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# Refinement of the Crystal Structure of Helvite, $Mn_4(BeSiO_4)_3S$*

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The crystal structure of helvite, $Mn_4(BeSiO_4)_3S$, space group $P\bar{4}3n$, $a=8{\cdot}294\pm0{\cdot}007$ Å and $Z=2$, has been refined using counter-diffractometer data to $R=4{\cdot}0\%$. The Si–O and Be–O distances are $1{\cdot}623\pm0{\cdot}003$ and $1{\cdot}638\pm0{\cdot}003$ Å respectively. Tetrahedral coordination of Mn(II) has been confirmed, with Mn–S $=2{\cdot}432\pm0{\cdot}002$ Å, and $3\times$ Mn–O $=2{\cdot}082\pm0{\cdot}004$ Å.

## Introduction

The mineral helvite is a tektosilicate of the idealized formula $Mn_4(BeSiO_4)_3S$. It is one of a number of isotypic, isometric phases characterized by rings of four tetrahedra in each of the faces of the unit cell which are linked together forming rings of six tetrahedra about each of the cell corners. Interest in the compound lies primarily in the structural effects which arise from the introduction of beryllium into tetrahedral sites, and in the nature of the supposed fourfold coordination of Mn(II).

Helvite from Hørtekollen, Norway, was reported to have the space group $P\bar{4}3n$ ($T_d^4$) with $a=8{\cdot}19$ Å by Barth (1926) utilizing powder photographs. From rotation photographs, Gottfried (1927) determined that $a=8{\cdot}52$ Å and that the space group is $T_d^4$ for a sample of helvite from an unreported source. Both Barth and Gottfried noted that helvite appeared to be isotypic with sodalite, $Na_4(AlSiO_4)_3Cl$.

Table 1. *Final fractional coordinates*

Standard errors are in parentheses.

| | *x* | *y* | *z* |
|---|---|---|---|
| O | 0·1418 (3) | 0·1404 (3) | 0·4171 (4) |
| | 0·137* | 0·133* | 0·416* |
| Mn | 0·1693 (1) | 0·1693† | 0·1693† |
| | 0·175* | | |
| Si | 0 | $\frac{1}{2}$ | $\frac{1}{4}$ |
| Be | $\frac{1}{2}$ | 0 | $\frac{1}{4}$ |
| S | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |

* Fractional coordinates, Pauling (1930).
† $z=y=x$

A sample from Schwarzenberg, Saxony, was analyzed by Pauling (1930) using oscillation photographs, for which he obtained $a=8{\cdot}25$ Å. Assuming a sodalite structure in which beryllium replaces aluminum, manganese replaces sodium, and sulfur replaces chlorine, he determined the structural parameters for helvite listed in Table 1. Glass, Jahns & Stevens (1944), in a paper describing the general mineralogy of the helvite group of minerals, reported $a=8{\cdot}273\pm0{\cdot}005$ Å for a sample of helvite also from Saxony.

## Experimental

In this investigation, crystals from Schwarzenberg, Saxony, were studied. Several chemical analyses have been reported for helvite from this region (see Hintze, 1897; Doelter, 1914, or Glass *et al.*, 1944). From these analytical data a composite formula has been calculated for the unit-cell contents: $(Mn, Fe)_{7{\cdot}33-7{\cdot}57}Be_{5{\cdot}29-6{\cdot}56}Si_{6{\cdot}05-6{\cdot}10}O_{23{\cdot}92-25{\cdot}47}S_{1{\cdot}72-1{\cdot}73}$. Previous workers (in particular, see Pauling, 1930) demonstrated that the idealized unit-cell contents are $(Mn, Fe)_8(BeSiO_4)_6S_2$. Analysis of powder photographs, using silicon ($a=5{\cdot}430$ Å) as an internal standard, yielded a value of $a=8{\cdot}294\pm0{\cdot}007$ Å. Weissenberg photographs using Cu $K\alpha$ radiation confirmed that the space group is $P\bar{4}3n(T_d^4)$.

Intensity data were measured for a complete octant of reciprocal space using a tetrahedral crystal (0·26 mm on an edge) mounted on a Weissenberg-geometry single-crystal diffractometer. Pulse-height analysis was used with Mo $K\alpha$ radiation, in conjunction with a monochromating graphite crystal. All intensity data were corrected for both Lorentz–polarization factors and absorption ($\mu_{lin}=51{\cdot}4$ cm$^{-1}$). The data consisted of 408 non-zero reflections. Symmetry related reflections were averaged to produce 116 observed structure factors.

