Hydrogen Bond Studies

67.* The Crystal Structure of Rubidium Trihydrogen Selenite, RbH$_3$(SeO$_3$)$_2$

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The crystal structure of RbH$_3$(SeO$_3$)$_2$ has been determined from three-dimensional single crystal X-ray diffractometer data obtained at room temperature. Four formula units crystallize in an orthorhombic unit cell of dimensions: $a = 5.9192(2)$, $b = 17.9506(5)$, and $c = 6.2519(3)$ Å. The space group is $P2_12_12_1$. The structure consists of two types of chains at a right angle. One chain is built up of H$_2$SeO$_3$ molecules linked by 2.594(8)-Å hydrogen bonds and the other of HSeO$_3^-$ ions linked by 2.571(12)-Å hydrogen bonds. These two types of chains are cross-linked by a third hydrogen bond of length 2.521(7) Å. The rubidium ion is surrounded by eight oxygen atoms forming a distorted cube. The Rb$^+$–O distances are in the range 2.94–3.19 Å.

Introduction

Crystals of the alkali trihydrogen selenites, MH$_3$(SeO$_3$)$_2$, have been found to show a variety of dielectric properties and crystal structures [for a review see Ref. (*1*)]. To be able to explain these different properties it is necessary to have detailed structural information.

The present investigation forms part of a series of X-ray and neutron diffraction studies of hydrogen-bonded ferroelectric and related compounds in progress at this Institute. The previous paper was a neutron diffraction study of LiH$_3$(SeO$_3$)$_2$ (*2*), and the next will be an X-ray diffraction study of NH$_4$H$_3$(SeO$_3$)$_2$ (*3*).

Experimental

Crystals of RbH$_3$(SeO$_3$)$_2$ were prepared from an aqueous solution of Rb$_2$CO$_3$ and SeO$_2$ in the stoichiometric ratio. The solution was heated to 80°C. On cooling to room temperature small almost spherical single crystals were obtained. Their melting point was found to be 57°C, which agrees very well with the reported value of 57.1°C (*1*).

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The intensity data were collected at room temperature on a Stoe–Philips computer controlled four-circle diffractometer with a graphite monochromator using MoKα radiation and ω–2θ scan. Different combinations of scan time and filter selection were used with the intention of measuring all reflections to about the same precision.

Three standard reflexions with integrated intensities of 3500, 4000, and 47 000 counts, respectively, were measured at regular intervals to provide a check on crystal and electronic stability. The two weaker reflexions showed no significant changes, whereas the intensity of the strongest one first underwent a continuous increase of 10% and then stabilized. All reflexions obtained up to this point were later remeasured. It was then found that the increase had affected only the high-intensity reflexions. This increase was probably due to an alteration in the nature of the extinction effects present. It could be that the mosaic structure had been changed because of radiation damage. As the data used in the refinements were those collected after the test reflexion had stabilized, no scaling was necessary.

A total of 1172 independent reflexions having $\sin \theta/\lambda$ less than 0.74 Å^{-1} were recorded. Out of these, 934 had intensities greater than $3\sigma_{count}$. The intensities were corrected for Lorentz, polarization, and absorption effects (spherical

crystal). The calculated linear absorption co-efficient was 189.7 cm^{-1}. The crystal was approximately spherical with a radius of 0.0376 mm. The transmission factors were in the range 0.356–0.373.

Space Group and Unit Cell

The space group was determined from Weissenberg photographs recorded with $CuK\alpha$ radiation. The diffraction symmetry and systematic absences of these photographs suggested the noncentrosymmetric orthorhombic space group $P2_12_12_1$.

The unit-cell dimensions were obtained from powder photographs recorded in a Guinier–Hägg XDC-700 focussing camera using $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å), with silicon ($a = 5.43054$ Å at 25°C) as an internal standard. A least-squares treatment of the observed θ-values from 63 reflexions provided the parameters given in Table I.* The b-axis was found to be about twice the value reported by Shuvalov et al. (1).

Structure Determination

The structure was solved by direct methods according to Karle and Karle (4). The normalized structure factor E_h was defined by $E_h{}^2 = F_h{}^2/\epsilon \sum f_{jh}^2$, where $\epsilon = 2$ when h is $h00$, $0k0$, or $00l$, and $\epsilon = 1$ otherwise; f_j is the atomic scattering factor for the jth atom in the unit cell containing N atoms. The set of reflexions used for the choice of origin, the enanthiomorph and those given symbolic phases are shown in Table II.

The procedure for fixing the origin in a non-

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least-significant digits.

