

# The Crystal Structure of Tris(selenourea) Sulfate Selenourea Solvate Dihydrate

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The crystal structure of tris(selenourea) sulfate selenourea solvate dihydrate,  $(su)_3SO_4 \cdot su \cdot 2H_2O$ , has been determined by X-ray methods, and refined by least-squares procedures. The crystals are triclinic, space group  $P\bar{1}$  (No. 2), with  $a = 8.8802(10)$  Å,  $b = 12.166(2)$  Å,  $c = 8.7222(15)$  Å,  $\alpha = 90.27(2)^\circ$ ,  $\beta = 92.60(2)^\circ$ ,  $\gamma = 100.907(11)^\circ$ , and two formula units per unit cell.

The tris(selenourea) ion possesses an approximately linear three-selenium system with Se–Se–Se bond angle  $168.29(5)^\circ$  and Se–Se bond lengths of  $2.6336(15)$  Å and  $2.6639(15)$  Å. The atoms in each selenourea group of the ion are co-planar. The three selenium atoms and the carbon atoms of the terminal selenourea groups are nearly co-planar, as are the three selenium atoms and the carbon atom of the middle group. These two planes make an angle of  $75.3^\circ$  with each other.

The dimensions of the uncomplexed selenourea molecule are nearly the same as found in the selenourea groups of the tris(selenourea) ion.

The oxygen atoms of the sulfate ion are disordered.

Tris(selenourea) sulfate selenourea solvate dihydrate,  $(su)_3SO_4 \cdot su \cdot 2H_2O$ , was first prepared by Verneuil<sup>1</sup> by air oxydation of an aqueous solution of selenourea containing sulfuric acid. It is referred to in Beilstein<sup>2</sup> as  $C_4H_{18}O_5N_8SSe_4 = [C_2H_6N_4Se_2 + H_2SO_4] + 2CH_4N_2Se + H_2O$ . From the X-ray study, the salt is a dihydrate. By further oxydation of the solution, first the tris(selenourea) sulfate and then the formamidinium diselenide sulfate crystallize.

The crystal structure determination was started since it was thought that the compound might contain a linear four-atom sequence of selenium

atoms. It turned out to have the known linear three-selenium system, with the fourth selenourea molecule as solvate. Since this molecule, in the crystals, is only bonded by hydrogen bonds, the structure gives the dimensions of a uncomplexed selenourea molecule.

## CRYSTAL DATA

The salt,  $(su)_3SO_4 \cdot su \cdot 2H_2O$ , forms reddish-brown prisms, space group  $P\bar{1}$  (No. 2), with  $a = 8.8802(10)$  Å,  $b = 12.166(2)$  Å,  $c = 8.7222(15)$  Å,  $\alpha = 90.27(2)^\circ$ ,  $\beta = 92.60(2)^\circ$ ,  $\gamma = 100.907(11)^\circ$ ,  $Z = 2$ ,  $D_m = D_x = 2.24$  g/cm<sup>3</sup>,  $\mu(MoK\alpha) = 86.9$  cm<sup>-1</sup>.

The dimensions of the crystal used for data collection were about  $0.1 \times 0.1 \times 0.1$  mm.

Collection of X-ray data was done by means of a Siemens AED diffractometer, using Nb-filtered  $MoK\alpha$  radiation,  $\lambda(\alpha_1) = 0.70926$  Å. For determination of cell parameters,  $\theta$  settings for 20 reflections with  $\theta$ -values in the range  $20$  to  $24^\circ$  were measured by the method of K. Maartmann-Moe<sup>3</sup> and evaluated by means of a least-squares program.

Intensity data were collected using a "five value" measuring procedure. The net count of three reference reflections, each measured two times at intervals of 50 reflections, was approximately constant during the collection period. The lower limit for observed reflections was set equal to two times the standard deviation in net intensity. Of 5294 reflections with  $\theta < 30^\circ$ , 125 showed extraordinary high or erratic background counts and were omitted from the data. 3496 reflections were found to be stronger than the lower limit. The remaining reflections were judged as unobserved and set equal to the limit.

The intensities were corrected for absorption and extinction. The extinction coefficient was found to be  $5.1 \times 10^{-3}$ .

