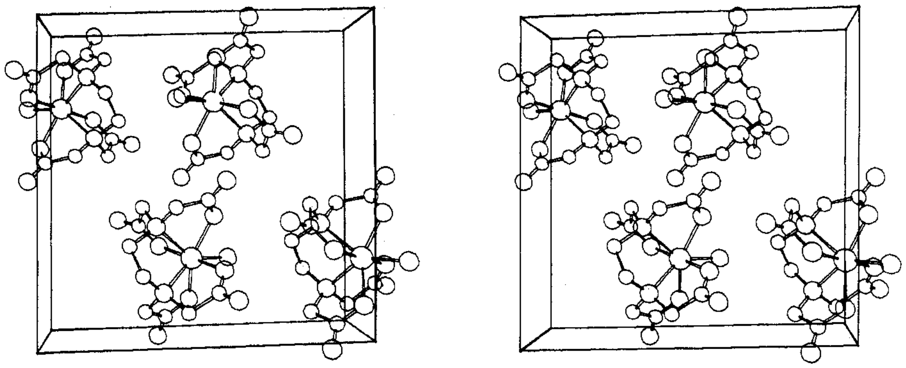

Figure 3.—Three-dimensional view of the crystal packing in a unit cell of $Sn^{IV}(OH_2)Y$ down the *y* axis. The *x* axis is vertical and the *z* axis is horizontal. The origin of the box is at 0,0,0.

W···O(4*) contacts are 2.734 ± 0.005 and 2.679 ± 0.005 Å, within the normal range for this type of interaction.[29] The hydrogen bonds appear to be fairly linear as indicated by O–H···O angles of 167 and 169°. Other details of the hydrogen-bonding geometry are given in Table VIII. The crystal contains no other close intermolecular contacts.

Anisotropic thermal motion appears to be most pronounced in the oxygen atom of the water molecule and in those carboxyl oxygens (O(2) and O(2*)) not involved in hydrogen bonding; the hydrogen-bonded pair O(4) and O(4*) also show fairly high anisotropy, however. Anisotropy decreases somewhat in the five-membered rings and especially at the nitrogen atoms, which act as bridgeheads between three rings: see Figure 1 and Table II. The isotropic temperature factors of the hydrogen atoms, which range between 0.5 and 4.8 Å², are subject to large errors because of the presence of the heavy atom.

**Acknowledgment.**—We thank P. P. North for kind assistance with the experimental work.

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[29] W. C. Hamilton Tnd J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

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# The Crystal Structure of Tetraselenium Bis(hydrogen disulfate)

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A single-crystal X-ray diffraction study of the compound $Se_4(HS_2O_7)_2$, tetraselenium bis(hydrogen disulfate), shows that it crystallizes in the monoclinic space group $P2_1/c$, with the following unit cell dimensions: $a = 7.721$ (2), $b = 5.606$ (2), $c = 17.202$ (7) Å, $\beta = 109.78$ (2)°; density (measured) = 3.1 (1) g cm$^{-3}$ and density (calculated) = 3.18 g cm$^{-3}$ for $Z = 2$. A three-dimensional structure determination was based upon the 552 observed reflections measured on a quarter-circle GE diffractometer using Mo K$\alpha$ radiation. Refinement by full-matrix least-squares methods of the parameters of all the atoms, except hydrogen, with anisotropic temperature factors, gave an unweighted $R$ factor of 0.066. The $Se_4^{2+}$ cation lies on a center of symmetry and is, within the accuracy of the experiment, strictly square planar, with Se–Se equal to 2.283 (4) Å. The anions are linked through hydrogen bonds into chains along the $b$ axis. All the terminal S–O bonds are of the same length, 1.43 (2) Å, except the S–O(H) bond which is 1.56 (2) Å. The resultant asymmetry of the anion is reflected in an asymmetric bridge (S–O = 1.59 (2) and 1.67 (2) Å, S–O–S = 123 (1)°) and the deviations of the O–S–O angles from tetrahedral. These results are compared with the anion in $NO_2^+HS_2O_7^-$, for which a new refinement has been performed.

