Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Trithallium hydrogen bis(sulfate), $Tl_3H(SO_4)_2$, in the super-ionic phase by X-ray powder diffraction

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Received 2 April 2002
Accepted 10 May 2002
Online 12 June 2002

The structure of trithallium hydrogen bis(sulfate), $Tl_3H(SO_4)_2$, in the super-ionic phase has been analyzed by Rietveld analysis of the X-ray powder diffraction pattern. Atomic parameters based on the isotypic $Rb_3H(SeO_4)_2$ crystal in space group $R\overline{3}m$ in the super-ionic phase were used as the starting model, because it has been shown from the comparison of thermal and electric properties in $Tl_3H(SO_4)_2$ and $M_3H(SO_4)_2$ type crystals (M = Rb, Cs or NH_4) that the room-temperature $Tl_3H(SO_4)_2$ phase is isostructural with the high-temperature $R\overline{3}m$-symmetry $M_3H(SO_4)_2$ crystals. The structure was determined in the trigonal space group $R\overline{3}m$ and the Rietveld refinement shows that an hydrogen-bond $O-H\cdots O$ separation is slightly shortened compared with $O-H\cdots O$ separations in isotypic $M_3H(SeO_4)_2$ crystals. In addition, it was found that the distortion of the SO_4 tetrahedra in $Tl_3H(SO_4)_2$ is less than that in isotypic crystals.

Comment

The $Tl_3H(SO_4)_2$ crystal is one of a family of $M_3H(XO_4)_2$ compounds (M = Rb, Cs or NH_4, and X = S or Se), known as zero-dimensional hydrogen-bonded systems. The $M_3H(XO_4)_2$ crystals exhibit very interesting characteristics. First, the hydrogen bonds are isolated. Secondly, deuterated crystals show a drastic isotope effect at the low-temperature phase transition. Thirdly, they undergo a super-ionic phase transition from the low-temperature ferroelastic phase of the monoclinic system to the high-temperature paraelastic phase of the trigonal system; for example, $Rb_3H(SeO_4)_2$ and $Cs_3H(SeO_4)_2$ undergo super-ionic phase transitions at 449 and 456 K, respectively.

Recently, it was found that $Tl_3H(SO_4)_2$ undergoes a super-ionic phase transition at 239 K and displays super-ionic conductivity even at room temperature (Matsuo *et al.*, 2001), in spite of the fact that other $M_3H(XO_4)_2$-type crystals are good insulators at room temperature. This interesting feature of the $Tl_3H(SO_4)_2$ crystal would result from the change to the crystal structure due to placing Tl in the M site. Therefore, the determination of the structure of the $Tl_3H(SO_4)_2$ crystal in the super-ionic phase is very important for understanding the origin of the super-ionic phase transition in $M_3H(XO_4)_2$-type crystals. However, no atomic coordinates of $Tl_3H(SO_4)_2$ in the super-ionic phase were known, although the unit-cell parameters at room temperature had been previously determined by Peter & Jolibois (1973) from X-ray powder diffraction measurements. It is very difficult to prepare good quality single crystals of this compound. Therefore, we have measured the X-ray powder diffraction pattern and determined the crystal structure of $Tl_3H(SO_4)_2$ in the super-ionic phase using Rietveld analysis.

It is known that $M_3H(XO_4)_2$-type crystals belong to the trigonal system, space group $R\overline{3}m$, in the highest-temperature phase below the melting point (Baranov *et al.*, 1987; Merinov *et al.*, 1990; Łukaszewicz *et al.*, 1993). Chen *et al.* (2000) recently deduced that a new $(NH_4)_3H(SO_4)_2$ phase above 433 K also has $R\overline{3}m$ symmetry. Moreover, $(NH_4)_3H(SeO_4)_2$, which is one of the $M_3H(XO_4)_2$-type crystals, is known to undergo four phase transitions at T_{I-II} = 335 K, T_{II-III} = 308 K, T_{III-IV} = 275 K and T_{IV-V} = 181 K (Gesi, 1977; Osaka *et al.*, 1979). Phase I, space group $R\overline{3}m$, and phase II, space group $R\overline{3}$, are super-ionic conductors (Pawłowski *et al.*, 1990; Łukaszewicz *et al.*, 1993). The phase transition at T_{I-II} is characterized by a small change in the temperature gradients