The structure was solved by Patterson and Fourier methods, and with the weighting scheme,  $w = 1/\delta^2(F)$ , refined by least-squares procedures to an  $R$ -value of 0.041. The value of  $s = [w_i(\Delta F_i)^2 / (N - V)]^{1/2}$ , where  $N$  is the number of reflections and  $V$  is the number of variables, was 1.80. During the refinement the matrix was divided into two blocks.

The oxygen atoms of the sulfate ion were found to be disordered. Two sets of oxygen positions were picked from the Fourier map. After alternating

refinements on temperature and on population parameters, the latter were chosen to be 0.67 for one set and 0.33 for the other set. The final difference Fourier map shows peaks up to  $0.7 \text{ e}/\text{\AA}^3$ , mainly in the region of the sulfate ion.

Calculations were made by the X-Ray System, Version of June 1972<sup>4</sup> with some adjustments done by K. Maartmann-Moe of this Institute.

The final atomic coordinates and temperature parameters are listed in Table 1. Lists of observed and calculated structure factors are available from the author on request.

Table 1. Positional and thermal parameters. The isotropic temperature factor is  $\exp[-8\pi^2 U(\sin\theta/\lambda^2)]$  and the anisotropic factor is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$ . The isotropic and anisotropic values have been multiplied by 100 and 1000, respectively.

	<i>z</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Se <sub>1</sub>	-0.06934(5)	0.40979(4)	0.24189(6)	32.7(7)	25.1(7)	32.5(7)	8.6(2)	1.2(2)	3.4(2)
Se <sub>2</sub>	0.15776(5)	0.40910(4)	0.05813(6)	34.1(7)	19.1(7)	36.4(7)	5.9(2)	-9.4(2)	0.3(2)
Se <sub>3</sub>	0.34230(5)	0.40282(4)	-0.17286(6)	33.2(7)	27.1(7)	32.3(7)	9.6(2)	1.0(2)	1.4(2)
Se <sub>4</sub>	0.30529(6)	0.59594(4)	0.39984(6)	40.1(7)	28.1(7)	41.8(7)	3.4(2)	-12.7(2)	-1.0(2)
C <sub>1</sub>	-0.0197(5)	0.3029(4)	0.3848(5)	31(3)	29(3)	28(3)	8(2)	3(2)	1(2)
C <sub>2</sub>	0.0339(5)	0.2766(4)	-0.0352(5)	33(3)	23(2)	27(3)	7(2)	-2(2)	1(2)
C <sub>3</sub>	0.4508(5)	0.2936(4)	-0.0921(6)	29(3)	28(3)	37(3)	5(2)	2(2)	3(2)
C <sub>4</sub>	0.4479(5)	0.6989(4)	0.5170(5)	31(3)	31(3)	29(3)	6(2)	3(2)	-1(2)
N <sub>1</sub>	-0.1017(5)	0.2016(3)	0.3766(5)	53(3)	32(2)	38(3)	2(2)	-11(2)	8(2)
