Acta Cryst. (1996). C**52**, 1061–1063

$Rb_3H(SeO_4)_2$ at 4 K by Neutron Powder Diffraction†

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(*Received 31 March 1995; accepted 10 August 1995*)

Abstract

The monoclinic structure of trirubidium hydrogen bis[tetraoxoselenate(2−)], $Rb_3H(SeO_4)_2$, has been refined from neutron powder diffraction data collected at 4 K, revealing the peculiarities of the so-called zero-dimensional hydrogen-bond network. The hydrogen bridge, with an O···O distance of 2.473 (4) Å, is non-linear [O—H···O 173 (2)°] with the H atom disordered between two symmetry-constrained positions of half occupancy [H···H 0.34 (3) Å]. The disorder might be static.

Comment

$Rb_3H(SeO_4)_2$ (TRHSe) is a member of a family of proton conductors with the general formula $M_3H(XO_4)_2$, where M = K, Rb, Cs and X = S, Se. At elevated temperatures, the family is characterized by two-dimensional disordered proton subsystems with rhombohedral symmetry. All members show one or more ferroic phase transitions to monoclinic or triclinic ordered phases with so-called zero-dimensional hydrogen-bond networks.

For TRHSe, an ordered phase has been found below 447 K which is probably stable down to 2 K. The structure is known to be monoclinic with space group *A*2/*a* (Makarova, Verin & Shchagina, 1986). The first structural study of this compound was an X-ray structure analysis in which the H-atom position was not refined (Makarova, Verin & Shchagina, 1986; Baranov *et al.*, 1987). Bohn *et al.* (1995) were the first to try to to determine the positions of the light atoms, including the H atom, by Rietveld refinement against neutron powder diffraction data. However, the data were of low accuracy as a low-resolution diffractometer was used. The studies cited above were carried out at room temperature; temperature-dependent X-ray structural studies on a deuterated sample have been presented by Ichikawa, Gustafsson & Olovsson (1992).

In the course of our investigations of TRHSe, we have performed a neutron powder diffraction experiment at 4 K on the high-resolution powder diffractometer (HRPD) at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. The spontaneous strain in TRHSe in the monoclinic phase is low (about 5 × 10^{-3}), hence it is absolutely necessary to use a high-resolution diffractometer in order to resolve the structural peculiarities of the hydrogen-bond system. It should be pointed out that there have been only two structural neutron diffraction experiments carried out on the selenium-containing compounds [$Cs_3D(SeO_4)_2$ in space group $P2_1/m$: Belushkin, Ibberson & Shuvalov, 1993; Bohn *et al.*, 1995], thus, such direct determinations of the H- or D-atom positions are very scarce (this is also true for the sulfate-containing compounds).

The structural parameters of the heavier atoms are similar to those determined by Makarova, Verin & Shchagina (1986) and Baranov *et al.* (1987) using X-rays. The basic features can be seen in Fig. 1(*a*).

The distances between the Rb and O atoms are significantly smaller than those determined previously (Makarova, Verin & Shchagina, 1986; Baranov *et al.*, 1987; Bohn *et al.*, 1995). This is plausible, as these distances tend to decrease with decreasing temperature. This has also been observed for the deuterated homologue by Ichikawa, Gustafsson & Olovsson (1992).

The typical distortions of the SeO_4 tetrahedra within the SeO_4—H—SeO_4 moieties, as discussed, for example, by Ichikawa, Gustafsson & Olovsson (1992), were verified by this study. The Se—O(2) distance is longer than the other three Se—O distances, three of the O—Se—O angles are larger than the ideal tetrahedral value and three of the angles are smaller. The O(2)···O(1) and O(2)···O(3) distances are smaller than the other O···O distances as a consequence of the orientation of the hydrogen bridge.