## Introduction

The group VI elements, sulfur, selenium, and tellurium, dissolve in strong acids such as fluorosulfuric, sulfuric, and disulfuric acids to give intensely colored solutions. The results of cryoscopic, conductometric, and spectroscopic experiments on solutions of selenium in these solvents have shown the presence of the polyatomic cation $Se_4^{2+}$.[1] A number of compounds containing the $Se_4^{2+}$ cation have been prepared and characterized by analytical and spectroscopic methods.[2] $Se_4^{2+}(HS_2O_7^-)_2$ was the first of these compounds to be prepared, and since it readily formed a well-defined crystalline solid, it was selected for an X-ray structure investigation. The purpose of the study was to demonstrate unambiguously the existence of the $Se_4^{2+}$ cation and to determine its structure. A preliminary report has already appeared.[3]

## Experimental Section

The preparation of the compound $Se_4(HS_2O_7)_2$ from selenium and 65% oleum has been described previously.[2] Slow crystallization from the viscous mother liquor yielded bright orange needle-

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[1] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

[2] J. Barr, D. B. Crump, R. J. Gillespie, R. Kapoor, and P. K. Ummat, *Can. J. Chem.*, **46**, 3607 (1968).

[3] I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Commun.*, 853 (1968).

TABLE II

ATOMIC POSITIONAL AND TEMPERATURE PARAMETERS FOR $Se_4(HS_2O_7)_2$[a]

| Atom | $x$ | $y$ | $z$ | $U_{11}$, Å$^2$ | $U_{22}$, Å$^2$ | $U_{33}$, Å$^2$ | $U_{12}$, Å$^2$ | $U_{13}$, Å$^2$ | $U_{23}$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Se(1) | 0.0730 (4) | 0.2777 (5) | 0.0620 (2) | 0.0309 (15) | 0.0307 (15) | 0.0320 (14) | 0.0036 (8) | 0.0080 (12) | 0.0076 (14) |
| Se(2) | 0.2013 (4) | 0.5258 (5) | −0.0085 (2) | 0.0280 (15) | 0.0366 (15) | 0.0335 (14) | 0.0003 (18) | 0.0122 (12) | 0.0060 (12) |
| S(1) | 0.6031 (8) | 0.0405 (11) | 0.1158 (4) | 0.021 (3) | 0.026 (3) | 0.020 (3) | 0.000 (3) | 0.002 (3) | 0.001 (4) |
| S(2) | 0.7924 (8) | 0.3398 (11) | 0.2529 (4) | 0.027 (3) | 0.022 (3) | 0.028 (3) | −0.002 (3) | 0.010 (2) | −0.000 (3) |
| O(1) | 0.748 (2) | 0.068 (3) | 0.082 (1) | 0.049 (9) | 0.039 (10) | 0.040 (8) | −0.013 (14) | 0.020 (8) | −0.005 (14) |
| O(2) | 0.536 (2) | −0.198 (3) | 0.119 (1) | 0.053 (9) | 0.032 (10) | 0.036 (8) | −0.010 (12) | 0.015 (7) | 0.005 (10) |
| O(3) | 0.466 (2) | 0.221 (3) | 0.090 (1) | 0.033 (9) | 0.031 (9) | 0.048 (8) | 0.019 (5) | −0.014 (12) | 0.001 (12) |
| O(4) | 0.701 (2) | 0.091 (3) | 0.217 (1) | 0.036 (8) | 0.031 (7) | 0.030 (12) | −0.004 (15) | 0.008 (14) | −0.002 (15) |
| O(5) | 0.902 (3) | 0.430 (3) | 0.209 (1) | 0.048 (9) | 0.047 (12) | 0.037 (8) | −0.022 (15) | 0.017 (8) | 0.001 (12) |
| O(6) | 0.874 (2) | 0.298 (3) | 0.342 (1) | 0.052 (12) | 0.039 (10) | 0.024 (12) | −0.009 (15) | 0.012 (15) | −0.014 (8) |
| O(7) | 0.629 (3) | 0.516 (3) | 0.244 (1) | 0.056 (9) | 0.028 (11) | 0.044 (9) | 0.014 (5) | 0.027 (10) | 0.004 (8) |

[a] Estimated standard deviations in the final figures quoted are given in parentheses. The expression used to calculate the temperature effects is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$.

shaped crystals. These were filtered in a dry atmosphere, washed repeatedly with liquid sulfur dioxide, and finally pumped dry at 50°. The crystals were handled in a drybox and mounted in thin-walled quartz capillary tubes (3-mm diameter tubes from the Pantax Co.) for the subsequent X-ray examination.

