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THE CRYSTAL AND MOLECULAR STRUCTURE OF SODIUM GOLD(I) THIOSULFATE DIHYDRATE

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Helena Ruben, Allan Zalkin, M. O. Faltens  
and David H. Templeton

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT  
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The Crystal and Molecular Structure of Sodium Gold(I) Thiosulfate Dihydrate<sup>1</sup>

BY HELENA RUBEN, ALLAN ZALKIN, M. O. FALTENS, AND DAVID H. TEMPLETON

X-ray diffraction study of a single crystal of  $\text{Na}_3 \text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$  shows that it is monoclinic with  $a = 18.206 \pm 0.006$ ,  $b = 11.355 \pm 0.006$ ,  $c = 5.436 \pm 0.004 \text{ \AA}$  and  $\beta = 97.87 \pm 0.05^\circ$ . The space group is  $P2_1/a$  with four formula units per unit cell. The X-ray density is  $3.14 \text{ g/cm}^3$ . The gold is located between the two thiosulfate groups in a near linear arrangement (S-Au-S,  $176.5^\circ$ ). The average Au-S bond distance is  $2.28 \pm .01 \text{ \AA}$ , the S-S distance is  $2.06 \pm .01 \text{ \AA}$  while the S-O distance is  $1.46 \pm .01 \text{ \AA}$ . The three sodium atoms are surrounded by irregular polyhedra of oxygen neighbors.

### Introduction

One of the authors, Faltens, had been studying aurous ( $\text{Au}^{\text{I}}$ ) and auric ( $\text{Au}^{\text{III}}$ ) compounds to elucidate their internal bonding.<sup>2</sup> Auric and aurous compounds are textbook examples of  $\text{dsp}^2$  (square-planar) and  $\text{sp}$  (linear) hybridization respectively. Similar electric field gradients about the gold atoms might be expected as well as similar electric quadrupole splittings as observed via the Mossbauer effect. Instead the quadrupole splittings for the aurous chloride was observed to be an order of magnitude larger than that for the auric chloride. In addition to the gold halides ( $\text{AuCl}$  and  $\text{AuCl}_4$ ) other gold compounds including sodium gold(I) thiosulfate dihydrate<sup>3</sup> were investigated, and the quadrupole splitting was observed to be consistently larger for the aurous compounds. This crystal structure investigation of  $\text{Na}_3\bar{\text{Au}}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$  was undertaken to remove any doubt of its identity and to establish the nature of the environment of the gold atom.

Experimental

Sodium gold(I) thiosulfate<sup>3,4</sup> was prepared by adding 21 grams of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  to about 75cc of water. A 40% (by weight) solution of NaOH was added by drops until a vivid red-orange precipitate started to form. This solution was poured into a mechanically stirred solution of 50 grams.  $\text{Na}_2(\text{S}_2\text{O}_3) \cdot 5\text{H}_2\text{O}$  in 100cc of water, causing no visible change. The order of pouring is important because if the solutions are mixed in the reverse order, the black precipitate of gold sulfide results. While still stirring vigorously, 4 molal  $\text{HNO}_3$  drops were added at a rate that allowed the disappearance of any red coloration before the next drop was added. The acid was added until the red-orange precipitate was dissolved and the red coloration no longer formed. This solution, approximately 200cc, was filtered through a "fine" sintered glass funnel and 800cc of ethyl alcohol added to the filtrate. The white flocculent precipitate which formed was collected on a similar glass funnel and washed with ethanol (about 100cc) then recrystallized twice by dissolving the sodium gold(I) thiosulfate in a minimum of water and precipitating with four volumes of ethanol. The specimen for this study was prepared by dissolving a small amount in a minimum of water, adding two volumes of ethanol and allowing the crystals to grow overnight in the dark, as most gold compounds are photosensitive.

A clear thin crystal plate approximately .17 x .07 x .02mm was mounted along the c axis on the end of a thin pyrex glass fiber. A second crystal was mounted on its b axis, but since it was fractured, it was not suitable for taking data, but was useful in obtaining the

monoclinic  $\beta$  angle.