The O(2)···O(2) distance of 2.473 (4) Å represents a short hydrogen bridge. Within the hydrogen bridge, two H-atom positions with occupancies of one-half were found (O—H/2···H/2—O). The alignment is clearly non-linear, with an O(2)—H···O(2) angle of 173 (2)° [see Fig. 1(*b*)]. As there is an inversion centre in the middle of the short hydrogen bridge and the H···H distance of 0.34 (3) Å is just below the resolution limit of the experiment, this symmetry-constrained structural model is not necessarily unambiguous [*cf.* Thomas (1992), and references therein]. However, a second possible model, in which the H atom was placed on the inversion centre and a cigar-shaped anisotropic displacement factor was used to describe the spatial distribution

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† Dedicated to Professor W. Prandl on the occasion of his 60th birthday.

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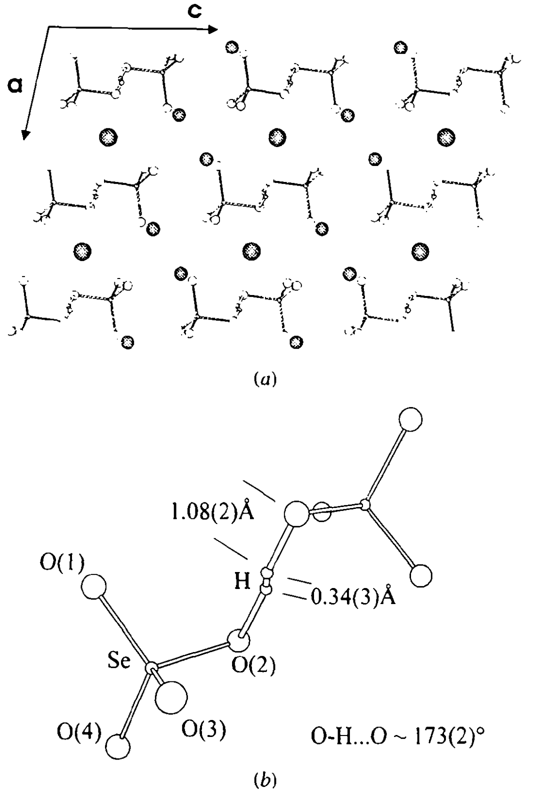
of the H atom, resulted in a worse refinement with an R factor more than 1% higher.

The deuterated sample shows another phase transition at about 90 K to a ferroelectric phase where the D atoms are ordered in an asymmetric O—D···O hydrogen bridge (Gesi, 1980). Therefore, the model proposed here for TRHSe, in which the H atom lies in a double-minimum potential well, is plausible. The O—H distance of 1.08 (2) Å and the H-atom displacement factor of 0.015 (3) $Å^2$ give no indication of a dynamically disordered proton subsystem, and at 4 K the disorder should be static. These structural details could not be resolved by Bohn *et al.* (1995); even a linear hydrogen bridge can be deduced from their data, as their e.s.d.'s are more than five times larger than those in the present study. The misalignment of the H atoms found here can also be seen from the Se—O(2)—H and Se—O(2)···H angles, which are 110.1 (8) and 103.4 (6)°, respectively.

The H-atom positions in the potassium sulfate homologue $K_3H(SO_4)_2$ were found by difference Fourier analysis of X-ray single-crystal data (Noda, Uchiyama, Kafuku, Kasatani & Terauchi, 1990; Noda, Kasatani, Watanabe & Terauchi, 1992). The maxima corresponding to the H atoms occur in the opposite sense to that found here, such that the S—O(2)—H angle is smaller than the S—O(2)···H angle (for temperatures above 100 K). A neutron diffraction experiment should show whether these Fourier maxima are artefacts or represent the real positions of the H atoms.



(*a*)

(*b*)

Fig. 1. (*a*) A projection onto the (010) plane of the structure of $Rb_3H(SeO_4)_2$ at 4 K. The Rb atoms are represented by shaded circles, Rb(1) atoms being the larger ones. (*b*) A perspective projection onto the (101) plane of the binding geometry of the hydrogen bridge. In the centre of the hydrogen bridge there is an inversion centre. The hydrogen bridge is non-linear with the Se—O(2)—H angle larger than the Se—O(2)···H angle.