TABLE I

CRYSTAL DATA[a]

Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a	5.9192(2) Å
b	17.9506(5) Å
c	6.2519(3) Å
V	664.287 Å^3
Z	4
D_x	3.42 g/cm^3
μ_{calc} (Mo$K\alpha$)	189.7 cm^{-1}

[a] 25°C.

TABLE II

STARTING SET PARAMETERS FOR PHASE DETERMINATION

h	$|E_h|$	ϕ_h	
1, 23, 0	3.03	$\pi/2$	origin
3, 0, 4	1.76	0	
0, 11, 3	2.01	$\pi/2$	
0, 5, 8	1.70	$\pi/2$	enanthiomorph
1, 3, 1	2.82	a	symbolic phases
4, 0, 2	2.53	b	
4, 20, 1	2.15	c	

centrosymmetric space group is discussed in detail by Hauptman and Karle (5). By using the formula $\phi_h \approx \langle \phi_k + \phi_{h-k} \rangle_{k_r}$, where ϕ_h is the phase related to $|E_h|$ and k_r means that only the phases corresponding to the largest $|E_k|$ are considered, the phases of the symbols were found to be $a \approx -\pi/2$, $b = \pi$, and $c \approx 0$. From these considerations 41 reflexions could be assigned phases and used as input to the tangent refinement,

$$\tan \phi_h \approx \sum |E_k \cdot E_{h-k}| \sin (\phi_k + \phi_{h-k})/ \sum |E_k \cdot E_{h-k}| \cos (\phi_k + \phi_{h-k}).$$

After a few cycles the phases of 121 reflexions with $|E| > 1.49$ were accepted and an E-map could be calculated. This yielded the coordinates for the rubidium and selenium atoms and, after a least-squares refinement based on these three heavy atoms, a difference Fourier calculation gave the positions of the oxygen atoms.

Refinement

The structure was refined by minimizing the function $\sum w(|F_o| - |F_c|)^2$ using the full matrix least-squares program LINUS. Each reflexion was assigned a weight inversely proportional to the estimated variance of the observation w: $w = 1/\sigma^2(F)$ where $\sigma^2(F) = \sigma_{count}^2 \mid (F^2)/4F^2 + k \cdot F^2$. The first term is based on counting statistics and the second is an empirical correction term to take account of other errors in the data. The constant k was chosen to be 0.0004. The refinement was based on the 934 reflexions with intensities $>3\sigma_{count}$. The parameters refined comprised 27 positional and 54 anisotropic thermal parameters, one overall scale factor, and one isotropic extinction parameter.

The positions of the hydrogen atoms could not be found in the difference Fourier maps. However, the Se–O distances clearly indicate to which oxygen atoms the three hydrogen atoms are

covalently bonded (cf. the "Description and Discussion ..." section below). The coordinates of the hydrogen positions were therefore calculated assuming linear $O \cdots O$ hydrogen bonds, with the atoms 1.05 Å from O(1), O(3), and O(6), respectively. They were included in the last cycles of calculation with fixed parameters. The isotropic thermal parameter for each was assumed to be 6.0 Å^2.

The atomic scattering factors used for Se and O were those calculated by Hanson et al. (6), for Rb$^+$ those calculated by Cromer, Larson, and Waber (7), and for H as calculated by Stewart, Davidson, and Simpson (8). The scattering factors of Se and Rb$^+$ were corrected for anomalous dispersion according to Cromer (9). The final agreement factors were:

$$R = (\sum ||F_o| - |F_c||/\sum |F_o|) = 0.030, \quad \text{and}$$

$$R_w = (\sum w(|F_o| - |F_c|)^2)/\sum wF_o^2)^{1/2} = 0.034.$$

The standard deviation of an observation of unit weight $\sigma_1 = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 1.07, where m is the total number of observations and n the number of parameters varied. The final parameters are given in Tables III and IV, the observed and calculated structure factors in Table V. The observed F_o values are corrected for extinction using the expression

$$|F_o|_{corr} = |F_o|\left(1 + \frac{\bar{T} \cdot p \cdot |F_c|^2 \cdot g \cdot \lambda^3}{12.593 \cdot V^2 \cdot \sin 2\theta}\right)^{1/4},$$

where λ is in Å, V is the unit cell volume in Å^3, and $p = 2 \cdot (1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)$ (which is strictly valid only for unpolarized X-rays) (10). The mean path length through the crystal $\bar{T}$ for a particular

reflexion is appropriately corrected for absorption. The refined value of the isotropic extinction parameter is $g = 4043(325)$. This corresponds to a mosaic spread parameter of approximately 14 sec or a domain size of 0.3 nm, depending upon whether a Zachariasen (11) Type I or Type II description is assumed. The extinction correction factors as given above were in the range 1.00–1.25.