The crystals were aligned on our G.E. XRD-5 hand-operated diffractometer equipped with a quarter-circle Eulerian cradle, scintillation counter and pulse height discriminator. A molybdenum anode tube ( $\lambda_{K\alpha 1} = 0.70926\text{\AA}$ ,  $\lambda_{K\alpha 2} = 0.71354\text{\AA}$  and  $\lambda_{K\beta} = 0.632253\text{\AA}$ ) operated at 45 kilovolts, 20 milliamperes was used. The X-rays were filtered by a 3.0 mil zirconium filter. Cell dimensions were determined from a series of measurements along the  $h00$ ,  $0k0$  and  $00l$  directions using peaks where the  $K\alpha 1$ ,  $K\alpha 2$  and  $K\beta$  X-rays were resolved. All measurements were made at room temperature. The intensities were measured with a take-off angle of  $4^\circ$ . 1965 independent reflections were observed and counted for ten seconds each using the stationary-crystal stationary-count technique. These are all of the data in a quarter of the sphere of reflection where  $2\theta < 50^\circ$  or  $\sin\theta/\lambda < 0.596$ . Background was plotted as a function of  $2\theta$  and applied routinely to the reflections with the exception of a minority of intensities where they were measured individually because of streaking from lower orders. The most intense reflection (511) was about 2303 counts per second.

The absorption parameter  $\mu$  was calculated to be  $145\text{cm}^{-1}$  for  $\text{MoK}\alpha$  X-rays. An absorption correction using the program HORSE<sup>5</sup> was applied to the data, and resulted in substantial improvement of the final agreement.

The standard deviation of the intensities and the structure factors were estimated as follows. The standard deviation of the intensity,  $I$ , is  $\sigma(I) = [C + B + (qI)^2]^{1/2}$ , where  $C$  is total count,

B the background and  $q$  (taken here as 0.07) is an arbitrary fraction of the intensity which has been included to account for such non-random errors in the data as extinction, and the lack of stability of the electronic circuits of the instrument. The standard deviation of the structure factor, by the method of finite difference, is taken as  $\sigma(F) = F_0 - [F_0^2 - sc(I)/Lp]^{1/2}$ .  $s$  is the scaling factor in the equation  $F_0 = (sI/Lp)^{1/2}$ . For the reflections where  $I \leq \sigma(I)$ ,  $\sigma(F) = [sc(I)/Lp]^{1/2}$ .  $Lp$  is the Lorentz-polarization correction.

Our unpublished full-matrix least-squares program minimizes the function  $R_2^2$ , where  $R_2^2 = \sum \underline{w}(\Delta F)^2 / \sum \underline{w}F_0^2$ .  $F_0$  and  $F_c$  are observed and calculated structure factors, and  $\Delta F$  is the difference of their magnitudes. The weighting factor  $\underline{w}$  is  $1/\sigma^2(F)$ . The program accommodates both the real and imaginary parts of the dispersion correction.

Scattering factors for neutral gold,  $Na^+$ , neutral sulfur and oxygen<sup>6</sup> were used and modified for dispersion by adding -2.36, 0.0, 0.1 and 0.0 electrons<sup>7</sup> respectively. The imaginary dispersion terms were modified by adding 8.89, 0.04, 0.16 and 0.0 to gold, sodium, sulfur and oxygen respectively.

The anisotropic temperature factor has the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ .  $\beta_{ij}$  values in  $\text{\AA}^2$  units are reported for the thermal parameters:  $\beta_{ii} = 4\beta_{ii}/a_i^*a_i^*$ , where  $a_i^*$  is the  $i$ th reciprocal cell length.