N <sub>2</sub>	0.0923(5)	0.3307(3)	0.4881(5)	45(3)	40(3)	34(3)	5(2)	-9(2)	4(2)
N <sub>3</sub>	0.0539(5)	0.1800(3)	0.0162(5)	47(3)	21(2)	41(3)	5(2)	-16(2)	3(2)
N <sub>4</sub>	-0.0659(5)	0.2853(3)	-0.1462(5)	44(3)	29(2)	42(3)	8(2)	-19(2)	-1(2)
N <sub>5</sub>	0.4207(5)	0.1938(3)	-0.1556(5)	47(3)	25(2)	62(3)	13(2)	-15(2)	-5(2)
N <sub>6</sub>	0.5523(5)	0.3192(3)	0.0200(5)	48(3)	38(3)	46(3)	12(2)	-14(2)	-1(2)
N <sub>7</sub>	0.4500(5)	0.8072(3)	0.5045(6)	50(3)	28(3)	60(3)	5(2)	-16(2)	-2(2)
N <sub>8</sub>	0.5464(5)	0.6653(3)	0.6139(5)	43(3)	36(2)	47(3)	9(2)	-19(2)	-7(2)
S	0.25058(13)	0.00830(9)	0.24651(14)	32.9(9)	24.3(8)	34.4(9)	4.6(5)	-7.6(5)	2.0(5)
O <sub>5</sub>	0.6575(7)	0.1204(4)	0.1352(6)	61(3)	43(3)	49(3)	11(2)	4(2)	-7(2)
O <sub>6</sub>	0.8385(6)	0.8793(4)	0.3767(7)	50(3)	47(3)	57(3)	5(2)	1(2)	-7(2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
O <sub>1</sub>	0.4127(7)	-0.0087(5)	0.2615(7)	5.39(16)	H <sub>41</sub>	-0.087(6)	0.345(5)	-0.168(6)	4.7(16)
O <sub>2</sub>	0.2451(7)	0.1232(5)	0.2807(7)	4.90(17)	H <sub>42</sub>	-0.121(6)	0.223(4)	-0.185(6)	5.2(16)
O <sub>3</sub>	0.1994(6)	-0.0151(5)	0.0820(6)	4.91(16)	H <sub>51</sub>	0.468(8)	0.141(6)	-0.129(8)	11(3)
O <sub>4</sub>	0.1575(8)	-0.0724(6)	0.3360(8)	6.97(20)	H <sub>52</sub>	0.347(8)	0.173(6)	-0.223(8)	10(2)
O <sub>11</sub>	0.3240(15)	-0.0669(11)	0.1713(16)	6.5(4)	H <sub>61</sub>	0.592(6)	0.264(5)	0.054(6)	5.8(18)
O <sub>22</sub>	0.3031(12)	0.1288(8)	0.2213(12)	3.2(2)	H <sub>62</sub>	0.574(6)	0.382(5)	0.047(6)	5.3(18)
O <sub>33</sub>	0.0804(11)	-0.0181(8)	0.2017(11)	3.5(2)	H <sub>71</sub>	0.521(6)	0.854(4)	0.558(6)	6.4(17)
O <sub>44</sub>	0.2592(11)	-0.0127(8)	0.4206(12)	3.9(2)	H <sub>72</sub>	0.392(7)	0.832(5)	0.457(7)	9(2)
H <sub>11</sub>	-0.079(7)	0.158(5)	0.442(8)	8(2)	H <sub>81</sub>	0.612(6)	0.720(5)	0.668(6)	6.1(18)
H <sub>12</sub>	-0.171(5)	0.181(4)	0.312(6)	3.5(14)	H <sub>82</sub>	0.563(7)	0.592(5)	0.617(7)	7.0(20)
H <sub>21</sub>	0.108(7)	0.266(5)	0.547(7)	8(2)	H <sub>1</sub>	0.587(9)	0.084(7)	0.152(10)	11(4)
H <sub>22</sub>	0.137(6)	0.387(7)	0.502(7)	6.3(20)	H <sub>2</sub>	0.681(7)	0.090(5)	0.079(7)	5(2)
H <sub>31</sub>	0.115(5)	0.175(4)	0.095(5)	4.0(14)	H <sub>3</sub>	0.828(8)	0.917(6)	0.434(7)	6(3)
H <sub>32</sub>	-0.001(5)	0.118(4)	-0.021(5)	3.3(14)	H <sub>4</sub>	0.915(8)	0.912(6)	0.356(8)	7(3)