The unit cell parameters of $a$ = 7.721 (2), $b$ = 5.606 (2), $c$ = 17.202 (7) Å, and $\beta$ = 109.78 (2)° were found by least-squares refinement of the angular parameters of 24 reflections with $2\theta$ lying between 5 and 40° measured on a GE XRD-6 diffractometer, using Mo K$\alpha$ radiation ($\lambda_{\alpha_1}$ 0.70926 Å). Precession photographs of the $0kl$ and $hk0$ planes, using Cu K$\alpha$ radiation, and Weissenberg photographs of the $h0l$, $h1l$, and $h2l$ planes, using Mo K$\alpha$ radiation, showed that the systematic absences were as follows: $h0l$, $l$ odd; $0k0$, $k$ odd. These results unambiguously indicate that the space group is $P2_1/c$ (no. 14, $C_{2h}{}^5$). A pycnometer experiment using Fluorolube MO-10 oil as the displaced liquid gave the density as 3.1 (1) g cm$^{-3}$. This is in good agreement with the value of 3.18 g cm$^{-3}$ calculated on the basis of two molecules of $Se_4(HS_2O_7)_2$ in the unit cell. Since the space group is centrosymmetric, the $Se_4{}^{2+}$ ion, if it exists as a discrete unit, must possess a center of symmetry.

Intensity measurements were made from a cylindrical crystal 0.3 mm in length and 0.07 mm in diameter mounted with its $b$ (needle) axis coincident with the $\phi$ axis of a GE XRD-6 diffractometer. Since the absorption coefficient for Mo K$\alpha$ radiation is 11.2 mm$^{-1}$, no absorption correction was deemed necessary. The reflections in the range $2.5° \leq 2\theta \leq 30.0°$ were recorded with a symmetric $\theta$–$2\theta$ scan of 2.25° at a scan rate of 2°/min, while those in the range $30.0° \leq 2\theta \leq 45.0°$ were recorded in a similar manner at 1°/min. Stationary 40-sec background counts were taken at the extremes of the $2\theta$ scan for each reflection. Zirconium-filtered Mo K$\alpha$ radiation was used for all the intensity measurements. Five standard reflections, chosen to be randomly distributed in the sphere of reflection with $2\theta < 40°$, were recorded at frequent intervals to monitor the stability of the crystal and the generator. Since no time-dependent trend was observed, the maximum intensity variation being of the order of ±3%, all intensity measurements were put on a common scale without further correction.

A total of 1967 reflections with $(\sin \theta)/\lambda \leq 0.54$ were measured and the recorded intensities were corrected for background, Lorentz, and polarization effects. Beyond $(\sin \theta)/\lambda = 0.54$ very few reflections had a measurable intensity. A standard deviation ($\sigma$) was calculated for each intensity from the formula

$$\sigma = (I - K(B_1 + B_2)(1 - K))^{1/2}$$

where $I$ is the total integrated intensity, $B_1$ and $B_2$ are the two background counts, and $K$ = (counting time for $I$)/[counting time for $(B_1 + B_2)$]. Equivalent reflections were combined to give a total of 985 reflections of which the 552 that had $I > 3\sigma$ were used in the structure determination and refinement.

## Solution and Refinement of the Structure

The positions and estimated isotropic temperature factors of the selenium atoms found in the preliminary structure determination[3] were refined by three cycles of full-matrix leasts quares to give $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.33. A three-dimensional Fourier map then revealed the positions of the sulfur atoms. Three further cycles of refinement reduced $R_1$ to 0.20. Seven peaks in the vicinity of the sulfur atoms found in the subsequent three-dimensional Fourier maps were assigned to oxygen atoms. Three cycles of least-squares refinement allowing the positional coordinates and isotropic temperature factors of all atoms to vary reduced $R_1$ to 0.072. At this point the structure was allowed to refine with anisotropic temperature factors to give $R_1$ = 0.066. Although the anisotropic temperature factors do not represent a significant improvement over the isotropic ones (see ref 4), they can be interpreted in terms of a physically reasonable model and so are included in Table II and are discussed below. A final refinement was performed with the weighting scheme introduced by Cruickshank[5]

$$w = [6.00 - 0.08F_o + 0.001F_o{}^2]^{-1}$$

reducing $R_2$ $[= \Sigma(w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}]$ to 0.060. The final value of $R_1$ including all 985 reflections was 0.097.