## Results

Unit Cell and Space Group. The space group is  $P2_1/a$  ( $C_{2h}^5$ ) and contains four formula units per monoclinic unit cell. The cell dimensions at  $23^\circ$  are  $a = 18.206 \pm .006$ ,  $b = 11.355 \pm .006$ ,  $c = 5.436 \pm .004 \text{ \AA}$  and  $\beta = 97.87 \pm .05^\circ$ . The errors are subjective estimates. The volume is  $1113.19 \text{ \AA}^3$ . With four formula units per unit cell, the density calculated from the X-ray data is  $3.14 \text{ g/cc}$  which is to be compared with the literature value of  $3.09 \text{ g/cc}$ .<sup>8</sup>

Determination of the Structure. The gold atom location was deduced from a three dimensional Patterson function. A Fourier phased by the gold atom revealed the locations of the sodium and sulfur atoms. A least square refinement of this partial structure using isotropic temperature factors resulted in  $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.21$ . With anisotropic thermal parameters on the gold atom the R factor went to 0.19. A difference Fourier revealed the oxygen atom locations. Final full-matrix, all atoms anisotropic, refinement brought R to 0.078 after several cycles. After making the absorption correction the final agreement was  $R = 0.055$ .

The final results are shown in Tables I, II, and III. Table I lists the observed and calculated structure factors. The final positional parameters with their standard deviations are listed in Table II, where the standard deviations are estimated by the least squares procedure assuming that the discrepancies represent random errors. The anisotropic thermal parameters are listed in Table III.

Attempts at locating the hydrogen atoms were unsuccessful. The difference Fourier showed many more peaks than the four hydrogen atoms present in the structure. Attempts to refine four of the peaks that were near the water oxygen atoms resulted in positions that gave unacceptable hydrogen-oxygen bond distances. The data are apparently inadequate to detect the hydrogen atoms. This is not surprising considering the big absorption correction and the presence of such a heavy atom as gold.

Description of the Structure. The most significant structural feature in this compound is the  $\text{Au}(\text{S}_2\text{O}_3)_2^{-3}$  anion. A schematic drawing is shown in Fig. 1. The S - Au - S angle is short of linearity by about  $3.5^\circ$ . The variation of the Au - S(3) and Au - S(4) bond distances are less than  $3\sigma$ , Table IV, and is not considered to be significant. The Au - S - S bond angles are somewhat intermediate between a right and a tetrahedral angle, being somewhat closer to the latter. Each terminal sulfur atom has a tetrahedral configuration of a sulfur and three oxygen atoms and is consistent with thiosulfate in sodium thiosulfate pentahydrate.<sup>9</sup> The two S - S distances in the anion are different by 3 to  $4\sigma$  from each other, but this difference is not considered by the authors to be significant. The average S - O bond distance of all six such bonds is  $1.458\text{\AA}$ , and no individual value is greater than one  $\sigma$  from this average.

The dihedral angle between the two planes defined by atoms Au - S(3) - S(2) and Au - S(4) - S(1) is  $67^\circ$  (see Fig. 4).

The three sodium ions are well encapsulated in irregular coordination spheres of oxygen atoms. Na(1) is coordinated by six oxygen atoms ranging in distances of 2.36 to  $2.63\text{\AA}$ . Two of these

oxygen atoms come from the two waters of hydration. Na(2) is also coordinated by six oxygen atoms at distances from 2.35 to 2.54Å only one of which comes from a water of hydration. Na(3) is coordinated to five oxygen atoms ranging in distance from 2.34 to 2.53Å, with one water of hydration involved.

Of the four hydrogen atoms only one appears to be involved in a "conventional" O - H.....O hydrogen bond within this structure; that would be the donor water oxygen O(8) to O(5) at a distance of 2.75Å.

Hydrogen bonding to sulfur is not particularly a well documented effect, and if it does exist must certainly be fairly weak. Bonds of this type have been suggested<sup>10</sup> in S - H.....S at 3.86Å and N - H.....S at 3.35Å. In this context water O(7) in this structure offers a possibility of O - H.....S hydrogen bonding. O(7) is centered in an irregular tetrahedron consisting of Na(1), Na(2), S(3), and S(4). The S(3) - O(7) - S(4) angle is approximately 104° and the O - S distances are 3.24 and 3.33Å respectively.