## Refinement

Least-squares refinement was carried out using the program *SFLSQ*5, which utilizes the full matrix, written and kindly made available by C. T. Prewitt. Initial fractional coordinates were those given by Pauling (Table 1). Refinement was carried out on the coordinates, the isotropic temperature factors, and the scale factor, using unit weighting. The refinement converged

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with $R=5{\cdot}1\,\%$. At this point, refinement of anisotropic temperature factors was initiated and the weighting scheme was changed to a modification of the weighting scheme suggested by Hughes (1941). The scheme was altered to take into consideration the number of individual structure factors averaged to produce the final value of the observed structure factor.

As refinement progressed, it became evident that for structure factors with magnitudes below the minimum observed values, estimated values based on standard counting statistics were uniformly too large. These structure factors were all superstructure reflections ($h+k+l=2n+1$). Refinement was therefore continued, omitting these reflections and using corrections for anomalous scattering. The $R$ value converged at a value of 2·1%. This $R$ value represented refinement on 94 reflections averaged from 324 separate intensity measurements. The final atom parameters (for the refinement with $R=2{\cdot}1\,\%$) are listed in Tables 1 and 2. Using these parameters, a final $R$ value of 4·0% was obtained for the full set of 116 structure factors. The final structure-factor data are listed in Table 3.

Table 2. *Final anisotropic temperature factors* ($\times 10^4$)

Standard errors are in parentheses.

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| O | 21 (4) | 22 (4) | 31 (4) | 12 (4) | 3 (3) | −3 (3) |
| Mn | 38 (1) | 38* | 38* | 5 (1) | 5* | 5* |
| Si | 19 (5) | 23 (3) | 23† | 0 | 0 | 0 |
| Be | 31 (21) | 17 (12) | 17† | 0 | 0 | 0 |
| S | 45 (2) | 45‡ | 45‡ | 0 | 0 | 0 |