The atomic scattering curves for Se, S, and O were taken from ref 6 and the values for Se and S were corrected for dispersion. All computations were performed on a CDC-6400 computer, using the least-squares program ORFLS and the Fourier program FOURR-A of the X-ray 67 system.

A final difference Fourier map was calculated in an attempt to find the hydrogen atom. The map was essentially featureless, the highest peaks having values of the order of 0.2–0.3 e$^-$/Å$^3$, but none of these was in a position that could be interpreted chemically as a hydrogen atom.

Table I, which lists the observed and calculated structure factors, has been deposited.[7] The final positional and thermal parameters for all atoms are listed in Table II.

## Discussion

The bond lengths and angles are given in Tables III and IV. The four Se atoms lie close to each other at the corners of a square centered on a center of symmetry (see Figure 1). This square is surrounded by a

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(4) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(5) D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961.

(6) "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959.

(7) Table I, a listing of structure factor amplitudes, will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE III

BOND DISTANCES (Å) AND ANGLES (DEG) AROUND THE SELENIUM ATOMS[a]

| | | | |
|---|---|---|---|
| Se(1)-Se(2) | 2.280 (4) | Se(2)-Se(1)-Se(2)′ | 90.1 (2) |
| Se(1)-Se(2)′ | 2.286 (4) | Se(1)-Se(2)-Se(1)′ | 89.9 (2) |
| Se(1)-O(1) | 2.89 (2) | Se(2)-O(3) | 2.75 (2) |
| Se(1)-O(3) | 2.93 (2) | Se(2)-O(2) | 3.17 (2) |
| Se(1)-O(5) | 3.33 (2) | Se(2)-O(5) | 3.27 (2) |
| Se(2)-O(1)′ | 2.69 (2) | | |

[a] The primed atoms are related to the unprimed ones by inversion through the center of symmetry at the center of the $Se_4^{2+}$ ion.

TABLE IV

BOND DISTANCES (Å) AND ANGLES (DEG) FOR THE $HS_2O_7^-$ IONS IN $Se_4(HS_2O_7)_2$ AND $NO_2(HS_2O_7)$[a]

| | $Se_4(HS_2O_7)_2$ | | $NO_2HS_2O_7$ |
|---|---|---|---|
| | Uncor | Cor | Uncor |
| S(1)-O(1) | 1.44 (2) | 1.45 | 1.53 (2) |
| S(1)-O(2) | 1.44 (2) | 1.46 | 1.47 (2) |
| S(1)-O(3) | 1.42 (2) | 1.45 | 1.43 (3) |
| S(1)-O(4) | 1.67 (2) | 1.67 | 1.70 (2) |
| S(2)-O(4) | 1.59 (2) | 1.60 | 1.59 (3) |
| S(2)-O(5) | 1.41 (2) | 1.42 | 1.44 (2) |
| S(2)-O(6) | 1.46 (2) | 1.47 | 1.52 (2) |
| S(2)-O(7) | 1.56 (2) | 1.58 | 1.57 (2) |
| S(1)-S(2) | 2.86 (2) | | 2.87 (1) |
| O(1)-O(5) | 2.90 (2) | | 2.73 (3) |
| O(3)-O(7) | 2.99 (2) | | 3.04 (3) |
| O(4)-S(1)-O(1) | 105 (1) | | 100 (1) |
| O(4)-S(1)-O(2) | 99 (1) | | 98 (1) |
| O(4)-S(1)-O(3) | 104 (1) | | 109 (1) |
| O(2)-S(1)-O(3) | 116 (1) | | 109 (1) |
| O(2)-S(1)-O(1) | 117 (1) | | 125 (2) |
| O(1)-S(1)-O(3) | 113 (1) | | 113 (2) |
| O(4)-S(2)-O(5) | 112 (1) | | 108 (1) |
| O(4)-S(2)-O(6) | 104 (1) | | 100 (2) |
| O(4)-S(2)-O(7) | 106 (1) | | 103 (1) |
| O(5)-S(2)-O(6) | 120 (1) | | 121 (1) |
| O(5)-S(2)-O(7) | 109 (1) | | 110 (2) |
| O(6)-S(2)-O(7) | 105 (1) | | 112 (1) |
| S(1)-O(4)-S(2) | 123 (1) | | 123 (2) |
| Twist angle | 14 (2) | | 16 (3) |
| O(7)-H—O(2) | 2.57 (2) | | 2.66 (3) |