TABLE I  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SODIUM GOLD(I) THIOSULFATE DIHYDRATE

Table with columns for h, k, l, F<sub>o</sub>, F<sub>c</sub>, and multiple columns of structure factor values. Includes a note at the bottom: \*Zero weighted state

TABLE II

POSITIONAL PARAMETERS<sup>a</sup>

ATOM	X	Y	Z
AU	.07361(3)	.06692(5)	.1479( 1)
S(1)	.0006( 2)	.3396( 3)	.2178( 5)
S(2)	.2592( 2)	.0358( 3)	.1207( 5)
S(3)	.1591( 2)	-.0366( 3)	-.0338( 6)
S(4)	-.0063( 2)	.1713( 3)	.3497( 6)
NA(1)	.2176( 3)	.3252( 5)	.3495(10)
NA(2)	.1254( 3)	-.4095( 4)	.3159( 9)
NA(3)	.4129( 3)	-.1027( 5)	.2427(10)
O(1)	.0762( 5)	.3809( 8)	.2892(17)
O(2)	-.0521( 5)	.4044( 8)	.3419(16)
O(3)	-.0179( 5)	.3425(10)	-.0505(15)
O(4)	.3108( 5)	-.0169( 9)	-.0319(16)
O(5)	.2543( 5)	.1633( 8)	.0916(16)
O(6)	.2783( 5)	.0010( 8)	.3803(15)
O(7)	.1652( 5)	-.2179( 9)	.4284(19)
O(8)	.3387( 5)	-.2627( 8)	.3212(17)

<sup>a</sup>Standard deviations appear in parenthesis.

TABLE III

ANISOTROPIC THERMAL PARAMETERS<sup>a</sup>

ATOM	B11	B22	B33	B12	B13	B23
AU	2.02( 2)	1.84( 3)	2.58( 3)	.18( 2)	.31( 2)	-.23( 2)
S(1)	1.82(12)	1.71(12)	1.41(11)	.02(10)	.15( 9)	.03(10)
S(2)	1.99(12)	1.73(12)	1.05(11)	.03(10)	.14( 9)	.04( 9)
S(3)	2.10(13)	2.15(14)	2.03(13)	.38(11)	.11(10)	-.52(11)
S(4)	2.57(14)	1.88(14)	3.01(15)	.19(11)	.93(11)	.02(12)
NA(1)	4.33(28)	2.62(25)	2.47(22)	1.05(21)	.19(19)	.35(19)
NA(2)	2.70(22)	2.13(22)	1.97(20)	.07(17)	.19(17)	-.09(17)
NA(3)	2.65(23)	2.90(24)	2.57(23)	-.25(19)	.30(18)	-.22(19)
O(1)	2.13(38)	2.48(41)	3.12(43)	-.45(31)	-.17(31)	.44(34)
O(2)	2.53(38)	2.29(39)	2.71(40)	.41(31)	.98(31)	-.10(31)
O(3)	2.95(42)	4.46(52)	1.56(36)	.02(39)	-.64(30)	-.19(35)
O(4)	2.66(40)	3.00(42)	2.03(37)	.67(34)	.31(30)	-.30(33)
O(5)	3.12(41)	1.95(37)	2.15(35)	-.52(32)	-.47(30)	.40(31)
O(6)	3.20(40)	1.92(39)	1.52(34)	.08(31)	-.21(29)	.07(29)
O(7)	2.51(40)	3.25(46)	3.91(46)	-.01(35)	.85(35)	.31(39)
O(8)	4.30(50)	2.09(40)	2.40(39)	-.34(35)	-.05(35)	-.43(32)

<sup>a</sup>Standard deviations appear in parenthesis.