* $\beta_{33}=\beta_{22}=\beta_{11}$; $\beta_{23}=\beta_{13}=\beta_{12}$

† $\beta_{33}=\beta_{22}$

‡ $\beta_{33}=\beta_{22}=\beta_{11}$

Table 3. *Observed and calculated structure factors*

| h | k | l | $F_o$ | $F_c$ |
|---|---|---|---|---|
| 2 | 2 | 0 | 31.7 | 35.2 |
| 1 | 3 | 0 | 66.0 | 62.8 |
| 2 | | | 26.1 | 26.2 |
| 3 | | | 146.6 | 148.9 |
| 0 | 4 | 0 | 68.3 | 62.5 |
| 1 | | | 3.3 | 0.1 |
| 2 | | | 56.7 | 58.5 |
| 3 | | | 5.2 | 0.3 |
| 4 | | | 132.0 | 130.5 |
| 1 | 5 | 0 | 41.9 | 43.4 |
| 2 | | | 21.1 | 21.2 |
| 3 | | | 71.7 | 71.5 |
| 4 | | | 3.4 | 0.2 |
| 5 | | | 18.4 | 17.5 |
| 0 | 6 | 0 | 126.9 | 129.4 |
| 1 | | | 19.2 | 19.3 |
| 2 | | | 43.9 | 42.9 |
| 3 | | | 19.3 | 18.9 |
| 4 | | | 7.1 | 7.0 |
| 5 | | | 17.2 | 17.3 |
| 6 | | | 49.5 | 49.3 |
| 1 | 7 | 0 | 18.8 | 17.9 |
| 2 | | | 17.6 | 17.6 |
| 3 | | | 58.8 | 58.5 |
| 4 | | | 3.6 | 0.0 |
| 5 | | | 14.1 | 14.2 |
| 6 | | | 13.1 | 13.7 |
| 7 | | | 37.4 | 37.1 |
| 0 | 8 | 0 | 23.9 | 22.1 |
| 1 | | | 4.2 | 0.7 |
| 2 | | | 50.4 | 48.9 |
| 3 | | | 3.1 | 0.0 |
| 4 | | | 51.5 | 51.9 |
| 5 | | | 3.7 | 0.5 |
| 1 | 9 | 0 | 29.5 | 30.2 |
| 2 | | | 13.5 | 14.0 |
| 3 | | | 51.3 | 52.4 |
| 4 | | | 4.3 | 0.5 |
| 5 | | | 30.4 | 30.1 |
| 1 | 2 | 1 | 124.5 | 125.2 |
| 2 | 3 | 1 | 53.1 | 51.5 |
| 1 | 4 | 1 | 115.0 | 115.4 |
| 2 | | | 23.0 | 23.4 |
| 3 | | | 13.9 | 17.1 |
| 2 | 5 | 1 | 49.0 | 50.7 |
| 3 | | | 2.3 | 0.5 |
| 4 | | | 74.1 | 75.0 |
| 1 | 6 | 1 | 29.5 | 29.5 |
| 2 | | | 3.5 | 0.3 |
| 3 | | | 15.5 | 15.5 |
| 4 | | | 16.2 | 17.9 |
| 5 | | | 52.1 | 52.5 |
| 2 | 7 | 1 | 54.4 | 51.9 |
| 3 | | | 3.0 | 0.4 |
| 4 | | | 45.2 | 46.4 |
| 5 | | | 3.1 | 0.7 |
| 6 | | | 22.8 | 23.4 |
| 1 | 8 | 1 | 61.6 | 61.8 |
| 2 | | | 15.3 | 15.1 |
| 3 | | | 28.6 | 28.9 |
| 4 | | | 3.2 | 0.2 |
| 5 | | | 39.1 | 40.1 |
| 2 | 9 | 1 | 38.1 | 37.4 |
| 3 | | | 4.1 | 0.6 |
| 4 | | | 8.1 | 8.3 |
| 5 | | | 5.3 | 0.2 |
| 1 | 0 | 2 | 31.0 | 29.9 |
| 2 | 2 | 2 | 57.5 | 55.3 |
| 3 | 3 | 2 | 29.1 | 27.1 |
| 2 | 4 | 2 | 80.1 | 78.0 |
| 3 | | | 21.3 | 21.6 |
| 4 | | | 82.5 | 80.5 |
| 3 | 5 | 2 | 54.3 | 54.5 |
| 4 | | | 18.3 | 19.3 |
| 5 | | | 21.8 | 20.5 |
| 2 | 6 | 2 | 35.5 | 35.5 |
| 3 | | | 3.0 | 0.0 |
| 4 | | | 5.5 | 7.7 |
| 5 | | | [illegible] | 0.1 |
| 6 | | | 53.3 | 53.4 |
| 2 | 7 | 2 | 33.5 | 34.1 |
| 3 | | | 15.5 | 15.7 |
| 4 | | | 34.3 | 35.0 |
| 5 | | | 3.2 | 0.5 |
| 2 | 8 | 2 | 35.0 | 34.9 |
| 3 | | | 14.5 | 14.7 |
| 4 | | | 41.7 | 43.3 |
| 5 | | | 12.7 | 12.5 |
| 3 | 9 | 2 | 8.9 | 8.2 |
| 4 | | | 13.0 | 11.8 |
| 5 | | | 40.4 | 40.1 |
| 3 | 4 | 3 | 58.3 | 57.6 |
| 4 | | | 26.9 | 27.9 |
| 3 | 5 | 3 | 89.1 | 88.7 |
| 4 | | | 16.7 | 16.6 |
| 5 | | | 26.5 | 25.1 |
| 4 | 7 | 3 | 24.9 | 25.6 |
| 5 | | | 3.1 | 0.7 |
| 6 | | | 5.8 | 3.5 |
| 3 | 8 | 3 | 45.0 | 43.0 |
| 4 | | | 3.2 | 0.4 |
| 5 | | | 15.3 | 13.8 |
| 4 | 9 | 3 | 24.4 | 25.4 |
| 5 | | | 5.5 | 0.5 |
| 4 | 4 | 4 | 70.1 | 72.1 |
| 5 | 5 | 4 | 45.9 | 47.4 |
| 4 | 6 | 4 | 31.8 | 33.1 |
| 5 | | | 13.8 | 13.9 |
| 6 | | | 19.0 | 18.8 |
| 5 | 7 | 4 | 35.2 | 35.4 |
| 6 | | | 10.7 | 11.4 |
| 4 | 8 | 4 | 57.5 | 53.3 |
| 5 | | | 5.5 | 0.1 |
| 5 | 5 | 5 | 36.9 | 36.8 |
| 5 | 7 | 5 | 32.4 | 32.9 |
| 5 | 8 | 5 | 29.8 | 31.5 |

