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Cs$_3$H(SeO$_4$)$_2$ at 300 K by High-Resolution Neutron Powder Diffraction

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Abstract

The monoclinic room-temperature structure of tricaesium hydrogen bis[tetraoxoselenate(2−)] was refined from high-resolution neutron powder diffraction data. Special emphasis was given to the precise location of the H atom and the determination of the hydrogen-bond network. A Fourier analysis clearly shows that the H atom is distributed over two symmetry-equivalent positions of half occupancy [H···H = 0.52 (2) Å] around an inversion centre. The hydrogen bridge is non-linear [O—H···O = 173 (2)°] with an O···O distance of 2.506 (7) Å.

Comment

Cs$_3$H(SeO$_4$)$_2$ (TCHSe) is a member of a family of compounds with the general formula M_3H(XO$_4$)$_2$ (M = Rb, Cs, K, NH$_4$; X = S, Se). The isostructural rhombohedral proton-conducting phases of this family are well known. The two-dimensional proton conductivity results from the disorder of the H atoms over partly occupied symmetry-equivalent positions. Until now, structural studies of this family were mainly performed using X-ray diffraction (for TCHSe see Merinov, Bolotina, Baranov & Shuvalov, 1988, 1991; Merinov, Baranov & Shuvalov, 1990; Ichikawa, Gustafsson & Olovsson, 1992), making it impossible to clarify the exact positions of the light atoms, which is the basic knowledge required for an understanding of the proton-conducting mechanism.

Our group recently performed the first neutron powder diffraction experiments on Rb$_3$H(SeO$_4$)$_2$ at different temperatures (Bohn *et al.*, 1995; Melzer, Sonntag & Knight, 1996; Melzer, Wessels & Reehuis, 1996). The only neutron diffraction study of Cs$_3$H(SeO$_4$)$_2$ until now was of a deuterated specimen, Cs$_3$D(SeO$_4$)$_2$, at 5 K (Belushkin, Ibberson & Shuvalov, 1993). We have recently reported the first-high resolution neutron powder diffraction experiment on the proton-conducting phase of TCHSe at 473 K (Sonntag, Melzer & Knight, 1997). In this work, we present a structural investigation of the hydrogen-bond network in TCHSe at room temperature, based on a high-resolution neutron powder diffraction experiment performed on the D2B instrument of the ILL at Grenoble.

TCHSe at room temperature is monoclinic with space group *C*2/*m*. The structure is built from Cs atoms coordinated by O atoms belonging to SeO$_4$ tetrahedra. These tetrahedra are linked into isolated pairs by hydrogen bonds. Cs atoms and SeO$_4$ tetrahedra form mixed layers parallel to a pseudo-hexagonal plane alternating with layers containing only Cs atoms. For a more detailed description of the structure see Bohn *et al.* (1995) and Melzer, Wessels & Reehuis (1996).

The initial parameters for our refinement were taken from Merinov *et al.* (1988). We started the refinement with the H atom situated on the inversion centre in the middle of the hydrogen bridge and with isotropic displacement parameters for all atoms. As the displacement parameter of the H atom refined to a large value, we then determined anisotropic displacement parameters for the H atom. A much better fit was obtained and the *R* factor decreased by about 1.5%, reflecting the cigar-shaped behaviour of the H-atom motion in the hydrogen bridge. Within experimental error, all the refined structural parameters of the heavy atoms were in good agreement with the initial values. In the proton-conducting phase at 473 K, the elongated vertex O atoms O(2) of the SeO_4 tetrahedra are distributed with equiprobable occupancies of 1/3 over three symmetry-equivalent positions. Consequently, there are three equiprobable hydrogen bridges, each with an occupancy of 1/3. The H atoms are distributed in a double-minimum potential over two symmetry-equivalent positions with site occupancies of 1/6. This strong disorder leads to fast proton conduction (Sonntag *et al.*, 1997). Using a similar model for our room-temperature data with a double-minimum potential for the hydrogen bridge and a site occupancy of 1/2 for the H atom did not change the structural parameters of the heavy atoms (including O) and the improvement in the *R* factors was insignificant. Fig. 1 shows the observed, calculated and difference profiles for this model.