[a] The correction for thermal motion is discussed in the text. The twist angle is defined as the average of the three smallest angles occurring between the projections of opposite S-O bonds onto the plane perpendicular to S(1)-S(2).

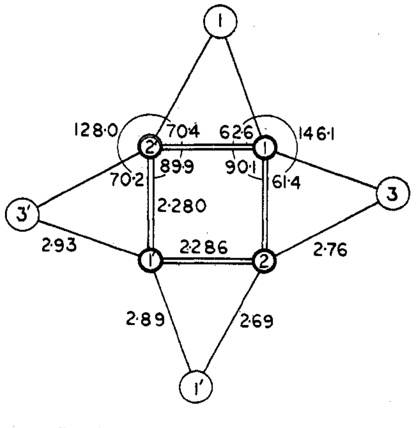


Figure 1.—The $Se_4^{2+}$ ion and its environment. Double circles are Se; single circles, O atoms.

TABLE V

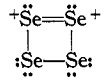
Equation of the Plane of the $Se_4^{2+}$ Ion Referred to Orthogonal Axes with $x$ (in Å) Paralell to $a$, $y$ (in Å) Paralell to $b$, and the Origin at the Center of the Ion: $-0.010x + 0.629y + 0.780z = 0$

Distances (Å) of Atoms from the Plane

| | | | |
|---|---|---|---|
| Se(1) | 0 | O(1) | −0.521 |
| Se(2) | 0 | O(3) | +0.176 |

rectangle of four oxygen atoms from four different $HS_2O_7$ groups in such a way that all eight atoms lie in a single plane whose equation is given in Table V. Each oxygen atom has two selenium neighbors at distances between 2.69 and 2.93 Å and *vice versa*. These comparatively long Se-O distances are very much larger than those of 1.635 Å found in $SeO_4^{2-}$,[8] suggesting that the bonding between the selenium and oxygen atoms is primarily ionic and that the compound should be formulated $Se_4^{2+}(HS_2O_7^-)_2$.

**The $Se_4^{2+}$ Ion.**—The $Se_4^{2+}$ ion has Se-Se bonds of length 2.283 (4) Å and is, within experimental error, a square of $D_{4h}$ symmetry, even though the only symmetry required by the crystal is $C_i$. The tensors describing the thermal motions of the selenium atoms have $D_{4h}$ symmetry with their maximum values, corresponding to an rms displacement of 0.20 Å, along the normal to the square and their minimum values (0.16 Å) along the lines from the selenium atoms to the center of the square. One model which can account for these observations assumes that the square is rigid with its three translational components of thermal motion equal (0.16 Å). It is librating in its own plane with an rms amplitude of 3.2° and is also librating around its diagonals with an rms amplitude of 4.5°. In an alternative model the translational component of the thermal motion normal to the square is assumed to be larger than that in the plane, and the amplitude of libration around the diagonals is correspondingly reduced. Depending on the particular assumptions made, a correction for thermal motion between 0.004 and 0.011 Å must be made to the Se-Se bond length, resulting in the true Se-Se distance lying between 2.287 and 2.294 Å. This length is significantly less than that of 2.34 (2) Å found in the $Se_8$ molecule,[9] indicating some degree of multiple bonding. Such a result is consistent with a valence bond description of the molecule involving resonance structures of the type



Alternatively the structure can be understood in terms of the molecular orbital theory discussed in ref 3 and 10 in which the relatively short Se-Se bond is explained in terms of the delocalization of the six π-type electrons. According to simple Hückel theory these constitute an aromatic sextet and provide a π-bond order of 0.5. Confirmation of this bond order is provided by the normal-coordinate analysis by Gillespie and Pez[11] of the ir and Raman spectra. The intense yellow-orange color of the $Se_4^{2+}$ ion ($\lambda_{max}$ 410 nm, $\epsilon$ 8000) is to be expected from the dipole-allowed excitation of an electron from the highest filled π orbital, which is of symmetry $e_g$ and almost nonbonding, to the lowest empty π orbital ($b_{2u}$). Stephens has recently shown that the results of his magnetic circular dichroism (MCD) experiments[12] are consistent with such a model.