Absolute Configuration

Since the effect of anomalous dispersion was included in the structure factor calculation, a determination of the absolute configuration was possible (12). Refinement of a structure having an absolute configuration opposite to that in Table III converged with agreement factors $R(-) = 0.036$ and $R_w(-) = 0.041$. Use of Hamilton's R-test (13) indicates a high significance for the absolute configuration given in Table III.

TABLE III

ATOMIC COORDINATES ($\times 10^5$)

	x	y	z
Se(1)	21630(14)	39527(4)	29576(12)
Se(2)	73113(14)	24215(4)	16878(12)
Rb	26034(15)	08289(4)	23398(13)
O(1)	18958(119)	42057(28)	02738(86)
O(2)	50635(98)	22483(34)	31855(138)
O(3)	49313(87)	42686(28)	34067(103)
O(4)	77185(96)	33470(24)	18904(88)
O(5)	08180(90)	46152(28)	42379(106)
O(6)	95210(96)	20750(31)	32267(145)

TABLE IV

ANISOTROPIC THERMAL PARAMETERS ($\times 10^5$)[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Se(1)	1418(21)	107(2)	1290(18)	−24(5)	−54(20)	−16(5)	131(1)	157(1)	162(1)
Se(2)	1546(23)	145(2)	1179(18)	−15(6)	199(21)	−38(5)	143(1)	155(1)	174(1)
Rb	1538(21)	169(2)	1541(19)	39(6)	70(22)	35(5)	159(1)	166(1)	180(1)
O(1)	3253(251)	216(18)	1135(132)	−242(57)	−408(166)	110(41)	140(9)	173(9)	257(9)
O(2)	1871(177)	281(22)	2787(249)	−243(51)	574(207)	−52(67)	152(10)	218(11)	252(11)
O(3)	1365(154)	153(16)	2242(183)	−1(40)	−70(165)	−51(46)	155(9)	157(8)	212(9)
O(4)	2093(169)	119(14)	2408(158)	14(44)	677(204)	42(40)	139(8)	170(11)	237(10)
O(5)	1483(162)	172(17)	2382(185)	60(45)	102(160)	−332(50)	123(11)	166(9)	242(9)
O(6)	1981(185)	216(20)	3111(263)	225(50)	−1023(207)	−113(66)	143(11)	192(10)	274(11)

[a] The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The root mean square components R_i ($\times 10^3$ Å) of thermal displacement of the atoms along the ellipsoid axes are also listed.

TABLE V

Observed and Calculated Structure Factors[a, b]