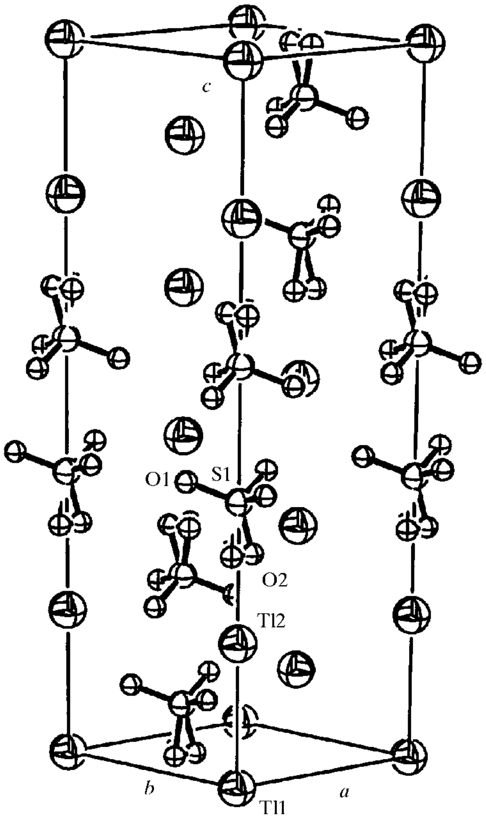

Figure 1
A view of the unit cell of $Tl_3H(SO_4)_2$. The O2 atom occupies three equivalent positions with probability $\frac{1}{3}$.

DOI: 10.1107/S0108270102008569

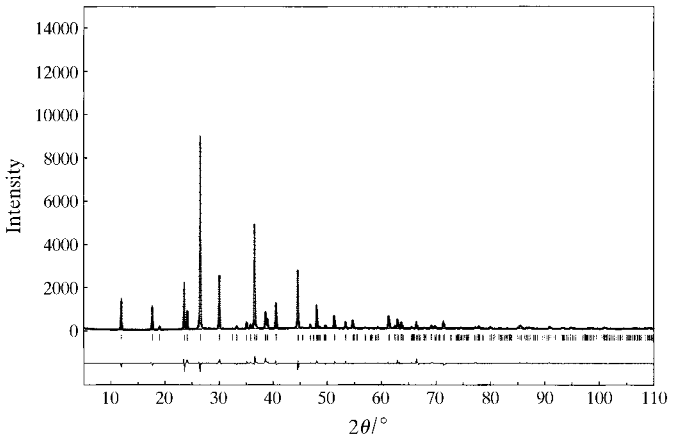

Figure 2
The fitted diffraction profile for $Tl_3H(SO_4)_2$, showing calculated (line), observed (+) and difference (lower) profiles.

of the dielectric constant and electrical conductivity (Pawłowski *et al.*, 1990). The $Tl_3H(SO_4)_2$ crystal also undergoes four phase transitions above 77 K, at T_{I-II} = 267 K, T_{II-III} = 239 K, T_{III-IV} = 196 K and T_{IV-V} = 156 K (Matsuo *et al.*, 2001).

In phases I and II, $Tl_3H(SO_4)_2$ is a super-ionic conductor similar to $(NH_4)_3H(SeO_4)_2$. Furthermore, in the phase transition at T_{I-II} = 267 K, the slopes of the dielectric constant and electrical conductivity show the same temperature dependence as $(NH_4)_3H(SeO_4)_2$ (Matsuo *et al.*, 2001). These facts indicate that the room-temperature $Tl_3H(SO_4)_2$ phase is isostructural with the high-temperature $R\bar{3}m$-symmetry $M_3H(XO_4)_2$ crystals. Therefore, a starting model based on the isotypic $Rb_3H(SeO_4)_2$ crystal in space group $R\bar{3}m$ of the super-ionic phase was used in the determination of the structure of the super-ionic phase of $Tl_3H(SO_4)_2$.

In the $M_3H(XO_4)_2$-type crystal, it is also known that the O2 atom which forms the hydrogen bond statistically occupies three equivalent positions with probability $\frac{1}{3}$ in the super-ionic phase (Baranov *et al.*, 1987; Merinov *et al.*, 1990). We used a similarly disordered model here. Selected geometric parameters are given in Table 1. The crystal structure is shown in Fig. 1 and the fitted diffraction profile for $Tl_3H(SO_4)_2$ is shown in Fig. 2.

The structure of $Tl_3H(SO_4)_2$ consists of isolated SO_4 tetrahedra with Tl atoms distributed between them. The unit-cell volume of $Tl_3H(SO_4)_2$ is 674.65 (6) Å^3. This is very small in comparison with the unit-cell volumes of 733.5 Å^3 for $Rb_3H(SeO_4)_2$ (Baranov *et al.*, 1987) and 839.0 Å^3 for $Cs_3H(SeO_4)_2$ (Merinov *et al.*, 1990) in the super-ionic phase. In the subsequent discussion, the crystal data for $Rb_3H(SeO_4)_2$ and $Cs_3H(SeO_4)_2$ are taken from Baranov *et al.* (1987) and Merinov *et al.* (1990), respectively.

