pnnn$) followed by further distortion, we can reasonably relate the structure of **1** to that of **4** by trigonal distortion plus additional distortion. Among the positions derived from the $4b$ site of $Pn\bar{3}m$ ($1a$, $1e$, $1f$, and $1g$ in $P\bar{1}$), only $1a$ accommodates a tetrameric water cluster; the other three sites are left vacant in the structure of **1**. Only trigonal distortion desymmetrizes four equivalent $4b$ positions of $Pn\bar{3}m$ into three equivalent and one nonequivalent positions ($3e$ and $1a$ sites in $R\bar{3}m$). The $1a$ site of $P\bar{1}$ in the structure of **1** corresponds to the $1a$ site of $R\bar{3}m$ in the structure of **2** and the $1a$ site of $R\bar{3}$ in the structure of **3**, which accommodate the 43 and 55 Å^3 voids. Smaller cations in **1** lead to the enlargement of the cavity, which then accommodates the water molecules of crystallization. The increased number of hydrogen bond donors of methylammonium cation (3 in **1** vs. 2 in **2** and 1 in **3**) makes the cavity hydrophilic and helps stabilize the water tetramer.

In contrast to the dimethylammonium and trimethylammonium cations in **2** and **3** that donate hydrogen bonds to three and two Keggin anions, the methylammonium cations in **1**, excluding N3B, interact with only one Keggin anion, as shown in Table 2. Each methylammonium cation is disordered over three sites, on each of which the cation interacts with a different anion. Since this cation has only one methyl group, its NH_3^+ moiety are allowed to interact with various O atoms in its proximity without giving rise to steric repulsion by the methyl group. The fact that **1** retains an arrangement of cations and anions similar to **2** and **3** even in the absence of hydrogen bonds connecting Keggin anions clearly illustrates that electrostatic interactions govern the crystal structure of compounds **1**–**3**. The arrangement or the disordered methylammonium cations is not symmetric and the cavity accommodating the cation is distorted, as shown in Figure 3. Together with the inclusion of a water tetramer that is incompatible with trigonal symmetry, the symmetry of compound **1** is further lowered to triclinic.

Hydrogen Bond Distances. The average distances of the hydrogen-bonded N···O pairs are 3.121, 3.044, and 3.097 Å in **1**, **2**, and **3**, as listed in Table 2. The longer N···O distance in **3** than that in **2** contradicts the general tendency that the hydrogen bond donor strengths of tertiary ammonium cations are stronger than those of secondary ammonium cations.[16,17] As described above, the replacement of dimethylammonium cation with trimethylammonium cation results in a shift of the cation and rotation of the anion, caused by the steric repulsion between C4 and $O12^{V}$, as shown in Figure 3. The shift of the cation shortens the hydrogen bond to the bridging O atom (3.025 Å for N1···O5 in **3** vs. 3.120 Å for N1···O5 in **2**), while the rotation of the anion lengthens the hydrogen bond to the terminal O atom (3.169 Å for $N1\cdots O13^{vii}$ in **3** vs. 2.967 Å for $N1\cdots O10^{vi}$ in **2**). Although we have no decisive justification for the mechanism of the lengthening of the average hydrogen bond distance in **3**, it should be noted that the steric hindrance exerts an influence on the hydrogen bond distances, especially for those between bulky donors (tertiary ammonium cation, in this case) and acceptors (Keggin anion, in this case).

Hydrogen Bond Networks. The most prominent structural feature in **1** is the inclusion of a discrete cluster of a four-membered water ring with C_i symmetry, which is one of the predominant structural motifs of water clusters in organic molecular crystals.[18] The water tetramer in **1** is planar with O···O distances of 2.844 and 2.908 Å. Two Keggin anions assist the water tetramer via four hydrogen bonds, sandwiching the water cluster between them. One of the disorder components of a methylammonium cation (comprising C3B and N3B) has short contacts with two Keggin anions and one water tetramer, forming an extended ladder-like hydrogen bond motif. However, all the other methylammonium cations show interactions with only one Keggin anion; therefore, the extent of the ladder-like motif should be limited to a restricted area. Compounds **2** and **3** exhibit hexagonal hydrogen bond motifs, as shown in Figure 2. Each Keggin anion is involved in three such motifs, leading to the formation of a honeycomb-like two-dimensional extended network of the hydrogen bond perpendicular to their threefold axes.

Conclusion

The structures of **1–4** show similar packing structures of cations and anions, although they crystallize into different space group types. This clearly demonstrates that the ionic interactions between the cations and the anions dominate their three-dimensional arrangements, at least when the sizes of the cations are sufficiently small. The effect of hydrogen bonds is restricted to applying distortion to these basic frameworks. It was also shown that steric hindrance is an important factor in determining the hydrogen bond distances.

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Supporting Information

Table S1 lists fractional coordinates for compounds **1–4**. For **2** and **3**, parameters with respect to primitive rhombohedral axes are listed to facilitate comparisons with those for **1** and **4**. Figures S1–S3 show intermolecular interactions between Keggin anions and methylammonium or K cations in **1** and **4**. Figures S4–S6 show ORTEP diagrams of compounds **1–3**. Figures S7–S9 show powder diffraction patterns of compounds **1–3**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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