0,K,L				1,K,L				2,K,L				3,K,L		

(Full-page tabulated numerical data of observed and calculated structure factors, arranged in repeated four-column index blocks labeled 0,K,L · 1,K,L · 2,K,L · 3,K,L, with columns H K L, Fobs, Fcalc.)

```
15  1  562  555      10  5  468  473      8  2  533  534      9  4  218  207
15  2  474  476      10  6  320  294      8  3  191  183      9  5   84   73*
15  3  229  239      10  7  209  228      8  4  419  440     10  0   52   10*
15  4  113  116*     11  0  155  176      8  5  226  226     10  1  281  306
15  5  119  111*     11  1  510  520      8  6  143  167*    10  2  144  178
15  6  196  192      11  2  282  288      9  0  458  463     10  3  419  414
16  0  149  167      11  3  606  606      9  1  713  712     10  4  251  227
16  1  170  182      11  4  225  226      9  2  330  327     10  5  321  308
16  2  255  243      11  5  409  413      9  3  431  442     11  0  173  137
16  3    0   73*     11  6  186  190      9  4   75   36*    11  1  360  394
16  4    0   58*     12  0  869  872      9  5  180  214     11  2  221  215
16  5  199   63*     12  1  558  551      9  6  176  167     11  3  366  377
16  6   27   90*     12  2  570  561     10  0   78  107*    11  4  145  179*
17  0  669  688      12  3  262  261     10  1  474  470     12  0  373  381
17  1  302  297      12  4  238  207     10  2  264  245     12  1  222  222
17  2  494  483      12  5  119   88*    10  3  211  210     12  2  367  360
17  3  121   95*     12  6  213  183     10  4  165  189     12  3   97  104*
17  4   44  132*     13  0  342  332     10  5  153  185     13  0  324  311
17  5  183  212      13  1  233  244     10  6  140  139*    13  1  203  214
18  0   77   61*     13  2  224  241     11  0  427  433     13  2  196  197
18  1  346  350      13  3  231  238     11  1  209  209     13  3   74  118*
18  2  170  139      13  4   83  102*    11  2  209  290     13  4  140  128*
18  3  380  372      13  5   58  125*    11  3  217  181     14  0  189  197
18  4  130  173*     13  6  105  119*    11  4  148  169     14  1  266  263
18  5  224  215      14  0  274  267     11  5  221  224     14  2    0   90*
19  0  290  276      14  1  464  456     11  6  196  177     14  3  169  171
19  1   95  122*     14  2  181  211     12  0  266  246     15  0  324  323
19  2  341  342      14  3  234  245     12  1  280  276     15  1  140  126*
19  3  247  256      14  4  170  160     12  2  282  285     15  2  244  278
19  4  319  323      14  5  216  191     12  3  296  286     16  0  119  129*
19  5  227  235      14  6  237  220     12  4  174  178     16  1    0   23*
20  0   64   10*     15  0  274  298     12  5  193  178     16  2  189  205
20  1  208  206      15  1  153  175     13  0  280  305     17  0  166  152
20  2  288  290      15  2  360  356     13  1  167  163     17  1  186  160
20  3  282  278      15  3  171  201     13  2  376  395
20  4  311  307      15  4  259  263     13  3  322  320          7,K,L
21  0  346  355      15  5  130  104*    13  4  388  404
21  1  120  103*     16  0   43   74*    14  0  292  290      0  1   22   91*
21  2  253  257      16  1  313  315     14  1  245  251      0  2  177  154
21  3  130  105*     16  2  293  290     14  2  382  392      0  3    0   50*
22  0  150  156      16  3  402  423     14  3  252  246      0  4   65   85*
22  1   94   54*     16  4  363  368     14  4  327  337      1  0  247  233
22  2  230  223      16  5  339  328     14  5   99   86*     1  1   30   92*
22  3  120  110*     17  0  123  118*    15  0  319  307      1  2  378  394
23  0  567  566      17  1  168  177     15  1  323  332      1  3  147  179*
23  1  133   96*     17  2  262  267     15  2  339  266      1  4  321  337
23  2  422  395      17  3  357  344     15  3  243  210      2  0  508  497
                     17  4  195  175     15  4  137  162*     2  1  168  184
      4,K,L          17  5  249  259     16  0  291  314      2  2  387  407
                     17  6  212  218     16  1  201  191      2  3   46   68*
 0  0 2118 2095      18  0  350  323     16  2  160  264      2  4  262  276
 0  1  103  103      18  1  166  170     16  3  129  139*     3  0    0    8*
 0  2 1464 1462      18  2  228  217     17  0  135  111*     3  1  431  435
 0  3  246  258      18  3    0   87*    17  1  356  358      3  2   45   21*
 0  4  339  348      18  4    0   56*    17  2  111   96*     3  3  250  254
 0  5  289  301      18  5   80   16*    17  3  280  286      3  4  312  302
 0  6  141  168      19  0  255  262     18  0  112   60*     4  0  315  347
 0  7  267  266      19  1  145  139     18  1  165  161      4  1  266  252
 1  0  600  612      19  2  205  171     18  2  116   73*     4  2  166  137
 1  1  524  515      19  3  178  109*    18  3  364  359      4  3  145  182*
 1  2  432  431      19  4  118   95*    18  4  112  118*     5  0  211  229
 1  3  486  495      20  0  483  492     19  0  239  244      5  1  116  112*
 1  4  433  445      20  1    0   41*    19  1  161  179      5  2  172  259