The crystal structure of the isoelectronic species $S_2N_2$

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[8] B. Morosin, *Acta Crystallogr., Sect. B*, **25**, 19 (1969).

[9] R. E. Marsh, L. Pauling, and J. D. McCullough, *ibid.*, **6**, 71 (1953).

[10] J. D. Corbett, *Inorg. Nucl. Chem. Lett.*, **5**, 81 (1969).

[11] R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, **8**, 1229 (1969).

[12] P. J. Stephens, *Chem. Commun.*, 1496 (1969).

has recently been determined in the compound $S_2N_2(SbCl_5)_2$.[13] The $S_2N_2$ fragment is also a planar ring with S–N bond lengths of 1.619 (5) Å. According to a correlation of bond order with bond length in S–N compounds,[14] this corresponds to a bond order of approximately 1.3. More recently the structure determination of $Te_4(Al_2Cl_7)_2$[15] has shown the existence of a square $Te_4^{2+}$ ion and Raman[16] and MCD[12] studies indicate that a square $S_4^{2+}$ ion also exists. Corbett[10] has interpreted the square $Hg_4$ rings in $Na_3Hg_2$ in terms of an $Hg_4^{6-}$ ion having a similar valence electron configuration to that proposed for $Se_4^{2+}$, but it seems likely that there is some delocalization of electrons from the $Hg_4$ ring onto neighboring Na atoms. In the case of the square $As_4$ and $Sb_4$ rings in the skutterudite structures,[17] magnetic measurements indicate that delocalization is so extensive that it is no longer possible to treat the rings as isolated ions.

**The $HS_2O_7^-$ Ion.**—The short distance O(7)–O(2) (2.57 Å) between $HS_2O_7^-$ ions and the long S(2)–O(7) bond (1.56 Å) suggest that the anions are hydrogen bonded into chains along the *b* axis with the hydrogen atom attached to O(7) (see Figures 2 and 3). Curiously, the only other $HS_2O_7^-$ ion whose structure has been determined, that in $NO_2HS_2O_7$ (see Appendix), not only has the same conformation but an identical hydrogen-bonding scheme between the ions, the translation vector between ions being $b = 5.606$ Å in the $Se_4^{2+}$ crystals and $c = 5.55$ Å in the $NO_2^+$ crystals. The arrangements of adjacent chains is however different: in the former case they are related by a twofold screw axis; in the latter, by a center of inversion. With similar conformations, the $HS_2O_7^-$ ions in the two crystals should have similar bond lengths and angles (see Table IV and Figure 4). In general this is true, although there are several differences larger than twice the estimated standard error. It would, however, be unwise to assume that these differences are necessarily significant.

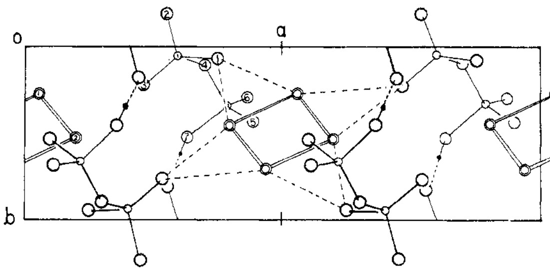

Figure 2.—Projection of $Se_4(HS_2O_7)_2$ down *c*. Two unit cells are included along *a*, but only the ions lying between $z = -0.25$ and $z = +0.25$ are shown. The large single circles are O, the small single circles are S, and the double circles are Se atoms.