TABLE IV

INTERATOMIC DISTANCES (Å) IN SODIUM GOLD THIOSULFATE DIHYDRATE<sup>a, b</sup>

Atoms	Dist.	Atoms	Dist.	Atoms	Dist.
Au -S(3)	2.280(3)	S(4) -O(1)	2.858(10)	Na(2)-O(4)	2.390(11)
Au -S(4)	2.272(3)	S(4) -O(2)	2.774(10)	Na(2)-O(6)	2.459(10)
S(1)-O(1)	1.457(9)	S(4) -O(3)	2.904(10)	Na(2)-O(7)	2.348(11)
S(1)-O(2)	1.458(9)	Na(1)-O(1)	2.626(10)	Na(3)-O(1)	2.532(11)
S(1)-O(3)	1.451(9)	Na(1)-O(4)	2.494(11)	Na(3)-O(2)	2.381(11)
S(1)-S(4)	2.051(5)	Na(1)-O(5)	2.460(11)	Na(3)-O(3)	2.383(11)
S(2)-O(4)	1.463(9)	Na(1)-O(6)	2.473(10)	Na(3)-O(4)	2.423(10)
S(2)-O(5)	1.458(9)	Na(1)-O(7)	2.355(11)	Na(3)-O(8)	2.338(11)
S(2)-O(6)	1.461(9)	Na(1)-O(8)	2.399(11)	O(1) -O(4)	2.885(12)
S(2)-S(3)	2.069(5)	Na(2)-O(1)	2.540(10)	O(1) -O(8)	2.940(12)
S(3)-O(4)	2.770(10)	Na(2)-O(2)	2.433(10)	O(2) -O(8)	2.940(12)
S(3)-O(5)	2.881(9)	Na(2)-O(3)	2.392(10)	O(5) -O(8)	2.751(12)
S(3)-O(6)	2.936(9)				

<sup>a</sup>Table contains all interatomic distances 3.00Å or less.

<sup>b</sup>Estimated standard deviations are indicated in parentheses.

SELECTED ANGLES IN SODIUM GOLD THIOSULFATE DIHYDRATE<sup>a</sup>

S(3) - Au -S(4)	176.5(2)	O(2)-Na(2)-O(3)	88.0(4)
O(1) -S(1)-O(2)	112.0(7)	O(2)-Na(2)-O(4)	150.7(5)
O(1) -S(1)-O(3)	109.9(7)	O(3)-Na(2)-O(6)	170.6(5)
O(2) -S(1)-O(3)	112.3(7)	O(4)-Na(2)-O(6)	81.8(4)
O(4) -S(2)-O(5)	112.2(7)	O(4)-Na(2)-O(7)	118.8(5)
O(4) -S(2)-O(6)	110.5(7)	O(6)-Na(2)-O(7)	92.4(4)
O(5) -S(2)-O(6)	112.1(7)	O(1)-Na(3)-O(2)	82.0(4)
Au -S(3)-S(2)	103.6(1)	O(1)-Na(3)-O(3)	117.7(4)
Au -S(4)-S(1)	104.1(1)	O(1)-Na(3)-O(4)	126.6(5)
O(1)-Na(1)-O(4)	68.5(3)	O(1)-Na(3)-O(8)	74.1(4)
O(1)-Na(1)-O(5)	116.6(4)	O(2)-Na(3)-O(8)	146.8(5)
O(1)-Na(1)-O(6)	80.2(4)	O(3)-Na(3)-O(8)	113.3(5)
O(1)-Na(1)-O(7)	156.6(5)	S(3)- O(7)-S(4)	103.9(2)
O(1)-Na(1)-O(8)	71.5(4)	S(3)- O(7)-Na(1)	101.4(3)
O(4)-Na(1)-O(6)	79.5(4)	S(3)- O(7)-Na(2)	114.2(3)
O(5)-Na(1)-O(7)	80.7(4)	S(4)- O(7)-Na(1)	123.6(3)
O(5)-Na(1)-O(8)	107.0(4)	S(4)- O(7)-Na(2)	89.4(2)
O(7)-Na(1)-O(8)	88.9(4)	Na(1)-O(7)-Na(2)	123.5(4)
O(1)-Na(2)-O(2)	80.8(4)	Na(1)-O(8)-Na(3)	97.4(3)
O(1)-Na(2)-O(3)	90.6(4)	Na(1)-O(8)-O(5)	117.2(4)
O(1)-Na(2)-O(7)	167.7(5)	Na(3)-O(8)-O(5)	113.2(4)

<sup>a</sup>Standard deviation is in parentheses and refers to the least significant digit.