 1  5  173  166      20  2  225  237     19  2  103  140*     5  3  284  264
 1  6  368  367      20  3  337  332     20  0  198  213      5  4  188  173
 1  7  141  116      21  0   22   24*    20  1  106   24*     6  0  150  154
 2  0  317  315      21  1  295  280     20  2  140  183      6  1    0   78*
 2  1  132  128      22  0   71   91*                         6  2  159  186
 2  2  204  196      22  1  140  154*         6,K,L           6  3   52   86*
 2  3  385  379                                              6  4  119   96*
 2  4  532  539          5,K,L           0  0  797  800      7  0  198  205
 2  5  282  301                          0  1   39   36*     7  1   81   23*
 2  6  430  431       0  1   81   70*    0  2  567  561      7  2  339  345
 2  7  215  202       0  2  416  410     0  3  105   70*     7  3  132  110*
 3  0   54   28*      0  3  178  187     0  4  191  191      8  0  358  357
 3  1  317  309       0  4  295  289     0  5  159  190      8  1    0   43*
 3  2   26   72*      0  5  166  163     0  6   70   16*     8  2  355  328
 3  3  592  588       0  6    0   44*    1  0  379  378      8  3  148  150
 3  4  152  177       0  7    0   35*    1  1  445  436      9  0  232  203
 3  5  232  249       1  0  187  176     1  2  218  215      9  1  105  103*
 3  6   35   63*      1  1   90   95*    1  3  412  412      9  2  361  358
 3  7   83  101*      1  2  378  380     1  4  134  127      9  3  114   91*
 4  0  153  132       1  3  314  312     1  5  173  197     10  0  223  233
 4  1  359  360       1  4  423  427     1  6  249  240     10  1   86   11*
 4  2  265  255       1  5  421  426     2  0   47   54*    10  2  287  297
 4  3  641  642       1  6  232  213     2  1  283  274     10  3  156  114*
 4  4  526  520       1  7  253  253     2  2  205  202     11  0  125  148*
 4  5  470  471       2  0  663  658     2  3  340  350     11  1  249  259
 4  6  367  365       2  1  314  313     2  4  346  346     11  2   87   79*
 4  7  231  235       2  2  567  570     2  5  174  183     11  3  172  182
 5  0  191  173       2  3  280  288     2  6  301  297     12  0  195  160
 5  1  810  814       2  4  414  417     3  0    0   16*    12  1  165  204
 5  2  343  345       2  5  353  346     3  1  192  190     12  2  189  154
 5  3  542  544       2  6  101   72*    3  2   32   17*    13  0  153  135*
 5  4  404  402       2  7  271  246     3  3  230  203     13  1   87  102*
 5  5  251  270       3  0   59   86*    3  4  145  149     14  0  242  224
 5  6  380  390       3  1 1175 1168     3  5  110   83*
 5  7   74   92*      3  2  131  136     3  6    0    7*         8,K,L
 6  0 1521 1533       3  3  557  548     4  0  345  359
 6  1  547  539       3  4  174  182     4  1  156  137      0  0  300  301
 6  2 1062 1048       3  5  114   67*    4  2  528  537      0  1    0   15*
 6  3  207  196       3  6  258  244     4  3  249  246      0  2  219  255
 6  4  296  308       4  0  197  165     4  4  340  349      0  3  253  253
 6  5   93  115*      4  1  608  619     4  5  161  197      1  0  282  267
 6  6  203  178       4  2  292  298     4  6  136  141      1  1  143  133*
 6  7  202  235       4  3  229  222     5  0  563  553      1  2  312   45*
 7  0  756  770       4  4  366  295     5  1   79   21*     2  0  196  201
 7  1  133  130       4  5  240  224     5  2  462  467      2  1  100  127*
 7  2  453  455       4  6   55   84*    5  3  162  177      2  2   75   49*
 7  3  207  196       5  0  239  236     5  4  613  619      3  0   43   26*
 7  4  294  297       5  1  334  332     5  5  574  572      3  1   96   44*
 7  5  142  149       5  2  123  128     6  0  143  150      4  0   62   44*
 7  6  218  229       5  3  295  266     6  1  494  484      4  1  199  197
 8  0  328  327       5  4  319  311     6  2    0   82*     5  0   59   32*
 8  1  422  418       5  5  201  203     6  3  232  233      5  1  213  119
 8  2  262  262       5  6  383  383     6  4  388  116*     5  2  314  334
 8  3  297  303       5  7  111  115*    6  5  545  550      6  0    0   12*
 8  4  329  338       6  0  244  249     7  0  162  186      6  1  276  282
 8  5  100  112*      6  1  289  297     7  1  334  349      6  2  102   37*
 8  6  337  340       6  2  208  197     7  2  223  225      7  0  289  290
 8  7  159  153       6  3  336  331     7  3  179  151      7  1  114   77*
 9  0    0   46*      6  4  165  160     7  4  143  139*
 9  1  405  401       6  5  247  236     7  5  150  134
 9  2  333  332       6  6  197  186     8  0  293  312
 9  3  412  419       7  0  147  148     8  1  151  184
 9  4  320  323       7  1  178  175     8  2  121  135*
 9  5  151  128       7  2  522  542     8  3  274  274
 9  6  208  181       7  3  337  327     8  4  143   95
 9  7  166  137       7  4  516  536     9  0  203  210
10  0  157  182       7  5  294  295     9  1  300  286
10  1  352  354       7  6  320  319     9  2  189  208
10  2  281  276       8  0  627  651     9  3  238  230
10  3  589  613       8  1  110   93*
10  4  425  431
```