The O—H···O hydrogen-bond distance of 2.626 (6) Å in $Tl_3H(SO_4)_2$. is slightly shorter than in the $Rb_3H(SeO_4)_2$ (2.67 (2) Å) and $Cs_3H(SeO_4)_2$ (2.71 Å) crystals. The S—O1 and S—O2 bond lengths in $Tl_3H(SO_4)_2$ are 1.644 (6) and 1.640 (8) Å, respectively; thus, the S—O2 distance is very similar to the S—O1 distance. In contrast, in the isotypic $M_3H(SeO_4)_2$ crystals, the Se—O2 distances [1.682 (9) Å for $Rb_3H(SeO_4)_2$ and 1.70 (2) Å for $Cs_3H(SeO_4)_2$] are considerably longer than the Se—O1 distances [1.617 (3) Å for ($Rb_3H(SeO_4)_2$) and 1.662 (8) Å for $Cs_3H(SeO_4)_2$]. Thus, in $Tl_3H(SO_4)_2$, the distortion of the SO_4 tetrahedra is less than that of the isotypic $M_3H(SeO_4)_2$ crystals.

It is known that the super-ionic phase transition is accompanied by a ferroelastic phase transition from the low-temperature ferroelastic phase to the high-temperature paraelastic phase. That is, the distortion in the crystal is closely related to the super-ionic phase transition. Therefore, the changes of the crystal structure due to filling the *M* sites with Tl, in conjunction with the lesser distortion of the SO_4 tetrahedra in comparison with the distortion of the tetrahedra in the isotypic crystals, would be the primary causes of the super-ionic phase transition at lower temperatures.

In this work, the coordinates of the H atom could not be determined, because H atoms migrate rapidly in the crystal in the super-ionic phase (Matsuo *et al.*, 2001).

Experimental

Crystals of $Tl_3H(SO_4)_2$ were obtained from aqueous solutions of Tl_2SO_4 and H_2SO_4 in a molar ratio of 3:2. The crystals were grown by slow evaporation from a saturated solution at 313 K after several recrystallizations for purification.

Crystal data

$Tl_3H(SO_4)_2$
M_r = 806.28
Trigonal, $R\bar{3}m$
a = 5.9376 (4) Å
b = 5.9376 (4) Å
c = 22.0966 (9) Å
V = 674.65 (6) Å^3
Z = 3
D_x = 5.946 (1) Mg m^{-3}
Cu *Kα* radiation
μ = 106.6 mm^{-1}
T = 293 K
Specimen shape: flat sheet
15 × 20 × 1 mm
Specimen prepared at 313 K
Particle morphology: plate-like, white

Data collection

Rigaku RINT-1400 diffractometer
$\theta/2\theta$ scans
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
$2\theta_{min}$ = 5.000, $2\theta_{max}$ = 110.0°
Increment in 2θ = 0.006°

Refinement

R_p = 0.065
R_{wp} = 0.094
R_{exp} = 0.076
S = 1.23
$2\theta_{min}$ = 5.000, $2\theta_{max}$ = 110.0°
Increment in 2θ = 0.006°
Profile function: pseudo-Voigt
268 reflections
38 parameters
H-atom parameters not refined
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.01
Preferred orientation correction: March–Dollase function, axis (001) (Dollase, 1986)

Table 1
Selected geometric parameters (Å, °), including the O2···O2 hydrogen-bond distance.

S1—O1	1.644 (6)	O1···O2^{ii}	2.586 (7)
S1—O2	1.641 (8)	O2···O2^{iii}	2.626 (6)
O1···O1^{i}	2.65 (1)		
O1—S1—O1^{i}	107.52 (6)	O1—S1—O2^{ii}	103.85 (6)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $\frac{1}{3}+y, x-\frac{1}{3}, \frac{2}{3}-z$.

The diffraction data were analyzed by the Rietveld method, with the atomic parameters of the isotypic $Rb_3H(SeO_4)_2$ in its super-ionic phase as a starting model (Baranov *et al.*, 1987). The profile shape was represented by a pseudo-Voigt function. In addition to the profile, lattice and structure parameters, the zero-point shift, ten background parameters, and the scale factor were determined with corrections for preferred orientation along (001) (the crystal shapes were very thin plates). Isotropic thermal vibrations were assumed. The interatomic distances and bond angles were calculated with *ORFFE* (Busing *et al.*, 1964).

Data collection: *RINT Server Software* (Rigaku, 1988); cell refinement: *RIETAN*2000 (Izumi & Ikeda, 2000); data reduction: *RINT Server Software*; program(s) used to solve structure: *RIETAN*2000; program(s) used to refine structure: *RIETAN*2000; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 2001); software used to prepare material for publication: *RIETAN*2000.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1021). Services for accessing these data are described at the back of the journal.

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