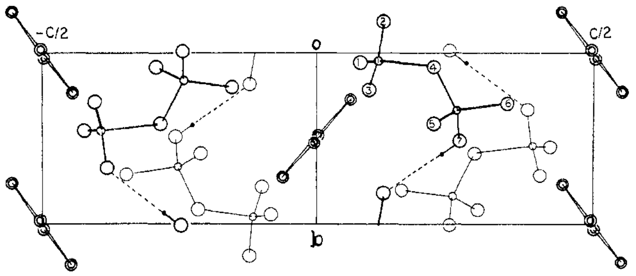

Figure 3.—Projection of $Se_4(HS_2O_7)_2$ down *a*.

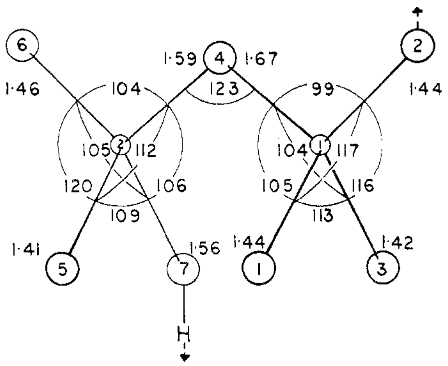

Figure 4.—The $HS_2O_7^-$ ion in $Se_4(HS_2O_7)_2$. The large circles are O; the small circles are S atoms.

The tensors describing the thermal motion of the $HS_2O_7^-$ ion in $Se_4(HS_2O_7)_2$ are consistent with a rigid ion librating with rms displacements of 3–4° around the axes perpendicular to the S–S vector and about 8° around an axis parallel to this vector, together with an isotropic translational motion with rms displacements of 0.14 Å. The resultant corrections to the S–O bond lengths lie between 0.006 and 0.026 Å (see Table IV).

Except for the S–O(H) bond, the uncorrected terminal S–O bond lengths average 1.43 Å in the tetraselenium compound and 1.48 Å in the nitronium compound. In the latter case the deviations from the mean appear to be significant but do not correlate with any of the features in the environment of the ion. In the $Se_4^{2+}$ structure the S(2)–O(H) bond is significantly longer than the other terminal S–O bonds (1.57 Å) introducing an asymmetry which is reflected in an asymmetry of the S–O–S bridge, the S(2)–O(4) bond of 1.59 Å being shorter than the S(1)–O(4) bond of 1.67 Å. The deviation of the O–S–O angles from tetrahedral is also significant and can be described by a decrease of about 4–5° in angles where one of the oxygen atoms is bonded to another sulfur or hydrogen atom and a further reduction of about 3° in angles where all these four atoms are coplanar. There is of course a corresponding increase in the other angles compensating for these reductions. Similar effects are also observed in $S_2O_7^{2-}$,[18] $S_3O_{10}^{2-}$,[19] and $S_5O_{16}^{2-}$,[20] and are in general agreement with the theories of Cruickshank,[21] Gillespie and Robinson,[22] and Baur.[23] The two former theories give a correlation between order and bond length and it is interesting to note that the total bond order around each sulfur atom in either theory is close to 6, the lower bond order of the S–O(H) bond at one end of the ion being almost exactly compensated for by the increased

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TABLE VI

ATOMIC POSITIONAL AND TEMPERATURE PARAMETERS FOR $NO_2(HS_2O_7)$[c]