Table 2. Dimensions of the selenourea groups in the tris(selenourea) ion and of the selenourea molecule. Bond lengths (Å) and angles (°). Standard deviations are given in parentheses.

The tris(selenourea) ion					
Se <sub>1</sub> –C <sub>1</sub>	1.903(5)	Se <sub>2</sub> –C <sub>2</sub>	1.925(4)	Se <sub>3</sub> –C <sub>3</sub>	1.903(5)
C <sub>1</sub> –N <sub>1</sub>	1.308(6)	C <sub>2</sub> –N <sub>3</sub>	1.300(6)	C <sub>3</sub> –N <sub>5</sub>	1.308(6)
C <sub>1</sub> –N <sub>2</sub>	1.306(6)	C <sub>2</sub> –N <sub>4</sub>	1.302(6)	C <sub>3</sub> –N <sub>6</sub>	1.295(6)
N <sub>1</sub> –H <sub>11</sub>	0.82(7)	N <sub>3</sub> –H <sub>31</sub>	0.87(5)	N <sub>5</sub> –H <sub>51</sub>	0.86(8)
N <sub>1</sub> –H <sub>12</sub>	0.82(5)	N <sub>3</sub> –H <sub>32</sub>	0.87(5)	N <sub>5</sub> –H <sub>52</sub>	0.87(7)
N <sub>2</sub> –H <sub>21</sub>	0.96(7)	N <sub>4</sub> –H <sub>41</sub>	0.81(6)	N <sub>6</sub> –H <sub>61</sub>	0.86(6)
N <sub>2</sub> –H <sub>22</sub>	0.73(6)	N <sub>4</sub> –H <sub>42</sub>	0.87(5)	N <sub>6</sub> –H <sub>62</sub>	0.78(6)
Se <sub>1</sub> –C <sub>1</sub> –N <sub>1</sub>	118.0(3)	Se <sub>2</sub> –C <sub>2</sub> –N <sub>3</sub>	117.9(3)	Se <sub>3</sub> –C <sub>3</sub> –N <sub>5</sub>	117.6(4)
Se <sub>1</sub> –C <sub>1</sub> –N <sub>2</sub>	120.7(3)	Se <sub>2</sub> –C <sub>2</sub> –N <sub>4</sub>	120.1(3)	Se <sub>3</sub> –C <sub>3</sub> –N <sub>6</sub>	120.4(4)
N <sub>1</sub> –C <sub>1</sub> –N <sub>2</sub>	121.3(4)	N <sub>3</sub> –C <sub>2</sub> –N <sub>4</sub>	122.0(4)	N <sub>5</sub> –C <sub>3</sub> –N <sub>6</sub>	121.9(5)
C <sub>1</sub> –N <sub>1</sub> –H <sub>11</sub>	115(4)	C <sub>2</sub> –N <sub>3</sub> –H <sub>31</sub>	122(3)	C <sub>3</sub> –N <sub>5</sub> –H <sub>51</sub>	123(5)
C <sub>1</sub> –N <sub>1</sub> –H <sub>12</sub>	124(3)	C <sub>2</sub> –N <sub>3</sub> –H <sub>32</sub>	121(3)	C <sub>3</sub> –N <sub>5</sub> –H <sub>52</sub>	123(5)
H <sub>11</sub> –N <sub>1</sub> –H <sub>12</sub>	121(5)	H <sub>31</sub> –N <sub>3</sub> –H <sub>32</sub>	117(4)	H <sub>51</sub> –N <sub>5</sub> –H <sub>52</sub>	113(7)
C <sub>1</sub> –N <sub>2</sub> –H <sub>21</sub>	111(3)	C <sub>2</sub> –N <sub>4</sub> –H <sub>41</sub>	121(4)	C <sub>3</sub> –N <sub>6</sub> –H <sub>61</sub>	115(3)
C <sub>1</sub> –N <sub>2</sub> –H <sub>22</sub>	126(5)	C <sub>2</sub> –N <sub>4</sub> –H <sub>42</sub>	118(4)	C <sub>3</sub> –N <sub>6</sub> –H <sub>62</sub>	118(4)
H <sub>21</sub> –N <sub>2</sub> –H <sub>22</sub>	124(6)	H <sub>41</sub> –N <sub>4</sub> –H <sub>42</sub>	121(5)	H <sub>61</sub> –N <sub>6</sub> –H <sub>62</sub>	127(5)
The selenourea molecule					
Se <sub>4</sub> –C <sub>4</sub>	1.867(4)				
C <sub>4</sub> –N <sub>7</sub>	1.319(6)	N <sub>7</sub> –H <sub>71</sub>	0.88(5)	N <sub>8</sub> –H <sub>81</sub>	0.91(5)
C <sub>4</sub> –N <sub>8</sub>	1.311(7)	N <sub>7</sub> –H <sub>72</sub>	0.75(7)	N <sub>8</sub> –H <sub>82</sub>	0.93(6)
Se <sub>4</sub> –C <sub>4</sub> –N <sub>7</sub>	120.3(4)	C <sub>4</sub> –N <sub>7</sub> –H <sub>71</sub>	118(4)	C <sub>4</sub> –N <sub>8</sub> –H <sub>81</sub>	116(4)
Se <sub>4</sub> –C <sub>4</sub> –N <sub>8</sub>	120.9(4)	C <sub>4</sub> –N <sub>7</sub> –H <sub>72</sub>	125(5)	C <sub>4</sub> –N <sub>8</sub> –H <sub>82</sub>	123(4)
N <sub>7</sub> –C <sub>4</sub> –N <sub>8</sub>	118.8(4)	H <sub>71</sub> –N <sub>7</sub> –H <sub>72</sub>	117(6)	H <sub>81</sub> –N <sub>8</sub> –H <sub>82</sub>	119(5)

### THE TRIS(SELENOUREA) ION AND THE UNCOMPLEXED SELENOUREA MOLECULE

Distances and angles in the tris(selenourea) ion are given in Fig. 1 and Tables 2 and 3. The unit cell contents are shown in Fig. 2.