Experimental

Single crystals of $Rb_3H(SeO_4)_2$ were grown by slow evaporation of an aqueous solution of stoichiometric quantities of Rb_2CO_3 and H_2SeO_4. The colourless single crystals, with sizes up to 3 mm^3, were carefully ground and checked for their quality by Guinier powder diffractometry. No impurities or abnormal peak broadening were found.

Crystal data

$Rb_3H(SeO_4)_2$
$M_r = 543.32$
Monoclinic
$A2/a$
$a = 10.38719\ (8)$ Å
$b = 6.03925\ (2)$ Å
$c = 15.29563\ (7)$ Å
$\beta = 102.8246\ (4)°$
$V = 935.572$ $Å^3$
$Z = 4$
$D_x = 3.857$ Mg m^{-3}

Neutron radiation
Cell parameters from whole diffractogram
$d = 0.66–2.52$ Å
$T = 4$ K
Powder

Data collection

High-resolution powder diffractometer (HRPD) at ISIS
Time-of-flight neutron diffraction
Flight path = 95.9872 m

Backscattering geometry, $2\theta_{av} = 168.329°$
$d_{min} = 0.66$ Å
$d_{max} = 2.52$ Å
1731 reflections

Refinement

Least-squares refinement against χ^2
$R_p = 0.0325$
$R_{wp} = 0.0382$
$R_{exp} = 0.0209$

$R_{wI} = 0.0773$
$\chi^2 = 3.34$
4515 observations
30 structure variables
46 variables in total

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

	x	y	z	U_{iso}
Rb(1)	1/4	0.7561 (7)	0	0.0091 (8)
Rb(2)	0.6519 (3)	0.7346 (5)	0.1945 (2)	0.0079 (5)
Se	0.4628 (2)	0.2269 (4)	0.1168 (1)	0.0066 (5)
O(1)	0.3995 (4)	0.0160 (6)	0.1572 (2)	0.0096 (8)
O(2)	0.4427 (3)	0.1767 (5)	0.0065 (2)	0.0085 (6)
O(3)	0.6213 (3)	0.2418 (6)	0.1547 (2)	0.0084 (6)
O(4)	0.3882 (3)	0.4570 (6)	0.1283 (2)	0.0108 (8)
H†	0.009 (2)	0.023 (3)	0.004 (1)	0.015 (3)

† Site occupancy 0.5.

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

Rb-atom coordination				
Rb(1)—O(1^{i})	× 2	3.000 (4)	Rb(2)—O(1^{iv})	3.070 (5)
Rb(1)—O(2^{i})	× 2	3.222 (5)	Rb(2)—O(1^{v})	3.140 (5)
Rb(1)—O(2^{ii})	× 2	3.241 (4)	Rb(2)—O(1^{vi})	2.874 (5)
Rb(1)—O(3^{ii})	× 2	2.964 (3)	Rb(2)—O(2^{vii})	3.060 (4)
Rb(1)—O(4^{iii})	× 2	2.815 (4)	Rb(2)—O(3)	3.040 (5)
Average		3.048	Rb(2)—O(3^{iv})	3.125 (5)
			Rb(2)—O(3^{viii})	2.909 (4)
			Rb(2)—O(4)	3.179 (4)
			Rb(2)—O(4^{v})	3.080 (5)
			Rb(2)—O(4^{ix})	3.390 (5)
			Average	3.087
SeO_4 ion				
Se—O(1)		1.618 (4)	O(1)···O(2)	2.629 (5)
Se—O(2)		1.680 (4)	O(1)···O(3)	2.685 (5)
Se—O(3)		1.622 (4)	O(1)···O(4)	2.698 (5)
Se—O(4)		1.619 (4)	O(2)···O(3)	2.620 (5)
Average		1.635	O(2)···O(4)	2.669 (5)
			O(3)···O(4)	2.698 (5)
			Average	2.667
O(1)—Se—O(2)		105.7 (2)	O(2)—Se—O(4)	108.0 (2)
O(1)—Se—O(3)		111.9 (2)	O(3)—Se—O(4)	112.7 (2)
O(1)—Se—O(4)		112.9 (2)	Average	109.4
O(2)—Se—O(3)		105.0 (2)		
Hydrogen bridge				
O(2)···O(2^{x})		2.473 (4)	O(2)···H^{xi}	1.39 (2)
O(2)—H^{iii}		1.08 (2)	H···H^{xii}	0.34 (3)
O(2^{iii})—H···O(2^{xi})		173 (2)	Se—O(2)···H^{xi}	103.4 (6)
Se—O(2)—H^{iii}		110.1 (8)		