| Atom |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| a | b | x | y | z | U, Å² | $U_{11}$, Å² | $U_{22}$, Å² | $U_{33}$, Å² | $U_{12}$, Å² | $U_{13}$, Å² | $U_{23}$, Å² |
| S(1) | S(1) | 0.1559 (8) | 0.1752 (7) | 0.7698 (14) |  | 0.005 (3) | 0.014 (3) | 0.009 (2) | −0.003 (3) | 0.008 (4) | −0.010 (4) |
| S(2) | S(2) | 0.2970 (8) | 0.4264 (7) | 0.3359 (15) |  | 0.019 (3) | 0.013 (3) | 0.008 (3) | −0.004 (2) | −0.002 (4) | −0.006 (4) |
| O(1) | O(1) | 0.320 (2) | 0.065 (2) | 0.742 (5) | 0.028 (5) |  |  |  |  |  |  |
| O(2) | O(5) | 0.079 (2) | 0.204 (2) | 1.009 (4) | 0.026 (5) |  |  |  |  |  |  |
| O(3) | O(4) | 0.028 (3) | 0.153 (3) | 0.633 (6) | 0.041 (6) |  |  |  |  |  |  |
| O(4) | O(6) | 0.222 (2) | 0.368 (2) | 0.625 (5) | 0.020 (5) |  |  |  |  |  |  |
| O(5) | O(2) | 0.417 (2) | 0.293 (2) | 0.291 (5) | 0.022 (5) |  |  |  |  |  |  |
| O(6) | O(3) | 0.351 (2) | 0.595 (2) | 0.321 (5) | 0.029 (6) |  |  |  |  |  |  |
| O(7) | O(7) | 0.129 (2) | 0.447 (2) | 0.186 (4) | 0.016 (4) |  |  |  |  |  |  |
| O(8) |  | 0.680 (3) | 0.093 (3) | 0.609 (6) | 0.047 (7) |  |  |  |  |  |  |
| O(9) |  | 0.773 (3) | 0.257 (3) | 0.294 (6) | 0.032 (6) |  |  |  |  |  |  |
| N(1) |  | 0.726 (3) | 0.171 (3) | 0.465 (6) | 0.029 (6) |  |  |  |  |  |  |

[a] Atom corresponding to the convention used in Table IV. [b] Atom given by Steeman and McGillavry.[26] [c] See Table II for explanation.

order of the adjacent bridge bond. This kind of asymmetry has also been observed in a number of pyrophosphates.[24,25]

## Appendix

### The Refinement of the Structure of $NO_2{}^+HS_2O_7{}^-$

In connection with our work on $Se_4(HSO_7)_2$ we have refined the structure of $NO_2HS_2O_7$ using the X-ray intensities measured by Steeman and MacGillavry,[26,27] who first reported the structure. Since these intensities were already on the same relative scale, only one scale factor was refined, but the reflections designated as unobserved or unreliable by the original authors were omitted in the present work, reducing the number of measurements from about 500 to 360. The positional parameters quoted in the original paper and isotropic temperature factors for all the atoms (except S for which anisotropic temperature factors were used) were allowed to refine using the full-matrix least-squares program CUDLS. Scattering factors for all the atoms were taken from ref 6. As the results were not sensitive to the weighting scheme, unit weights were used throughout. $R_1$ dropped from 0.16 to 0.125.

The refined atomic parameters are summarized in Table VI, and the molecular geometry of the anion is given in Table IV. Although $R_1$ was not much reduced, there were some significant changes in the bond distances, notably that of S(1)–O(1) which dropped from the anomalously large value of 1.64 Å to the still large but more likely value of 1.53 Å. The standard errors quoted are those based on the final round of least-squares refinement and are likely to be rather low. The difference in the lengths of the two N–O bonds (0.96 (4) and 1.06 (4) Å) is probably not significant and the O–N–O angle (178 (7)°) does not differ significantly from 180° but the error is large and the conformation of the ion is consistent with the bent model for $NO_2{}^+$ proposed by Cruickshank in $(NO_2)_2S_3O_{10}$.[19] The structure of the anion and the hydrogen-bonding scheme are discussed in the main text.

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# Notes

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## The Preparation and Properties of a Chromium(III)–Plutonium(V) Complex[1]

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It has been known for some time that Cr(III) can form complexes with $UO_2{}^+$ [3] or $NpO_2{}^+$ [4] as ligands. These complexes may be made by the reduction of $UO_2{}^{2+}$ or $NpO_2{}^{2+}$ with $Cr^{2+}$ or, in the case of neptunium, by direct substitution on $Cr^{3+}$(aq).[4] Attempts to make the corresponding plutonium complex by the reduction of $PuO_2{}^{2+}$ failed, presumably due to the rapid reaction of the complex with $Cr^{2+}$.[3] We now report the successful preparation of the plutonium complex by the *oxidation* of Pu(IV) by Cr(VI). In agreement with early work[5] we have found that Pu(IV) is oxidized moderately rapidly by excess Cr(VI) in dilute $HClO_4$. However, after the Pu(IV) has been consumed, only about half the total plutonium is Pu(VI);[6] several days are required before all the plutonium appears as Pu(VI). That which is oxidized

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(2) Graduate student summer employee.

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