During refinement, the form-factor scale factors were allowed to vary. With the exception of beryllium, all factors remained at their initial values within standard error (oxygen, 100% O; manganese, 88·9% Mn, 11·1% Fe; silicon, 100% Si; sulfur, 100% S). The Mn form factor scale factor refined to a value of 0·890 ± 0·003, for example. The final unit-cell contents as determined by our refinement were $(Mn_{7\cdot11}Fe_{0\cdot89})_8(Be_{5\cdot73}Si_{0\cdot27})_6Si_6O_{24}S_2$. The calculated density for this formula ($3{\cdot}25$ g.cm$^{-3}$) agrees well with the literature values of 3·17 and 3·20 g.cm$^{-3}$. The relative amounts of Fe and Mn were determined by X-ray fluorescence analysis, subsequent to the refinement. The value of 15% Fe so determined is in good agreement with values used in the refinement.

## Discussion

Table 4 contains a list of bond lengths and angles, with estimated standard errors, as calculated using the program *ORFFE* (Busing, Martin & Levy, 1964) and Table 5 gives the magnitudes and orientations of the principal axes of the thermal ellipsoids. The estimated standard errors were computed utilizing the final least-squares variance–covariance matrix and lattice-parameter standard errors. Included in Table 4 for comparison with the present results are data from a refinement of the crystal structure of sodalite (Löns & Schulz, 1967).

The high-spin manganese(II) ion is on a triad axis, tetrahedrally coordinated by three oxygens (2·082 Å), and one sulfur (2·432 Å). Corliss, Elliot & Hastings, (1956) reported that MnS with the zincblende structure has the lattice parameter $a=5{\cdot}606$ Å. The calculated Mn–S bond length for the manganese tetrahedra is 2·427 Å, in excellent agreement with the value determined for helvite. Bond lengths calculated by employing effective ionic radii of Shannon & Prewitt (1969), and extrapolating values of ionic radii for tetrahedrally coordinated Mn(II) and sulfur ions from the corresponding octahedrally coordinated values, yielded Mn–S and Mn–O distances of 2·45 and 2·02 Å respectively.* The resulting Mn–S distance is in good agreement with the one observed in helvite. The Mn–O distance (2·08 Å) is somewhat larger than that predicted, however. The difference cannot be explained by the presence of smaller Fe(II) ions substituting for manganese.

Helvite and sodalite provide an unusual opportunity to compare the effects on the tetrahedral framework of two dissimilar cations on the T sites (Be,Al) and of very different non-framework cations (Mn,Na). The silicon containing tetrahedra in these two structures have dimensions which are identical within 2σ. Similarly, while the bond lengths reflect differences in ionic radii, the bond angles for the Be and Al tetrahedra are also markedly alike for helvite and sodalite respectively. The principal difference is in the small Si–O–T (T = Al, Be) angle of helvite. The value of this angle has been proposed to be a qualitative measure of the degree of *d–p π* bonding in the silicate framework (Cruickshank, 1961; Brown, Gibbs & Ribbe, 1969) such that a bond angle of 180° corresponds to the maximum *d–p π* inter-

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* The tetrahedrally coordinated Mn(II) ionic radius was predicted by comparison with similar changes from octahedral to tetrahedral coordination for Fe(II), Cr(IV), and Zn(II). These gave values of the Mn(II) ionic radius of 0·67, 0·66, and 0·66 Å respectively. The tetrahedrally coordinated sulfur ionic radius was predicted using a similar comparison with changes in oxide ionic radii.

action. In sodalite, both Al and Si have 3*d* orbitals available for such interactions. In helvite, beryllium has no available orbitals of the correct symmetry to produce interactions of this type with the oxygens coordinating it. Therefore the small Si–O–Be angle (128·20°) is expected as a result of the lesser $\pi$ contribution to the bonding of the framework in helvite.