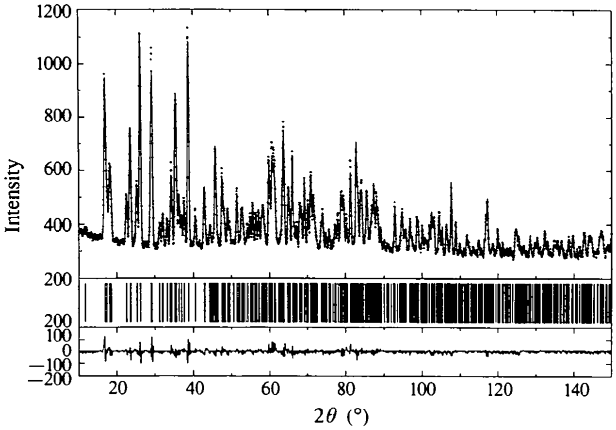

Fig. 1. Observed, calculated and difference neutron diffraction patterns for $Cs_3H(SeO_4)_2$ at room temperature.

A Fourier analysis was carried out to clarify whether the H atom is situated on the inversion centre in the middle of the hydrogen bridge with anisotropic displacement parameters (model 1) or is disordered in a double-minimum potential over two symmetry-equivalent positions with an isotropic displacement parameter (model 2). This clearly showed a double-minimum potential for the H atom in the hydrogen bridge (see Fig. 2), thus confirming model 2. The two symmetry-equivalent positions of the H atom, each with an occupancy of 1/2, are separated by 0.52 (2) Å. The O(2)···O(2) distance of 2.506 (7) Å shows that the hydrogen bridge in TCHSe is short. The O(2)—H distance of 1.01 (2) Å is typical for a hydrogen bridge and the O(2)—H···O(2) angle of 173 (2)° shows that it is non-linear. Fig. 3 shows two SeO_4 tetrahedra connected *via* a hydrogen bridge projected onto the (001) plane.

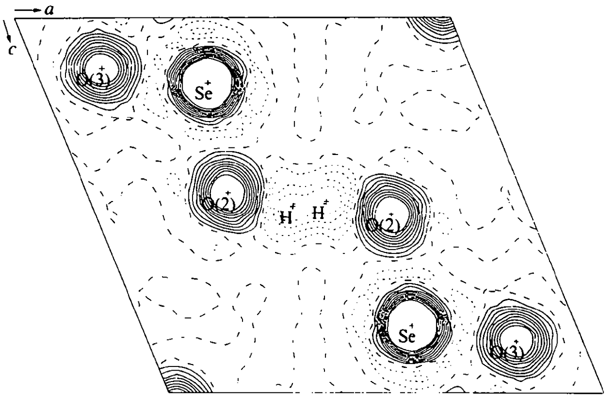

Fig. 2. A Fourier map of the scattering density (at y = 0) showing clearly the double-minimum potential of the H atom in the hydrogen bridge.

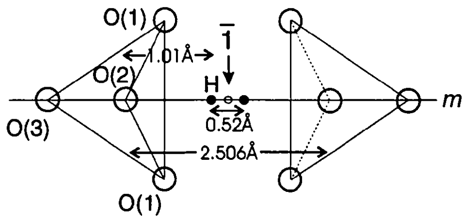

Fig. 3. Two SeO_4 tetrahedra connected *via* a hydrogen bridge projected onto the (001) plane. In the middle of the hydrogen bridge there is an inversion centre. The O(2), O(3) and H atoms are situated on a mirror plane (*m*).

Experimental

Single crystals of $Cs_3H(SeO_4)_2$ were prepared by slow evaporation of an aqueous solution containing stoichiometric quantities of Cs_2CO_3 (Aldrich Chemical Co. No. 255645) and H_2SeO_4 (Merck No. 12325) with H_2O (Merck No. 15333) in a ratio of 0.3 (2 molar solution of H_2SeO_4). The crystals were platelet-shaped with maximum dimensions 3 × 3 × 1 mm. They were carefully ground and checked for impurities by X-ray diffraction. No additional impurities were found.

Crystal data

$Cs_3H(SeO_4)_2$
M_r = 685.63
Monoclinic
$C2/m$
a = 10.8883 (4) Å
b = 6.3877 (1) Å
c = 8.4404 (3) Å
β = 112.448 (2)°
V = 542.56 (3) Å^3
Z = 2

Neutron radiation
λ = 1.5946 Å
T = 300 K
White

Data collection

Backscattering geometry
High resolution powder diffractometer D2B at ILL, Grenoble

Specimen mounting: vanadium can, diameter 10 mm, height 40 mm
$2\theta_{\min}$ = 10.0, $2\theta_{\max}$ = 160.0°
Increment in 2θ = 0.05°