[a] The four columns are, in order, k, l, $10|F_o|$ and $10|F_c|$.

[b] Reflexions marked with an asterisk were not used in the refinements.

Computer Programs

The structure was solved with an IBM 1800 version of the program PHASE written by Koenig (14). The final calculations were done on the CDC 3600 computer in Uppsala using programs briefly described by Jönsson and Liminga (15).

Description and Discussion of the Structure

General

The structure is illustrated in Figs. 1–4. Bond distances and angles are listed in Table VI, with some distances also shown in the figures. The atomic arrangement of the heavy atoms in the asymmetric unit is illustrated in Fig. 1. As was pointed out earlier, it was not possible to find the positions of the hydrogen atoms from the difference Fourier maps. However, as in the case of $LiH_3(SeO_3)_2$ (2), the Se–O distances very clearly indicate that the hydrogen atoms are bonded to O(1), O(3), and O(6). From these considerations it is possible to formally describe the asymmetric unit as consisting of an Rb^+ ion, an $HSeO_3^-$ ion, and an H_2SeO_3 molecule. The $HSe(2)O_3^-$ ions are connected by hydrogen bonds $O(2)\cdots HO(6)$, forming S-shaped chains running in the [100]-direction (Fig. 2). The molecules $H_2Se(1)O_3$ are
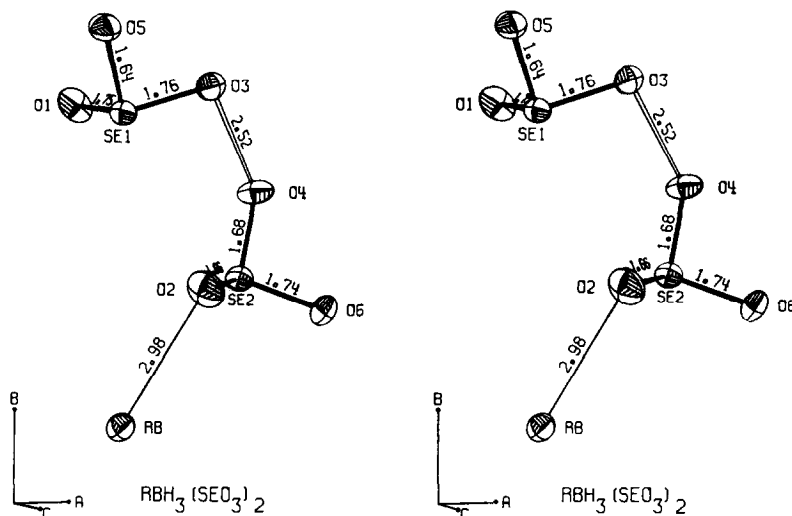
FIG. 1. A stereoscopic illustration of the heavy atoms of the asymmetric unit in $RbH_3(SeO_3)_2$. The ellipsoids are scaled to include 50% probability. Covalent bonds are filled, $O\cdots O$ hydrogen bonds are open, and ionic bonds are drawn as single lines.
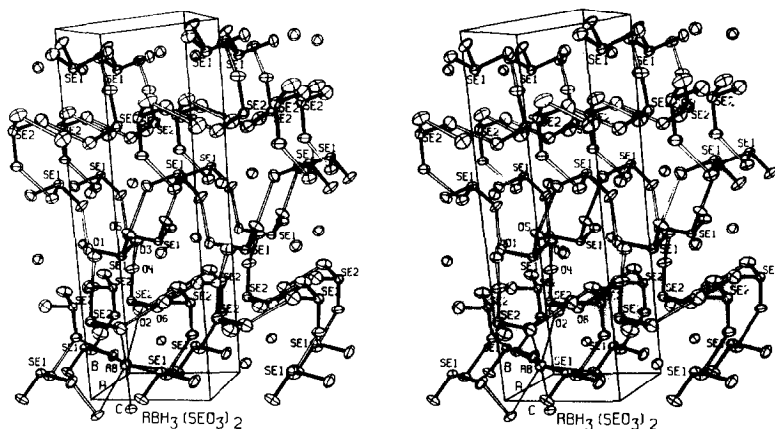
FIG. 2. A stereoscopic view of the structure showing the different types of chains.
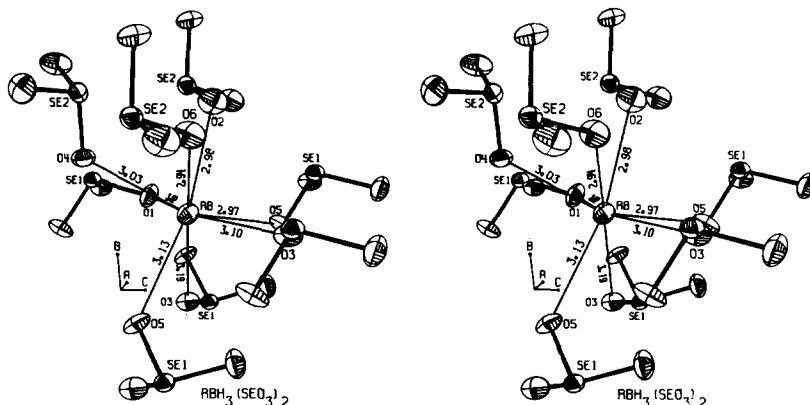
FIG. 3. A stereoscopic pair of drawings showing the rubidium ion and its surroundings.
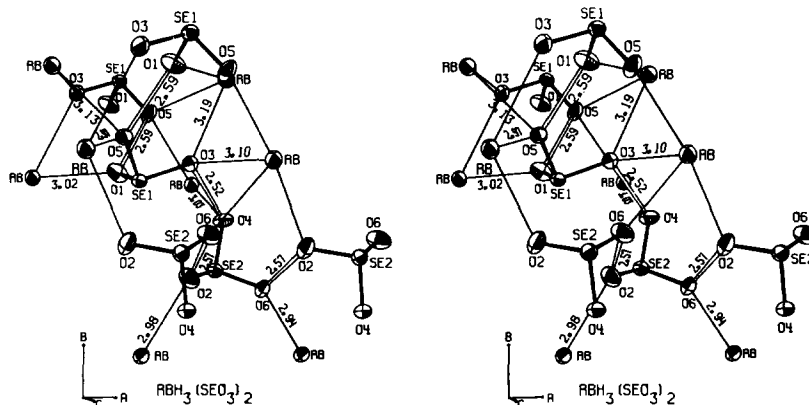