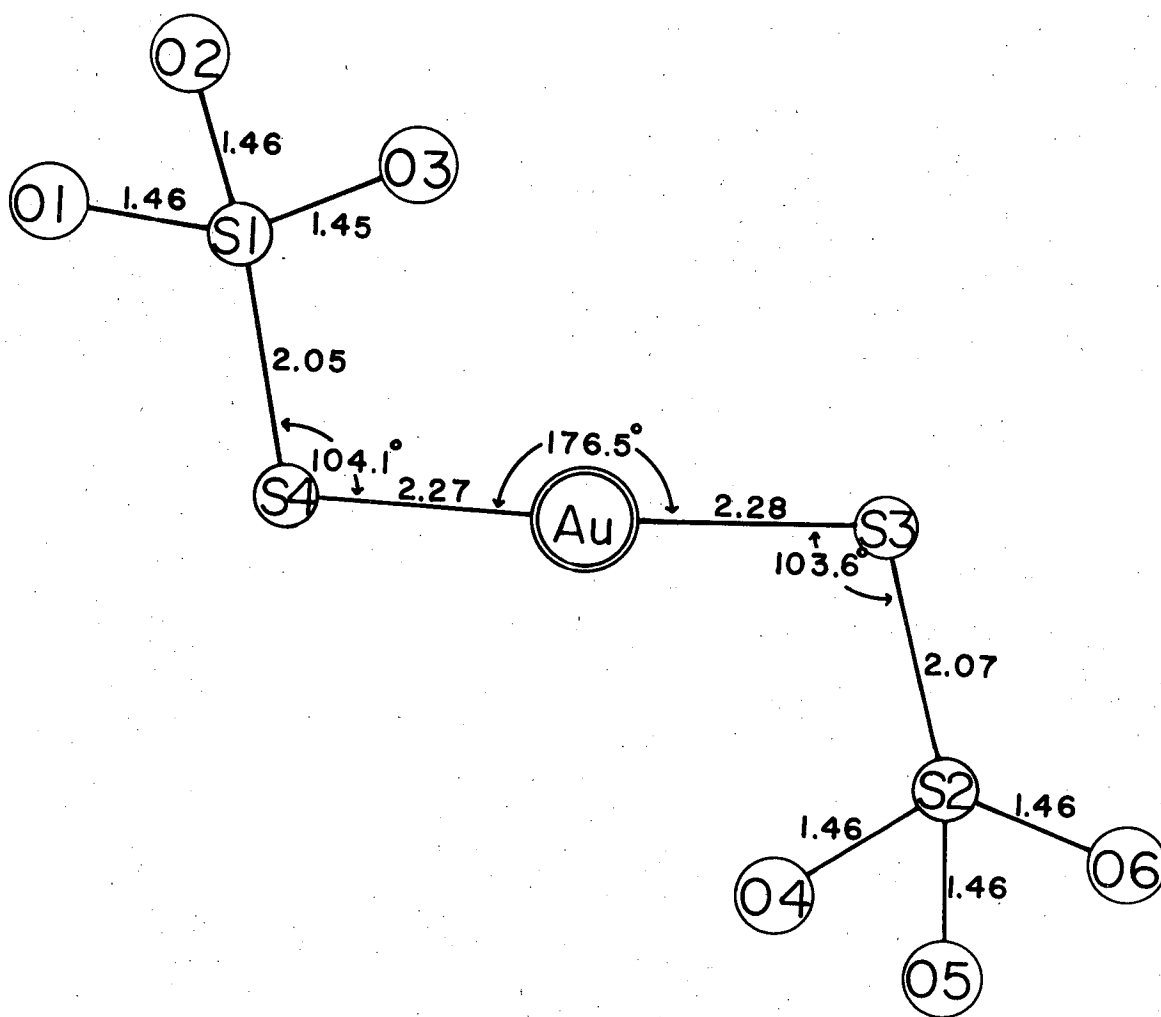
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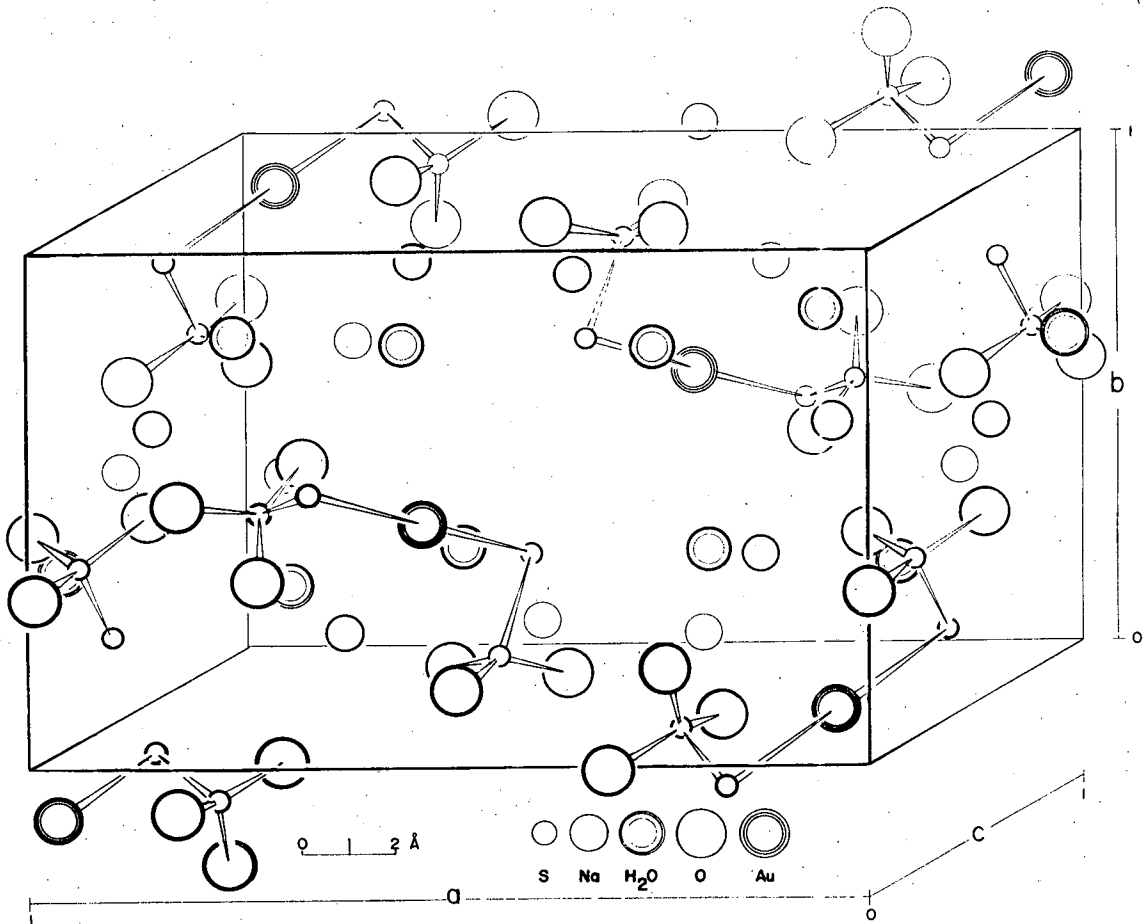
Figure Captions