The crystal structure of the tris(selenourea) ion in the tris(selenourea) dichloride and the corresponding dibromide,<sup>5</sup> has been determined earlier. The selenourea groups are bonded together through a linear Se–Se–Se system. The bonding is of the three-centre four-electron type with Se–Se bond lengths about 0.31 Å longer than a single covalent Se–Se bond. The central selenium atom has a T-shaped coordination being bonded to the two selenium atoms and to a carbon atom.

As seen from Table 3 the Se–Se–Se system in the three structures shows only small variations. In the present structure, the Se–Se–Se system is more symmetrical and the sum of the two Se–Se bond lengths is a little smaller. This is in accordance with

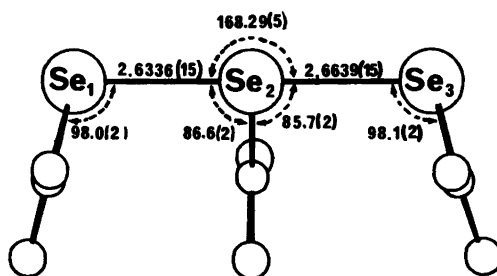


Fig. 1. The tris(selenourea) ion in (su)<sub>3</sub>SO<sub>4</sub>.su.2H<sub>2</sub>O.

Table 3. Se—Se bond lengths (Å) and Se—Se—Se angles (°) in tris(selenourea) ions.

	Se <sub>1</sub> —Se <sub>2</sub>	Se <sub>2</sub> —Se <sub>3</sub>	∑Se—Se	∠Se—Se—Se
(su) <sub>3</sub> Cl <sub>2</sub> ·H <sub>2</sub> O <sup>5</sup>	2.597(2)	2.717(2)	5.314	173.81(6)
(su) <sub>3</sub> Br <sub>2</sub> ·H <sub>2</sub> O <sup>5</sup>	2.624(2)	2.712(2)	5.336	173.89(9)
(su) <sub>3</sub> SO <sub>4</sub> ·su·2H <sub>2</sub> O	2.6336(15)	2.6639(15)	5.2975	168.29(5)

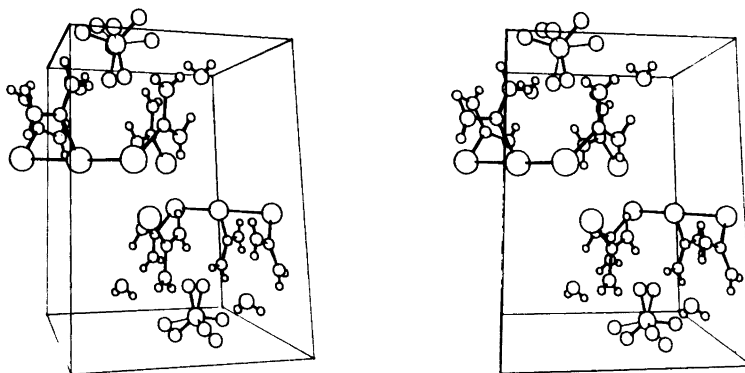


Fig. 2. A stereoscopic pair of drawings showing the content of the unit cell.

the trend found in the crystal structures of three salts of the triselenocyanate ion,<sup>6</sup> but opposite to what is found when the tris(selenourea) ion in the dichloride and in the dibromide is compared.

The Se—Se—Se angle in the present structure is 5.6° smaller than in the two dihalide structures. The bending is also in a different direction. In the dihalides it is such that the —C(NH<sub>2</sub>)<sub>2</sub> groups are

moved away from each other. In the present structure the bending is at about right angle to this. The distances of the atoms from the least-squares planes through Se<sub>1</sub>Se<sub>2</sub>Se<sub>3</sub>C<sub>1</sub>C<sub>3</sub> and through Se<sub>1</sub>Se<sub>2</sub>Se<sub>3</sub>C<sub>2</sub> are in both cases about 0.14 Å for Se<sub>2</sub>, —0.07 Å for Se<sub>1</sub> and Se<sub>3</sub>, while the carbon atoms are in the planes. The dihedral angle between these two planes is 75.3°.