FIG. 4. A stereoscopic view of the hydrogen bond scheme.

also hydrogen bonded together via O(1)H···O(5), forming similar chains in the [001]-direction.

Puckered sheets of –Se(1)–Se(1)– and –Se(2)–Se(2)– chains with chain direction at right angles thus alternate in the [010]-direction. The different types of chains are interlinked through the third hydrogen bond O(3)H···O(4) to form a three-dimensional network. The network is further stabilized by ionic bonds Rb$^+$–O.

The Rubidium Ion

The rubidium ion is surrounded by eight oxygen atoms forming a distorted cube (Fig. 3 and Table VI). The Rb$^+$–O distances are between 2.939(6) and 3.192(5) Å. As can be seen in Figs. 2 and 3, Rb$^+$···O bonds are formed with oxygen atoms situated both in the same and in adjacent chains, thus stabilizing the structure both within and between different chains.

The Selenium and Oxygen Atoms

There are two independent selenium atoms present in the structure. They are covalently

bonded to three oxygen atoms, each forming a pyramid with Se–O distances 1.640(6)–1.757(5) Å (Fig. 1 and Table VI). The angles O–Se–O are between 98.09(26)°, and 104.93(29)° (Table VI). Distances and angles are in good agreement with those in LiH$_3$(SeO$_3$)$_2$ (2) and KH$_3$(SeO$_3$)$_2$ (16). As in these cases, it is to be expected that the Se–O distances are dependent upon whether or not a hydrogen atom is covalently bonded to the oxygen atom. From consideration of the Se–O distances, it is clear that the hydrogen atoms are covalently bonded to O(1), O(3) and O(6), having Se–O distances 1.746(5), 1.757(5), and 1.739(7) Å, respectively. The oxygen atoms O(2), O(4), and O(5), with Se–O distances 1.656(7), 1.683(4), and 1.640(6) Å, respectively, thus serve as acceptor atoms in the hydrogen bonds.

The Hydrogen Bond System

The details of the hydrogen bond system are shown in Fig. 4. It consists of three different hydrogen bonds. The first O(1)H···O(5), 2.594(8) Å, connects the H$_2$Se(1)O$_3$ groups

TABLE VI

INTERATOMIC DISTANCES AND ANGLES IN $RbH_3(SeO_3)_2$[a]