Table 4. *Bond lengths and angles*

Standard errors are in parentheses.

| Helvite* | | Sodalite† | |
|---|---|---|---|
| Silicon tetrahedra: | | Silicon tetrahedra: | |
| Si—O | 4 × 1·623 (3) Å | Si—O | 4 × 1·628 (4) Å |
| O—O | 4 × 2·622 (4) | O—O | 4 × 2·629 (8) |
| | 2 × 2·704 (6) | | 2 × 2·714 (8) |
| O—Si—O | 4 × 107·8 (1)° | O—Si–O | 4 × 107·7° |
| | 2 × 112·9 (2) | | 2 × 113·0 |
| Beryllium tetrahedra: | | Aluminium tetrahedra: | |
| Be—O | 4 × 1·638 (3) Å | Al–O | 4 × 1·728 (4) Å |
| O—O | 4 × 2·649 (4) | O—O | 4 × 2·806 (8) |
| | 2 × 2·725 (6) | | 2 × 2·855 (8) |
| O—Be—O | 4 × 107·9 (1)° | O—Al–O | 4 × 108·5° |
| | 2 × 112·6 (2) | | 2 × 111·3 |
| Si—O—Be | 128·2 (2) | Si—O–Al | 138·3 |
| Manganese tetrahedra: | | Sodium tetrahedra: | |
| Mn–S | 2·432 (2) Å | Na–Cl | 2·730 (4) Å |
| Mn–O | 3 × 2·082 (4) | Na–O | 3 × 2·351 (8) |
| S—O | 3 × 3·835 (5) | | |
| O—O | 3 × 3·238 (7) | | |
| S—Mn–O | 3 × 116·1 (1)° | | |
| O—Mn–O | 3 × 102·1 (1) | | |

* This work.
† Löns & Schulz (1967).

Brown *et al.* (1969) have further noted that the Si–O bond length should be affected by the T atom. The near equality of the Si–O bond lengths in both sodalite and helvite is thus seemingly inconsistent with this bond model. This direct comparison between Si–O distances in sodalite and helvite is not necessarily reasonable, however, because Löns & Schulz assumed the Si–O bond in sodalite was affected by limited Al substitution (10%), while analysis for helvite indicates less than 3% Al in the silicon sites.

The Si–O–Be angle in tugtupite, $Na_4(AlBeSi_4O_{12})$ (Cl,S) (Danø, 1966) is 143·4°, significantly larger than that in helvite. Significant *d–p* $\pi$ contributions to the bonding are indicated by the other Si–O–T angles, 157·4 and 141·9 (T = Si) and 135·9° (T = Al). In beryl, $Al_2(BeSi_2O_6)_3$ (Gibbs, Breck & Meagher, 1968) the Si–O–Be angle is 127·0°, in good agreement with that of helvite, while the Si–O–Si angle is 168·3°, again indicating significant $\pi$ bonding in the framework. The change in Si–O–Be angle in going from helvite to tugtupite (isotypic with helvite) is consistent with the hypothesis that $\pi$-bonding through the Si–O–Si and Si–O–Al linkages controls the detailed geometry of the framework and thus the Si–O–Be angle. In helvite, where all oxygen atoms bridge between Si and Be, the framework is free to contract as required by the Mn(II) ion, which is unusually small for the tektosilicate structures. Similarly, in beryl, where all the oxygen atoms in the Be tetrahedron bridge to Si, the framework is again free to contract about the Al atoms occupying octahedral sides. Thus, the framework geometry appears to be controlled by both the nature of covalent bonding and the size of the non-framework cations present. Clearly more studies on Si–Be framework minerals is needed to firmly establish the ranges of Si–O–Be angles to be expected in these compounds.

Qualitatively, the differences in the lattice parameter, *a*, that occur in going from sodalite ($a = 8·87$ Å, Löns & Schulz, 1967) to helvite ($a = 8·29$ Å) and even among the helvite group itself [danalite $(Fe,Mn)_4(BeSiO_4)_3S$, $a = 8·19$ Å; genthelvite $(Zn,Fe)_4(BeSiO_4)_3S$, $a = 8·11$ Å; Glass *et al.* (1944)] can be easily explained. By considering changes in ionic radii alone, substituting beryllium for aluminum and manganese for sodium, decreases in *a* of 0·34 Å and 0·76 Å respectively are predicted. A combination of both, plus restrictions on the relative

Table 5. *Magnitudes and orientations of principal axes of thermal ellipsoids*

Standard errors are in parentheses.