Symmetry codes: (i) $\frac{1}{2}-x, 1+y, -z$; (ii) $x-\frac{1}{2}, 1-y, z$; (iii) $\frac{1}{2}-x, y, -z$; (iv) $x, 1+y, z$; (v) $\frac{1}{2}+x, 1-y, z$; (vi) $1-x, \frac{1}{2}-y, \frac{1}{2}-z$; (vii) $1-x, 1-y, -z$; (viii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ix) $1-x, \frac{3}{2}-y, \frac{1}{2}-z$; (x) $1-x, -y, -z$; (xi) $\frac{1}{2}+x, -y, z$; (xii) $-x, -y, -z$.

All reflections could be indexed in space group *A*2/*a*. The principle design of HRPD is described elsewhere (Ibberson, David & Knight, 1992). The refinement was carried out using *TF*12*LS* (Mark 4.12), a program based on the Cambridge Crystallography Subroutine Library (David, Ibberson & Matthewman, 1992). Initial structural parameters were taken from Makarova, Verin & Shchagina (1986).

The authors are grateful to A. Bohn for the sample preparation.

Lists of intensity data and complete geometry, together with a plot of observed, calculated and difference profiles, have been deposited with the IUCr (Reference: JZ1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1063–1065

$CsLaNb_2O_7$

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(*Received 14 July 1995; accepted 21 November 1995*)

Abstract

The title compound, caesium lanthanum diniobium heptaoxide, belongs to the $ARNb_2O_7$ (A = K, Rb, Cs; R = La, Nd) family of compounds and crystallizes as a layered structure in which the Cs^+ ions are located in the interlayer gap formed by double perovskite $LaNb_2O_7$ layers. The single-crystal X-ray refinement of the structure of $CsLaNb_2O_7$ reported here is the first for a member of this family.

Comment

The alkali metal–rare earth niobium oxides $ARNb_2O_7$ (A = Na, K, Rb, Cs; R = La, Nd) have layer structures formed from double perovskite layers of composition RNb_2O_7 (Dion, Ganne & Tournoux, 1986; Gopalakrishnan, Bhat & Raveau, 1987). This family of compounds is divided into two groups by a difference in the conformation of adjacent perovskite layers; for A = Na and K adjacent layers are staggered, while for A = Rb and Cs they are eclipsed. The lattice parameters for $CsLaNb_2O_7$ [a = 3.908 (1), c = 11.160 (4) Å] agree well with the values determined from X-ray powder diffraction data [a = 3.905 (2), c = 11.185 (6) Å; Gopalakrishnan *et al.*, 1987].

Recently, the crystal structures of $KLaNb_2O_7$ (Sato, Abo, Jin & Ohta, 1992) and $RbLaNb_2O_7$ (Armstrong & Anderson, 1994) were refined by the Rietveld method, and were found to have a supercell. The present study shows that $CsLaNb_2O_7$ has no supercell. The lattice parameters of $KLaNb_2O_7$ [a = 3.9060 (1), b = 21.6030 (7), c = 3.8879 (1) Å] are related to those of