Each of the four selenourea groups, the three groups of the tris(selenourea) ion and the uncomplexed selenourea molecule, is planar within the errors. The carbon and nitrogen atoms are all trigonal planar, in accordance with sp<sup>2</sup>-hybridization at the atoms.

The plane of the terminal selenourea group, Se<sub>1</sub>, and of the central selenourea group, Se<sub>2</sub>, make an angle of 14.1° with each other. The dihedral angle between the planes of the Se<sub>2</sub> and Se<sub>3</sub> groups is 17.6°.

The differences in the bond lengths and angles in the various selenourea groups are small. The Se—C bond length is 1.867(4) Å in the uncomplexed selenourea molecule, 1.903(5) Å in both terminal selenourea groups of the tris(selenourea) ion and 1.925(4) Å in the middle group. These variations of the Se—C bond lengths seem to be significant.

The mean value of the Se—C bond lengths in the

Table 4. Dimensions of the sulfate ion. O<sub>N</sub> denotes an oxygen atom with population parameter 0.67 and O<sub>NN</sub> an atom with population parameter 0.33. Bond lengths (Å) and angles (°).

S—O <sub>1</sub>	1.493(6)	O <sub>1</sub> —S—O <sub>2</sub>	109.6(3)
S—O <sub>2</sub>	1.439(6)	O <sub>1</sub> —S—O <sub>3</sub>	106.3(3)
S—O <sub>3</sub>	1.495(6)	O <sub>1</sub> —S—O <sub>4</sub>	109.2(4)
S—O <sub>4</sub>	1.420(6)	O <sub>2</sub> —S—O <sub>3</sub>	108.2(3)
		O <sub>2</sub> —S—O <sub>4</sub>	115.5(4)
		O <sub>3</sub> —S—O <sub>4</sub>	107.5(3)
S—O <sub>11</sub>	1.397(15)	O <sub>11</sub> —S—O <sub>22</sub>	118.1(7)
S—O <sub>22</sub>	1.473(10)	O <sub>11</sub> —S—O <sub>33</sub>	109.1(6)
S—O <sub>33</sub>	1.517(10)	O <sub>11</sub> —S—O <sub>44</sub>	109.1(7)
S—O <sub>44</sub>	1.542(10)	O <sub>22</sub> —S—O <sub>33</sub>	106.8(6)
		O <sub>22</sub> —S—O <sub>44</sub>	108.3(6)
		O <sub>33</sub> —S—O <sub>44</sub>	104.5(5)

Table 5. Hydrogen-oxygen distances (Å). H<sub>NN</sub> and H<sub>N</sub> are hydrogen atoms bonded to nitrogen atoms and to water oxygen, respectively.<sup>a</sup>

H <sub>11</sub> ···O <sub>4E</sub>	2.28(7)	H <sub>42</sub> ···O <sub>11D</sub>	2.37(5)	H <sub>72</sub> ···O <sub>44A</sub>	2.42(7)
H <sub>11</sub> ···O <sub>44E</sub>	2.50(6)	H <sub>42</sub> ···O <sub>33D</sub>	2.59(6)	H <sub>81</sub> ···O <sub>2H</sub>	2.12(5)
H <sub>12</sub> ···O <sub>5C</sub>	2.14(5)	H <sub>51</sub> ···O <sub>1F</sub>	2.41(8)	H <sub>81</sub> ···O <sub>22H</sub>	2.07(5)
H <sub>21</sub> ···O <sub>6H</sub>	2.03(7)	H <sub>51</sub> ···O <sub>11F</sub>	2.25(8)		
H <sub>31</sub> ···O <sub>2</sub>	2.11(5)	H <sub>52</sub> ···O <sub>6G</sub>	2.07(7)	H <sub>1</sub> ···O <sub>1</sub>	2.02(8)
H <sub>31</sub> ···O <sub>22</sub>	2.12(5)	H <sub>61</sub> ···O <sub>5</sub>	2.07(6)	H <sub>2</sub> ···O <sub>3F</sub>	2.10(7)
H <sub>31</sub> ···O <sub>3</sub>	2.56(5)			H <sub>2</sub> ···O <sub>11F</sub>	2.20(6)
H <sub>31</sub> ···O <sub>33</sub>	2.50(5)	H <sub>71</sub> ···O <sub>1H</sub>	2.42(5)	H <sub>3</sub> ···O <sub>44H</sub>	1.99(7)
H <sub>32</sub> ···O <sub>3D</sub>	2.00(4)	H <sub>71</sub> ···O <sub>2H</sub>	2.42(5)	H <sub>4</sub> ···O <sub>4B</sub>	2.14(7)
H <sub>32</sub> ···O <sub>33D</sub>	2.00(4)	H <sub>71</sub> ···O <sub>22H</sub>	2.40(6)	H <sub>4</sub> ···O <sub>33B</sub>	2.10(7)
H <sub>42</sub> ···O <sub>4D</sub>	2.22(5)	H <sub>71</sub> ···O <sub>44H</sub>	2.47(5)		