| | Principal axis | R.m.s. displacement | Angle to $+a$ | Angle to $+b$ | Angle to $+c$ |
|---|---|---|---|---|---|
| O | 1 | 0·057 (14) | 45·0 (9·0) | 133·0 (9·0) | 100·0 (8·0) |
| | 2 | 0·105 (8) | 110·0 (88·0) | 95·0 (98·0) | 159·0 (115·0) |
| | 3 | 0·108 (7) | 51·0 (58·0) | 43·0 (21·0) | 108·0 (131·0) |
| Mn | 1 | 0·106 (2)* | 114·1 (0·0) | 114·1 (0·0) | 35·3 (0·0) |
| | 2 | 0·106 | 65·9 (0·0) | 65·9 (0·0) | 144·7 (0·0) |
| | 3 | 0·129 (2) | 54·7 (0·0) | 54·7 (0·0) | 54·7 (0·0) |
| Si | 1 | 0·081 (11) | 0 | 90 | 90 |
| | 2 | 0·089 (6)† | 90 | 90 | 180 |
| | 3 | 0·089 | 90 | 90 | 0 |
| Be | 1 | 0·076 (28)* | 90 | 90 | 0 |
| | 2 | 0·076 | 90 | 90 | 180 |
| | 3 | 0·104 (36) | 0 | 90 | 90 |
| S | 1 | 0·120 (4)‡ | 0 | 90 | 90 |
| | 2 | 0·120 | 90 | 0 | 90 |
| | 3 | 0·120 | 90 | 90 | 0 |

* 2 = 1; † 3 = 2; ‡ 3 = 2 = 1.

orientation of the tetrahedra by the existence of changes in *d–p* π-bonding contributions can explain the observed difference of 0·58 Å in the lattice parameters of sodalite and helvite. The changes in ionic radii in the series Mn(II), Fe(II), and Zn(II) cause the decrease in *a* in the helvite group. On this basis, the predicted difference between each of the members is 0·07 Å, in good agreement with those observed (0·10 Å, helvite to danalite, and 0·08 Å, danalite to genthelvite).

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# The Structure of Hydrogen Triuranate†

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Hydrogen triuranate, $H_2U_3O_{10}$, is triclinic, space group $P\bar{1}$, with $a$=6·802 (5), $b$=7·417 (16), $c$=5·556 (5) Å, $\alpha$=108·5 (4), $\beta$=125·5 (1), and $\gamma$=88·2 (2)°. Measured density is 6·7 g.cm$^{-3}$ and the computed value is 6·85 g.cm$^{-3}$ for the one formula weight. The structure was resolved with 756 independent reflections recorded with an automatic diffractometer utilizing the double-filter technique. A least-squares refinement, based on $F$, gave an $R$ value of 6·0%. The configuration of oxygen atoms about U(1) (at origin) is an octahedron, while the coordination about U(2) (in general positions) is a pentagonal bipyramid. Apex oxygen atoms lead to shared U(2)–U(1)–U(2′) bipyramids and octahedra to give triuranate groups along $c^*$. The apex (uranyl) oxygen atoms of each bipyramid form part of an octahedral array of oxygen atoms about the point 0 ½ 0 of the unit cell as a 'center'. The hydrogen atoms can be shown to be associated with oxygen atoms of this octahedron.

## Introduction

One of the phases in the $UO_3$–$H_2O$ system is a composition previously considered to be the 'hemihydrate', $UO_3.\frac{1}{2}H_2O$. Infrared (IR) observations by Urbanec (1966) show, however, that the compound does not contain lattice or coordinated water; hence, the composition should be formulated as $H_2U_2O_7$ or as $U_2O_5(OH)_2$. Early X-ray studies (Vier, 1944) assigned monoclinic symmetry to this phase, but subsequent observations (Staritsky & Walker, 1952) led to triclinic symmetry with $a$=6·87, $b$=7·42, $c$=5·57 Å, $\alpha$=107·5, $\beta$=125, and $\gamma$=89·5°. Based on a measured density of 6·7 g.cm$^{-3}$, these parameters lead to three formula weights of the hemihydrate in the unit cell and a calculated density of 6·78 g.cm$^{-3}$. No further structural work appears to have been performed on this compound.

Our investigation was carried out as part of a continuing study of uranium oxide systems, and particularly because of the bearing this hydrate has on the structure of certain oxides. Interest in the phase also stems from the fact that the assigned unit cell does not contain an integral number of water molecules and that our analytical data gave U:$H_2O$ ratios approaching 3:1, rather than 2:1. In addition, the IR spectrum shows a remarkable similarity to transition metal tri-

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† Based on work performed under the auspices of the U. S. Atomic Energy Commission.

‡ On leave from Augustana College, Sioux Falls, South Dakota.