- Fig. 1 Schematic drawing of  $\text{Au}(\text{S}_2\text{O}_3)_2^{-3}$  anion.
- Fig. 2 Molecular packing in the unit cell of Sodium Gold(I) Thiosulfate Dihydrate.
- Fig. 3 Stereo view of Sodium Gold(I) Thiosulfate Dihydrate showing examples of the bonding of the sodium atoms.



XBL 707-1307

Fig. 1



MUB-11223

Fig. 2

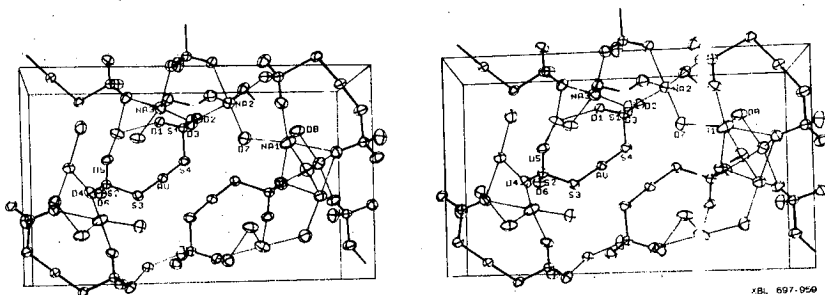


Fig. 3

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