<sup>a</sup> An atom marked with A denotes an atom at (x,1+y,z), B at (1+x,1+y,z), C at (x-1,y,z), D at ( $\bar{x}$ , $\bar{y}$ , $\bar{z}$ ), E at ( $\bar{x}$ , $\bar{y}$ ,1-z), F at (1-x, $\bar{y}$ , $\bar{z}$ ), G at (1-x,1-y, $\bar{z}$ ), and H at (1-x,1-y,1-z).

crystal structure of the trigonal form of selenourea<sup>7</sup> is 1.86(3) Å. In the crystal structures of the formamidinium diselenide ion the Se-C bond length is 1.94(1) Å in the dichloride<sup>8</sup> and 1.943(4) Å in the diiodide.<sup>9</sup> The planes of the selenourea groups, both in the present structure and the structure of the formamidinium diselenide ion, are at approximately right angles to the Se-Se bond. Thus, the  $\pi$  orbitals of the carbon atoms are parallel to the Se-Se bonds and this is unfavourable for  $\pi$  contribution to the Se-C bonds. The Se-C bond length in the structures of the formamidinium diselenide ion is nearly the same as in the middle selenourea group of the present structure, and might be taken as the length of a single covalent Se-C<sub>sp2</sub> bond. The shortening of the bond in the terminal groups may be explained by looking at the bonding in the three-selenium sequence as a resonance between Se-Se Se and Se Se-Se, a covalent bond and no bond. The selenium atom of the non-bonded selenourea group might then participate to some extent in a  $\pi$  bonding with the carbon and nitrogen atoms. In the uncomplexed selenourea molecule, this effect is stronger and the Se-C bond is shorter.

The C-N bond lengths in the four selenourea groups are not significantly different.

#### THE PACKING IN THE CRYSTALS

Both of the terminal selenium atoms have, in *trans* position to the C-Se bond, a slight approach from selenium atoms of one neighbouring tris(selenourea) ion. The Se<sub>1</sub>···Se<sub>2</sub>' ( $\bar{x}$ ,1-y, $\bar{z}$ ) distance is

3.5835(15) Å, and the angle C<sub>1</sub>-Se<sub>1</sub>···Se<sub>2</sub>' is 174.0(2)°. The distance of Se<sub>2</sub>' from the plane of Se<sub>2</sub>Se<sub>1</sub>C<sub>1</sub> is 0.30 Å. The Se<sub>3</sub>···Se<sub>1</sub>' distance is 3.6616(15) Å, the angle C<sub>3</sub>-Se<sub>3</sub>···Se<sub>1</sub>' is 164.7(2)° and the distance of Se<sub>1</sub>' from the plane of Se<sub>2</sub>Se<sub>3</sub>C<sub>3</sub> is 0.16 Å.

The central selenium atom, Se<sub>2</sub>, has no close contact in *trans* position to the C<sub>2</sub>-Se<sub>2</sub> bond, the fourth coordination site of square planar coordination at Se<sub>2</sub>. In the structure of tris(selenourea) dihalides,<sup>5</sup> such contacts occur to halide ions.

The amino nitrogen atoms have hydrogen bonds to oxygen atoms in the sulfate ions and water molecules (Table 5). Four of the amino hydrogen atoms do not have contact with oxygen atoms.

Each of the oxygen atoms of the water molecules, themselves bonded to two hydrogen atoms, has close contacts with two other hydrogen atoms. The arrangement is approximately tetrahedral. The H-O bond lengths are found from 0.68(7) to 0.75(16) Å and the H···O lengths are from 2.03(7) to 2.14(5) Å. The angles at the oxygen atoms, are in the range 95(8) to 125(6)°.

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