A. Distances (Å)		B. Angles in degrees	
Se(1)–O(1)	1.746(5)	O(1)–Se(1)–O(3)	98.87(31)
–O(3)	1.757(5)	O(1)–Se(1)–O(5)	103.68(29)
–O(5)	1.640(6)	O(3)–Se(1)–O(5)	98.09(26)
		O(2)–Se(2)–O(4)	104.93(29)
Se(2)–O(2)	1.656(7)	O(2)–Se(2)–O(6)	102.96(36)
–O(4)	1.683(4)	O(4)–Se(2)–O(6)	101.76(27)
–O(6)	1.739(7)		
		O(1)$_{5553}$–Rb–O(2)	72.71(17)
O(1)H···O(5)$_{5642}$	2.594(8)	O(1)$_{5553}$–Rb–O(4)$_{4553}$	61.27(15)
O(6)H···O(2)$_{5563}$	2.571(12)	O(2) –Rb–O(6)$_{4551}$	67.63(16)
O(3)H···O(4)	2.521(7)	O(4)$_{4553}$–Rb–O(6)$_{4551}$	78.88(19)
		O(3)$_{4563}$–Rb–O(5)$_{5454}$	84.32(15)
Rb–O(1)$_{5553}$	3.021(7)	O(3)$_{4563}$–Rb–O(5)$_{5563}$	72.17(15)
–O(2)	2.982(6)	O(3)$_{6454}$–Rb–O(5)$_{5454}$	68.87(13)
–O(3)$_{4563}$	3.099(6)	O(3)$_{6454}$–Rb–O(5)$_{5563}$	65.00(15)
–O(3)$_{6454}$	3.192(5)	O(1)$_{5553}$–Rb–O(3)$_{6454}$	61.22(14)
–O(4)$_{4553}$	3.031(5)	O(2) –Rb–O(5)$_{5563}$	77.81(17)
–O(5)$_{5563}$	2.972(6)	O(4)$_{4553}$–Rb–O(5)$_{5454}$	94.54(15)
–O(5)$_{5454}$	3.134(5)	O(6)$_{4551}$–Rb–O(3)$_{4563}$	64.17(19)
–O(6)$_{4551}$	2.939(6)		

[a] Atoms outside the asymmetric unit are specified by a subscript which indicates how the atomic parameters can be derived from those in the asymmetric unit. The first three digits code the lattice translation (the asymmetric unit is in cell 555) and the fourth digit specifies the symmetry operation: $1 = x, y, z$; $2 = 1/2 - x, -y, 1/2 + z$; $3 = 1/2 + x, 1/2 - y, -z$; $4 = x, 1/2 + y, 1/2 - z$.

to form S-shaped chains and the second bond O(2)···HO(6), 2.571(12) Å, connects the $HSe(2)O_3^-$ groups in a similar way. The third bond, O(3)H···O(4) 2.521(7) Å, links the Se(1)- and Se(2)-chains. This scheme is completely different from that found in $LiH_3(SeO_3)_2$ (2), but to discuss it in detail it is necessary to know the accurate hydrogen positions.

Acknowledgments

References

1. L. A. SHUVALOV, N. R. IVANOV, N. V. GORDEEVA, AND L. F. KIRPICHNIKOVA, Sov. Phys.-Crystallogr. 14, 554 (1970).

2. R. TELLGREN AND R. LIMINGA, J. Solid State Chem. 4, 255 (1972).

3. R. TELLGREN, D. AHMAD, AND R. LIMINGA, Chemica Scripta in press.

4. J. KARLE AND I. L. KARLE, Acta Crystallogr. 21, 849 (1966).

5. H. HAUPTMAN AND J. KARLE, Acta Crystallogr. 9, 45 (1956).

6. H. P. HANSON, F. HERMAN, J. D. LEA, AND S. SKILLMAN, Acta Crystallogr. 17, 1040 (1964).

7. D. T. CROMER, A. C. LARSON, AND J. T. WABER, Acta Crystallogr. 17, 1044 (1964).

8. R. F. STEWART, E. R. DAVIDSON, AND W. T. SIMPSON, J. Chem. Phys. 42, 3175 (1965).

9. D. T. CROMER, Acta Crystallogr. 18, 17 (1965).

10. P. COPPENS AND W. C. HAMILTON, Acta Crystallogr. Sect. A 26, 71 (1970).

11. W. H. ZACHARIASEN, Acta Crystallogr. 23, 558 (1967).

12. J. A. IBERS AND W. C. HAMILTON, Acta Crystallogr. 17, 781 (1964).

13. W. C. HAMILTON, Acta Crystallogr. 18, 502 (1965).

14. D. F. KOENIG, Private communication.

15. P.-G. JÖNSSON AND R. LIMINGA, Acta Chem. Scand. 25, 1729 (1971).

16. F. HANSEN, R. GRØNBAEK HAZELL, AND S. E. RASMUSSEN, Acta Chem. Scand. 23, 2561 (1969).