Refinement

$R_p = 0.029$
$R_{wp} = 0.039$
$R_{\text{exp}} = 0.021$
$R_B = 0.069$
$2\theta_{\text{min}} = 10.0$, $2\theta_{\text{max}} = 152.5°$
Increment in $2\theta = 0.05°$
Excluded region(s): none
Least-squares refinement against χ^2
Profile function: pseudo-Voigt
31 parameters
All H-atom parameters refined
Preferred orientation correction: none

Table 1. *Fractional atomic coordinates and isotropic displacement parameters (Å^2)*

	x	y	z	U_{iso}
Cs(1)	0	0	0	0.020 (1)
Cs(2)	0.1976 (5)	0	0.6081 (6)	0.028 (1)
Se	0.4266 (3)	0	0.2342 (3)	0.0174 (5)
O(1)	0.4862 (3)	0.2123 (4)	0.6893 (4)	0.0254 (6)
O(2)	0.3921 (4)	0	0.0209 (5)	0.0294 (8)
O(3)	0.2883 (5)	0	0.2633 (5)	0.0323 (9)
H†	0.525 (1)	0	0.005 (2)	0.028 (3)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Cs-atom coordination			
Cs(1)—O(1$^{\text{i}}$) ×4	3.159 (3)	Cs(2)—O(1$^{\text{iii}}$) ×2	3.217 (6)
Cs(1)—O(2$^{\text{ii}}$) ×4	3.431 (2)	Cs(2)—O(1) ×2	3.246 (5)
Cs(1)—O(3) ×2	3.077 (4)	Cs(2)—O(1$^{\text{iv}}$) ×2	3.138 (4)
Average	3.251	Cs(2)—O(2$^{\text{v}}$)	3.314 (5)
		Cs(2)—O(3)	3.412 (8)
		Cs(2)—O(3$^{\text{vi}}$) ×2	3.358 (2)
		Average	3.264
SeO$_4$ ion			
Se—O(1$^{\text{vii}}$) ×2	1.640 (3)	O(1)···O(1$^{\text{viii}}$)	2.712 (3)
Se—O(2)	1.694 (5)	O(1)···O(2$^{\text{ix}}$)	2.666 (4)
Se—O(3)	1.615 (6)	O(1)···O(3$^{\text{ix}}$)	2.698 (5)
Average	1.647	O(2)···O(3)	2.689 (7)
		Average	2.691
O(1$^{\text{ix}}$)—Se—O(1$^{\text{vii}}$)	111.5 (2)	O(1$^{\text{ix}}$)—Se—O(2) ×2	106.2 (2)
O(1$^{\text{ix}}$)—Se—O(3) ×2	111.9 (2)	O(2)—Se—O(3)	108.7 (2)
		Average	109.4
Hydrogen bridge			
O(2)···H	1.51 (2)	O(2)—H$^{\text{x}}$	1.01 (2)
O(2)···O(2$^{\text{x}}$)	2.506 (7)	H···H$^{\text{x}}$	0.52 (2)
O(2)···H—O(2$^{\text{x}}$)	173 (2)	Se—O(2)···H	105.4 (7)
Se—O(2)—H$^{\text{x}}$	112 (1)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (v) $x, y, 1 + z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (vii) $1 - x, y, 1 - z$; (viii) $x, -y, z$; (ix) $1 - x, -y, 1 - z$; (x) $1 - x, -y, -z$.

Neutron diffraction measurements were performed at the high-resolution powder diffractometer D2B of the ILL in Grenoble (Hewat, 1986) in the high intensity mode. The 64 counters, spaced at 2.5° intervals, were moved by steps of 0.05° to give a complete diffractogram up to 160° in 2θ.

The program *FULLPROF* (Rodriguez-Carvajal, 1992) was used to refine the structure.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1168). Services for accessing these data are described at the back of the journal.

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A New Hexagonal κ Phase of Al–Cr–Ni

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Abstract

A new hexagonal aluminium–chromium–nickel phase, $Al_{14.4}Cr_{3.4}Ni_{1.1}$, is described. The structure includes 12 icosahedral clusters in the unit cell, each of which consists of a transition metal (TM) atom at the center and 11 aluminium and one TM atom on the fivefold vertices of the icosahedron. Pairs of the clusters are linked along the c axis by sharing a triangular face. Two pairs of the clusters are joined by two trigonal antiprisms, constructing a column along the c axis. Six such columns are included in the unit cell and form the crystal structure. The second neighboring atoms connecting the columns are on the threefold axes of the icosahedral cluster.

Comment

It is important to know approximate crystalline structures for the understanding of quasicrystals. One of the